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STANDARD REFERENCE MATERIALS AND MEANINGFUL MEASUREMENTS

Standard Reference Materials and Meaningful Measurements

Proceedings of the 6th Materials
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Edited by

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Abstract

This book presents the proceedings of the 6th Materials Research Symposium on "Standard Reference Materials and Meaningful Measurement" held at the National Bureau of Standards, Gaithersburg, Maryland, on October 29 through November 2, 1973. The symposium was sponsored by the NBS Institute for Materials Research. The purpose of the symposium was to explore ways that Standard Reference Materials (SRM's) could be used more effectively to bring about meaningful measurements both on a national and international scale, to explore the meaning of meaningful measurements, and to review the major paths now used to reach these measurements.

Starting with the relationship of SRM's to a national measurement system, the symposium reviewed SRM activities at the international level, various national programs, and industrial needs. The use of statistics, selection criteria, and steps for certifying SRM's were reviewed. Fifteen panel sessions reviewed the current status of SRM's and outlined future needs.

Key Words: Certification; certified reference materials; materials; meaningful measurements; measurement; reference materials; SRM's; standards; standard materials; standard reference materials.

PREFACE

This Symposium, the sixth in a continuing series sponsored by the Institute for Materials Research of the National Bureau of Standards, had two major purposes: one internal to NBS, the other addressed to both national and international needs. In the first instance, it was hoped that information concerning national needs for Standard Reference Materials (SRM's) would be authoritatively presented so as to provide future guidlines for the NBS-SRM program. In this regard we can judge the Symposium to have been successful, but in an uneven way. Representatives from several U.S. industries and technological areas presented current and anticipated measurement problems that might be resolved, at least in part, through the instrumentality of SRM's and the "meaningful measurement" concept. Unfortunately, several important measurement technological areas were poorly represented and their needs were not so well stated or set forth. Hopefully, these proceedings will serve in an educational role to help enlighten those industries where SRM's are lacking or where better measurement technology could be brought to bear. Especially fruitful and important for internal NBS planning and guidance were the various panel discussions and recommendations. If these were to be useful for NBS or even U.S. purposes alone, then one might question the need for these proceedings to be distributed on an international scale. However, it is our hope, widely concurred in by the attendees and by speakers from other countries, that the findings and recommendations could, by a not too tortuous extrapolation, have meaning and utility for other national programs.

The second major purpose of the Symposium was to serve as a forum for a discussion of international SRM needs and possible modes of cooperation. Seven major industrial nations, one multinational agency, and three international agencies, presented the current status of their SRM activities. Without exception all these speakers stressed the need for closer and more active cooperation between nations, and endorsed the concept, expressed by the writer, that international mechanisms were required to bring about an effective cooperation and collaboration. Since more than one year has passed between the closing of this Symposium and the publication of these proceedings, it is appropriate to use this space to bring the reader up to date concerning international developments that have occurred in the interim. In the week following this Symposium, seven international agencies and observers from 12 countries met at NBS at the invitation of the Organization of Legal Metrology to explore the need for and possibilities of bringing about cooperation on the international scale for SRM's. This ad hoc group unanimously recommended the formation of a new International

Commission on Reference Materials (ICRM) and set forth some guidelines as to its objectives and scope of work. The group also asked the International Organization for Standardization (ISO) to call the founding meeting of the new Commission and to provide initial secretariat services. Subsequently, ISO formally accepted these tasks. It is now anticipated that the founding session of the ICRM will take place early in 1975, probably in Geneva, Switzerland. This ad hoc group also clearly indicated and recommended that from a logical and linguistic point of view the term "Standard Reference Materials" ought to be changed to "Reference Materials" as the generic name for the entire class of materials currently placed under the phrase "Standard Reference Materials." Thus reference materials produced and certified by, say, the International Atomic Energy Agency (IAEA) would be designated IAEA Certified RM's.

Of the importance of these subjects and discussions in the context of today's technological world we have no doubt; whether we will be successful in fulfilling these purposes time will be the judge.

J. Paul Cali

CONTENTS

PAGE

Preface
Welcome -- R. W. Roberts. 1

Standard Reference Materials and Meaningful Measurements -- An Overview
R. D. Huntoon 4

Possibilities for International Cooperative Efforts in Standard Reference Materials
J. P. Cali. 57

Activity by the International Organization for Standardization with Respect to Standard Reference Materials
F. L. LaQue 68

The Analytical Quality Control Programme of the International Atomic Energy Agency
O. Suschny and D. M. Richman. 74

The Activities of the European Economic Community in the Field of Reference Materials and Methods
K. F. Lauer and H. Laurent. 103

Calibration and Test Materials for Physicochemical Measurements
H. Kienitz. 118

Selection Criteria of a Material as Standard Reference Material and Steps for Certification
G. Milazzo. 127

Statistics and Standard Reference Materials
J. Mandel 146

National SRM Program in France
G. Denegre and A. Marschal. 161

National RM Program in Germany (FRG)
R. J. A. Neider 167

The Current Status of SRM Activities in Japan
T. Tsuchiya 189

National SRM Programs in Poland
T. Plebanski. 201

PAGE

Reference Materials in the United Kingdom
J. D. Cox 224

The National Standard Reference Materials Program in the U.S.A.
H. T. Yolken. 237

The SRM Story at NBS
R. E. Michaelis 246

The Role of the American National Standards Institute in National and International Consensus Standards Programs
R. P. Trowbridge. 258

ASTM in the U.S. Measurement System
W. T. Cavanaugh 267

Chemical Composition Control Problems and Solutions Related to Metals and Alloys
R. S. Cremisio. 275

Measurement Problems in Physical and Mechanical Properties of Industrial Metals and the Use of SRM's
J. Convey 298

High-Purity Compounds: An Overview
A. J. Barnard, Jr. 320

Industrial SRM Needs and Measurement Problems in Inorganic Materials - Chemical Properties
V. A. Stenger 336

Industrial Standard Reference Material (SRM) Needs: Organic Materials
J. Mitchell, Jr. 355

"Meaningful Measurement" in Clinical Chemistry
J. H. Boutwell. 366

Standard Reference Materials and Environmental Monitoring
E. W. Bretthauer, G. B. Morgan, and
R. E. Jaquish 387

SRM Needs and Measurement Problems in Science - Chemical Properties
T. W. Mears 395

PAGE

Air and Water Pollution Panel. 411

Cement Panel 435

Industrial Chemicals Panel 454

Clinical Analytical Chemistry Panel. 465

Metals (Chemical Properties) Panel 517

Glass and Ceramics Panel 583

Metals (Physical Properties) Panel 610

Nuclear Materials (Fuels) Panel. 643

Petroleum Panel. 655

Ores and Geological Materials Panel. 695

Plastics Panel 733

Radioactive Materials Panel. 751

Rubber and Rubber Compounds Panel. 754

Metrology Panel. 759

Intercomparison, Quality Control, and Statistics Panel . 804

WELCOME
STANDARD REFERENCE MATERIALS AND MEANINGFUL MEASUREMENTS

Richard W. Roberts
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Good morning and welcome to the National Bureau of Standards and the 6th Materials Research Symposium on Standard Reference Materials and Meaningful Measurements. I hope you will enjoy your visit to NBS and that you find this Symposium both rewarding and informative.

In some respects this has been a difficult conference to arrange, for the subject matter may appear to be either narrow or broad, depending on one's viewpoint. If we consider the first part of the Conference title, Standard Reference Materials, and think of these materials in terms of their production, the measurement of their properties, and their certification, then we are speaking of a relatively few scientists actively engaged in this process. But when we consider the second part of the Conference title, Meaningful Measurements, then we include a great many scientific activities whose results are expressed in numerical terms. On this basis then, our scope is very large indeed.

Let me give you two contrasting examples of measurement activities in the U.S. alone: the first, a measurement system well-established and based on SRM's and reference methodology; the second, where pioneering efforts to bring about meaningful measurement are just underway. In the production of steel in this country, approximately 100 million (1×10^8) samples are analyzed per year to assure the quality of the end product. Because this measurement system is based upon SRM's and methods of demonstrated accuracy, the analytical results are accurate to within 1-2% of the "true" value, thus assuring compatibility of measurement within this industry. It is interesting from an economic point of view to note that through an expenditure of about 50 cents per analysis, or about 50 million dollars per year, the quality of 14 billion dollars worth of steel is assured with very little waste.

In contrast to that meaningful measurement system is the situation in our clinical chemistry laboratories where the tradition of measurement based on SRM's and reference methodology is only beginning. This year in the U.S. between 3-4 billion measurements will be made at a cost to the patient of 4-6 billion dollars. Some clinical laboratory directors estimate that between 10-25% of all these measurements must be repeated because of error or because the results are so questionable as to provide no useful information to the physician. At the lower figure of 10%, this is an unnecessary economic cost of 300-400 million dollars per year.

It would be absolutely unfair of me to stop at this point in the clinical story, leaving a very negative picture. Few groups of scientists are more critical of their own measurement deficiencies, or working harder to correct them, than the clinical chemists and clinical pathologists of this nation. Furthermore, we should recognize that biological systems are extremely complex and difficult to work with, especially in view of the fast turn-around time demanded for most analyses. Now that clinical SRM's and reference methods are being made available, I am sure that progress in this field will be rapid. The economic incentive alone to improve measurement systems is very great and presents opportunities for all of us.

As Dr. Huntoon will show in his paper, one of the best ways to improve measurement systems, that is, to assure compatibility throughout a measurement infrastructure, is through the use of SRM's and reference methodology. In terms of what constitutes meaningful measurement, and how it may be attained and assured, we are in a sense holding an educational conference.

I am sure all of you here today recognize that the observations I have made relative to the situation in the U.S. are pertinent to the entire world, and for this reason I take special pleasure in greeting our friends and colleagues from other nations and representatives from several international agencies. The time is ripe to mount a determined effort to bring about international cooperation so that all the world may benefit from more meaningful measurement in the fields of health, environmental protection, industrial productivity enhancement, and in science itself.

This conference has one more very important goal, that of learning of further additional needs for SRM's and of obtaining the information required to place these needs in a rational order of priority. To learn these needs we have invited and welcomed representatives from many industries -- ferrous and non-ferrous metals, glasses, ceramics, ores, nuclear power, rubber, petroleum, and several others. These representatives will meet in open panel discussion groups to discuss needs for SRM's and reference methodology, and to help us establish their relative priority. The results of these discussions will be incorporated in the published proceedings, thus providing NBS with a set of future needs and priorities that will have a great influence on the shape of our program over the next few years. I would also hope that these proceedings will receive appropriate consideration as the international efforts now taking shape become more firm and intensive. As an example of the international efforts currently underway, NBS is hosting next week a meeting called by the Office of International Metrologie Legale to explore on an ad hoc basis with several other inter- and multi-national organizations possibilities for international action in the area of Standard Reference Materials. Dr. van Male, President of the OIML, who will chair the sessions, has assured me that any of you, who so desire, may attend these sessions as unofficial observers.

Again, I welcome all of you to this conference and to the National Bureau of Standards.

STANDARD REFERENCE MATERIALS AND MEANINGFUL MEASUREMENTS
AN OVERVIEW

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I. Introduction

In our national measurement system no station stands alone. The measurements made at each become endowed with a meaningfulness that goes beyond what can be achieved at the station and comes by virtue of coupling the station·to the rest of the system. Standard Reference Materials are an important means for coupling station to system. Their full potential is only now becoming generally recognized as indicated by their rapid growth in kind and quality in the last decade.

Producers and distributors of Standard Reference Materials (SRM's) assume and carry special obligations and responsibilities in our nNational measurement system. Many measurement stations throughout the system rely upon SRM's to bring full status of membership and the important endowment of meaningfulness that accompanies it. Failure on the part of the producer to meet his commitments destroys the integrity and validity of all measurements referred to his SRM's and of the products or decisions based upon those measurements.

Rudyard Kipling put the idea very strikingly in one of his brief poems.

> The careful text-books measure,
> Let all who build beware,
> The load, the strain the pressure
> That materials can bear.
>
> For when the creaking girder
> Lets down the grinding span
> The blame for loss or murder
> Will rest upon the man.
> Not upon the stuff, the man.

Our purpose is to examine broadly the vital role of SRM's in the measurement system and to develop in perspective an understanding of the opportunities and obligations that face the producers of SRM's.

As is often the case with those closely associated with a technical field, interest in the sophisticated details and the press of events tend to limit awareness and understanding of the broad implications of the activity and of its actual or potential important relationships with other endeavors. Thus it is often valuable to step back and examine the forest after acquiring mature understanding of the trees.

This overview should be received in that context. No recent discoveries or breakthroughs are to be announced. Rather we undertake an ordering and structuring of what is already well known to gain insight into important relationships and display them in relevant perspective.

We begin with the simple act of measurement at one of the front line stations of the measurement system. The result of this act of measurement -- "a measurement" -- may or may not be meaningful depending upon the need for it, the uses to which it will be put, the integrity of the Station operations, and the nature of the endowment of meaningfulness brought to the station via its interfaces with the measurement system. We therefore first examine briefly the station, its operation, and the validity of its output based solely upon local factors. We then turn attention to the endowment and examine the means for achieving compatibility with the total system and the implications for meaningfulness.

Attention then turns to system fundamentals such as selection of measurement units, concepts of independently realizable and coherent units, and relationships between compatibility and accuracy. All along the way the specific possibilities for involvement of SRM's in the process will be identified and given special emphasis. The strict requirements for stability and integrity emerge naturally.

Finally, the measurement infrastructure of the measurement system, which provides the essential hardware and software necessary for the transfer of meaningfulness, will be examined and its exciting challenges highlighted.

It may be helpful to keep in mind a specific measurement example to apply to the ideas and concepts as they develop. For example, the measurement station may be a technician using a thermistor type of thermometer to measure the body temperature of a patient in a hospital. Or, it may be an engineer with a volt meter measuring the potential (with respect to ground) in a complex electronic circuit. We shall subsequently refer to them as the thermometer or volt meter examples.

II. A Measurement Station

We start with the measurement station, schematically indicated in figure 1. The components are : (1) The measurand, the thing or entity to be measured. (2) The station standard and scale. For each act of measurement this standard-scale combination provides a local realization of the appropriate fraction or multiple of the unit of measure. (3) A set of instrumentation, by means of which the measurand can be compared with the locally realized standard-scale to yield a number characterizing the measurand.

Two additional, essential components are not shown. These are (4) the operator, or measurer, who operates the hardware and (5) the software -- a set of instructions on how to manipulate the hardware and how to realize the full endowment of meaningfulness available to the station. This software may be explicit in the form of documents such as manuals and instruction sheets, or implicit, i.e., in the head of the operator as a result of past education, training, and experience.

In any case the software must be present in explicit or implicit form in an amount adequate for the regular station operations, and must be used as intended not filed away except when needed to impress visitors.

These components will be referred to as station elements. Table 1 groups them for ready reference.

Table 1. Station Elements

1. Measurand
2. Local standard-scale
3. Comparator
4. Operator - Technician
5. Software

The obvious purpose of the station is to make valid, useful measurements. This implies a process, which we give the name - an act of measurement, that utilizes the station elements to arrive at a numerical result - the measurement. There are many ways to describe a measurement station and its process. We need a characterization, around which to build the discussion and to help avoid misunderstanding. The one we shall use, with no implication that it is the only or best one, is outlined in table 2.

Table 2. Station Process

- Specify Measurand
- Declaration
  - Quantity
  - Unit
  - Replications
- Act of Measurement
  - Coupling
  - Comparing and realization
  - Recording
- Replication
- Result
  - Magnitude
  - Uncertainty

The first step in the process is to make a clear, clean, precise determination and identification of the measurand. Despite the apparently absurd obviousness of this step, where failure negates the whole process, many have been known to forget its importance. They thereby introduce irrevocable error and uncertainty at the very start of the process.

Consider the thermometer example. We seek the temperature of the patient. The measurand may be the mouth, rectum, or armpit and we must be clear which it will be.

Some associated chain of inference in the software will relate the temperature of the measurand to the body temperature of the patient. The essential point in step 1 is clarity and specificity in the identification of the measurand.

The second step involves a decision and a declaration. There must be a clear indication of what physical attribute of the measurand is to be measured, i.e., length, temperature, voltage, mass, etc.

This essential step, also often honored in the breech, provides opportunity for error and misunderstanding. Often one attribute is measured and used via the software, to infer the value of another attribute. In the thermometer example the resistance of the thermistor is measured, its temperature is inferred, and from it the patient's temperature. Another example is the measurement of gas pressure or liquid volume in a container to determine its temperature.

In some instrumentation, the indication is direct in terms of the quantity to be measured with the inferential conversion built in. In others, the operator makes the inference. Again there must be clear understanding of the chain of inference, if error is to be avoided.

It follows immediately, once the quantity to be measured is identified, that the unit in which the measurement is to be expressed, must also be indicated. Otherwise the measurement has limited but not necessarily zero usefulness.

The popular vacuum-tube checkers in most drug stores are an example in point. They measure an unspecified attribute of the tube in question, known to the manufacturer and service technicians, and give readings on a scale marked good - poor - bad with no units indicated. They clearly serve a practical and useful purpose, but they do not tell what is wrong, and are frequently erroneous because other tube parameters can confuse the reading. What would we think of a doctor who had his oral thermometer marked in red and green bands labeled sick and well.

For our purposes we insist upon specification of the unit and name it, i.e., meter, kilogram, kelvin, knot, pound, volt, ampere, and so on.

It is also preferable to include in step two prior to action, a statement of the number of replications of the act of measurement that will constitute a "measurement." This, if adhered to, avoids a natural tendency to let the results of the measurement influence the process -- a bad habit, to be avoided, unless one is trouble shooting the measurement station hardware or process.

In the third step, the operator utilizes the station hardware, according to established procedures, to perform the act of measurement. We use the term "act of measurement" to describe the whole station process, or step three, as appropriate. At this stage, the skill and integrity of the operator become crucial.

The measurand must be properly coupled to the comparator. Here an unwary operator can be easily led astray. What the instrumentation sees is what the measurand actually presents to it. This may or may not be what the operator thinks it presents. For example, a thermometer measures only its own temperature. It is up to the operator to see that the thermometer comes to thermal equilibrium with the measurand. A cold oral thermometer takes time to come to equilibrium with the patient. This is the essence of the coupling problem. Put another way - "A volt meter measures the voltage at its terminals." The operator must be sure that the insertion of the instrument did not change the value of the measurand present before the insertion. Thus the coupling problem has two aspects: (a) the instrument must truly see the measurand, not something else; and (b) the coupling of the measurand to the instrumentation must not change the measurand, more than local expected errors will tolerate (unless it does so in an understood and calculable manner so that appropriate corrections can be made). (We are not concerned here with measurements of such sensitivity and exactness that we become involved with the Uncertainty Principle of Heisenberg, which places fundamental limits upon exactness of measurement.)

When satisfied with the coupling between measurand and instrumentation, the operator turns to his station instrumentation, which performs two functions either explicity or implicitly. The instrumentation (1)realizes in terms of station standards the appropriate fraction or multiple of the declared unit, and (2) compares the measurand with it to arrive at a numerical value to be assigned to the measurand. This assigned numerical value tagged with an identifying unit (three feet, ten kilograms, sixteen milliamperes, etc.) completes an act of measurement.

Replication of this act of measurement the declared number of times, N, recording N results, and calculating the mean of N results produces a measurement. We will call it an N-fold measurement and, when we use the term, we mean the result of the process just described. Also a single act of measurement, N=1, which is commonly all that is done on one measurand, at a typical station, with no replication or averaging, can be called a measurement.

Once a station customer is given a measurement or an N-fold measurement he naturally asks: "How accurate is it? What trust can I place in it? Would other stations give the same answer?" Often a measurement carries with it, in addition to the required unit designation, a statement of percent uncertainty, e.g., 16 ma ± 5 percent, 380 kwh ± 1/2 percent. Unless explained properly, such appendages may propagate more confusion than clarification.

In any case, the customer is really asking for some satisfactory enlightenment about the endowment of meaningfulness that comes with the measurement. The extent of endowment he feels to be necessary will depend upon the use to be made of the measurement. The customer wants to be satisfied that the N-fold measurement will meet his needs, and he does not want to wait for or pay for an endowment that far surpasses his requirements. Thus in measurement, as in most technical undertakings, cost is a vital consideration and the product should match the needs of the user.

Evidently the endowment of meaningfulness carried along with a measurement is a vital attribute. In fact the whole system of units and measures and the National and International Measurement Systems, with their extensive infra-structures, exist to enable stations to acquire the proper endowment needed.

We shall not define what we mean by meaningfulness or by the endowment. The concepts will acquire connotation and meaning as the discussion proceeds.

At this stage the station process has realized an appropriate fraction or multiple of the unit, compared the measurand with it, and provided a numerical result. We next turn attention to the validity of the station process.

III. Local Validity

A. The Beginning of Meaningfulness

The endowment of meaningfulness that accompanies an N-fold measurement from a typical station is not usually developed just for that measurement alone. It is generally developed by and for the station, and accompanies all similar measurements made there. The endowment includes a number of characteristics and/or entities each of which is necessary but not sufficient for meaningfulness, but are sufficient, in the aggregate, to insure the required or desired level of meaningfulness.

The first set of these entities relates to what may be called local validity or local quality assurance. These the station must have or there is no point in its existence. To draw upon a few cliches as a matter of emphasis, we paraphrase:

> Meaningfulness like charity begins at home.
> To thine own station be true.
> Do this or all else is meaningless.

B. Operator qualifications

The station operator must have integrity, capability, and experience.

Here we pause to highlight integrity. Measurement is a physical process undertaken to arrive at a quantitative numerical result in a repeatable, verifiable manner, independent of such extraneous emotional or psychological influences as desires, needs, political pressures, consequences, etc. All who are involved in the measurement chain must have the integrity to insist upon and to deliver objective quantitative values.

> If for example measurements are "fudged" to reduce shrinkage, parts that should mate will not do so and no amount of rationalization

will eliminate the loss.

Lack of integrity in the measurement process is self defeating and winds up nullifying the whole undertaking by loss of confidence in the measurements. Similar strictures, of course, do not apply to those who wish to interpret the results of measurements. Integrity in the sense used here should not be confused with the ever present uncertainties in the measurement process that can not be completely eliminated and that will be covered later.

Personal integrity is a required characteristic for the whole measurement system and is not limited to station operators. In the remainder of the discussion it will be assumed that this essential requirement for integrity is understood, is present, and needs no further emphasis or comment.

The need for technical competence and experience on the part of the station operator is obvious. He clearly must know enough about the station hardware to use it properly for the measurements he is undertaking, and he must have sufficient experience with the equipment to know if it is functioning properly. A thorough familiarity with station software as it relates to the measurements being made is also a prerequisite. Each situation is so specific that details would be too extensive to be appropriate here. Suffice it to say, the competence and experience must match the desired sophistication level of the particular station.

C. Hardware Requirements

Station instrumentation (hardware) must clearly be of a level of sophistication to yield results the inherent uncertainties of which are acceptable for the intended use. An operator, properly qualified, and backed up by proper software should be able to judge the adequacy of the hardware, and its state of repair. We assume it to be adequate for the undertakings of the station.

D. Local Dispersion

If the operator were to make a very, very large number of measurements upon the same measurand and record the results he would find a dispersion in the results, and if he were to make a chart of the results plotting as Y the number of measurements giving the value X he would get a dispersion curve similar to that shown in figure 2.

The data from which the curve is plotted can be treated statistically to yield the mean for the process, M_p, and the standard deviation for the process, σp. The various statistical parameters for this kind of station are commonly given the name local precision parameters or station process precision.

If repetition of the set of measurements leading to the curve of figure 2 gives a significantly different curve, the station process is out of control and there can be no worthwhile endowment of meaningfulness. Also if the distribution of data scatters erratically and does not lead to a reasonable distribution curve, control is missing and must be provided. Statistical tests for assessing the state of control can be found in standard text books. We assume the station measurement process is in proper control. (The operator must be trained to recognize symptoms of failure to maintain control.)

In any typical production type measurement station, a dispersion curve like that for figure 2 will be undertaken rarely if at all. It is time consuming and costly, but it is needed, must exist somewhere, and commonly is provided by the manufacturer of the station hardware, either as a curve or as a statement of guaranteed precision, i.e., 5, 1, or 1/10 percent, or σp equals 1 or 5 percent.

The operator may make only one measurement, then want to make some statement about its accuracy. With the information at hand, the best he can say, by referral to his dispersion curve (figure 2), is that his measurement has three chances in four (or 19 in 20) of being within error δ of the mean, M_p, which would be obtained if the full curve were run. In figure 2, 75 percent of the measurements fall between the two ordinates marked 75 percent and the chances are thus three out of four that any one of the measurements will fall between them. Similarly for the 19-1 and the 95 percent ordinates. Please note carefully, however, that the single measurement is *assumed* to come from the same population as that which produced the dispersion curve (figure 2). If this kind of stability from measurement to measurement does not exist, such inferences are not valid and no claims for deviation from the mean can be made. It thus emerges that *stability* of the measurement process is an essential ingredient for the development of an endowment of meaningfulness. This requirement for stability-in-time extends throughout the system and becomes a matter of grave concern to a national laboratory such as NBS. Also responsibility for stability rests heavily upon any producer of Standard Reference Materials for reasons that will become apparent.

If the station is not satisfied with the uncertainty associated with a single act of measurement, replication to give an N-fold measurement is in order. A new dispersion curve, figure 3, will be obtained for these N-fold measurements. It will have approximately the same mean, M_p, but σ_N will be smaller than σ_p. The relation is shown in the statistical text books to be: $\sigma_N = \frac{\sigma_p}{\sqrt{N}}$ NOTE: σ_N can not be reduced without limit as this relation indicates, for the stability of population upon which it rests will ultimately limit the σ_N that can be achieved. Only careful examination by experts can tell how far a station can improve its uncertainty by replication. Usually factors of three to five, i.e., 10-25 replications, are considered safe. However, replications are time consuming and costly at a busy station, and upgrading hardware to reduce σ_p may be more economical in the long run.

The dispersion curve (figure 2 or 3) with its mean, M_p, and standard deviations, σ_p or σ_N, represents what we may call self dispersion or local precision. More information is needed before any statement can be made about accuracy.

E. Accuracy

Accuracy is a term loosely used in many instances and often incorrectly used. To avoid possible confusion, we digress briefly to indicate the meaning of the term as used here.

The term accuracy presumes that there is a "right" or correct answer for the measurement on the particular measurand, and that the mean of a large number of replications would converge upon this correct answer as N grows larger and larger. Except in special situations* where the measurand comes with a tag giving the "correct" answer, this correct answer is not known. We seek to find it by making the measurements. Differences between a measurement and the "correct" value are no longer uncertainties, they are errors, and strictly speaking the term error should be used only where the correct value is known.

It is tempting to say that M_p for large N ($N \longrightarrow \infty$) is the correct answer, but even a small amount of consideration quickly shows what a shaky assumption this can be. If the

---

*While special, they are very important. Where a station receives a tagged measurand, such as an SRM, to be used to check out its local process and hardware the "correct" answer is that shown on the tag. It is assumed that the station that made the measurement shown on the tag met all the criteria for meaningfulness and that the tag value is to be trusted to be within stated limits.

hardware is not suitable for the job, or if it is so coupled to the measurand that the value presented for measurement is changed by the presence of the hardware (volt meter of too low internal resistance in the volt meter example), a bias is introduced that will lead to irreducible error in M_p no matter how many replications are made. Or suppose that the measurand is stated to be measured at temperature T_1, but through other hardware failures it is actually measured at T_2 where its presented value is different. A bias is again introduced.

If the operator can state with confidence that all bias has been eliminated from his measurements, he can then state that the limiting value of M_p for his station is the correct answer, in terms of the standards as maintained and realized at his station, for the physical attribute to be measured. (Remember that each act of measurement at the station includes the realization of the stated unit and a scale for the comparison with the unknown measurand.) The operator can never state absolutely that all bias has been removed. He can only say, and usually says, that the bias would not make his M_p in error by more than X percent from the correct value in terms of station standards. These bias error estimates can not usually be given in terms of a dispersion curve of error with an M and an σ. They are judgmental uncertainties for a number of interrelated parameters. History is replete with cases where important measurements have been found in error from biases far greater in magnitude than that estimated by the operator. However, we shall assume that the station operator has sufficient experience and judgment to eliminate all bias to the point where any residual is small compared with σ_N for normal station operation. This is a situation where measurement becomes a real and satisfying challenge to an operator, and meeting it can lead to a rewarding career in measurement.

On that basis, we can say, "for this station, M_p for large N represents the correct value in terms of station standards and the dispersion curve can be used as an error curve for estimating the error of any single N-fold measurement".

Why the insistence on the underlined words in terms of standards as maintained and realized at the station? Later, we shall see that a measurement accurate in terms of station standards may not be accurate in terms of other standards such as of the laboratory, region, nation, International Bureau of Weights and Measures, or in terms of the unit as conceptually defined by national or international agreement (i.e., ampere, volt, meter, second).

Now, we see that accuracy relates to a distribution of errors with respect to a postulated correct answer, the correctness being related to an indicated set of standards and unit realizations. In this sense accuracy can be called associated dispersion, i.e., dispersion associated with a particular correct answer. If the standards referred to are "in error," i.e., different from another set defined as "better," then a bias is also introduced, but this bias relates only to accuracy in terms of the "better" set of units and standards. Thus, accuracy statements should be of the form, "The chances are X to 1 that the error will not exceed Y percent in terms of standards as maintained by (----) station."

We are now in a position to make statements about the precision of the station measurement process and about the accuracy of measurement in terms of standards as maintained at the station.

Using the station dispersion curve (figure 2), we may ask what factors contribute to the spread of values displayed by it. They are:

1. Measurand dispersion. The measurand itself may appear different to the instruments by virtue of inherent fluctuations, surface roughness, electrical noise, microphonics, etc. These, if random and not constant, contribute to the observed σ_p. If not, they may introduce, in addition, a bias.
2. Coupling dispersion. The coupling to the comparator may introduce random changes such as contact resistance or thermal contact variations.
3. Comparator dispersion. The comparator has finite sensitivity and possibly internal self noise that introduces jitter into the indications as a contribution to σ_p.
4. The process of realization of the unit and scale from the local standard for each measurement, itself an experimental process, has a characteristic σ of its own.

These factors, if reasonably random, combine approximately according to the expression

$$\sigma_p^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \sigma_4^2 .$$

Often, σ_1 is overlooked because in many cases it is negligible. It should be explicitly considered before discarding. Combining σ_2, σ_3, and σ_4 gives the usual instrumentation errors. A properly experienced operator watches all four and reduces the most important ones to bring σ_p to a level that meets his needs in accuracy - cost trade off.

If all of the measurements made at the station were to be used "in situ" and never used in relation to similar or related measurements at any other station the endowment of meaningfulness described thus far would suffice. A do-it-yourself-carpenter could build or repair his own home with any arbitrary ruler and tape measure to fit his parts together - provided he did not buy, by size, important items from a store or order them from a catalog. However, these isolation conditions seldom exist. We are concerned with measurements that will be used outside the station in juxtaposition with similar or related measurements throughout society. This requires that a measurement made at any station should be meaningful, to an appropriate degree, to any user in society. Hence, meaningfulness becomes a much broader term and the requisite endowment provided at the station must be much more extensive and sophisticated.

IV. System-wide Validity

Broader Meaningfulness

We may now examine meaningfulness as applied to measurements from a station that is an element of a national (or international) measurement system. Clearly, the measurements should be useful to anyone who belongs to the society the system serves, and who has both the need and capability to make proper use of them.

To be more restrictive, but more understandable, is to say: "Within normal uncertainties of measurement, the result of a measurement on any particular measurand should be the same for any qualified station within the system." This implies that, for every qualified station, the measurements are made in terms of physical quantities, in units agreed upon by all stations in the system, and in terms of national (or international) realizations of those units as national (or international) standards. Thus system meaningfulness requires accuracy in terms of system standards instead of station standards. The station must somehow relate its standards to national system-wide standards.

Before examining how this relationship can be developed, it is helpful to take a broadbrush look at how measurements are in fact used.

Our national measurement system (NMS) undertakes, through its network of cooperating stations and with the aid of its measurement infra structure (MIS), to provide a quantitative measurement basis for two major classes of measurement uses -- A. Interchangeability and B. Decisions for Action -- and to make it available in (1) Public Affairs,

(2) Commerce and Industry, and (3) Science and Engineering.

A. Interchangeability

Measurements, as indicated in figure 4, provide interchangeability, as needed, in three important kinds of undertakings.

1. Interchangeability of Parts
   Our technologically-based society is found upon mass production of materials, piece-parts, subsystems for automobiles, refrigerators, and TV sets, to name a few. Economical operation of the vast network of producers and suppliers in the automobile industry, for instance, requires that nominally identical parts must mate wherever required without being individually fitted, i.e., parts, materials, and systems must be interchangeable. (Nuts and bolts must mate whenever nominally identical mates are brought together.) This can happen only if all measurements throughout the complex of suppliers are adequately compatible. Measurement stations yield compatible measurements and are said to be compatible if they give essentially the same measurement results on essentially identical measurands. Thus compatible measurements provide interchangeability of parts and are thus necessary to an industrial-type society.
2. Interchangeability in Exchange
   Similarly, modern commerce and mass markets require compatible measurements if there are to be common agreements on prices and amounts of commodities.
3. Interchangeability of Information
   Thirdly, our science and engineering proceed upon the results of information on properties, interactions, relationships, etc., carefully and quantitatively measured and recorded. If the information, so generated, in one laboratory is to be useful in any other laboratory both must make compatible measurements. (Also accurate measurements in terms of defined coherent units as explained later.) Thus compatible measurements make the discoveries of one available to all, and permit the progress in science and technology required to fulfill the goals of society.

B. Decisions for Action

In much of our social activity, measurements are not recorded and used to tag parts or to fill scientific reports. They are made and "consumed on the spot," so to speak, to make decisions for action. Figure 5 shows in one limited but striking area this aspect of measurement for decision.

The "weather persons" measure the air characteristics to plan and prepare for a flight or to change it, in course. Decisions on course, speed, and altitude are based upon weather data. Performance of the aircraft is displayed by flight instruments, which measure and report on many performance parameters such as air speed, engine temperature, fuel flow, hydraulic pressure, air temperature, altitude, and ground speed, to name a few. The consequences of lack of compatibility between ground station measurement, aircraft station measurements, and engineering and design measurements are obvious. Measurements-for-decision affect all of us in day-to-day living, ranging from the sophisticated, like (a) the air system indicated, (b) how much antibiotic to take, or (c) following the status of the unconscious patient on the operating table to the simple like (d) a glance at the thermometer to decide what clothing to wear, or (e) a glance at a clock to see if it is time to leave for work.

Compatibility of all the measurements (to the required and proper degree) is essential if they are to be useful. All of us have come to depend upon our measurement system to provide this essential compatibility. Where it does not, through failure, ignorance, or plain sloppiness, we suffer, at the least, frustration and, at worst, severe hardship, even death. Clearly then a most important ingredient for meaningfulness of a measurement is its endowment of compatibility. How does this endowment come about?

C. Acquisition of Compatibility

Consider the case of a measurement station that has progressed to the point of making measurements with a satisfactory σ_p and is adequately accurate in terms of its own station standards. It seeks to become a qualified station in the system. Figure 6 indicates this situation. The station undertakes to couple itself to the national system by establishing mutual relations with other qualified stations (QS) with the aid of the MIS.

The achievement of compatibility comes about through an exchange of measurements with the aid of the MIS so that the station standards can be adjusted to yield compatible measurements. This process or adjusting the instrumentation of an otherwise capable and functional station to yield compatible measurements is called harmonization. It is in this fundamental undertaking of harmonization that Standard Reference Materials find their main utility. Harmonization with a compatible qualified station in the system brings compatibility.

In fact mutual harmonization between any two stations will make them compatible. If either member of the pair harmonizes with another all three become compatible. This is the measurement system analog of the axion, "Things equal to the same thing are equal to each other."

Now if two stations undertake to harmonize and find that they are not already compatible one has to adjust (move over). Which one? No matter, either one will do. Generally the one with the smaller σ_p and better techniques or more experience will become master and the other will slave to it. Once the master-slave relation is established the compatibility of the slave depends upon his master.

If stations A and B harmonize with C all are compatible as in the left box of Figure 7. If stations D and E harmonize with F they also are compatible. However no member of the A-B-C clan is compatible with any member of the D-E-F clan. If C and F harmonize to each other or become slaves to G with whom they harmonize, then all, A to G, become compatible. (See the right hand box in figure 7.)

NOTE: the establishment of master-slave relations has made G the master for the entire group, and the compatibility of all measurements from the group depends on G.

Our national measurement system has grown in this way with a hierarchy of master-slave levels. Stations at one level are masters for those below and slaves for those above. This, of course, is not necessary. In principle one master would suffice with all others slaved to it. Such an arrangement is obviously impractical in a vast national system, and efficiency of operations requires the hierarchy of levels. Figure 8 shows the arrangement a little more strikingly. What it does not emphasize is the responsibility placed upon the top master. In effect he becomes top banana for the whole structure. If his standards are not stable the whole system is adrift. If he has a bias in his accuracy all stations have it. For a large network the responsibility is enormous. Fortunately, important checks and balances are at work to streamline the hierarchy and prevent disaster if the top station for any particular kind of measurement goes astray.

One of the interesting aspects of the hierarchy is a tradition that has grown into it. Namely each master station should have its σ_p about 3 to 10 fold better than all its slaves. This eases the harmonization process but, for a multiplicity of levels, places fantastic requirements on the σ_p for the top master station.

We call a system that has all stations compatible by virtue of a structure of master-slave relationships a compatibility coupled system. This implies other kinds of coupling.

Later we will see another. One of the virtues of a compatibly coupled system is that any new member that becomes compatible with some already qualified member station is immediately compatible with all other qualified stations in the system (at the same level of uncertainty of measurement).

Harmonization, the essential process of acquiring compatibility, can be achieved in several ways. Each has its own advantages and disadvantages and each is used. We shall explain them generally in relation to each other and specifically as individuals so that the importance of SRM's can be more readily understood in perspective.

Table 3. Modes of Harmonization

- Mutual
  - Active (SRT, SRM)
  - Passive (Calibration)
- Absolute (self)
  - Definition - Recipe
  - Standard Reference Data

Table 3 gives a classification of the modes. The most common is mutual harmonization. Two stations measure the same measurand and then after elimination of errors or biases by careful consideration they adjust their instrumentation to yield identical results (except for statistical uncertainties). This mutual undertaking can be approached in two ways. Station one can ship its instrumentation to station 2 (the master) and have station 2 use both sets of instrumentation to measure the same measurand and then adjust the equipment from 1 to agree with 2. Station two then returns equipment 1 to station 1 with a certificate indicating what was done. As far as station 1 is concerned the process is passive. Station 2 does all the work. This passive harmonization is called calibration and we say station 2 calibrated the instruments of station 1.

Figure 9 illustrates the process for a master and four slaves. There is also an active form of mutual harmonization. In this case station 2 measures a top quality stable measurand and sends it to station 1 with a tag carrying the results of the station 2 measurement. Station 1 then measures the measurand and compares its results with the tag. Station 1 adjusts its own instrumentation to bring the harmonization agreement. In this active process station 1 does most of the work and makes its own adjustment. A frequent refinement is to return the moving measurand to station 2 for recheck to see if it changed during the process. The measurands exchanged can be things, such as gauge blocks or weights, or they can be substances such as melting point substances, standard alloys, or chemicals. Thus we see that SRM's are, to put it succinctly, measurands, of the substance category, to be used in the active harmonization process to bring compatibility. Figure 10 illustrates this active harmonization with SRM's.

The other fundamental approach to harmonization is not a mutual undertaking at all. We shall call it absolute (or self) harmonization. In this case station 1 (no need for a station 2) works from first principles, starting with the definition of the unit, realizing it in terms of the stated procedures included in the definition, and using this unit as the station standard. The accuracy of the station measurements would then be expressed in terms of units realized independently by the station from the accepted definition. Measurements from any other station, whose local units are realized by absolute harmonization, will be automatically compatible with those from station 1 to the accuracy of each realization. Neither instrumentation nor measurands are exchanged. Only numerical information flows between stations. A set of stations absolutely harmonized are said to be accuracy coupled as opposed to compatibility coupled.

The use of standard reference data for absolute harmonization will be discussed later.

V. Mutual Harmonization

A. Statistical Approximations

Let σ_{p_1} and σ_{p_2} represent the local station precision for stations 1 and 2, respectively, as based upon a large number of measurements. Suppose station 1 measures the transfer measurand with N_1 replications and computes the mean value as M_1. Station 2 does likewise getting N_2 and M_2; N_2 need not be the same as N_1. We observe the difference D in the means M_1 and M_2. Replication of this procedure a large number of times will give dispersion curves of M_1, M_2, and D having:

$$\sigma_{M_1} = \frac{\sigma_{p_1}}{\sqrt{N_1}} \qquad (1)$$

$$\sigma_{M_2} = \frac{\sigma_{p_2}}{\sqrt{N_2}} \qquad (2)$$

$$\sigma_{D_{12}} = \sqrt{\frac{\sigma_{p_1}^2}{N_1} + \frac{\sigma_{p_2}^2}{N_2}} \qquad (3)$$

In any given harmonization undertaking, the dispersion of D's is not usually measured; it is inferred from equation 3.

What can be said about the dispersion curve at station 1 for subsequent N-fold measurements? If station 1 corrects its M_1 by the amount D taken from the two N-fold measurements (N_1 and N_2), the new dispersion curve to be used has $M = M_1 + D$. Since there is no way of knowing which of the possible D's was actually observed, we must merge the uncertainty of the D's into the σ_{M_1} to get:

$$\sigma_M = \sqrt{\frac{\sigma_{p_1}^{\ 2}}{N_1} + \sigma_{D_{12}}^{\ 2}} \qquad (4)$$

$$= \sqrt{\frac{2\sigma_{p_1}^{\ 2}}{N_1} + \frac{\sigma_{p_2}^{\ 2}}{N_2}} \qquad (5)$$

This approximation will serve our needs. Statistical textbooks should be consulted if more precise expressions are required. NOTE: the dispersion for the single N-fold measurement has had its variance increased by a factor of 2 due to the spread in differences D as well as in M_1. If station 2 had $N_2 = N_1$ and $\sigma_{p_2} = \sigma_{p_1}$ then the variance would be increased 3-fold. Three times as many replications would be needed to achieve the same dispersion. However, if

$\sigma_{p_2} = \frac{\sigma_{p_1}}{3}$, then for similar N's the uncertainties depend

mostly upon σ_{p_1} and N_1. Thus, we see why it helps to have the master station better than the slave by about a factor of three. This harmonization process has not lowered the quality of the station with the apparent increase in σ_M over σ_{p_1}. Its σ_p has not changed with respect to its own local standards, nor has its accuracy statements in terms of local standards. The greater uncertainty comes when the station makes accuracy statements in terms of the standards maintained and realized at the master station. Thus compatibility has a price; i.e., a loss of accuracy in terms of master standards, unless care is exercised to improve local precision to compensate.

If similar equations included a third station to which station 2 was slaved and a fourth to which 3 was slaved, and if the 3-fold improvement in σ_p were observed at each level, then the uncertainty in terms of upper level standards would depend mostly upon σ_p at the local level, a little bit on σ_p at the next level, and practically none on σ_p's of higher levels.

As harmonization proceeds upward, the lowest level station can make accuracy statements in terms of standards maintained at any level above it as far as harmonization has proceeded. This chain of harmonization upward to national standards is what is meant by the term "traceability." Lower level stations that are harmonized, hence compatible with a master station, are automatically compatible. No mutual harmonization is required between the lower level stations.

A compatible system of stations derived from the mutual harmonization process may be characterized by a single top station with a (national, international) system prototype standard for each measurement quantity. There is no higher station to refer to, and as long as harmonization is maintained on a current basis elsewhere in the structure, the whole structure is locked to the top station and moves with it if it drifts or allows biases to creep in.

Several top stations could be all mutually harmonized; but if differences develop, arguments arise about who is master and who is slave. Until resolved, the system breaks down into a noncompatible set of subsystems, each compatible within its own chain of couplings. Arrangements by which top stations agree to shift to a common value to provide full compatibility, in effect, provide a form of a top prototype standard, even though it may not exist as a real physical entity.

The decision to use the active or passive mode depends upon other factors such as trade-offs between cost, convenience, stability of results, quality of results, feasibility in a given case, the nature of the measurement to be made, the technological state-of-the-art, speed of operations, skills required, and the timeliness of the results.

However accomplished, the acquisition and maintenance of compatibility among all stations of the system confers upon the measurements of any qualified station an endowment of meaningfulness that allows them to be used with confidence and validity throughout the entire system. There is no magic about becoming a qualified station. An individual using a speedometer to control speed becomes one so long as the speedometer remains compatible with those of some other station such as the local police station. If the compatibility is not maintained, the consequences are obvious.

Turning from the considerations common to both modes it is helpful to examine briefly a few of the specifics related to each mode.

B. Passive Harmonization (Calibration)

This is perhaps the most commonly used mode. Manufacturers produce instruments, harmonize them to their station, as a master, and ship them to the slave stations with certificates of calibration, and statements about their σ_p and expectations of stability. The slave station uses them to make measurements accurate in terms of the standards as maintained by the manufacturer initially and then as maintained by the instrument itself until harmonized again at some later date. Faith must be placed in the stability of the instrument and in the manufacturer's claims about his calibration service and how often calibration must be repeated. For vast areas of practical measurement this has worked out well as an economical, practical approach to maintaining compatibility.

The obvious flaw is that the local station operator had no part in the harmonization process and he may unknowingly be introducing bias through improper use or care of the instruments. There is no feedback until some consequence, trivial to serious, emerges to let him know something is wrong. Suppose, however, as a safety precaution he had a set of stable measurands labelled with the "right" answer. He could measure them as necessary to insure that his own station was in measurement control. But this is active harmonization, which will be discussed shortly.

One consequence of the open-loop nature of the passive mode as compared to the closed-loop characteristic of the active mode, has been, in many cases, the failure to detect station incompetence. Certificates of calibration do not carry any guarantee that station measurements will be properly compatible. They only indicate that the staff at the master station adjusted them to give compatible measurements at the master station. Incompetent slave station operators have been known to point to calibration certificates as proof of validity of local measurements. As bad as this sounds, it must also be noted that a vast portion of our national system works in the open-loop passive mode and does quite well.

C. Active Harmonization

We have seen how closing the loop by giving the local station some labelled measurands to measure can prevent loss of compatibility and insure an endowment of meaningfulness. Given these measurands tagged with the result of a compatible measurement, it is not necessary to use the passive mode at all. The station can measure them and make its own local adjustments to become compatible. In this case, the compatibility is with the station that measured the measurand and labelled it.

In this mode, possible slave station incompetence is not by-passed. The operators at both stations are involved. Those at the master station must make sure that the labels put on the measurands are valid and compatible, i.e., come with the fullest endowment of meaningfulness that the master station can provide. Those at the slave station must measure and adjust repetitively until compatibility is achieved and maintained. Occasional re-referral to the measurand should keep the station in control if the measurand is stable.

In this active mode a third entity has been introduced in addition to the two sets of instrumentation -- master and slave. It is the transported measurand. We shall call it a harmonization device (HD). HD's can be substances, things, transfer instruments, or even publications.

Substances used because of their unique, carefully measured, stable properties to harmonize instrumentation used for the measurement of those properties are called Standard Reference Materials.

Things that have critical, but stable, parameters carefully measured can be used to harmonize local slave instruments for measuring the same physical quantity. These "thing-type" HD's can be called standard reference things. More commonly they are given specific names like gauge blocks for length measurement; standard masses or calibration weights, for mass measurement; standard resistances, for resistance measurement; standard cells, for voltage measurement; and so on for a great variety of things.

It is even possible for a small factory making piece parts to harmonize its stations by the use of the same kind of piece parts. It can acquire some from another factory, which has compatible stations, and use them as HD's for active harmonization of its own stations. This requires that the parts come carrying tags indicating the results of measurements made upon them. Alternatively, the factory can send some of its own parts away to be measured at some adequately compatible station and returned to serve as HD's.

Another useful HD is the standard transfer instrument. In this case the master station ships an instrument to the local station. The local station uses it along with its own instrument to measure any convenient measurand and then harmonizes its own instrument to agree with the standard one. This is just the reverse of passive calibration. Instead of adjusting the instrument shipped to it, the station recognizes the standard instrument to be master and harmonizes itself. Until very recent times gravimeters were calibrated by transfer instruments (pendulums) to establish the gravity station network over portions of the earth.

Finally, there is the HD called Standard Reference Data (SRD). These are published values of careful measurements of physical constants of nature or properties of materials that have been well characterized. In principle, any station can measure the physical constants, compare its results with the published values, and make the necessary adjustments to achieve compatibility. Or it can obtain some material for which values are published, characterize it according to published instructions, remeasure the properties, and adjust station instrumentation for compatibility, with the station that made the published measurements.

Since we are concerned with SRM's we shall not discuss the other HD's further, with one exception. We shall need to examine SRD again with respect to the stability of the overall measurement system that SRM's can then propagate.

To return to SRM's. This HD has great importance for our national system, even for the international one. Much of its potential remains to be utilized although much has already been done. In a large national system, it is clearly evident that we could, by proper use of SRM's, reduce the number of levels in the hierarchy of harmonization very greatly. One master station can, in principle, make a large number of nominally identical measurands, broadcast them to many, if not all, of the stations in the system, and be one master controlling a multitude of slaves. Thus we see the possibility of horizontal harmonization throughout the system with marked reduction in levels of the hierarchy. This in turn brings top level accuracy close to all local stations. Difficulties are evident. No one station could measure all the necessary HD's even if enough could be produced. A few measurands cannot be shipped everywhere and survive the wear and tear. Also, a great many eggs are placed in one basket with one station handling a multitude of measurements. Finally, not all kinds of measurement are amenable to SRM-type harmonization.

One evident solution is large scale production of the SRM. It is then divided into essentially identical measurands, and measurements are made on a sampling basis to determine the dispersion curve for the batch of pieces. This simplification comes at a price. The slave station is no longer informed of the measurements on its piece. This introduces a third component in the uncertainty in the harmonization process. If the sample spread can be kept small with respect to station σ_p's no harm is done. If it is comparable with the σ_p's then the spread goes from $\sqrt{\frac{2\sigma_p}{N}}$ to something like $\sqrt{\frac{3\sigma_p}{N}}$, Figure 11 is illustrative.

In addition to the compression of levels in the hierarchy, with attendant relief of strain from fabulous accuracy at the top station, the active mode brings other significant advantages.

As we have seen, perhaps the most important one is the closed-loop nature of the process. It includes local station personnel in the harmonization process. Incompetence is much more easily detected and the tendency to "kid one's self" about the state of measurement control of the station is reduced.

In addition, SRM's in many instances appear to be inherently stable HD's, much less prone to damage by shipment than things or instruments. To the extent that this is true, and where it is true, they provide means for monitoring and holding stable the compatibility of the stations linked by them. The significant advances in measurement quality among the relatively new medical measurement laboratories attest well to the potential of active harmonization by SRM's.

D. Properties of Compatibility Coupled Measurement System

The various modes and devices for harmonization are all designed to provide compatibility of measurement throughout the entire system. When all stations achieve compatibility, the chain is complete and we speak of accuracy in terms of national prototype standards. We can also speak of accuracy in terms of national or international realizations of defined units, or we can speak of accuracy in terms of the defined units themselves. If the top standards reflect these other accuracies, so also will the entire compatible network to the extent that compatibility is achieved.

As a review, the properties of a compatibility coupled system that have emerged are:

1. Compatibility with any station in a system brings compatibility with the rest of the system.
2. The top standards become responsible for the whole structure.
3. Accuracy in terms of top national standards is a form of national precision which must be related to defined units.
4. Real accuracy injected at any station propagates throughout the system (within statistical uncertainties).

5. Stability maintained at any station can detect system frift-in-time.
6. Compatibility is often easier to come by than accuracy (this emerges later).

E. Review of SRM's

In the light of what has been said, we can answer the question: "How do SRM's enrich the endowment of meaningfulness to station measurements?"

They provide: compatibility, stability, check on station performance, close ties to the NMS, extensive horizontal coupling, accuracy, economy, and validity-confidence-integrity; if the producer-supplier of the SRM's lives up to his obligations and responsibilities. That is, if he can honestly make the following statements.

1. "I know my compatibility and the standards with which I am compatible."
2. "I know how to measure."
3. "I made the measurements correctly."
4. "I kept the spread of my SRM's within guaranteed amounts.
5. "I am sure of their guaranteed stability."
6. "I realize all that depends upon the job I did. You can trust me. 'I'm the man to take the blame - (R. Kipling).'"

That is a mighty sobering responsibility for a producer-supplier to live up to and to guarantee. In this day of too much double talk, we must emphasize, "In measurement, double talk will not hide or absolve errors -- parts will not fit, patients will suffer or die, planes will crash, bridges will fall."

The producer must be sure of his measurement status and product status, and he must understand the system.

VI. Absolute Harmonization - Accuracy

We have already seen how mutual harmonization, if carefully and properly done, can couple a structure of measurement stations together so that each can make accuracy statements in terms of the others or in terms of national standards. Since all slave stations are then controlled by the top standard, the responsibility for full endowment of meaningfulness to all measurements gets placed squarely on the top station, which maintains the national standards.

Does it follow, then, that the rest of the system can relax and wait upon the top station for subsequent improvement and enrichment of the meaningfulness? In principle the answer could be, "Yes." However, it turns out that ample provision and opportunity exist for all high quality stations to contribute to improvement. It also follows that any respectable producer of SRM's must have and maintain a top quality measurement station to meet his responsibilities. He should then be able to make contributions to improve the MIS and should do so.

A. Independently Realizable Units

The measurement considerations so far have not covered the selection or identification of the top standard, which determines the measurement unit (for its physical quantity), for the whole system.

The agreed upon unit represented by the standard can be completely arbitrary. The Egyptians of ancient times used the cubit, the English the inch, and the French the centimetre, and so on. So long as the unit allows practical measurements, of the time, to be expressed in commonly understood and easily grasped numerical magnitude, like tenth, quarter, half, one, five, ten, one hundred, or several thousand there is little basis for choice among them. Units that require the ordinary person to handle magnitudes in the millions, billions, or millionths for everyday transactions find little acceptance, and this convenience seems to be a major factor determining the size of the unit. Once set however, and when use has become widespread, change to a different unit becomes a serious undertaking, because of all the extensive associated changes that must be made in records, machines, and instruments. The present difficulties in changing to the Metric System in the United States reflect this. There is nothing magic that makes a meter better than a yard for length measurements. It depends on the magnitude of vested interests and emotions linked to each.

While recognizing that the selection of the unit is an arbitrary choice, it was believed from early times that independent realization of the unit is highly desirable. Hence the definition of the cubit as the length of the Pharaoh's forearm or the inch by a number of barley corns laid in a row. The considerations of stability that become apparent as compatibility extends throughout a measurement system brought pressure to insure that these arbitrary definitions of the unit should not be capricious or subject to change from time to time as rulers or weather patterns changed. This was accomplished in early cases by realizing the definition in the form of a physical standard and then dropping the original definition and declaring the standard to be the unit thenceforth. Such standards that lose their independent reproducibility are called prototype standards. Until recent times, national and international standards for mass and length were of this kind, and all compatible measurements with respect to them can make valid accuracy statements in terms of them.

As science, industry, and technology grew and the dependence upon stability of the prototype standards became increasingly important, concern for their stability grew apace. Metrologists began to search for ways to define the units of measure in terms of some immutable properties of nature such as wavelengths of light, natural frequencies of atoms, or masses of nuclei. In the case of length and time-frequency, suitable definitions have been found and adopted -- length in terms of the wavelength of the red radiation of Kr atoms, and the second in terms of the hyperfine vibrations of Cs atoms.

For us the details are not so important. The principle has extensive repercussions. Once we express the agreed upon unit in terms of a recipe instead of a prototype standard then it becomes possible, in principle, for any measurement station to realize the unit in terms of the definition, and harmonize its own instruments with it. The station measurements must then be automatically compatible with those from all other stations based upon the same unit. No mutual comparisons are required and we call the harmonization absolute; and we call the units defined in this way independently realizable units.

NOTE: The realization of the unit at any station in an experiment. As always, experimental uncertainties are present, and these uncertainties must be reflected in the accuracy statements made by the station. Thus a station may say that the accuracy of a measurement in terms of the station standards is X $\pm$ δ but in terms of the defined unit is Y $\pm$ ε.

This introduces a new situation. Suppose several stations make independent realization of the unit as defined, and then undertake mutual harmonization. They may well find that they can make compatible measurements to say, δ uncertainty, if they agree upon one realization to use, but can make compatible measurements to only ε uncertainty if each station uses absolute harmonization. This situation can and does happen. It is usually resolved by leaving the independent realization of the units to a top national standards measurement station, and using mutual harmonization to provide compatibility coupling throughout the system. This is done when absolute harmonization leads to uncertainties greater than mutual harmonization permits or greater than the particular measurement requirement can tolerate. In this country numerous stations now realize the inch or centimeter with absolute harmonization and adequate accuracy for their purposes.

A careful measurement station must however indicate in connection with its accuracy statements, what the statements are in terms of. NBS stations make it clear that their accuracy statements are in terms of standards as realized and maintained at NBS or in terms of the defined unit. [For example voltage measurements may be stated to be accurate to one part in 10^7 in terms of the standard volt as maintained at NBS or accurate to five parts in 10^6 in terms of the volt (as defined).

Why then have these independently realizable definitions? The answer is clear. We can reassure ourselves that our top standards are not adrift by more than the errors associated with the absolute realizations. At the same time, the system can go ahead to take advantage of mutual harmonization wherever compatibility requirements exceed the capabilities of absolute harmonization in terms of the defined units.

B. Base and Derived Unit

The arbitrariness in the selection of the unit of measure extends to every physical quantity of interest. Each could be treated in the manner already described. But if we did so, we would find that the system of units and measures that resulted would loose much of its potential efficiency and practical usefulness. In addition to its obvious utility in commercial transactions and in the manufacture of piece parts for devices and appliances, measurement emerges as an indispensable tool in the development of the science and engineering, which form the basis of our complex technologically based society.

When we study science, we find that there are valuable and useful relationships among the units of measure. For example, among the physical quantities length, time, speed, and acceleration, we find the relations expressed by the equations: $L = K1\ S\ T$; $S = K2\ A\ T$. Here L stands for distance measured in length units, S stands for speed, T stands for time, and A for acceleration. The constants K1 and K2 are numbers inserted to make the equations true equations instead of proportionalities. Consider in more detail the first equation. Suppose, for the experiments that led to the formulation of the equation, we measured L in miles, T in hours, and S in Knots. Then K1 would be 0.87. But if we had instead measured L in nautical miles, we would have found $K1 = 1$.

For some other units we could make a table like table 4.

Table 4

L	S	T	K
mi	knot	hr	0.87
km	knot	hr	0.54
mi	mi/hr	hr	1.00*
mi	km/hr	hr	0.62*
km	km/hr	hr	1.00*
naut mi	knot	hr	1.00*

For any set of units selected, the experiments will show that there is a particular value of K_1 that will make the equation $L = K_1 S T$ a valid equation representative of the real world of physics. Table 4 could be greatly extended, but it serves to illustrate the point. For those with an asterisk, the value of K_1 is unity and the physical equation takes the form: $L = S T$, with no K_1 to remember. If we pick the units for any two of the three quantities and wish to have $K_1 = 1$, then the unit for the third quantity is determined.

We could produce a similar table and argument for the quantity A that relates to S and T in the second equation and arrange for $K_2 = 1$. Now among the four quantities: L, T, S, and A, we can pick two and, by putting $K_1 = K_2 = 1$, determine the other two. If we defined the units for L and T in an independently reproducible way, these two equations could serve to provide the basis for independently reproducible definitions for units S and A. These units for S and A would depend upon the actual numerical values used in the definition of the units for L and T. In this situation, the defined units for L and T are called base units, the units for S and A are called derived units, and we say that all four units are coherent. They are coherent with the two equation of physics: $L = S T$; $S = A T$.

Figure 12 illustrates the situation pictorially. An arrow indicates the physical equation that is injected to determine the magnitude of the unit for the physical quantity to which it points. The equations have been extended in the figure to include a fifth quantity, F (force), a sixth quantity, M (mass) -- another base unit, and a third equation to determine the unit for measurements of force: $F = M A$.

Another table, like table 4, could be made to show how we could use the three equations to set the units for F, S, and A, in an independently reproducible and coherent way once the three base units L, T, and M are set.

In fact one can proceed through all of physics adding quantities and units, and defining equations drawn from the physical equations found to represent experiments. If he does so, he will find that he has enough equations to set all but four base units. These four could be any four of all the units. Units for L, M, T, and θ (θ = Temperature) were agreed upon as base units early in the formulation of the basic ideas. Figure 13 shows a more extended picture of the relation among the units like that started in figure 12. It could be thought of as the genealogy of a coherent system of units.

Clearly a coherent system of units offers important advantages, and practical experience with a coherent system (the SI system) shows them to be very real. Among the most important are:

1. The equations of science and engineering are much simpler, easier to work with, and require no reference table of constants.
2. A coherent system can have only one unit for each quantity; for only one can be coherent. There can be many coherent systems, but in any one system this rule holds. The advantage of using only the meter instead of inch, foot, yard, rod, mile, furlong, etc., for length measurements is obvious.
3. Having only one unit in which to express all magnitudes requires some system for multiples and submultiples and leads naturally to the decimal system characteristic of SI, i.e., millimeter, centimeter, meter, kilometer, etc.
4. Compatible measurements suffice so long as the user limits himself to working with one physical quantity only (e.g., piece parts whose physical size is the only consideration). Where relations between quantities (as between mechanical and electrical quantities) are important, then the use of coherent units is a great advantage.
5. The coherent system of units requires an arbitrary, independently reproducible definition for only the base units. The equations that define the derived units also provide automatically one or more independently reproducible definitions for each new unit.

Since the United States has now been pushed into a corner with its English Customary Units and faces a period of transition to the use of SI, an understanding of the advantages of the SI system can be most helpful. In the light of the preceeding discussion of the advantages of a coherent system of units, we can say here that probably the greatest technical advantage of the SI system is that it is a coherent system. The enormous practical, as well as political, advantage is that all other major nations are using it or converting to it.

Since SRM's are intended to provide mutual harmonization by the active mode, what can we say about how they serve to enrich the endowment of meaningfulness with regard to accuracy and coherent systems of units?

First, we note that if the standards of a top station in a compatibility-coupled network are set to realize coherent units, then the stations throughout the chain will also realize coherent units. However, in a compatibility-coupled network with tight coupling, if any station makes measurements accurate in terms of the defined unit, this accuracy automatically propagates throughout the chain as soon as the top station adjusts to it via the compatibility network. It follows that any top quality station, e.g., good enough to produce high quality SRM's may find itself in a position to improve the accuracy of realization of a coherent unit. If it acts upon its opportunity, it can thereby enrich the endowment of all compatibility-coupled stations throughout the system. As the production of SRM's grows and spreads, such opportunities should become more numerous, and any dedicated sophisticated station operator should be on the alert to recognize them. Those who measure and publish standard reference data are in a similar position, but that is not a subject for this discussion.

VII. Stability

We have noted the importance of stability in a measurement system. We are now in a position to examine more explicitly how stability can be, and is, provided.

It is helpful to think of stability as affording compatibility across time. To have lasting usefulness for measurements, it is essential that measurements made upon the same measurand at different times should be compatible. This assumes that the measurand is not changing with time. But it follows that, if the measurand is not changing in time, it automatically provides the necessary basis for checking upon the stability of measurements. This makes the procedure for insuring stability of a measuring station or system sound absurdly simple. "Find some stable measurands and measure them from time to time." The trouble has been to find them.

Fortunately or unfortunately, compatibility coupling shifts the monkey up the line until it rides on the back of the top station. If his standards are stable all those harmonized with them will also be stable. In a coherent system all the derived units relate to the base units in terms of invariant definitions, so that their stability also depends, in principle and within measurement uncertainties upon the stability of the base units. Thus, it emerges that the top stations for measurement of mass, length, time, and temperature must acquire the necessary stability. If they succeed, the whole structure will endow all measurements (again in principle with due regard for measurement uncertainties) with stability in time.

As we have seen, the base units are arbitrary and can be defined in any convenient way. Now it emerges that they must be stable and that stability is a top priority consideration. Clearly the definition must not lead to a unit that fluctuates in time. Thus, the cubit and the inch as originally defined were based upon what we would consider to be improper definitions. The founding fathers of the SI system recognized this and turned to nature for stable properties around which to frame definitions. The meter was related to the circumference of the earth, the second was related to the period of the earth's rotation about its axis, the kilogram was related to a measured volume of water, and the kelvin, or degree of temperature, to the triple point of water.

The experiment to realize the meter was found to be in error; so the definition was changed to be the length that had been found and marked off on a particular platinum iridium bar. The second was good for a long time until it was learned that the period of rotation of the earth is not constant but varying about one quarter second per year. The definition of the kilogram was found wanting in its realization and was changed to be the mass of a particular platinum iridium cylinder. The triple point definition of the kelvin has met well the test of time. There was concern that the meter bar might be changing its length due to internal structural rearrangements associated with aging. There has also been concern that the surface chemistry of the standard kilogram may be changing and with it the amount of matter in the kilogram. Thus, the system emerged with base units of mass and length not defined in an independently reproducible manner and tied to physical bodies whose stability, while quite good, could not be guaranteed to within close enough limits.

There are sound scientific reasons to believe that the properties of individual atoms and molecules, of space around us, and of heavenly bodies in their orbits are stable in time or subject to predictable changes. Based upon such arguments, the international bodies concerned with measurement have redefined the base quantities of length and time in terms of atomic wave lengths and frequencies. These two are now considered to be stable until science can adduce valid reasons for doubt.

An independently reproducible definition for a stable mass unit has not yet been devised. However, recent developments at NBS in the measurement of crystal lattice spacings and densities indicate that the day for one may be near. The mass scale still depends upon an arbitrary prototype standard held at the top world station in Sevres, France. All others are harmonized with it. This should not be considered grounds for serious present concern because the stability is believed to be better than one part in one hundred million. (About the mass of ink in a single letter compared with the mass of the whole book.) Still it rankles.

The problems of stability are not settled practically, although they are in principle, once the base units and standards are stable as defined and realized by the top stations. Two main deficiencies arise.

The first is that the state-of-the-art for the realization of some of the derived units does not permit the realization to be achieved with small enough uncertainty to meet some practical compatibility requirements. In these cases the system reverts to the use of an arbitrary top standard as close to the defined unit as the state-of-the-art can recognize, and relies upon compatibility coupling. The top standard can then drift between the limits set by the uncertainties in its realization of the definition.

Here SRM's can play a key role. By finding a substance or atomic or molecular entity with invarient properties the top station can hold its measurements constants, though possibly in error, until such error can be detected and corrected. Samples of this same material can be disseminated throughout the system as SRM's to maintain compatibility and stability.

The second arises directly from the needs for harmonization to maintain stability at any local station. Experience teaches how often the equipment at any station must be checked to insure continued compatibility. If the station has at hand stable SRM's against which to check itself it can maintain its self sufficiency and stability. Experience then dictates how often new SRM's must be acquired to maintain acceptable stability. This shows how the broad practical status of every day stability for the measurement stations throughout the system is importantly dependent upon good stable SRM's, wherever they are feasible and practicable.

Fortunately nature provides a multiplicity of atoms, molecules, substances, and materials whose properties are of intense interest. These are examined in many laboratories, in many ways with ever improving equipment and techniques, as a basis for the development of science, engineering, and technology. Many of the properties thus carefully measured are believed to be time invariant. Hence their measurement and remeasurement provide, system wide, extensively redundant checks to detect any drift in the standards, units, or the compatibility coupling.

For example, the measurement of the wave length of red cadmium radiation over several decades gave evidence that the meter bar was maintaining a stable length. And today measurement of the speed of light would quickly show any drift of either the time or length units unless both drifted exactly in unison.

From one point of view, the fundamental physical constants can be thought of as natures stable measurands given to us to lock our measuring system into nature. From another they can be thought of as properties of God's perfect SRM (free space, full of radiation). Figure 14 indicates this. The fundamental constants h, m, k, and c represent the electromagnetic properties of space. But they can also determine our base units for us as shown in figure 15 in which we see the mutual relationships between the constants and the base units. For example we see that the electron mass can be used as a mass unit and the values of the constants h, m, c determine a natural length unit: $L = \frac{h}{mc}$. Both units will be many powers of 10 different from those we now use.

From such considerations it follows that arbitrary assignment of numerical values to the constants h, m, c, and k will fix the units M, L, T, and θ for a measuring system different from the one we now use. Assigning them the values we now observe experimentally will fix the units to be those in the system as it now exists.

If we should, in fact, some day establish communication with some distant civilization on another planet in this or another solar system we need only exchange values for h, m, c, and k to harmonize our measurement systems. When God said "let there be light," as chronicled in the description of creation in the Bible, He handed all civilization a perfect SRM for the establishment of a compatible intergalactic measuring system, with built in stability; one that truly provides compatibility across distance and time, and permits inclusion of coherence and accuracy.

The multitude of natural or man-made substances and materials provides a host of properties suitably invariant and isolable to serve as SRM's. When enough is known to permit precise characterization of the substance, so that any other investigator given the recipe can prepare it adequately, it can be used without being prepared and distributed as an SRM. Any top quality station can measure the properties of interest and publish the results.

Any other station can prepare the substance according to the published characterization and use it as if it were an SRM for harmonization purposes. The literature of science and engineering carries vast amounts of information on the properties of materials that in principle can be used in this way. However, to be satisfactory, enough must be known about the material so that the published characterization process, if followed, will yield a material whose properties are close enough to those of the parent material upon which the publication was based, to warrant trust in them. If so, compatible measurements are achieved; if not, the station goes astray.

Standard Reference Data (SRD) is the name given to published data on properties that are useful in this way. Much of the data of record today is not measured upon substances well enough characterized to allow their use as active harmonization means, except for stations having low compatibility requirements. However, a sizable portion of the data is of excellent quality, and the substances are readily enough characterized so that the published data is truly of measurement grade. The National Standard Reference Data System, centered at NBS, is engaged in extending this body of measurement grade data, in addition to improving the quality of the data for its many other important uses not germane to this discussion.

SRD of measurement grade becomes a serious competitor to SRM's whenever they come into direct competition. SRD puts the station on an independently reproducible basis for compatible measurements, compatible with the measurements and standards of the parent station that originally obtained and published the data. Accuracy, in terms of national standards or in terms of defined coherent units, will be as good as those of the parent station.

Since SRD must be stable, i.e., time invariant, to warrant the effort and the name, they afford a system wide redundant means for verifying and insuring measurement stability.

SRM's possess a great initial advantage. The required characterization process is much more limited. Enough must be known to insure that the measured properties are stable and the same (within statistics) for every sample of the SRM. If this is achieved, every slave station depending upon the SRM for harmonization is assured of having the same substance because it got a piece of the original.

There is no need for concern over competition between SRD and SRM's. Each finds its proper place where economic factors enter into trade offs of cost, timeliness, compatibility, and accuracy requirements. For the forseeable future there is ample need for both.

VIII. Measurement Infrastructure--MIS

We have seen how a local station can bring an endowment of meaningfulness to its measurements first by the quality of its own staff, equipment, and procedures and second by coupling itself to the national or international measurement system and the associated measurement infrastructure (MIS). Like the song "Love and Marriage" states, "You can't have one without the other." We take the first as accomplished and turn attention to the latter.

The coupling, of course, implies an interface between station and system across which information (software) and devices or substances (hardware) flow. The flow need not be unidirectional. When, however, it is all from system to station we will characterize the station as a sink station. When the station feeds the system it is serving as a source station. The implied interface we will call a tie point to the system.

From this point of view coupling to the system to acquire full endowment of meaningfulness can be described as finding a proper tie point.

The MIS is a complex, world-wide structure of institutions, establishments, metrologists, information, instrumentation, customs, procedures, and quantitative language, all in support of the measurement system to insure compatible, stable measurement stations throughout the structure. Important portions of the MIS are developed and supported by the family of nations, signatory to the Treaty of the Metre, and active in the Bureau of International Weights and Measures. Equally important portions of the MIS are maintained by those users of the MIS who develop source as well as sink characteristics. The MIS turns out to be, in an important degree, a self-expanding, self-generating structure, with stations playing dual roles, sometimes as a sink drawing upon the rest of the structure and sometimes as a source, becoming a part of the larger system to supply services to other stations, and even contributing to the general reservoir of knowledge, information, and capability.

Fortunately, in the development of the MIS the world has shown a sigular openness and freedom. Wherever the printed word can reach and transportation can provide hardware, tie points are available to those with the skill to make use of them. There is no organized arrangement to withhold vital information from any customer. And establishing compatibility with any qualified station brings instant world wide compatibility with all other qualified stations. All references to accuracy is intentionally omitted. Compatibility coupling suffices to bring to the station all the accuracy available in the MIS. If the station has need of this accuracy, it can be realized only if adequate compatibility has been established for it. If station demands for accuracy, in terms of defined units, exceed that in the MIS, the operator then moves into a special situation where he seeks to extend the state-of-the-art and becomes a leading specialist for that particular kind of measurement. He then feeds the MIS through his tie point and plays a different role in which creative invention becomes essential. Such source type contributions lead the system to its self expanding nature and are welcomed with enthusiasm.

Like the rest of technology, measurement technology has undergone rapid development, made fundamental changes, and is now moving in new directions. This movement could well be called a revolution in measurement. As is usual in times of rapid change, social institutions are slow to respond and old methods live beyond their usefulness. The MIS is no exception, continuing, as all SRM users well know, with passive modes of harmonization in the presence of active modes now available and growing. Improved SRM's are one important aspect of the revolution.

A. Characterization of Tie Points

An adequate tie point must provide to the station the capability to make compatible measurements to the levels of accuracy in terms of national standards, or defined units, to meet its needs. This must include both hardware, (instruments, SRM's or measurands) and software, (documents and information telling how to develop the capability). Ideally the tie point should offer alternative approaches suited to different levels of sophistication. Both the information and hardware should relate as closely as possible in kind and magnitude to the specific measurements to be made at the station. Describing to a station how to measure stellar distances will help little if the need is to measure the diameters of very small holes. The chain of inference to be used at the station must be kept small if the full potential of system endowment delivered to the station is to be realized. Thus, it becomes important to characterize tie points with some technical specificity about what they can supply.

B. Scale Extension

Perhaps the best parameter for the first dimension of an index of tie points is the magnitude on the scale of values at which the measurements are to be made. Once the unit for a measurement quantity has been defined and realized the scale is only begun. A chain of measurement must be established to provide national standards for compatibility coupling at all of the magnitudes needed by the system, downward from unity to 10^{-x} and upward to 10^{+x}. Figure 16 describes the process and figure 17 illustrates the spread of magnitudes involved in connection with the scale of masses from 10^{-24} kg for atomic particle masses to 10^{+24} kg for planetary masses. In the central regions, indicated by the black bar, direct measurements with smaller or larger standard masses (weights) can be used. Beyond this, indirect means involving a chain of inferences and experiments must be used. As the magnitudes get further displaced from unity the extended chain of measurements nearly always introduces more and more uncertainty. To indicate this it is helpful to use a chart that has along its abscissa a logarithmic scale of values for the measurement quantity unity in the center and running from 10^{-x} at the left to 10^{+y} at the right. The ordinate is an expression of accuracy or compatibility, with higher points indicating less uncertainty. Customarily, if the uncertainty is expressed as one-in-(x), then the increasing values up the ordinate scale represent increasing accuracy. Such charts are variously called accuracy or compatibility charts. A generalized chart of this form is shown in figure 18.

It demonstrates the typical situation that accuracy, in terms of the defined unit or in terms of the top standard representing the realization of that unit is the highest ordinate on the chart heavy curve (top). Accuracy falls off seriously at the extremes of the range. Such charts are useful for indicating other important features of the measurement system, at a particular magnitude for a particular quantity. As shown, the middle curve indicates what American industry or science need at the time of the chart. The lower curve shows what is required at the production measurement stations in industry. And the dots represent the capability of measurement stations for industrial standards laboratories. Notice that the middle "need" curve crosses the top curve of actuality on the right thus demonstrating a recognized unmet need. Segments, such as the dashes, can be used to indicate goals for existing research projects anywhere in the system. As can be seen, such charts give a very valuable picture of the state of the measurement system at any given time. Real charts of the actual situation have been made at NBS for almost all of the quantities for which national standards and dissemination systems are maintained.

Figure 19 shows a real chart for the physical quantity, length, as produced by NBS a few years ago. Figure 20 is another example for the case of the physical quantity temperature. These should be considered as illustrative for the discussion and not as a basis for any present decisions or actions. The differences in the status of the two quantities are quite marked and they reflect nearly as much about the relative nature of length and temperature measurements as about the state of the system.

Frequently, a natural physical constant (SRD) or an SRM can be found, or produced, that permits compatibility of measurement, in a limited range near a particular point on the abscissa, far in excess of the accuracy with which the point can be related to the defined unit. Masses of atomic magnitude are a case in point. The uncertainty in the measured mass of the carbon 12 nucleus in terms of the kilogram is about one part in 20,000. By defining a non-coherent atomic mass unit, such that the mass of carbon 12 in AMU is exactly twelve, compatible measurements of atomic masses can be made with modern instruments with accuracies in terms of the AMU of 1 part in 10^8 (approximately) and in terms of the kilogram to 1 part in 20,000. On the compatibility chart this situation would be represented by a small dot or short line far above the rest of the curve. On the accuracy curve (with respect to the kg there would be no such high point). An accuracy curve in terms of AMU's would show the high point. This illustrates again the importance of specifying the "in terms of" whenever making accuracy statements.

The electrical quantities such as voltage, current, resistance, impedence, capacitance and inductance pose special problems for the maker of accuracy charts. The accuracy is a function of alternating current frequency as well as measurement magnitude. These cover the range from dc through 50-60 Hz power frequencies, 30 - 30,000 Hz audio-frequencies to the upper radio frequencies of 10,000 GHz. Thus the chart should be displayed in three dimensions. The conventional approach is to give a cross section or slide at each important frequency.

Clearly no system can maintain capability at all abscissae for all quantities. A central laboratory must limit itself to the provision of tie point capability at selected important points and expect the using station to extend its own capability from the nearest tie point to meet its own needs. This means that a more realistic curve, reflecting these zones of capability, would be more like the dotted curve than the solid one shown in figure 21.

To illustrate the cases of different stations looking for a tie point to couple to the system we consider three cases P, Q, and R.

Point P on the curve as an example, is representative of a tie-point to the MIS showing that compatibility of 1 in 10^4 can be attained for measurements in the vicinity of magnitude 10^2.

A point such as Q represents a tie-point to the MIS where compatibility 1 in 10^3 is available at a magnitude 10^{-1}. It also represents the important case of a tie-point providing less than maximum state-of-the-art capability presumably with cheaper instrumentation and skill requirements on the part of the user. A tie-point such as Q could be a great help to an emerging establishment whose activities do not require the best there is. Q points are thus of significant importance in the practical, efficient, economical use of the MIS. Such less-than-best capability is commonly found at the secondary and lower echelons of a passive transfer MIS. In an active transfer, MIS Q points are characteristic of SRM's with more of a spread in values.

R point represents a tie-point reflecting needs beyond the present state-of-the-art. It is not a real point since capability indicated by it does not exist and cannot flow across the interface. Any station searching the MIS for this tie-point will find none. If the need is real and important enough, the station must undertake to develop the capability itself and become a source to the MIS or encourage some other more sophisticated station to undertake the improvement. NOTE: This compatibility chart provides a convenient indexing scheme for referencing tie-points. The need for measurement strikes the user as a need for compatibility or accuracy (α) at a range point (β) for a physical quantity (θ) like Q point in figure 21.

A user turns to the MIS and seeks a tie-point having capability α, at β for θ. If he looks in a catalog of tie-points (one does not yet exist) under coordinates $\alpha\beta\theta$, he hopes to find:

1. Names and locations of institutions that can provide the capability.
2. Indication of kinds of transfer available:
    a. Passive.

   b. Active - Kind of harmonization devices, SRM's, SRD, or SRT, available; and where to get them at what cost.

3. Reference to "how-to" documents. A document for each kind of transfer available at the tie-point, which shows how to establish compatible measurements with that transfer mechanism.
4. Other information that experience indicated to be valuable.

A code word for each $\alpha\beta\theta$ could indicate the essence of the service available at the tie-point.

The specification of a complete tie-point can now be given. It is one characterized by an $\alpha\beta\theta$ and meeting requirements 1 to 4. For the special case of the electrical quantities, an additional coordinate Hz (the frequency at which the measurement must be made) is added.

It would be great if such a lexicon were in existence at some central place for worldwide reference and use. But it does not yet exist. Although some parts are available at NBS and other national standards laboratories. Other parts exist throughout the system in uncataloged form, but nonetheless available to those who somehow learn of their existence.

In any case it becomes clear that a measurement station seeking to establish a particular competence should delineate carefully the quantities, magnitudes, and accuracies or compatibilities it honestly and practically requires. It should then turn to the nearest convenient station of the system for assistance in learning where to probe the system to get the necessary information on the state-of-the-art relative to capabilities and costs. When at a loss where to start, a letter to the NBS Office of Measurement Services will bring all the known pertinent information.

C. SRM's and MIS

It should now be quite evident that the SRM producer is an important component of the MIS. His associated measurement station, which must be of top quality, may well be of the sink type. But, in total, the SRM laboratory is a net source element providing tie-point capability for quantity θ at abscissa β for ordinate α; and, as we have seen, carries great responsibilities for accuracy, reproducibility, and stability. It should also provide software on how to use SRM's to best effect and how to avoid pitfalls. The software should also include explicit statements giving clearly and honestly the information on compatibility, accuracy, reproducibility, and stability that can realistically be attained by the proper use of the SRM's.

We emphasize finally that:

1. Any station in a measurement system that becomes compatible with any qualified station in the system becomes compatible with the whole system (statistics considered).
2. Any compatible station that can improve accuracy in terms of defined units provides that accuracy to the whole system.
3. Any station can be a source of improvement to the MIS and become a source station.

The self-generating nature of the MIS is one of its most inviting characteristics for it can, by its own self-improvements evolve to meet the developing needs of all elements of the national measurement system.

IX. Recapitulation

As we are mainly concerned with SRM's let us briefly summarize what SRM's contribute to the MIS. This will be a measure of their contribution to the endowment of meaningfulness for measurements of any capable, qualified measurement station. The contributions include:

1. Active harmonization devices.
2. Proof of station competence.
3. Compatibility with the coherent units.
4. Transfer of accuracy.
5. Help in the maintenance of stability.
6. Providing horizontal coupling to reduce the levels of the compatibility hierarchy.
7. Rapid inexpensive means for automatic process control.
8. Measurement results in real time to meet practical requirements for timeliness.

These contributions accrue if the SRM producer meets these requirements:

1. His station is in and is kept in measurement control at an adequate level.
2. The materials are properly characterized.
3. Their stability is verified and assured.
4. The sample dispersion is properly controlled and measured.
5. Nondamaging distribution means are provided.
6. Adequate "how to" software accompanies the SRM.
7. Unambiguous statements of accuracy, compatibility, stability, dispersion, are included in software.

We may say in conclusion that SRM's are and can continue to be an ever growing important asset of the MIS -- provided the producers fully realize how much depends upon their process integrity and that they fully meet the challenge this presents.

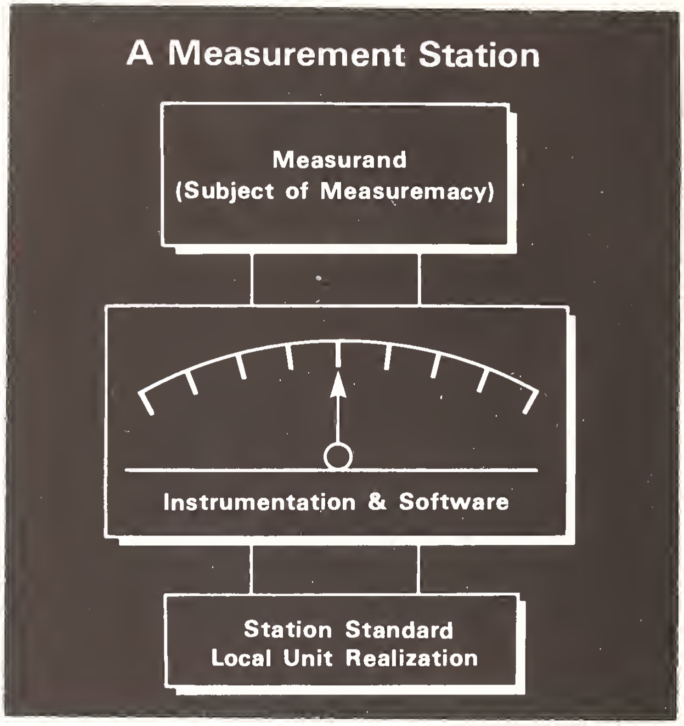


Figure 1. A Measurement System

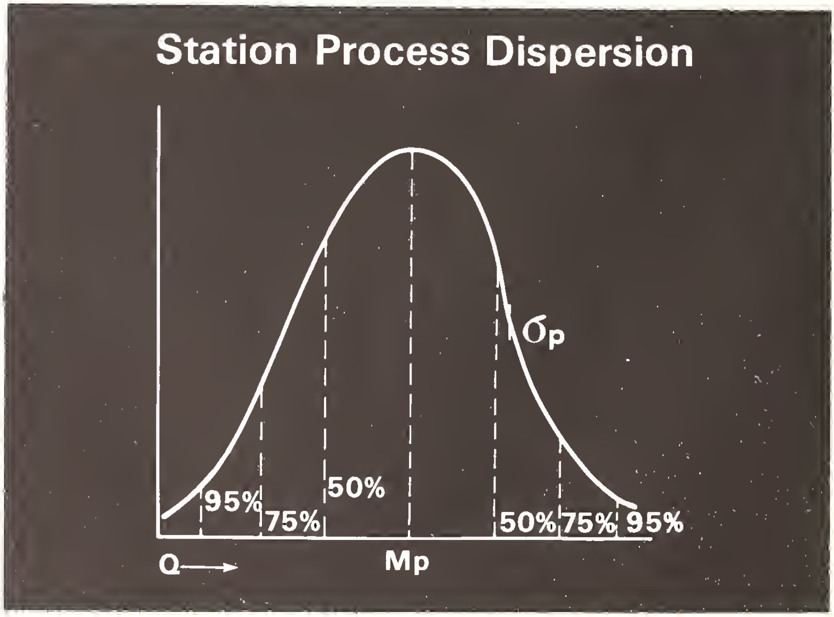
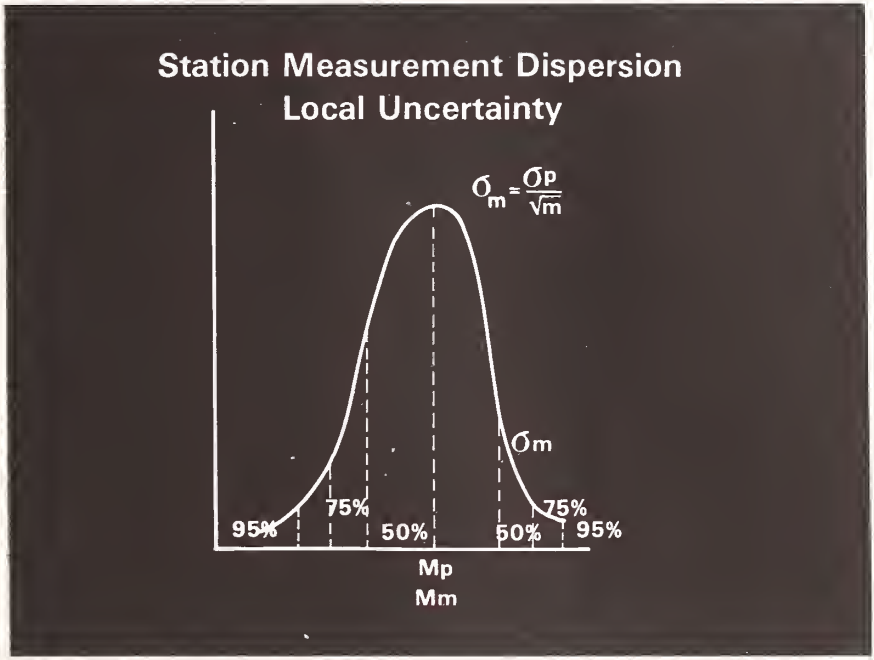
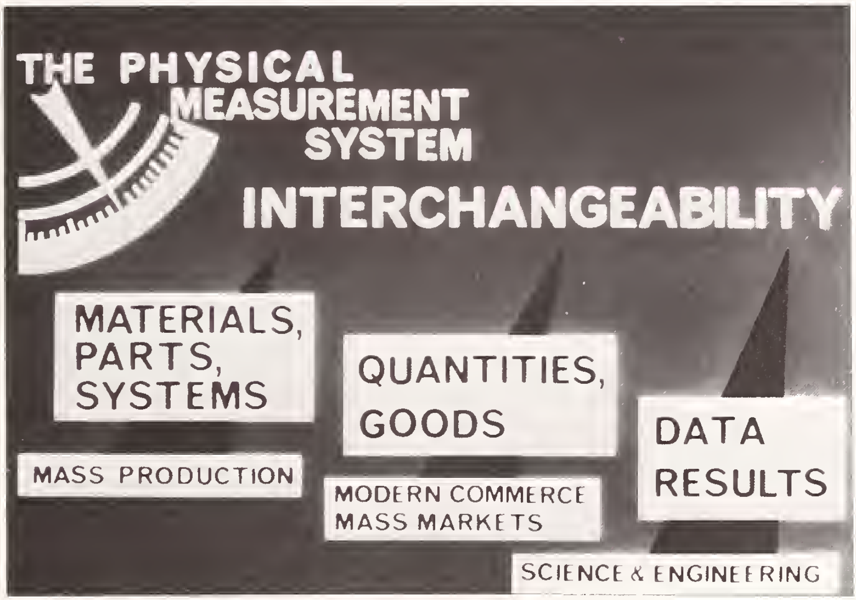


Figure 2. Station Process Dispersion



Station Measurement Dispersion
Local Uncertainty

Figure 3. Station Measurement Dispersion Local Uncertainty



THE PHYSICAL MEASUREMENT SYSTEM

INTERCHANGEABILITY

MATERIALS, PARTS, SYSTEMS

MASS PRODUCTION

QUANTITIES, GOODS

MODERN COMMERCE
MASS MARKETS

DATA RESULTS

SCIENCE & ENGINEERING

Figure 4. The Physical Measurement System Interchangeability

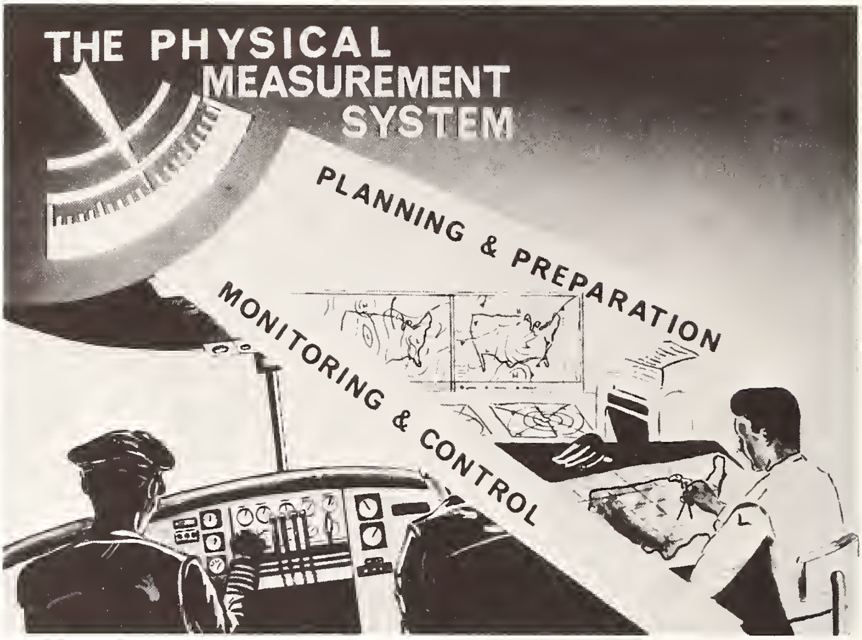
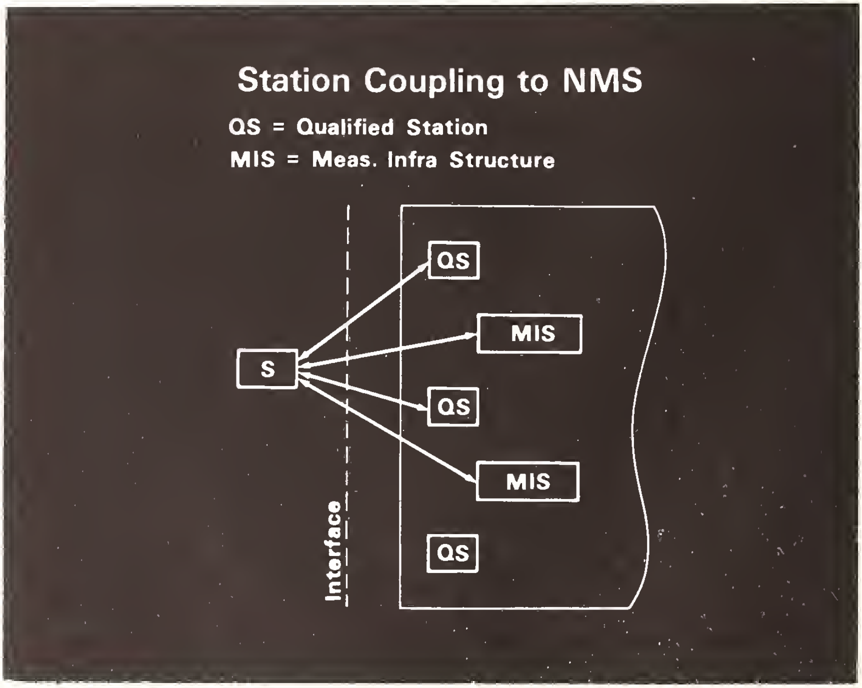


Figure 5. The Physical Measurement System



Station Coupling to NMS

QS = Qualified Station
MIS = Meas. Infra Structure

Figure 6. Station Coupling to NMS; QS = Qualified Station, MIS = Meas. Infra Structure

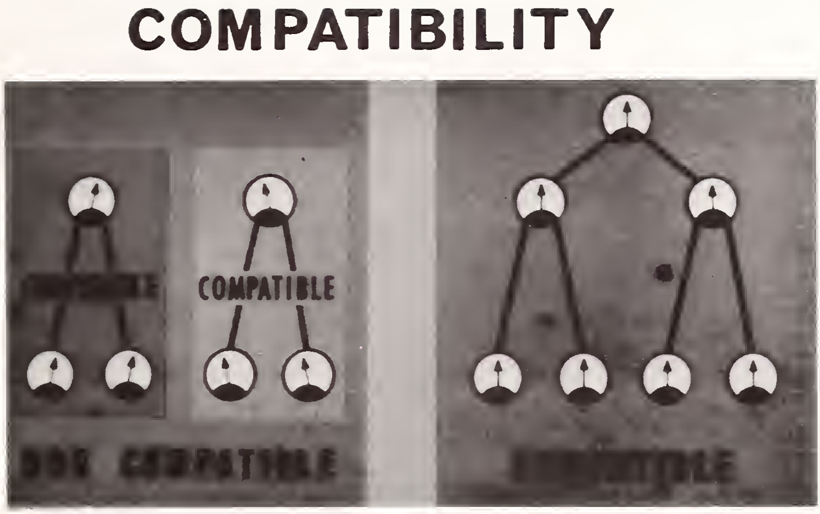


Figure 7. Compatibility

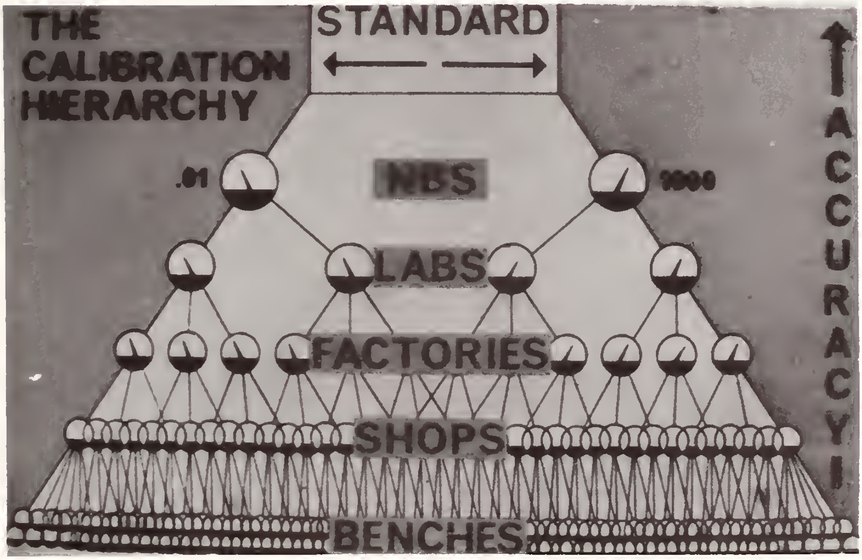


Figure 8. The Calibration Hierarchy

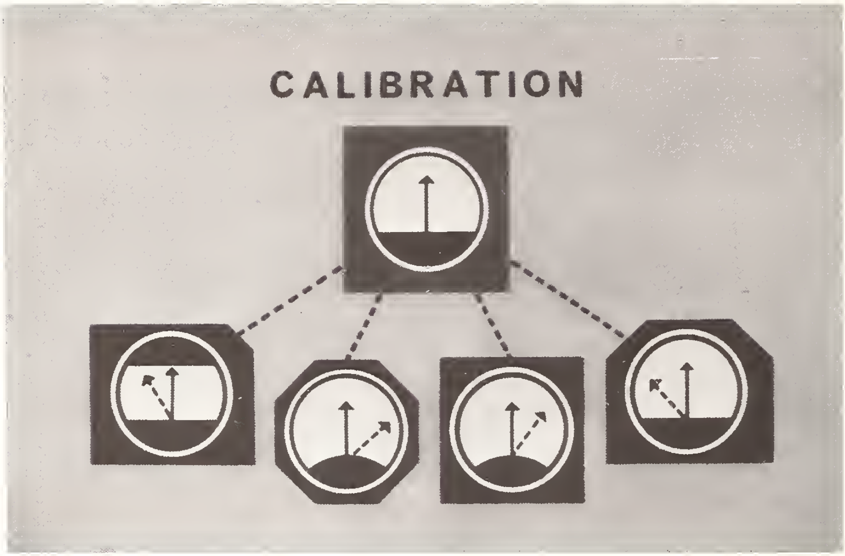


Figure 9. Calibration

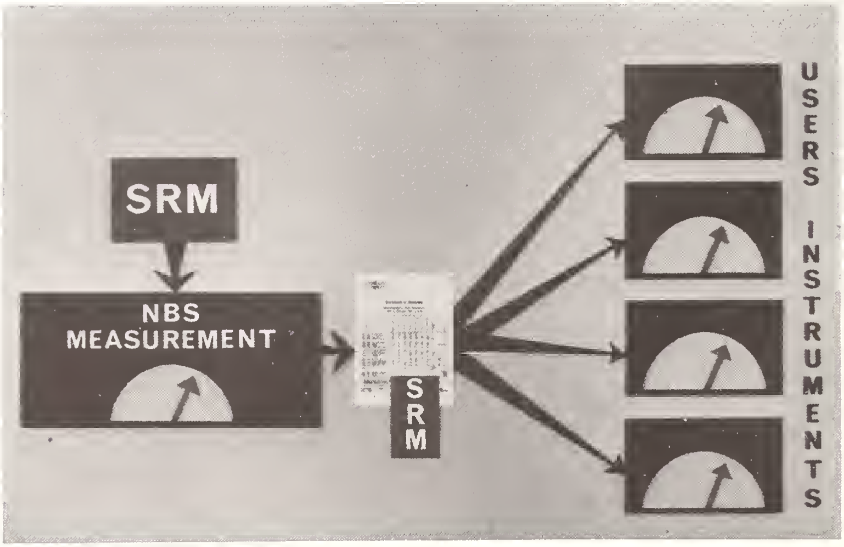
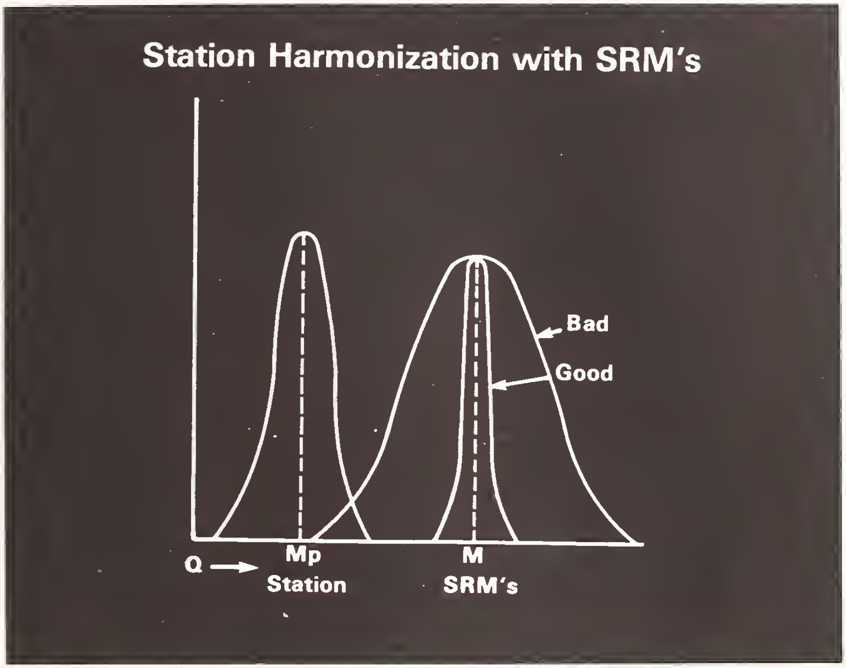


Figure 10. Active Harmonization with Standard Reference Materials



Station Harmonization with SRM's

Figure 11. Station Harmonization with SRM's

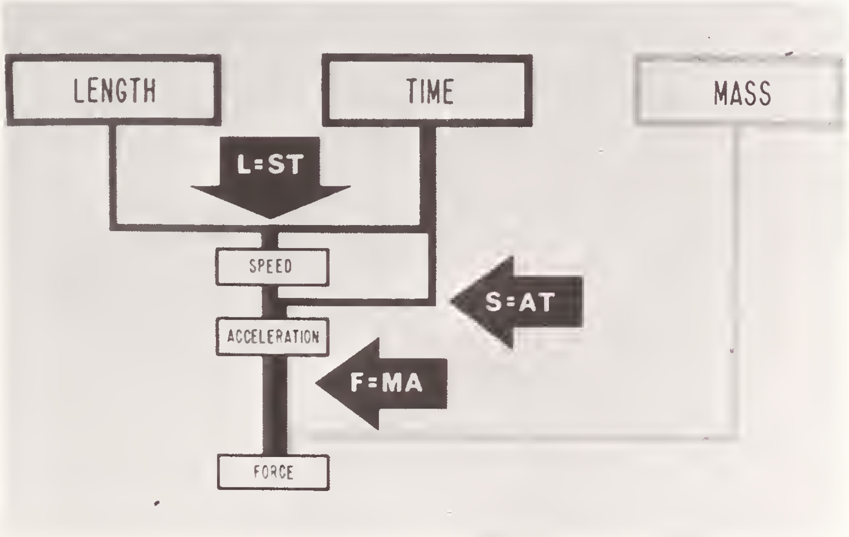


Figure 12. Formation of Coherent Derived Units

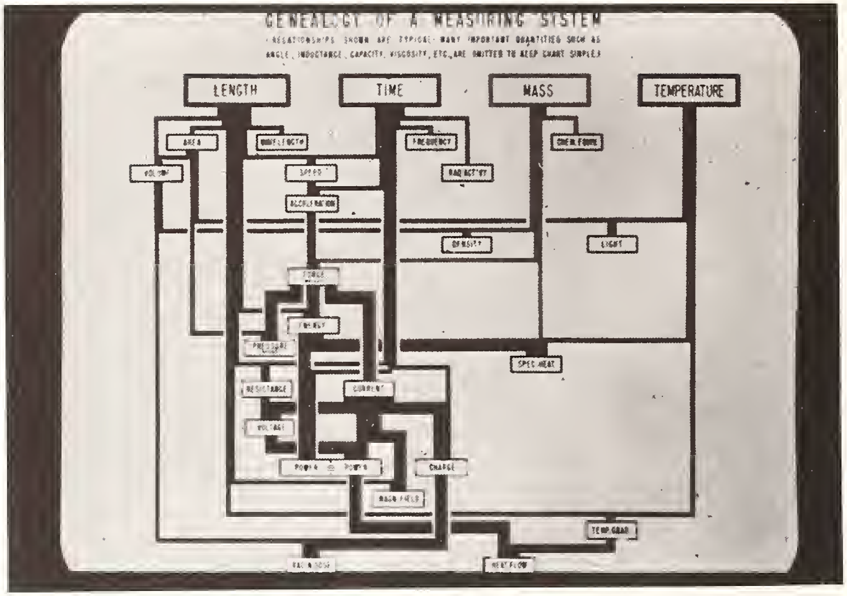


Figure 13. Genealogy of a Measuring System

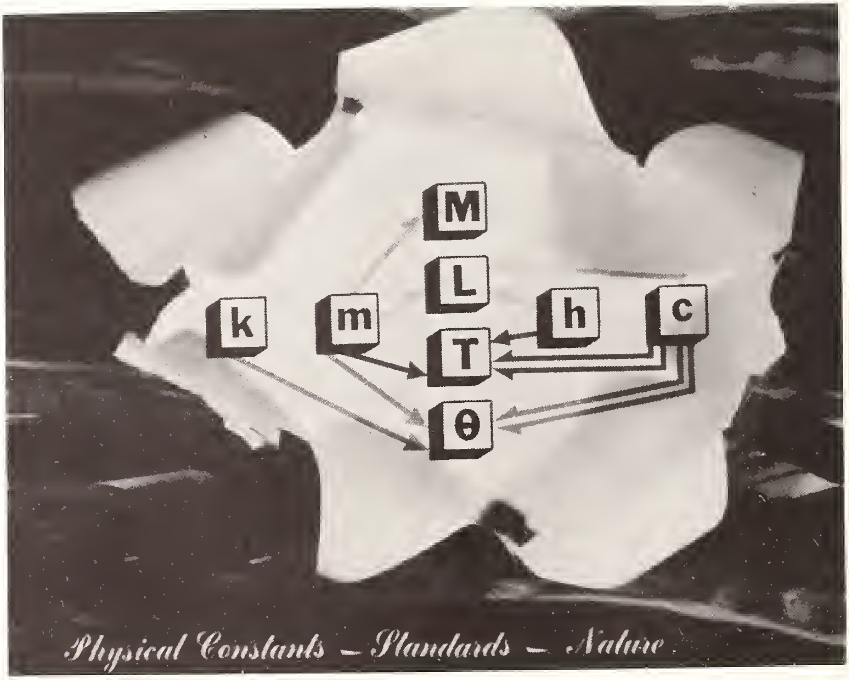
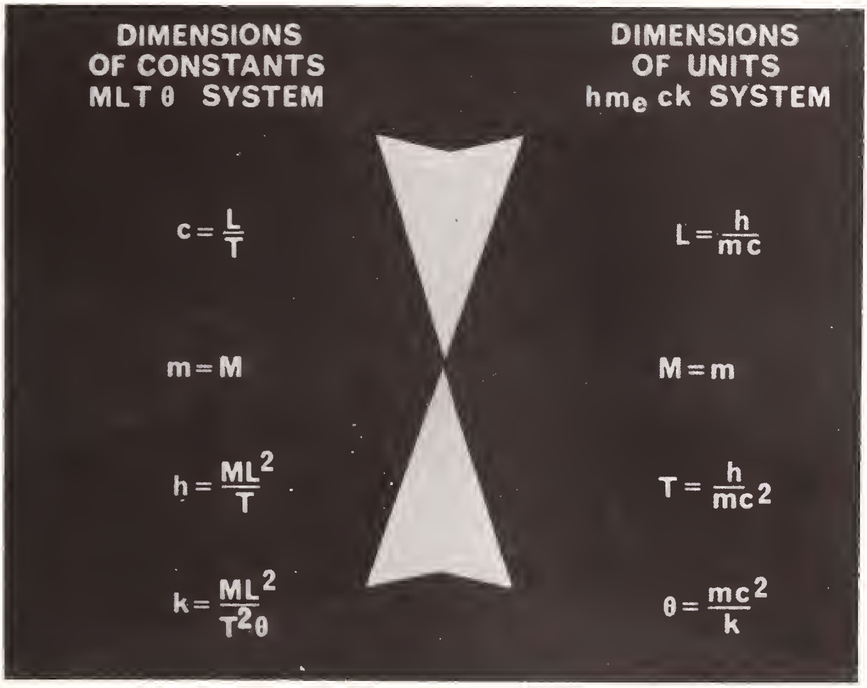


Figure 14. Natures SRM



DIMENSIONS
OF CONSTANTS
MLT θ SYSTEM

DIMENSIONS
OF UNITS
$hm_e ck$ SYSTEM

$c = \frac{L}{T}$

$m = M$

$h = \frac{ML^2}{T}$

$k = \frac{ML^2}{T^2 \theta}$

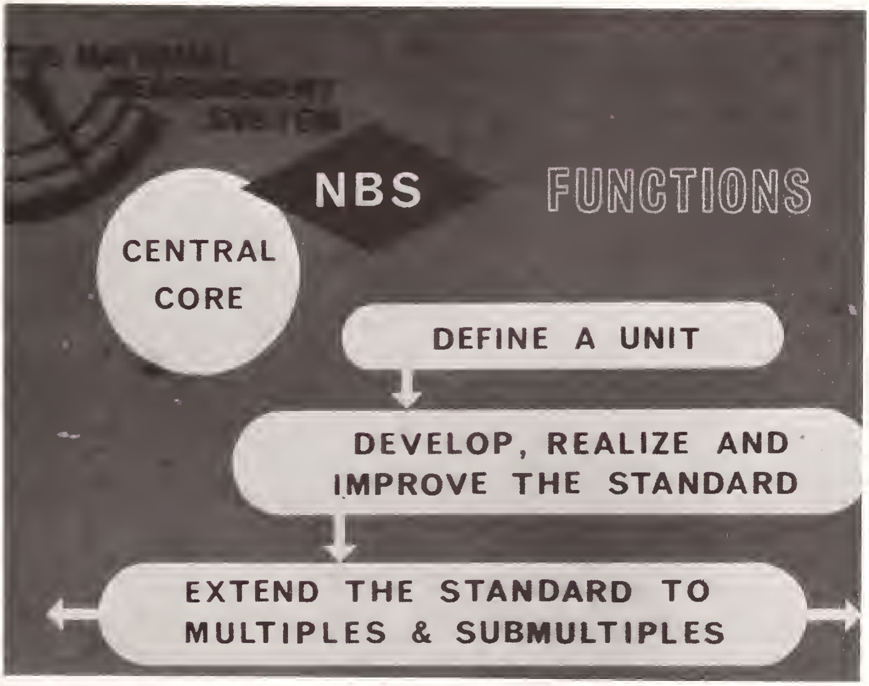
$L = \frac{h}{mc}$

$M = m$

$T = \frac{h}{mc^2}$

$\theta = \frac{mc^2}{k}$

Figure 15. Formation of Natural Units



THE NATIONAL MEASUREMENT SYSTEM

NBS

FUNCTIONS

CENTRAL CORE

DEFINE A UNIT

DEVELOP, REALIZE AND IMPROVE THE STANDARD

EXTEND THE STANDARD TO MULTIPLES & SUBMULTIPLES

Figure 16. Basis for the Measurement Infrastructure

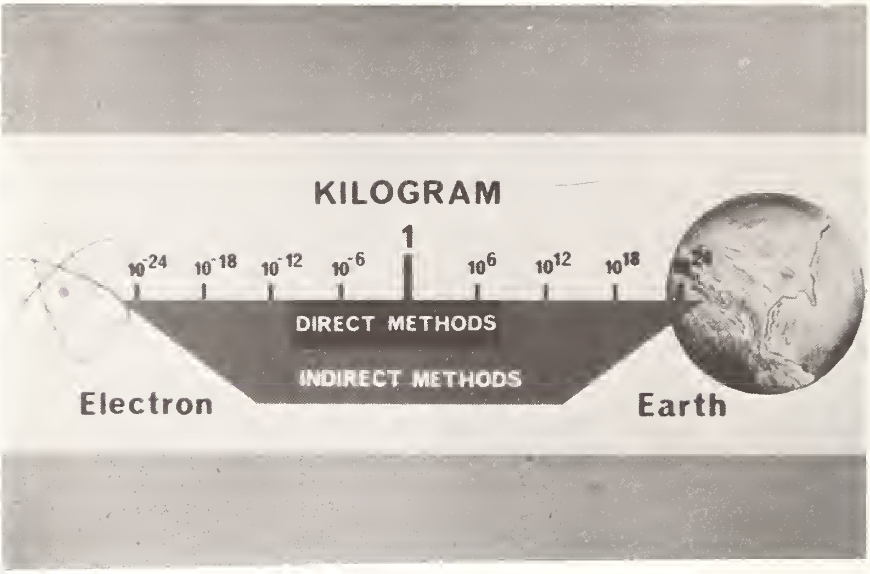


Figure 17. Range Extension

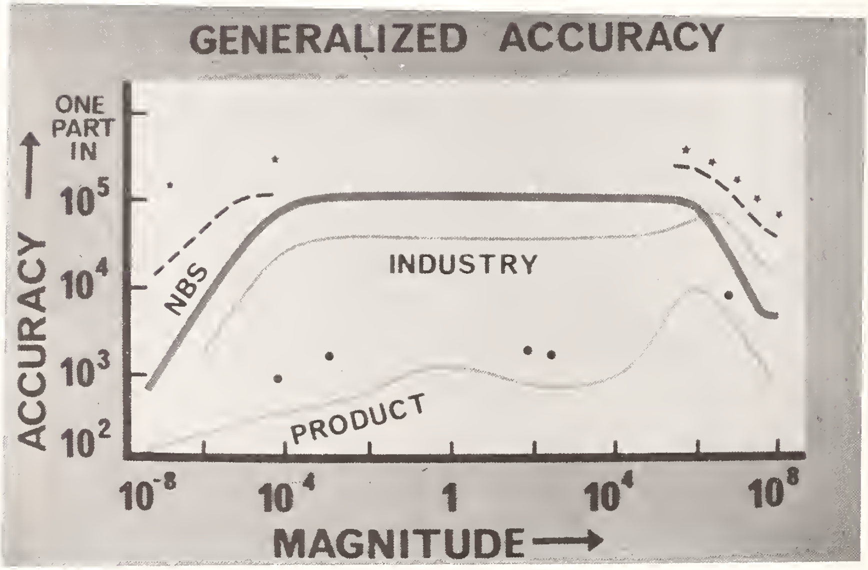


Figure 18. Accuracy - Compatibility Chart - Conceptual

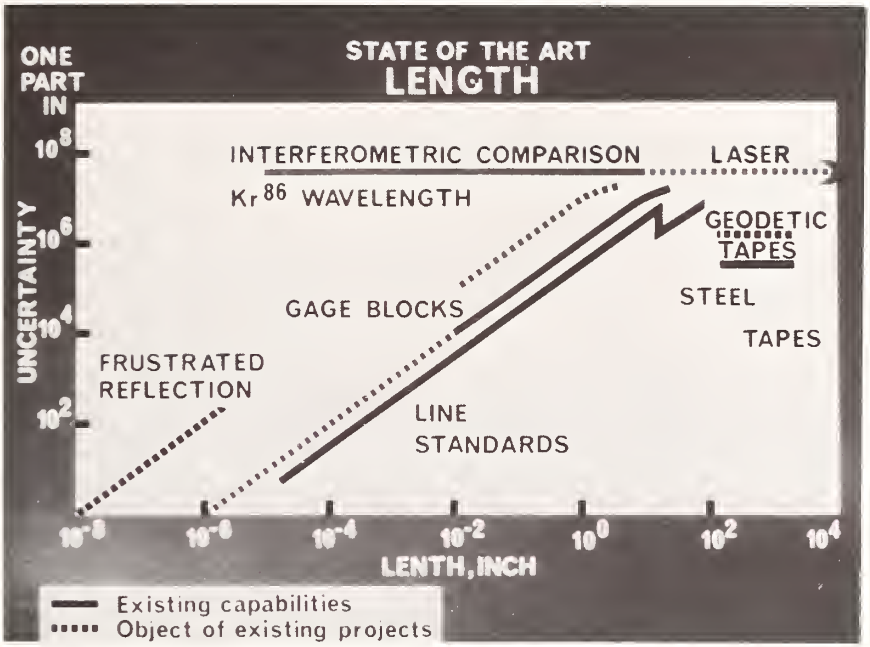


Figure 19. Accuracy Chart - Length

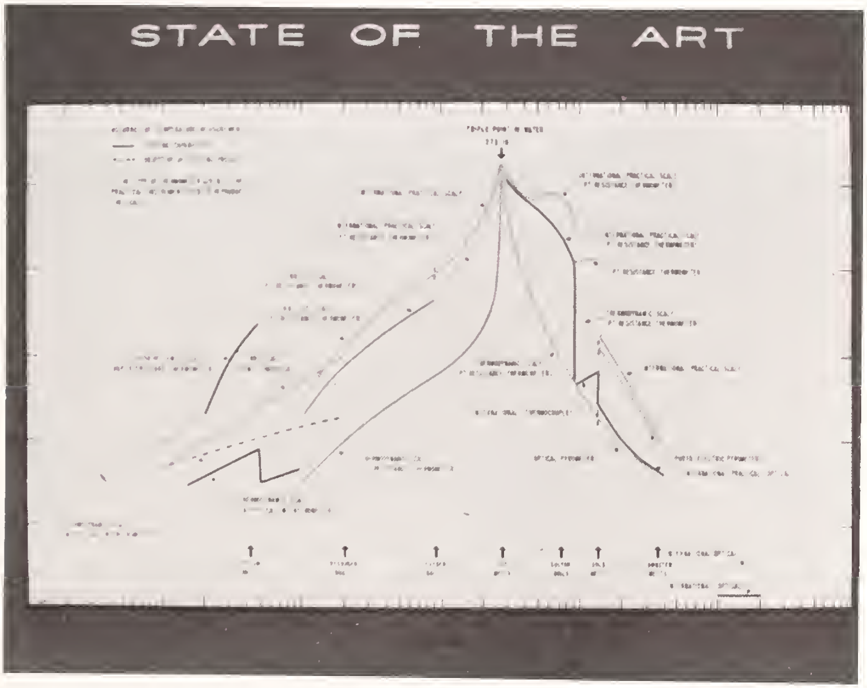


Figure 20. Accuracy Chart - Temperature

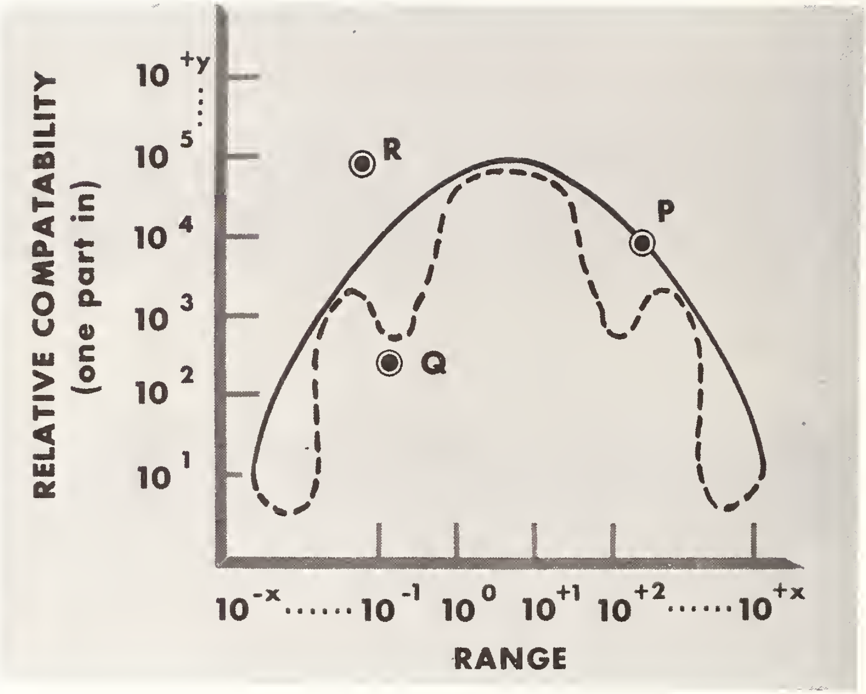


Figure 21. Characterization of the Points to MIS

POSSIBILITIES FOR INTERNATIONAL COOPERATIVE EFFORTS IN STANDARD REFERENCE MATERIALS

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National Bureau of Standards
Washington, D.C. 20234

I. Introduction

Serious efforts to establish international cooperation in the field of Standard Reference Materials (SRM's) have their origin no more than five years ago. At present, there is no international agreement on the definition of what constitutes an SRM, and because a comprehensive definition is not central to the purposes of this paper, the simple definition of an SRM as a "wellcharacterized material, produced in quantity, whose property or properties are certified by some authoritative body," is used. Admittedly, the process of internationalization would be long and tortuous, and will require substantial time and effort. Therefore, this process should be considered only if there are to be potential benefits of significant substance. In table 1 are listed some immediate and longer-term benefits that might accrue from a successful international program. If it were possible through an international agency to gather and widely disseminate information on all currently available SRM's, this would have a global effect. The effect would be to expand the use of a greater variety of SRM's and to increase the number of nations using them. For example, in 1968 the National Bureau of Standards (NBS) procured six different botanical materials as candidates for SRM's. These were to be used in agricultural, botanical, environmental, and to a lesser extent, health measurement applications. The materials were orchard leaves, citrus leaves, alfalfa, tomato leaves, aspen chips, and pine needles. In an agricultural sense these six materials represent more than 90 percent of all food, foraging, and forest crops used by man (excluding grains). Because of limited financial and manpower resources available to NBS, only the orchard leaves have been measured, certified, and issued to date. If a worldwide SRM information network had been in existence in 1968, it is possible that other nations and international agencies might have offered to take one or more of these candidate SRM's under their sponsorship. A possible result would be that several of these very important SRM's might be available today. Hopefully, a greater information exchange would help avoid unnecessary duplication in the production of SRM's.

With reference to the third item in table 1, because of present and past lack of international information exchange, there exists today in the United States, the United

Kingdom, Union of Soviet Socialist Republics, France, Germany, Japan, and several other countries, over 100 SRM's used in the iron and steel industries. These SRM's are essentially identical and such extensive duplication is not fully justifiable. Yet there is another side to this particular issue. The implication that country A should take responsibility for air pollution, while country B takes responsibility for health should not be drawn. On the contrary, it is very important that scientific competences in as many diverse fields as possible be built and maintained in many countries. But for specific SRM's, such as a coal SRM certified for its mercury content, it is wasteful to have, say, six of these from six different countries, when cadmium, lead and several other trace elements in coal are also needed. Coordination of efforts internationally to avoid this type of wasteful duplication is needed. Continuing on the subject of the international division of work, there is an important role to be played for the less-industrialized countries. In many of these nations, basic chemical analytical skills such as the traditional gravimetric and volumetric methods of analysis are better maintained and practiced than in many sectors of the highly-industrialized economies. In the highly-industrialized countries these skills have often been displaced by instrumental methods of analysis. Yet, for chemical composition SRM's, a good, well-carried out gravimetric analysis is to be preferred over many instrumental methods, because the former is likely to give results of greater accuracy, and it is accuracy that is often required in SRM's.

In Dr. Huntoon's paper he shows how measurement compatibility can occur through the use of SRM's. International compatibility through the wider use of SRM's will surely work in the direction of freer trade between nations. Several of the papers in this conference point out the economic and social benefits that accrue on the national level through the use of SRM's, and there is no reason why similar benefits should not accrue internationally.

The last item in table 1, educational benefits, requires some explanation. It simply is not possible to use SRM's in an intelligent manner unless the measurement scientist has an appreciation of matters such as: the measurement process in toto, accuracy and precision, systematic bias studies, compatibility, transfer mechanisms, and so on. Yet these are subjects that are not widely studied today or taught through any formal educational process, and it is for this reason that educational benefits accrue through the use of SRM's. Their use makes the scientist think not only of his own immediate problem, but of the way in which his actions can or will affect an entire measurement science or branch of technology.

At this juncture some potential pitfalls and difficulties of the internationalization process should be pointed out. It must be recognized that certain classes of SRM's are widely used in highly-competitive industrial applications and in areas where vital national interests are at stake. In these cases there are no easy answers and a certain amount of duplication in the production of these SRM's will undoubtedly be necessary. It is also recognized that countries at various stages of development will assess their needs differently and will set their priorities at variance with other countries. For example, countries at an early stage of industrialization will stress SRM's in the areas of agriculture, food, and health, while countries in intermediate stages of development might stress basic material SRM's of industrial importance. The more highly-developed countries will most likely place priority on SRM's for environmental protection and advanced technological application. The resolution of these and other difficulties will require good will and a willingness to compromise on the part of all nations.

II. Historical Perspective

Some significant events in the internationalization process are summarized in table 2. The first truly international effort in SRM's took place in 1969. The meeting was cosponsored by the International Commission of Weights and Measures (CIPM) and NBS. After three days of discussion, the 33 representatives from 15 countries and seven international agencies recommended that the International Bureau of Weights and Measures be asked to establish a facility or mechanism to: first, gather and disseminate information on SRM availability, characteristics, and prices; second, to coordinate information on SRM needs; third, to identify potential suppliers for SRM materials; and, finally, to coordinate information on potential SRM certifying facilities.[1] Unfortunately, at a later date the CIPM felt that within the limitations of its charter and resources available, that it could assume responsibility solely for the SI base unit metrological SRM's.

Largely because the CIPM felt it must thus limit the scope of its efforts, NBS has proceeded to work toward greater internationalization through bilateral agreements. Two such agreements are now in existence between NBS and the Bundesanstalt Für Materialprüfung (BAM) in Germany, and between NBS and the European Economic Community (EEC). Because this ongoing work is covered in later papers of these proceedings it will not be expanded on here. Other agreements or arrangements include the SRM-oriented work within the Organization for Economic Cooperation and Development, the work proceeding within the International Union of

Pure and Applied Chemistry and the work of the International Atomic Energy Agency, all covered in later papers. Finally, the long-term cooperation between the United States and Canada initiated during the 1960's when the copper-base SRM's were being developed is still another example of bilateral cooperation. An expansion of similar agreements and cooperative ventures between nations, either bilaterally or multi-laterally, or within international agencies would do much to further the internationalization process. This historical listing is not comprehensive, and other efforts are covered in the following papers by authors from other countries and international agencies.

The actions now underway within the International Organization of Legal Metrology (OIML, the last two entries of table 2), have the greatest potential in furthering the cause of SRM internationalization in a substantial way. At the 4th International Conference of Legal Metrology in October 1972, the Soviet Union proposed that OIML take responsibility for, "...the creation of international recommendations relative to SRM's." In the ensuing discussion, the United States delegation, believing that the question was too broad and complicated to resolve without further study, suggested that other international or multi-national organizations be invited to join with the OIML on an ad hoc basis to study the question of SRM internationalization and to make a recommendation to OIML for further action. As a result, the OIML invited nine inter- and multi-national organizations to meet with it at NBS on November 5-6, 1973. The recommendations of the ad hoc group are given in Appendix I, and if implemented, as now seems likely, then a truly effective international program will be launched in 1974.

III. Some Possibilities for Action

Given some evidence that nations are moving, though slowly and cautiously, toward an international cooperative mode, what are some of the possibilities for action?

The items in table 3 are arranged in a sequence ranging from easily implemented to implemented with difficulty. The first item, information gathering and dissemination, should require no more than a one to two man-year level of effort, although computerization is an important consideration. The assessment of needs and setting of priorities will require highly-knowledgeable and technically-trained scientists from a wide variety of scientific and technological fields. These range from basic to finishing industries, through health and environmental fields, to areas of basic science, and the coordination of this effort will be difficult.

Setting up a worldwide distribution network for SRM's may not be possible at all when one considers such practical difficulties as: clearing through customs, currency exchange, and language barriers. In fact, these very practical difficulties may prove to be the most difficult to implement.

Harmonization of national SRM programs means international agreement on: certification procedures; minimum requirements for the measurement process that leads to certification; assurance of unrestricted distribution; the reporting on a certificate in terms of accuracy, uncertainties, limitations on use, labeling requirements, etc. Many, if not most, of these problems will take the utmost patience and careful negotiations to resolve.

With regard to the last two items of table 3, it is not at all clear that such a degree of internationalization is even feasible at this time in man's history and development. As long range goals, the desirability and feasibility of a truly complete, self-sustaining international effort is worthwhile. Unfortunately, SRM's do enter into commercial transactions (via methods of test, e.g.,) and this immediately raises questions of great national economic importance, which are not easily resolved. On the other hand, in questions related to health and environmental protection, economic and political questions are not so overwhelming and agreement in such areas might be internationally feasible on a reasonable time scale.

IV. Recommendations

A series of recommendations for implementing and carrying forward an international cooperative effort in SRM's is shown in tables 4-6. These recommendations are grouped in three time categories - those possible of implementation within two years (table 4); those requiring a longer time span of two to five years (table 5); and long-range recommendations (table 6). Further, these should be viewed as personal recommendations of the author, and not in any official sense as representing the views of NBS or the United States.

Obviously, a truly international effort requires the sponsorship and overview of a recognized international agency. The recruitment of such an agency is not necessarily an easy task, since the carrying out of such an effort as is envisaged requires financial support and technical manpower resources. Unfortunately, the nations of the world cannot always support requests from the international agencies for additional monies or resources. Yet, this task, if it is to be successful, will require both. The tasks recommended in table 4 will require one to two man-years of continual effort at a total cost of $50,000 to $100,000 per year. The establishment of such a unit in an international agency would provide the nucleus for further growth and allow the implementation of the two to five year recommendations shown in table 5.

Additional financial support required by the agency would be minimal, if the supporting countries will pay the expenses of its scientists to attend the technical meetings that will be required to accomplish the first two tasks shown. If these highly-specialized meetings could be held in conjunction with other regularly scheduled meetings of the agency, then additional savings would be possible. Furthermore, a fair amount of this work can be done by correspondence and surveys, utilizing the agency staff already operating within the program.

A full-fledged international SRM program, shown in table 6, one where actual SRM's are produced, measured, certified, and issued under the sponsorship of the agency may be an unrealizable goal. Indeed it may prove to be an unnecessary or even an undesirable goal, so that these last recommendations are more in the nature of speculations than hard and fast recommendations. In any case, the realization of such far-reaching goals can only come about through an evolutionary process, one dependent upon the successful implementation of the goals or recommendations listed in tables 4 and 5.

As is the case in all of man's endeavors, the longer the time period, the greater the uncertainty, and the greater the need to maintain flexibility. If we can agree on the immediate and shorter term goals and if these can be successfully implemented and carried out, then the basis for a more complete, more comprehensive program for the future will have been laid. The time seems right to implement such a program and start to develop that ideal of cooperation that will benefit all the nations of the world.

Reference

[1] Astin, A. V., "Report on the Symposium on an International Standard Reference Materials Program," Metrologia, 6, No. 1, 33-34 (1970).

APPENDIX I

RECOMMENDATIONS OF THE AD HOC INTERNATIONAL MEETING ON REFERENCE MATERIALS, SPONSORED BY THE INTERNATIONAL ORGANIZATION OF LEGAL METROLOGY, 5-6 NOVEMBER 1973, AT THE NATIONAL BUREAU OF STANDARDS, WASHINGTON, D.C.

In order to have a definite plan of action result from this ad hoc meeting, we offer as a starting point for the purposes of discussion the following proposed plan:

1. That this ad hoc group recommends the formation of an independent International Commission on Reference Materials.
2. It is recommended that this Commission shall have the following objectives as a point of departure:
   a. to gather and disseminate information on Reference Materials as to their availability, ordering information, properties certified, etc.;
   b. to define Reference Materials in terms of uses, and to examine their role in international standards (in all aspects of the term) and trade;
   c. to recommend a plan of action on the international scale to increase the quantity and improve the quality of needed Reference Materials; to increase their usefulness and availability to help fulfill unmet needs; to foster cooperation among nations to accomplish these ends.
3. a. It is recommended that organizations or institutions active in this field on an international basis should be invited to participate in the International Commission. Participants of the informal meeting have suggested that the following organizations be included in the initial invitations:
      - ISO--International Organization for Standardization
      - IEC--International Electrotechnical Commission
      - IUPAC--International Union of Pure and Applied Chemistry
      - WHO--World Health Organization
      - IUPAP--International Union of Pure and Applied Physics
      - IUPAB--International Union of Pure and Applied Biology
      - UNESCO--United Nations Educational, Scientific and Cultural Organization

CIPM--International Committee of Weights and Measures
OIML--International Organization of Legal Metrology
IAEA--International Atomic Energy Agency
FAO--Food and Agricultural Organization of the United Nations
WMO--World Meteorological Organization

b. It is further recommended that the respective activity of each participant be discussed within the Commission.

4. Regional, multi-national and national organizations active in the field of Reference Materials should be invited to participate in the activities of the Commission.
5. It is recommended that the International Organization for Standardization (ISO) be asked to accept initial responsibility for the secretariat of this Commission.
6. It is recommended that the International Commission on Reference Materials establish a Working Group of experts on Reference Materials as soon as possible, to be responsible for accomplishing the objectives stated in 2. above.

The meetings were closed with a statement by A. J. van Male, expressing appreciation to the participants from the international organizations and to the observers from the various countries, for their attendance and interest. It was agreed that a draft report of the proceedings would be prepared by the National Bureau of Standards and forwarded to the OIML for approval and subsequent dissemination.

Table 1. Immediate Benefits

- Wider Availability
- Greater Variety
- Avoid Wasteful Duplication

Longer Term Benefits

- Compatibility of Measurements
- Freer International Trade
- Economic
- Social
- Educational

Table 2. Historical Perspective

1969 - CIPM-NBS Cosponsored ISRM Symposium

1970 - BAM-NBS Bilateral Informal Agreement

1970 - EEC-NBS Bilateral Informal Agreement

1971 - CIPM Assumes Responsibility for Metrological SRM's (SI Base Unit Only)

1972 - EEC Member States Establish EEC-Wide SRM Program

1972 - OIML Proposes Study of Some International SRM Aspects

1973 - OIML Calls Ad Hoc Study Group (Nov. 5-6, at NBS)

Table 3. Possibilities for International Action

- Information Gathering and Dissemination
- Assessment of Worldwide SRM Needs
- Assessment of Worldwide SRM Priorities
- Worldwide SRM Distribution Network
- Harmonization of National Programs
- Establishment of Worldwide Network of Cooperating Laboratories
- Production, Measurement, Certification of SRM's at the International Level

Table 4. Recommendations (Now)

Recruit an International Agency to Gather and Disseminate Information on:

- Current International and National SRM Programs
- SRM's Now Available
- SRM Availability and Ordering Information
- Laboratories Now Performing SRM Work
- National Measurement and Certification Procedures

Table 5. Recommendations (2-5 Years)

International Agency Establishes Formal Network and Technical Committees to:

- Establish Worldwide Needs for Additional SRM's Not Available
- Set Priorities on These Needs
- Encourage Cooperation Among Nations to Avoid Needless Duplication
- Maintain and Expand Information Network

Table 6. Recommendations (5 Years-Onward)

Establish Within (or Under the Aegis of) the International Agency a Formal Network to Produce, Measure, Certify, and Issue SRM's. This will include:

- Recruitment of National (and Other Qualified) Measurement Laboratories
- Qualification Procedures for Participating Laboratories
- Procedures to Assure Quality and Integrity of Work
- Procedures to Assure Non-Competition with National Programs
- Establishment of Distribution Network
- Financial Support (Eventual Goal - Self-Funding)

ACTIVITY BY THE INTERNATIONAL ORGANIZATION FOR STANDARDIZATION WITH RESPECT TO STANDARD REFERENCE MATERIALS

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Before dealing specifically with the interest of ISO in standard reference materials it may be useful for the benefit of those present who may not be familiar with ISO to present a brief description of it.

ISO is a confederation of the national standards bodies of 72 countries. Of these, 56 are full members and 16 are corresponding members. The latter are countries which do not as yet have standardization organizations capable of representing their countries as full members of the ISO. The United States is represented in ISO by the American National Standards Institute. ANSI, itself, is a confederation of the several organizations in the USA in which standards are developed. The American Society for Testing and Materials is an important member of ANSI. Memberships in ANSI are held also by many large companies.

Standards developed by such societies as ASTM are recognized by ANSI as American National Standards when they are found to be qualified for such recognition in accordance with ANSI criteria and procedures. Standards proposed for recognition as American National Standards are submitted for public review and comment prior to such recognition.

The National Bureau of Standards provides highly qualified technical personnel as participants in the many technical committees in which both national and international standards are developed. A fairly recent survey showed that NBS staff occupied more than twelve hundred positions on such standards development committees.

ISO is a non-governmental organization which, however, has established liaison arrangements with more than two hundred other international organizations, governmental and non-governmental, including the UN and such UN agencies as WHO, FAO, UNIDO and UNESCO, and the OILM.

There is a sister organization to ISO called the International Electrotechnical Commission, IEC. IEC deals with international standards needed in the electrical field. ISO handles all the rest.

ISO was established in 1947 as a successor to the International Federation of the National Standardizing Associations, ISA, organized in 1926. IEC was established in 1906. ISO is endeavoring to achieve recognition as a specialized agency for the development and promulgation of the world's needs for international standards in its field. Many of these are adaptable for use by reference in national and international regulations and trade agreements.

There is a strong current trend to action in many countries to adopt ISO and IEC international standards without substantial revision as national standards.

This trend has been accelerated by action taken by ISO to change the name of its product from ISO recommendation to ISO standards.

This is in line with a change in the mission of ISO. For many years its mission was to reconcile differences between the national standards of different countries.

Current emphasis is on the development of international standards in the first place. This has been referred to as a global approach to national standards in contrast to a national approach to global standards.

Development of ISO standards is in the hands of technical committees administered by secretariats held by the member countries of ISO. There are currently 145 ISO technical committees which include 494 sub-committees, 610 working groups and 100 special task groups. Each working day there are, on the average, eight ISO technical meetings. It has been estimated that about 50,000 individuals around the world are engaged in the technical activities of ISO.

Administration of the ISO programs is in the hands of the Central Secretariat with headquarters in Geneva, Switzerland. This has a staff of about 85 and a current budget of about 6 million Swiss francs. To this should be added another 50 million Swiss francs for the estimated costs of the 145 technical committee secretariats administered by the members of ISO.

The programs and management of ISO as delegated by the General Assembly which meets every three years are in the hands of a Council comprised of 14 member bodies. The members of the Council from the United Kingdom, France, Germany, the USSR, and the United States, are regularly sponsored for re-election. The other memberships on the Council are chosen by the ISO General Assembly and are rotated among the other members of ISO for overlapping three year terms.

The Council meets once a year and carries on much of its work by correspondence and through activities of several Council committees assigned specific areas of responsibility. These include, for example, an Executive Committee, EXCO, and a Planning Committee, PLACO.

The Council is responsible for approving the ISO budget and assessing membership dues.

The greatly increased recognition of the need for, and usefulness of, international standards has resulted in a tremendously accelerated activity in the development of ISO standards. As many ISO standards were issued during a recent three year period as were issued during the first 20 years of ISO's existence.

Another recent trend has been concern in ISO for what are called "standards for people" as distinct from "standards for industry." Standards for people are illustrated by the missions of such recent ISO technical committees as those established to deal with the methodology of measuring the qualities of air and water. The secretariat of the latter is held by the USA through ANSI, with major participation by the National Bureau of Standards and financial support by the National Science Foundation.

The immediate interest of ISO in a program related to standard reference materials was stimulated by a request for help with standard reference materials that are needed in connection with the measurement of certain pollutants encountered in waters.

In response to this approach ISO undertook a review of the possible scope of ISO requirements for standard reference materials that might justify the creation of a new committee of the ISO governing Council. The following is quoted from the results of this study:

> "ISO technical committees are sometimes called upon to prepare standards, usually dealing with test methods, which require the use of standard reference materials for performance of the test. These materials may be needed, for instance, to serve as standards or scales of reference, as calibrants, as reference materials for check testing or as ingredients for test mixtures.
>
> "The following are some of the examples already met with, which illustrate the requirement of standard reference materials for ISO standards:

a. As standards or scales of reference:
Test methods for assessing the color fastness or staining properties of textiles, plastics and other materials.

b. For calibration of measuring instruments and test procedures:
Test methods for measuring the reflectance properties and opacity of paper, board and pulps; polymer characterization of plastics.

c. For check testing or indirect verification of accuracy, reproducibility, etc., of instruments or methods;
Verification of machines for hardness testing of metals.

d. Standard ingredients for test mixtures:
Standard materials for compounding of test samples of rubber, for the determination of various properties of the rubber.

"Other requirements which are liable to arise include, for example, standards for coating thickness measurements, scales of reference for solid state analysis of metals by spark spectra, chemical or other products of known purity or known content of impurities/pollutants for verification or check testing, standards for particle size for control of test sieves, etc.

"Furthermore, there is an increasing trend in the technical world towards the use of instrumental or automated methods, particularly for rapid testing for purposes of routine checking or process control. Such methods very often rely on comparisons with standard reference materials.

"Prescription of reference materials in ISO standards raises a number of administrative or policy questions; to name only a few:

- assurance of availability and supply of the materials;
- arrangements for their custody;
- criteria to be fulfilled by laboratories for becoming approved custodians or suppliers;
- procedure for recommending individual laboratories and their appointment as approved institutions for the purpose of International Standards;
- consequence of subsequent failures;
- possible financial implications.

"At present there is no machinery in ISO for dealing with the above type of questions or for supervising that an ISO policy is applied reasonably consistently. The problems which arise from time to time cannot therefore be dealt with in a uniform manner. Individual technical committees are apt to make their own rules and to differ widely in their approach to the problem. When a certain laboratory has been selected by an ISO technical commitee it then has only the reference of that technical committee as its sole authority to act on behalf of ISO for all users of International Standards. Furthermore the same laboratory may be needed by more than one ISO technical committee, thus adding to the potential risks attendant on divergent approaches.

"It would therefore appear that there is a need for some form of a policy making and supervising body with all administrative, policy and coordinating functions in regard to standard reference materials for the purposes of ISO standards. Since these questions potentially affect all ISO technical committees, it would appear that such an organ would have to function centrally and be responsible to Council, i.e., it would be a Council committee.

"If Council decides to set up a new Council committee for the above purpose, it is suggested that the terms of reference of such a committee would include:

a. Principles relating to the publication of International Standards dependent on the use of standard reference materials.
b. Rules governing satisfactory upkeep and convenient availability of stocks of the standard reference materials and their supply on reasonable terms.
c. Rules governing selection or approval of laboratories or institutions, whether national or international, authorized to act as custodians or stockists and suppliers of standard reference materials for the purpose of International Standards.
d. Appointment of individual laboratories or institutions in particular cases, in consultation with the ISO technical committee(s) concerned."

On the basis of this study the ISO Council at its meeting in Washington last month (September 1973) adopted the following resolution 43/1973:

"Council establishes an ad hoc group to study further the proposal for the creation of a Council committee on standard reference materials. Council appoints Mr. W. Andrus as chairman of this group and invites him, in consultation with the Secretary-General, to nominate the

> members of this group. The group is requested to present its findings as early as possible."

It should be evident therefore that ISO recognizes the importance and need for international standard reference materials and that determination of the course to be taken by ISO in this matter is in good hands.

THE ANALYTICAL QUALITY CONTROL PROGRAMME OF THE INTERNATIONAL ATOMIC ENERGY AGENCY

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I. The Agency and Its Laboratories

The International Atomic Energy Agency was established in 1957 "...to accelerate and enlarge the contribution of atomic energy to peace, health, and prosperity throughout the world."

The formulative statute authorizes the Agency not only to "encourage and assist" peaceful atomic research, but also to "perform any operation or service useful in research on, or development, or practical application of, atomic energy for peaceful purposes." This authority, as well as other statutory functions, including the establishment or adoption of standards of safety in atomic energy operations, established the need for laboratory facilities; indeed, the statute specifically authorized the Agency to "acquire or establish any facilities, plant, and equipment useful in carrying out its authorized functions."

The Agency presently has three such facilities. The building of the Agency's main laboratory in Seibersdorf, adjacent to the Austrian Reactor Centre, was completed in 1961. The working space initially provided was 1700 square meters; a few hundred square meters were added to this later. In addition, several laboratory sections are presently located at the Agency's provisional headquarters in Vienna. A second facility is the Laboratory for Marine Radioactivity located in the Principality of Monaco, and the third is the International Centre for Theoretical Physics in Trieste, Italy. The total number of people employed in these facilities is 155, of which about two-thirds are scientists and technicians, and the rest administrative, secretarial, and maintenance staff. About 25 Member States are represented by the staff.

With a relatively small group staffing Agency Laboratories, it is mandatory that activities be selected with care to maximize the use of the talents and resources available to serve the objectives of the IAEA. Thus we seek to avoid activities that are better performed in the much larger and more elaborately equipped nuclear research centers in some of the Agency's Member States. There are problem areas, however, of an international nature that place a unique responsibility upon our laboratories.

One area concerns the establishment of international standards and regulations to ensure safety in atomic energy operations; another includes the development of safeguard procedures to prevent the diversion of fissionable materials from peaceful uses - this includes a limited amount of direct analytical work; and a third covers the provision of laboratory support to some of the Agency's technical assistance projects and coordinated research contract programmes.

Closely coupled with the establishment of standards and procedures is the availability of reference materials, chemical standards, and calibration services, which are described later.

Apart from activities associated with the Agency's role in regulation and safeguards, the laboratories also were designated to render scientific and technical services to Member States at their request. Many developing countries do not yet possess the necessary facilities for certain types of scientific work in which they are interested, e.g., relatively advanced investigations in connection with radioisotope applications, or reliable analysis of samples from prospecting operations to determine uranium ore concentrations.

The fields in which the laboratories operate and in which services can be provided are chemistry (including analytical, isotope, and radiochemistry using destructive and non-destructive techniques), physics (including isotope calibration by absolute counting techniques and neutron monitoring), medicine and health physics (including whole body counting, bioassay of radionuclides, and activation analysis for medical research purposes), agriculture (including isotope studies of fertilizer applications, genetic studies with radiation-induced mutant strains, and sterile male techniques of insect pest eradication), hydrology and environmental radioactivity (including marine radioactivity studies at the International Laboratory of Marine Radioactivity at Monaco).

Thus far the role of the laboratories has been emphasized. The laboratories report administratively to the same Division as the Industrial Applications and Chemistry (IAC) Section which also has responsibilities relevant to analytical quality control. The IAC Section responsibiities are complementary to those of the laboratories and emphasis is placed upon research support through coordinated contract programmes such as one on nuclear-based methods for trace element analysis; advice for technical assistance programmes which include equipment grants, training courses, and assignment of experts to assist Member States, the organization of symposia, siminars, panels, study groups, and the preparation of proceedings and technical reports. Although the IAC Section staff is small--four professionals --use is made of expert consultants to assist in planning and evaluating Agency activities.

II. Development of the Agency's Analytical Quality Control Programme

A. Radioisotope Calibration

Very early in the history of the laboratories the Physics Section became involved in the calibration of radioisotopes preparation. The Agency, in promoting the use of isotopes in medicine, science, and technology, but particularly in the medical field, found the need for a hard look at the validity of existing calibrations. Several groups of experts and panels convened by the Agency have, over the years, provided detailed directives on standardization and intercomparison activities of the laboratories. Initially, calibrated solutions mainly of short-lived radioisotopes were prepared by absolute methods and provided to laboratories in Member States against a small fee designed to recover direct expenses. Later, solid standard sources also were provided. Several thousand samples were distributed during the following years. The programme was terminated when an adequate supply of radioisotope standard sources had become available from commercial suppliers.

To prove and maintain its own capability in the absolute measurement of radionuclides, the laboratory also participated in intercomparisons organized by the Bureau International des Poids et Mesures at Paris.

Calibration services were extended by the Medical Section which built a phantom human head fitted with exchangeable phantom thyroids labelled with a mixture of barium-133 and cesium-137 to simulate iodine-131 radiation. The phantom was used in hundreds of clinical laboratories to check upon and improve the accuracy of thyroid function tests with iodine-131.

B. Intercomparison of Analytical Results

In the past ten years the Agency has been active in carrying out analytical intercomparisons of radioactive materials, of materials relevant to atomic energy programmes, and also of materials for which analysis by nuclear techniques has seemed preferable to other techniques.

During the early 1960's, the Seibersdorf laboratory had developed a capability in the determination of strontium-90 and other fall-out nuclides in environmental samples. The UN Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), concerned with calculation of human exposure rates to strontium-90 on a worldwide scale, found that the data on strontium-90 concentrations in food, soil, vegetation, and bones received by it from many countries were often of rather doubtful quality. When this occurred, the Agency's laboratory was able to have intercomparison samples prepared in bulk quantities to provide to the involved laboratories to check their methods. The number of materials available for this purpose was increased in later years and, in addition to strontium-90, other radionuclides, artificial as well as natural, were determined in them. In addition to "naturally contaminated" materials, spiked samples were occasionally used and not only intercomparison samples but also samples of known radionuclide content (reference materials) provided.

For intercomparison, the samples distributed were prepared to closely resemble those materials routinely analyzed by the participating laboratories. They were selected to have reasonable stability with a general composition similar to the materials routinely analysed and with a comparable concentration of the nuclides or elements to be determined. Homogeneity of the samples was, in all cases, assured down to the required size-range.

In recent years, the Monaco laboratory has contributed intercomparison materials for marine radioactivity studies and Seibersdorf some uranium and plutonium compounds to be used in safeguards work.

Also, a number of materials was added to serve the need of scientists working on trace-element determinations by nuclear-based methods, mainly neutron activation analysis.

C. Standard and Reference Materials

When many countries embarked on prospecting for uranium and other elements, sometimes under programmes assisted by the United Nations, the need arose for ore standards to check on results obtained both in the field and at the supporting laboratories. Three different ore types were used to prepare four batches of standards all in the 0.2 - 0.4% range of uranium concentrations. Certification of these was based on analyses carried out at several national laboratories. Recently, to satisfy demand for standards of lower-grade ores, two additional materials in the 0.01 -

0.05% range of uranium concentration were added. The Isotope Hydrology Section, meanwhile, prepared two water standards for isotopic ratio analysis. The oxygen and hydrogen isotope ratios were intercompared by 25 laboratories and these standards together with two older standards distributed in the past by the National Bureau of Standards, but since transferred to the IAEA, are now available from Vienna.

Our programme has evolved over the years. Many intercomparisons carried out at more or less regular intervals were replaced by the provision of reference samples available on a continous basis. The number of participants in intercomparisons has increased, partly through an increase in the number of laboratories interested in the types of analyses covered by these, and partly through improved publication of our activities. Continued evolution of our programme to assist Member States to improve their analytical capabilities is anticipated.

III. The Need for Analytical Quality Control in the Nuclear and Isotope Fields

It seems hardly necessary to stress the need for analytical quality control at a Symposium like the present one, which by its very title underlines the fact that meaningful measurements can only be obtained by recourse to standard reference materials or by similar forms of outside intervention or control. The results of the Agency's efforts in quality control in the nuclear and isotopes fields show that the situation in these fields is qualitatively similar to that in the areas covered by previous speakers. Quantitatively, however, it may be worse since the number of newcomers and inexperienced laboratories is relatively larger in nuclear techniques than in conventional chemistry. A few examples from the many results of intercomparisons that the Agency has collected, evaluated, and sometimes published in the course of the last few years [1-6], will show this.

The first example is an intercomparison of cesium-137 determinations in dried animal blood. [6] Forty-eight organizations took part in this effort, providing 217 individual results. Each laboratory received 2 kg of blood packed in an air-tight container. The material was prepared from fresh animal blood containing environmental levels of cesium-137. Homogeneity was verified by measuring the cesium-137 content of the material in randomly selected containers. The results of the determinations are shown in figure 1a. Using all the results received, one obtains an inter-laboratory mean cesium content and a standard deviation among laboratories of:

$$\bar{X} \pm S = 114.8 \pm 117.6 \text{ pCi/kg}$$

This value and the standard deviation of more than 100% is largely due to the influence of three laboratories submitting averages between 400 and 600 pCi/kg. By neglecting these results and the equally unlikely one at the other end of the range (13 pCi/kg) one arrives at the much likelier figure of:

$$\bar{X} \pm S = 86.3 \pm 24.6 \text{ pCi/kg}$$

This latter mean is shown as dotted horizontal line in figure 1a. The corresponding 95% confidence limits of the mean come to ± 7.4 pCi/kg. Two-thirds of the results submitted were obtained by (direct) gamma scintillation spectrometry, the other third by various radiochemical methods followed by beta radioactivity measurements. Calculated separately for each of these techniques the means are:

Beta counting	$\bar{X} \pm S = 71.2 \pm 23.8$ pCi/kg
Gamma spectrometry	96.7 ± 20.4 pCi/kg

The difference is significant at the 0.05% probability level and likely due to losses of cesium on ashing prior to radiochemical separation procedures. Separate distributions of results obtained with the two procedures are shown in figure 1b.

The second example is from two intercomparisons of the analysis of several radionuclides on air filters carried out on request of the Commission on Instruments and Methods of Observation of the WMO. [7] In the first one, organized in 1968-1969, six radionuclides were used, ^{54}Mn, ^{55}Fe, ^{90}Sr, ^{137}Cs, ^{144}Ce, and ^{239}Pu, at levels ranging from 10 pCi to 1 nCi. From the ten participating laboratories, no results were received for ^{55}Fe at the 1 nCi level. The majority of the results received for the other nuclides did not show unusual spread and their overall means did not deviate too much from the true value of the spike added. However, only three out of the ten laboratories reported on ^{239}Pu and only four on ^{144}Ce. Of the 31 averages received for all nuclides taken together, 5 had to be rejected as outliers.

A similar intercomparison was organized in 1972. The two cannot strictly be compared, since in the new intercomparison ^{106}Ru was substituted for ^{144}Ce and the activity levels of all nuclides was considerably higher than in the earlier intercomparison (the new one was aimed at analysis in emergency situations). Participation was much better, however, than in the earlier intercomparison (20 laboratories compared to 10), and the number of laboratory averages received was 84 based on 729 individual determinations. The results that can be seen in figure 2 show an interesting feature: the intralaboratory standard deviation and the corresponding standard error of each laboratory mean are usually small while the scatter of these means around their overall interlaboratory mean is considerable.

Obviously, the difference of a laboratory mean from the overall mean is mainly due to bias and cannot be much influenced by repetition of measurements. Excessive repetition under such circumstances must be considered a waste of effort. Laboratories were advised that more time should instead be devoted to the detection of the reason for the bias that leads to a standard deviation of up to 20% (in the case of ^{90}Sr) and that in some cases could be due to the use of biased radionuclide standards. Agreement between the overall mean and the nominal value, on the other hand, is good for most nuclides. All differences, except that for ^{239}Pu, amount to less than 3% and are fully accounted for by the standard error of the overall mean. In all, 24% of laboratory means had to be rejected in 1968, this figure was down to 15% in 1972.

The third example concerns the determination of uranium, thorium, and potassium in three different sediments, two shales with a silicate matrix from Germany and Sweden, and a limestone with a carbonate-sulfate matrix from Iran. Twenty-two participating laboratories returned a total of 134 results, each based upon from 1 to 6 individual determinations. Exactly one-half of the results was obtained by gamma spectrometry, 16 of these had to be rejected as highly improbable (outside the limits of 3 standard deviations from the mean of all the accepted results). The other half, obtained by methods such as neutron activation, fluorimetry, fission track counting, and a few others, contained only 2 objectionable results and had smaller standard deviations. The overall means of the two halves were not significantly different, however. All accepted values were therefore combined in the calculation of the overall means and their standard deviations:

Sediment	Uranium	Thorium	Potassium
1	104 ± 21 ppm	11.7 ± 2.6 ppm	2.92 ± 0.32%
2	3.7 ± 1.2 ppm	8.8 ± 3.1 ppm	1.75 ± 0.19%
3	3.3 ± 0.6 ppm	∿1.9 ppm	0.15 ± 0.06%

The normalized distribution (mean = 100) of all nine groups of results is shown in figure 3. For uranium, the range of values received is from 60 to 140% at 100 ppm and from 40 to 180% at 3 ppm. For thorium at 2 to 12 ppm the range extends from as low as 10% up to 600% of the mean. Most surprising perhaps is the wide scatter of results for potassium even though this element was present in much higher concentration than the other two. Even if we disallow the extreme values (one at 10 and one each at 250 and at 600%) the other values are still spread between 60 and 160% of the mean at the 0.1% concentration and not much less at the 2 to 3% concentration.

Figure 4 shows results obtained for the same 3 elements in urine samples. These determinations were carried out by laboratories whose function it is to determine body burdens of radioactive elements in nuclear industry workers. The amount, e.g., of plutonium used was about that generally taken to correspond to 15% of the permissible body burden. (A level of 4 pCi in a 24 h urine sample, usually rather more than 1 litre of urine, is assumed to correspond to the maximum permissible body burden.) The lowest value reported (20% of the mean) would indicate the presence of only 3%, the highest (400% of the mean) that of 80% of the permissible value. Or, putting it another way, the laboratory providing the high value would report the presence of the maximum body burden already when the amount of plutonium present in urine would in fact correspond to only one-quarter of the accepted figure, while the other would not sound the alarm until five times the permissible body burden would be reached.

It has been mentioned earlier that our investigations include not only radioactive materials but also materials in the analysis of which radiochemical and nuclear methods may be used to advantage. [8] Determinations of environmental mercury fall into this category. Mercury pollution from industrial as well as agricultural uses of the element has given rise to concern in the last few years and many laboratories have started to analyse for it in environmental materials. The concentrations looked for are of the order of between one and one hundred ppb and at this low concentration range the great sensitivity of neutron activation analysis for mercury has made this method one of the methods of choice. To assist laboratories to control their reliability and at the same time to assess the general status of analytical performance in this type of work, the Agency distributed nine different materials containing environmental concentrations of mercury. [9, 10] The results of the nine different intercomparisons is shown in table 1. As can be seen from the vertical column at the extreme right of the table, roughly one-third of the 407 individual values (92 laboratory averages) had to be excluded as grossly erroneous. The remaining results still gave standard deviations varying form 23 to 65% of the mean. A separate evaluation of the results according to the analytical methods employed did not show any difference in performance between neutron activation analysis, which was used by two-thirds of the participating laboratories, and atomic absorption, which was used by most of the others.

Finally, as an example of an application to multi-element analysis, the results of the intercomparison of the analysis of 13 metals deposited on air filters are shown in table 2. The filters were loaded by evaporating on them aliquots of suitable solutions of salts of the metals concerned. The quantities of the various elements on each filter varied from 0.2 micrograms for mercury and selenium up to 200 micrograms for iron. Batches of 10 filters were provided to each participating laboratory. Twenty-two laboratories submitted 171 laboratory mean results based on 876 individual determinations. A preliminary report based on less complete data has been published elsewhere. [7] As in previous cases, the standard deviations of individual laboratory means from the overall mean of 20 to 40% for most elements were found to be very much larger than the differences between individual measurements carried out at one and the same laboratory. Differences between the nominal quantities of metals added and the overall mean were 10% or less for all except three of the metals. For about half of the elements investigated, these differences were within one standard error, for slightly more than one-third within the range between 1 and 2 SE and only for two elements between 2 and 3 SE. This proves that no serious bias was introduced in the preparation of the samples used in this intercomparison.

Summing up the results of the intercomparisons reported here, which are only a small part of the total number organized by the Agency, it can be said that they illustrate the great need of laboratories for analytical quality control. Such intercomparisons are a useful first step in:

1. Assessing the analytical capabilities of laboratories,
2. Assisting in the improvement of analytical programmes, and
3. Evaluating the degree of reliability of data.

In some fields of analysis, relatively large errors can be tolerated. The intercomparisons described, however, have shown that even generous tolerance limits are often exceeded by a considerable number of laboratories. Continued quality control seems to be quite essential to achieve and retain reliability.

One problem has remained with us: the recognition of outliers. We have used different statistical criteria for their recognition, but are happy with none of them. Depending on the number of data received in each run, which varies considerably, and on their grouping, one or the other of the methods seems preferable, but none of them is really satisfactory for use with all the data.

IV. Present Status of the Agency's Analytical Quality Control Programme

The materials presently supplied are classified as follows:

1. Standard Materials (S): These have been analyzed at one of the Agency's laboratories or at one or several contractor laboratories, well known to be reliable. They are supplied with a certificate describing their general composition as well as stating the content of the element or nuclide of interest and the methods by which this value was obtained. Our uranium ore standards fall into this category, which previously included our radioisotope solution standards also. Occasionally the Agency also supplies standard samples prepared by national laboratories such as NBS.
2. Intercomparison materials (I): These are materials distributed free of charge for intercomparison purposes. The homogeneous distribution of elements or nuclides to be analyzed in them is ascertained; their absolute concentration, however, is not always known to us. They are distributed free of charge (except for postage if its cost is considerable) on the understanding that the laboratories ordering them report their results to us on a confidential basis for use in our calculations.
3. Reference materials (R): These are materials that have been previously used for intercomparisons so that their contents have been determined. Generally, the degree of accuracy with which these contents can be named is inferior to that pertaining to standard materials.

Table 3 lists all the materials scheduled for distribution in 1973 and 1974. Some of these materials are available from stock on a continuous basis. Most of the intercomparison samples for 1973 have already been sent out. For some of them the collection of results has been concluded and the evaluation started and, in a few cases, already completed.

Many of the analytical activities covered by these materials are of interest not only to the Agency but to other international, regional, and national bodies. Close cooperation is sought with these bodies with a view towards coordinating programmes. We enjoy good relations with the World Meteorological Organization (WMO) with whom we have exchanged ideas concerning our air filter studies [7] and who will be interested in anything we do to assist in improving accuracy in the determination of air pollution. In the field of samples of medical interest we are in contact with the World Health Organization; those of our stable element materials that are relevant to pesticide studies [5] and other agricultural applications have been discussed with representatives of FAO with whom the Agency has a Joint Division. We have in the past consulted or cooperated on standards and intercomparisons with many other organizations including the BIPM, UNSCEAR, IUPAC, ISO, EURATOM [11] and other international and interregional as well as with numerous organizations and offices, including, of course, the National Bureau of Standards. In addition, an informal network of reference laboratories has been set up by the Agency selected on the basis of their reputation and continued reliability, to assist in the analysis of reference materials.

V. Recent Recommendations to the Agency

A recent consultant's meeting on Labelled Chemicals and Nuclide Production Relevant to Nuclear Medicine (Copenhagen, 2-4 April, 1973) led to several recommendations indicative of the broader implications and need for analytical quality control. This group recommended that there be IAEA sponsored intercomparison activities carried out to assure good accuracy in radiopharmaceutical laboratories. They also recommended strongly that the Agency investigate reference materials needs in Member States with the objective of being responsive to such needs. It was, incidently, also noted that there is a need for a ^{133}Xe standard reference material for calibration purposes - a counting standard. In this context, WHO currently provides a few reference substances for quality control procedures.

A recent Panel on Practical Aspects of Neutron Activation Analysis (Vienna, 6-10 August, 1973) a subject that has been of major interest to the Agency for a long time, added further support to the importance of the Agency's programme. Although Neutron Activation Analysis is regarded by many groups, based on their own experience, as a generally reliable technique, wide-scale interlaboratory comparisons of NAA results on reference materials such as those organized by the Agency and others, have revealed significant discrepancies of results among the laboratories. [8] Concurrent intercomparisons of some other competing techniques have also shown that they are not better than NAA in this regard. The findings further underline the need for continuous control of the quality of analytical work, regardless of the analytical method employed.

The panelists recommended an expansion of the Agency's services by acting as a clearing house for information on the availability of reference materials and SRM's from reliable non-Agency sources. In its own production, the Agency should concentrate its efforts on reference materials and SRM's that are not currently available. Biological reference materials and SRM's were pointed out as being in relatively short supply and increasingly demanded. The need for larger batches of these materials was stressed - subject to considerations of storage life - since by the time a reference material becomes accepted as an SRM, the supply may often be nearly exhausted. The interlaboratory comparisons of analytical results should continue. In such studies the uncertainties in the standards used in the analyses of reference materials have been recognized as a major contributor to the large deviations observed among laboratories. In order to make a more realistic comparison and evaluation, it was suggested that the Agency provide, together with each set of reference materials to be analyzed for intercomparison, a "standard" for the elements of interest, to allow normalization of the results for comparison.

In the field of marine radioactivity studies, a panel that met in Vienna, 30 October to 3 November, 1972, recommended that the Monaco Laboratory should "continue the highly-successful programme of preparation and distribution of intercomparison samples of environmental material, both marine and freshwater ... contaminated with either fission-produced or activation-produced nuclides" as well as "the present programme of cooperation with Seibersdorf Laboratory in the preparation and distribution of standard reference samples ...(and) calibrated solutions suitable for yield monitoring and standardization in the analysis for transuranic elements."

Recommendations for SRM's in the field of medical isotope applications were made by a Consultants' meeting on analytical quality control for the WHO/IAEA joint research programme on trace elements in cardiovascular diseases, Vienna, 13-15 December, 1972, and for environmental monitoring by the IAEA/WHO Panel on environmental monitoring programme, Vienna, 6-10 November, 1972.

Finally a word about Reference Materials for nuclear fuel analysis. Here again as the result of a Consultants' Meeting (Vienna, 13-15 December, 1972), it was recommended that the Agency undertake several activities important for increased international cooperation with some concurrent improvement of the ability of scientists from different countries to be able to talk to one another and know that their data is comparable. These include preparation of a list of available materials - reference and also test materials - specifically uranium and plutonium materials, with the Agency in the coordination role in assisting and encouraging exchanges and intercomparisons of these materials. Test materials were defined as those normally satisfactorily characterized for their particular purpose, but not as fully as reference materials. It is likely that in this task the Agency would have the active cooperation of several supra-national organizations such as EURATOM.

The Agency was asked to encourage Member States to make internal national reference materials available to enhance international cooperation on the analytical chemistry of nuclear fuels and for the mutual benefit of all States concerned.

VI. Future Plans

To explore the results of programmes over the past decade and to advise the Agency on how to best help laboratories to achieve accurate measurements in the nuclear and radioisotope fields with adequate precision, sufficient speed, and at a reasonable cost, a Consultants' Meeting on Analytical Quality Control was convened by the International Atomic Energy Agency from 16-18 May, 1973, in Vienna. A systematic and practicable approach to this problem resulted from the meeting, and plans for reference materials, analytical quality control, and related matters are discussed in the following sections.

A. Supply and distribution of Standard Reference Materials

Having effectively completed and evaluated the results of a number of intercomparisons, consultant meetings, and panel reports, the need for continued distribution of standards, reference materials, and intercomparison samples has been clearly affirmed.

The future Agency programme will seek to emphasize certification of more standard reference materials with their content of radionuclides and stable elements, and to assist in the distribution of national standard reference materials for worldwide intercomparisons, where legal difficulties prevent their direct export from one country to another (i.e., uranium and plutonium).

Steps will be taken to establish priorities in introducing new standard reference materials and reference materials in the broad fields of analyzing radionuclides and stable elements in nuclear materials, rocks and ores, environmental, and medical samples. In this context, in the planning of any new standard reference materials programmes, continuous cooperation of the Agency with other international bodies will avoid possible duplication. With the objective of improving the accuracy of laboratories engaged in intercomparison studies, it is considered advisable to establish worldwide priorities for well-defined studies based on particular standard reference materials. It is considered better to carry out a few well-planned intercomparison studies on particular problems than to disperse the Agency's efforts over a large number of problems.

Standard reference materials must be produced with the highest quality, and it is essential that only well-established and recognized procedures be used to accomplish this goal. While we would like to be able to strengthen our own in-house scientific facilities and orient ourselves towards measurement work on standard reference materials, this would require a staff and facilities increase well beyond what appears practical for the IAEA in the near future.

We believe that a network of highly qualified laboratories should be encouraged to work together in the measurement work leading to certification. These may be university, industrial, or national laboratories. The emphasis must be placed on <u>quality</u>, i.e., to measure properties with capability, responsibility, and reliability. A large number of laboratories is not necessary and indeed may be a disadvantage. We believe the Agency can provide a focal point for such an effort, concentrating on requirements for nuclear-based methods of analysis and nuclear-analytical needs.

B. Analytical Quality Control Services and Other Matters

Since reliable analytical results are often the basis for critical discussions in assessing nuclear operations, environmental pollution, nutritional deficiencies, and mineral resource potential, it is of paramount importance for international organizations and their Member States to have at their disposition the services of analytical laboratories of assured reliability.

In reviewing the problems related to the Agency's Analytical Quality Control Services and its results, it was felt that the reliability of analytical data in the fields of radiochemistry and trace analysis could be appreciably improved. Through analysis of the causes of deficiency, it is believed that improvements can be achieved through:

1. Improved understanding of the analytical problems,
2. More information on suitable methods and equipment, and
3. Better analytical quality control work.

It is planned to continue the Analytical Quality Control Services based on the organization of intercomparison studies, but with the expanded objectives of including the survey of the analytical situation in a particular field, information dissemination, education, and improvement of methodology. The accuracy of the measurements in the participating laboratories is to be controlled through distribution and analysis of standard reference materials.

In the Agency's Safeguards programmes, improved availability and intercomparison opportunities involving reference materials for nuclear fuel analysis also will be useful. In the development of Safeguards procedures for evaluation the reliability of analytical data, considerable effort is being put forth to examine the systematics of chemical analysis, to identify the frequency of use of reference materials required, to define biases introduced by particular methodologies, etc. This kind of activity may be of considerable use outside the Safeguards programme, in monitoring for water or air pollution, for example. We plan to exploit the broader applicability of those activities.

In the field of nuclear fuel analysis one area of particular concern is the analysis of mixed uranium - plutonium oxide fuel materials. These are important to the advanced technological efforts in a number of Member States. Present analytical methods for assay for uranium or plutonium in mixed oxide materials are difficult to master. There is a need for a test material to examine the difficulties involved and it is anticipated that a coordinated research programme on some of the analytical problems of mixed uranium - plutonium oxide materials will be undertaken. This would involve obtaining a supply of well-characterized (U - Pu) oxide material to be used as a test material. Particular problems to be examined would include dissolution of mixed oxides and analysis for U and Pu in the presence of each other. It is expected that the opportunity for international intercomparison will be received favourably by all workers involved with the analysis of mixed oxides.

C. Areas of Priority

To meet the practical requirements of participating laboratories, the Agency may concentrate on providing the services discussed above in areas of high priority such as follows:

1. Uranium and thorium prospecting (more standard reference materials are required).
2. Environmental analysis for radionuclides, particularly with respect to radioactive waste disposal on land and into the ocean.
3. Environmental analysis for stable elements by nuclear-based techniques (such as analysis of Hg, Cd, As, and others).
4. Analysis for safeguards purposes.
5. Analysis in connection with isotope applications in the life sciences.

D. Cooperation with Other Organizations

It has been mentioned in preceding sections of this paper that the Agency has cooperated in the past with several international, interregional, and national organizations, institutions, and laboratories in the preparation of materials for analytical quality control and in the organization of intercomparisons. It is our firm intention to continue to do so in the future.

The costs of preparing certified reference materials are high and are influenced by the time and effort required. In view of the direct gain through elimination of significant analytical errors, however, costs should not be considered a limiting factor. The efficient use of materials that are expensive demands an awareness of purpose of use, and of secondary materials that may be adequate for many purposes.

We welcome any new initiative by national or international bodies to provide additional reference materials in the nuclear field. No single organization is capable of providing all the SRM's required even in this field alone.

International cooperation and careful distribution of work is necessary to use the available manpower and resources to the best effect.

VII. Summary

The International Atomic Energy Agency has distributed calibrated radioisotope solutions, standard reference materials, and intercomparison materials in the nuclear and radioisotope fields since the early 1960's. The purpose of this activity was to help laboratories in its Member States to assess and, if necessary, to improve the reliability of their analytical work and to enable them, in this way, to render better service in a large number of areas ranging from nuclear technology to isotope applications in medicine and environmental sciences. The usefulness and the need for this service was demonstrated by the results of many intercomparisons which proved that, without continued analytical quality control, adequate reliability of analytical data could not be taken for granted.

The scope and the size of the future programme of the Agency in this field has been delineated by recommendations made by several Panels of Experts. They have all agreed on the importance of it and made detailed recommendations in their areas of expertise.

The Agency's resources are limited and it cannot on its own undertake the preparation and distribution of all the materials that are needed. It can, however, offer a focal point to bring together different international and national bodies who have an interest in quality control materials. Cooperation is sought with these bodies to coordinate efforts, avoid duplication of work, and make the best use of available resources.

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Table 1. Summary of Intercomparison Results for Mercury

Material Analysed		Corn flour	Wheat flour	Animal blood	Fish solubles	Milk powder	Saw dust	Cellu-lose	Lacquer paint	Coloric material	All inter-compar-isons
Intercomparison Code		V-1	V-2	A-2	A-6	A-8	S-8	S-9	S-10	S-11	
Number of reported results	Individual determinations	67	58	43	62	45	39	38	29	26	407
	Laboratory averages	15	14	10	14	11	9	8	6	5	92
Number of values accepted	Individual determinations	36	26	35	48	21	22	33	11	22	254
	Laboratory averages	9	7	8	11	6	6	7	3	4	61
Number of values excluded	Individual determinations	31	32	8	14	24	17	5	18	4	153
	Laboratory averages	6	7	2	3	5	3	1	3	1	31
Total range of laboratory averages (ppb Hg)		2.45 - 200	2.5 - 74	4.1 - 49	32.8 - 300	2.3 - 24	29.7 - 1922	33.7 - 608	53.8 - 500	7.8 - 446	
Range of accepted laboratory averages (ppb Hg)		2.45 - 19.3	2.5 - 7.75	4.1 - 21.6	32.8 - 104	2.3 - 5.37	29.7 - 56	33.7 - 143	53.8 - 86	7.8 - 55	
Overall mean of accepted laboratory averages (ppb Hg)		10.3	4.6	13.0	62.6	4.5	41.5	74.5	72.3	30.7	
Standard deviation of overall mean	ppb Hg	6.6	2.2	6.0	23.0	1.1	10.1	38.7	16.6	19.3	
S	%	64.8	48.7	46.3	36.8	24.8	24.4	51.9	23.0	62.9	

Table 2. Air Filter Intercomparison - 1972/1973
Summary of Results

Element Determined	Means Received No.	Means Received Range	Accepted No.	Accepted Range	Added	Mean	Recovered S.D.		Recovered S.E.		Difference	
		µg		µg	µg	µg	µg	%	µg	%	µg	%
Arsenic	12	0.695 - 4.400	11	0.695 - 2.740	2.04	1.655	0.566	34.2	0.171	10.3	0.385	18.9
Barium	9	10.48 - 18.00	9	10.48 - 18.00	13.8	13.05	2.60	19.9	0.87	6.6	0.75	5.4
Cadmium	11	1.93 - 5.63	10	1.93 - 4.77	3.06	3.21	0.77	23.9	0.24	7.5	0.15	4.9
Chromium	16	1.30 - 7.50	14	1.30 - 4.20	1.85	2.28	0.76	33.4	0.21	8.9	0.43	23.1
Copper	15	0.816 - 8.333	14	0.816 - 6.000	3.04	3.22	1.26	39.1	0.34	10.4	0.18	9.7
Iron	21	112.4 - 291.6	21	112.4 - 291.6	194	191.4	41.1	21.4	8.96	4.6	2.6	1.3
Mercury	6	0.110 - 0.416	6	0.110 - 0.416	0.24	0.26	0.12	46.2	0.049	18.8	0.02	8.3
Manganese	19	3.000 - 8.350	19	3.000 - 8.350	4.2	4.64	1.29	27.8	0.30	6.3	0.44	10.5
Nickel	11	1.63 - 10.00	11	1.63 - 10.00	5.3	6.51	2.28	35.0	0.69	10.5	1.21	22.9
Lead	14	100.3 - 201.0	14	100.3 - 201.0	153	149.7	31.8	21.2	8.5	5.6	3.3	2.2
Selenium	7	0.507 - 1.040	7	0.507 - 1.040	0.85	0.769	0.160	20.9	0.061	7.9	0.081	9.5
Vanadium	10	1.635 - 10.42	9	1.635 - 2.500	2.16	2.05	0.27	13.1	0.090	4.3	0.11	5.1
Zinc	20	50.00 - 118.8	18	50.00 - 85.76	74	70.74	9.68	13.6	2.28	3.2	3.26	4.4

Table 3. IAEA Analytical Quality Programme 1973-1974

Code Name	Matrix	Elements or Nuclides to be Determined	Concentration or Activity Level	Sample Size	Class of Sample and Scheduled Year of Distribution 1973	1974	Remarks
Nuclear Materials							
SR-1	Uranium oxide product	U	87% U	5 g	I		
SR-2	Uranyl nitrate solution	U	200 g/l	2 x 10 ml	I		1
SR-2-1	Uranyl nitrate solution	U isotopic Composition	100 g/l total U 1.5 - 5% U-235	2 x 2 ml	I		1, 2
SR-3	Plutonium nitrate solution	Pu	20 g/l	2 x 10 ml		I	1
SR-3-1	Plutonium nitrate	Pu isotopic composition	90% Pu-239			I	1
Uranium ores							
S-1	Uranium ore: Torbernite	U	0.471% U_3O_8	100 g	S	S	
S-2	Uranium ore: Torbernite	U	0.313% U_3O_8	100 g	S	S	
S-3	Uranium ore: Carnotite	U	0.418% U_3O_8	100 g	S	S	
S-4	Uranium ore: Uraninite	U	0.375% U_3O_8	100 g	S	S	
S-12	Uranium ore: Pitchblende	U	0.014% U_3O_8	100 g	S	S	
S-13	Uranium ore: Pitchblende	U	0.039% U_3O_8	100 g	S	S	
Environmental materials							
W-1	Fresh water, low content of fission products and tritium	H-3 Sr-89, Sr-90, Cs-137	10 nCi/l 2 - 20 pCi/l	concentrated solution to be diluted	I,S	I,S	
W-2	Fresh water, high content of fission products and tritium	H-3 Sr-89, Sr-90, Cs-137	1 µCi/l 0.2 - 2 nCi/l	concentrated solution to be diluted	I,S	I,S	
W-3	Fresh water	Pb, Hg, Mn, Cr, As, Cd, V, Fe, Ni, Zn, Co, Cu, Mo, Se, Ba	10-100 times of natural fresh water levels	concentrated solution to be diluted	I	I	5

Table 3. IAEA Analytical Quality Programme 1973-1974 (continued)

Code Name	Matrix	Elements or Nuclides to be determined	Concentration or Activity Level	Sample Size	Class of Sample and Scheduled Year of Distribution 1973	1974	Remarks
Biological Materials for biomedical studies							
H-1	Human urine	U, Pu, Th		5 ml of concentrated solution	S	I,S	4
H-1/1	Human urine	Hg, Pb, Mn, Cr, As, Cs, V, Fe, Ni, Zn, Cu, Co, Se	natural content	1 litre	I	I	5
H-4	Animal muscle	multielement analysis	natural content	20 g	I	S	
H-5	Animal bone	multielement analysis	natural content	20 g		I	
H-6	Human blood serum	iodine	100 ng/g	5 ml	R		2
Biological Materials of marine origin							
AG-I-1	Fucus vesicelosus (Seaweed)	Co-60, Sr-90, Ru-106, Ag-110m, Cs-134, Cs-137, Ce-144, Pu-238, 239, 240	2 - 150 pCi/g	50 g	R	R	
MA-B-1	Anadara granosa (Clam)	Sr-90, Ru-106, Cs-134, Cs-137, Ce-144	1 - 100 pCi/g	50 g	I	R	3
MA-B-2	Opisthobranch gastropod	Co-57, Co-60, Cs-137, Ce-144	1 - 100 pCi/g	50 g	I	I	2,3
Soil							
Soil-5	Soil	As, Cd, Cr, Fe, Hg, Ba, Mn, Pb, V, Zn, Cu, Co	natural content	1000 g	I		5
Sediments							
SD-B-1	Marine sediment	Sr-90, Ru-106, Cs-134, Cs-137, Ce-144	1 - 100 pCi/g	100 g	I	R	2,3
SD-B-2	Marine sediment	Co-57, Co-60, Cs-137, etc.	1 - 100 pCi/g	100 g	I	I	3
SL-1	Lake sediment	As, Cd, Cr, Fe, Hg, Ba, Mn, Pb, V, Zn, Co, Cu	natural content	100 g	I		

Table 3. IAEA Analytical Quality Programme 1973-1974 (continued)

Code Name	Matrix	Elements or Nuclides to be determined	Concentration or Activity Level	Sample Size	Class of Sample and Scheduled Year of Distribution 1973	1974	Remarks
Air Samples							
Air-1	Simulated deposition on air filter	Pu, Sr-90 Mn-54, Fe-55, Ru-106, Cs-137	100 pCi, 10 nCi 0.5 - 3 μCi ea.	10 filters		I	
Air-2	Simulated deposition on Air Filter	Sr-89, I-131, Ce-144	200 nCi - 1 μCi ea.	10 filters		I	
Air-3 Air-3	Simulated deposition on Air Filter	Pb, Hg, Mn, Cr, As, Cd, V, Fe, Ni, Zn, Co, Cu, Mo, Se, Ba	100 - 0.1 μg of each element on each filter	10 filters		I	
Sea Water							
SW-A-1	Sea water	low level fallout radioactivity	background levels	50 litres	I	I	2, 3
SW-I-3	Sea water	Fission products Pu	10 - 300 pCi/l 0.5 pCi/l	5 litres	I	R	
Animal Materials							
A-1	Spray dried animal blood	Pu, U, Th	natural content	500 g		R	
A-2	Spray dried animal blood	As, Cd, Cr, Fe, Hg, Mn, Pb, Zn, Br, Co, Cu, Mo, Se	natural content	100 g		R	
A-3	Calcinated animal bone	Sr-90 5 pCi/g Ra-226 0.1 pCi/g	(low natural content)	100 g	R	R	
A-10	Calcinated animal bone	Sr-90, Ra-226	medium natural content	50 g	I		2
A-3/1	Calcinated animal bone	As, Cd, Cr, Fe, Hg, Mn, Pb, Zn, Co, Cu	natural content	100 g		R	5
A-6	Fish solubles	As, Cd, Cr, Fe, Hg, Mn, Pb, V, Zn, Co, Cu	natural content	100 g	I		5
A-7	Milk powder	Sr-90, Cs-137, Na, K, Ca, Sr, Ba, Cs	natural content	500 g	R	R	
A-7/1	Milk powder	As, Cd, Cr, Fe, Hg, Mn, Pb, Zn, Co, Cu	natural content	100 g		R	5
A-9	Milk liquid	Sr-89, Sr-90, Cs-137	0.5 - 2 nCi/l	5 ml of concentrated solution	I,S	I,S	4

Table 3. IAEA Analytical Quality Programme 1973-1974 (continued)

Code Name	Matrix	Elements or Nuclides to be Determined	Concentration or Activity Level	Sample Size	Class of Sample and Scheduled Year of Distribution 1973	1974	Remarks
Plant Materials							
V-1	Corn flour	Hg	10 ppb Hg	50 g	R	R	
V-2	Wheat flour	Hg	5 ppb Hg	50 g	R	R	
V-2/1	Wheat flour	As, Cd, Cr, Fe, Hg, Mn, Pb, Zn, Cu, Co	natural content	50 g		R	5
V-5	Wheat flour	iodine	5 ng/g	15 g	R		
V-4	Potatoes, mashed, dried	As, Cd, Cr, Fe, Hg, Mn, Pb, Zn, Cu, Co	natural content	50 g		R	5
Hydrological Standards							6
Vienna SMOW	Water	$^{18}O/^{16}O$ D/H	$(1193.4\pm2.5)\times10^{-6}$ $(155.76\pm0.05)\times10^{-6}$	25-50ml	S	S	8
SLAP	Water	$\delta^{18}O$ δD	-55.40 ± 0.13 per mil -426.8 ± 1.0 per mil	25-50ml	S	S	7
NBS-1	Water	$\delta^{18}O$ δD	-7.89 ± 0.03 per mil -46.7 ± 0.4 per mil	25-50ml	S	S	7
NBS-1A	Water	$\delta^{18}O$ δD	-24.27 ± 0.07 per mil -182.5 ± 0.4 per mil	25-50ml	S	S	7

Notes and Abbreviations:

I Intercomparison.

R Reference material.

S Standard material.

1 Each distribution consists of two samples, one made from pure uranium salt solution, the other one with different impurities added.

2 New Item for 1973.

3 Distributed from Monaco Laboratory.

4 To be made up to 1 litre with natural matrix.

5 For trace multielement analysis.

6 Distributed by the Section of Isotope Hydrology.

7 Difference in per mil vs Vienna SMOW, established by intercalibration of 25 laboratories.

8 $^{18}O/^{16}O$ Craig, H., Standard for reporting concentrations of deuterium and oxygen-18 in natural waters, Science, 133, 1833-34 (1961). This $^{18}O/^{16}O$ ratio reported is that of the SMOW defined by Craig. The Vienna-SMOW has, according to Craig, exactly the same isotopic ratio as the SMOW defined by him.

D/H Hagemann, R., Nief, G., and Roth, E., Absolute isotopic scale for deuterium analysis of natural waters. Absolute D/H ratio for (Vienna)-SMOW, Tellus, 22, 712-715 (1970).

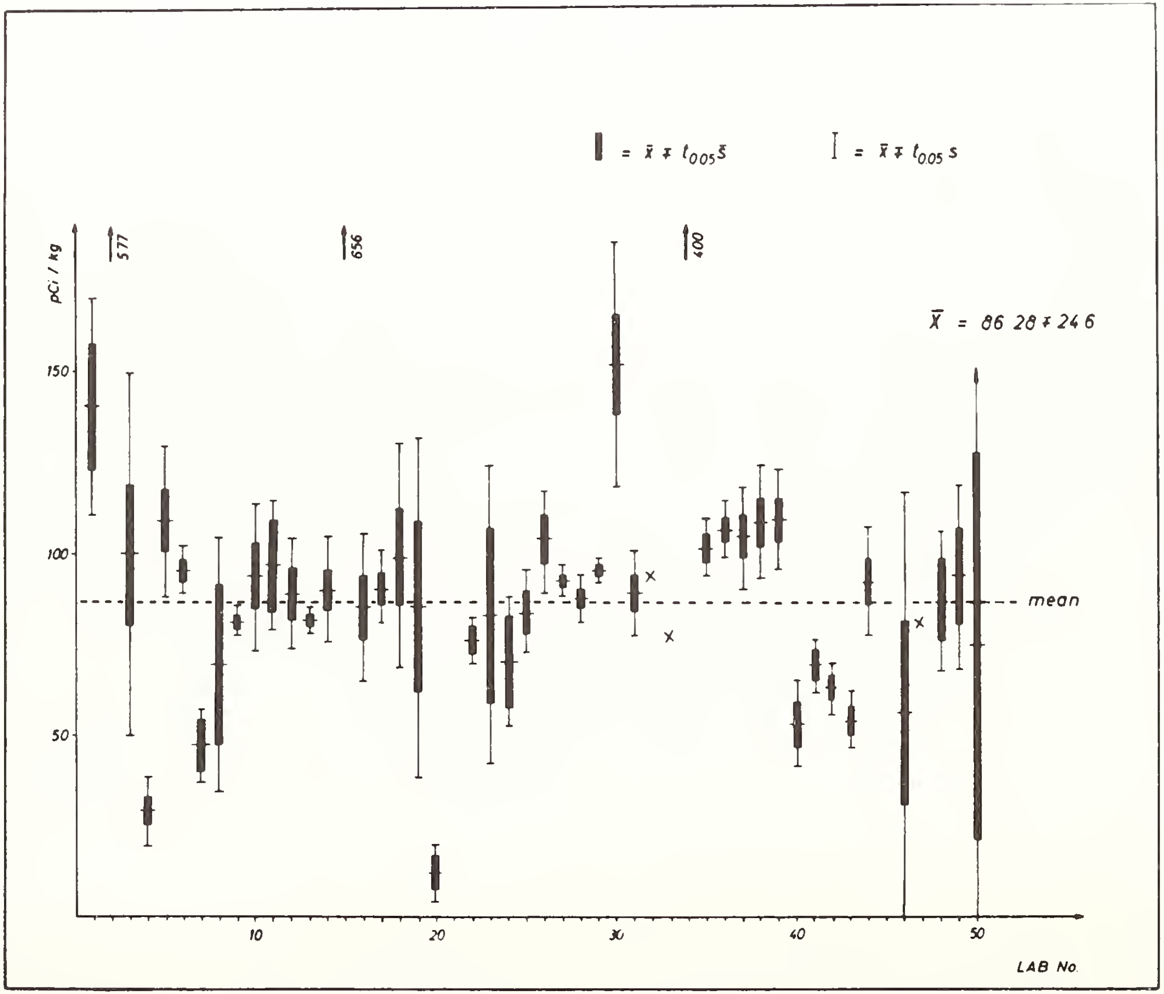

Figure 1a. The result of 217 determinations of Cesium 137 in dried animal blood performed by 48 organizations.

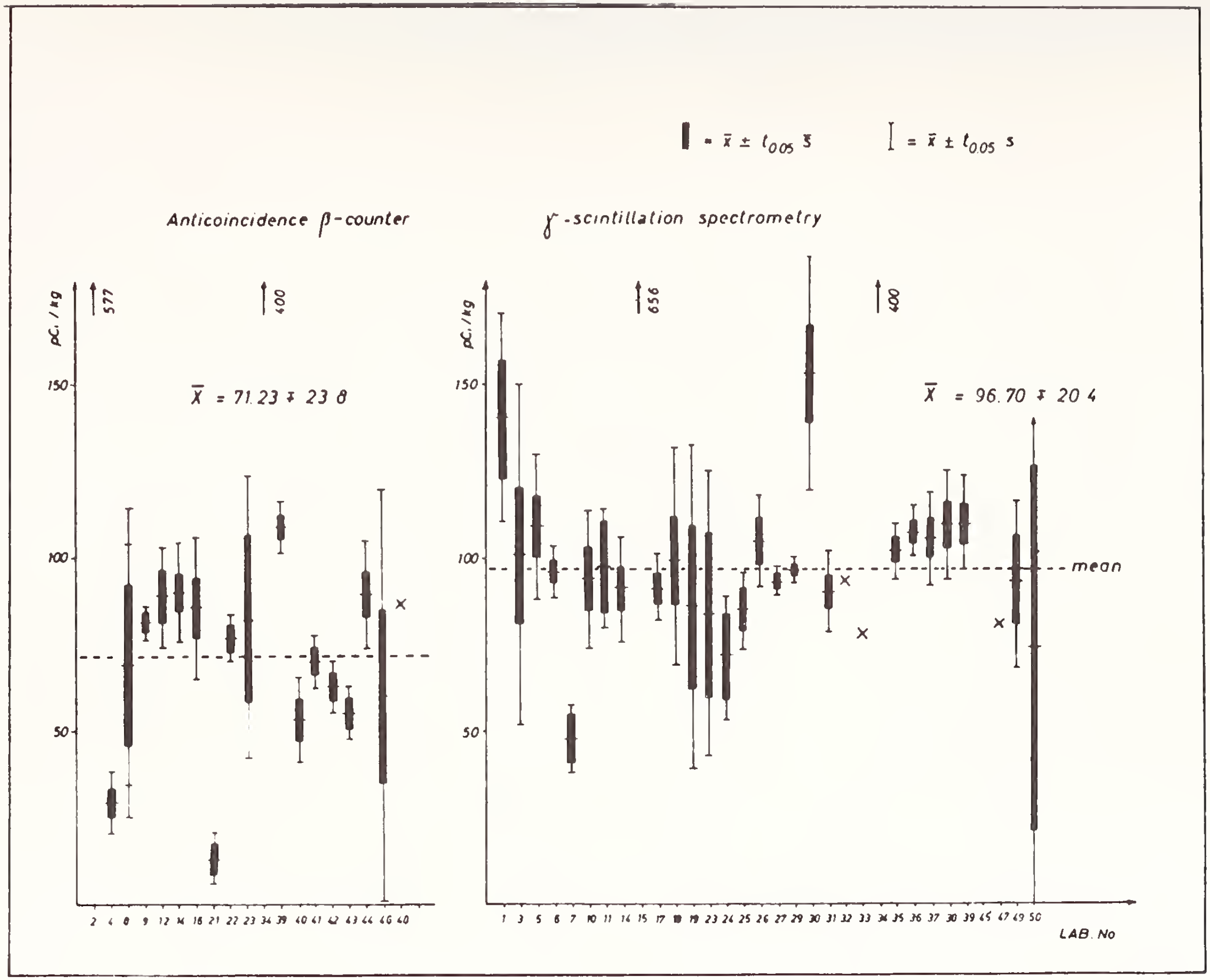

Figure 1b. The cesium 137 measurements of figure 1a are divided into those done by gamma scintillation spectrometry and all other methods.

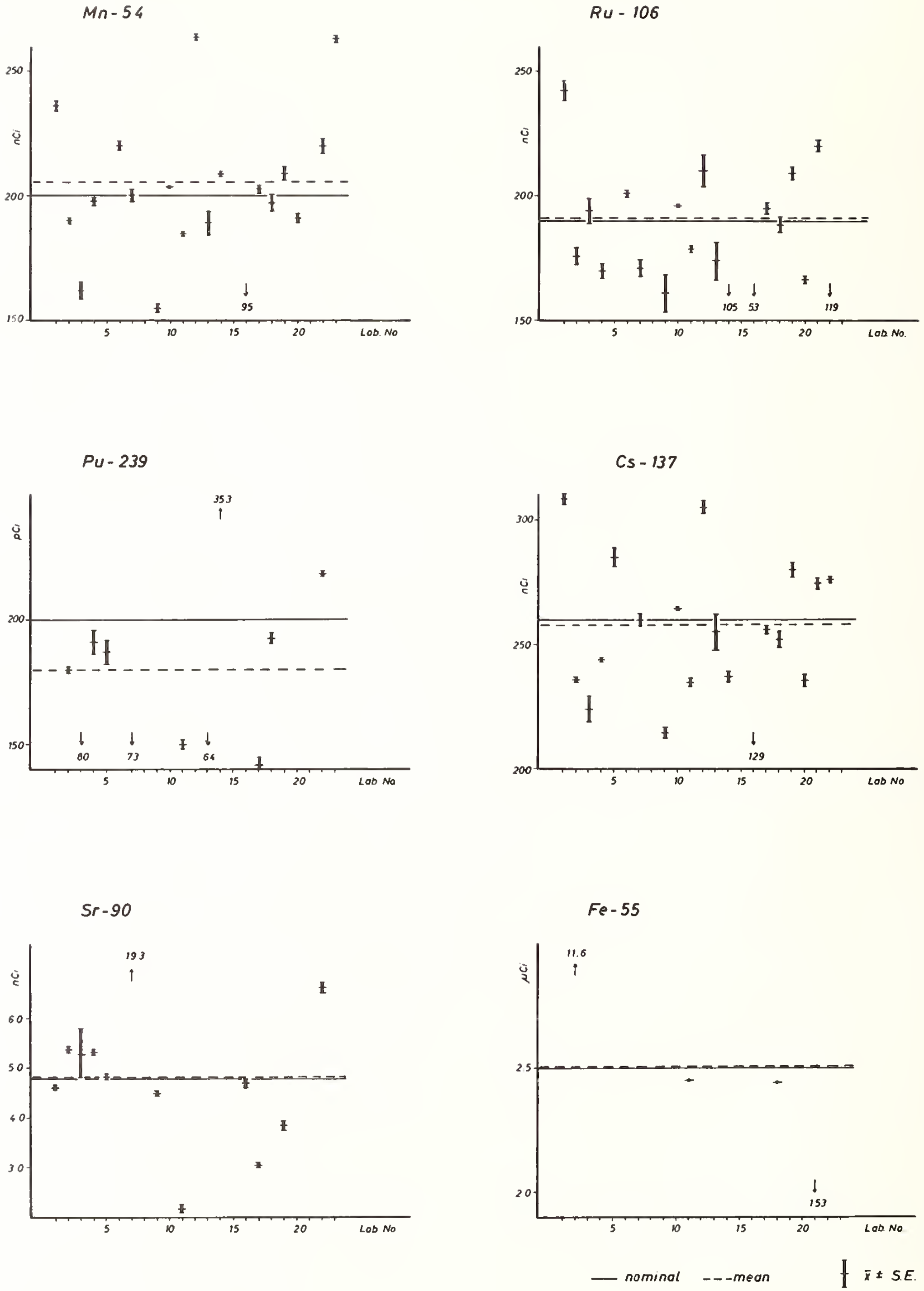

Figure 2. An intercomparison of six radionuclides on air filters in 1972 showed small intra-laboratory standard error, while the overall inter-laboratory means is large.

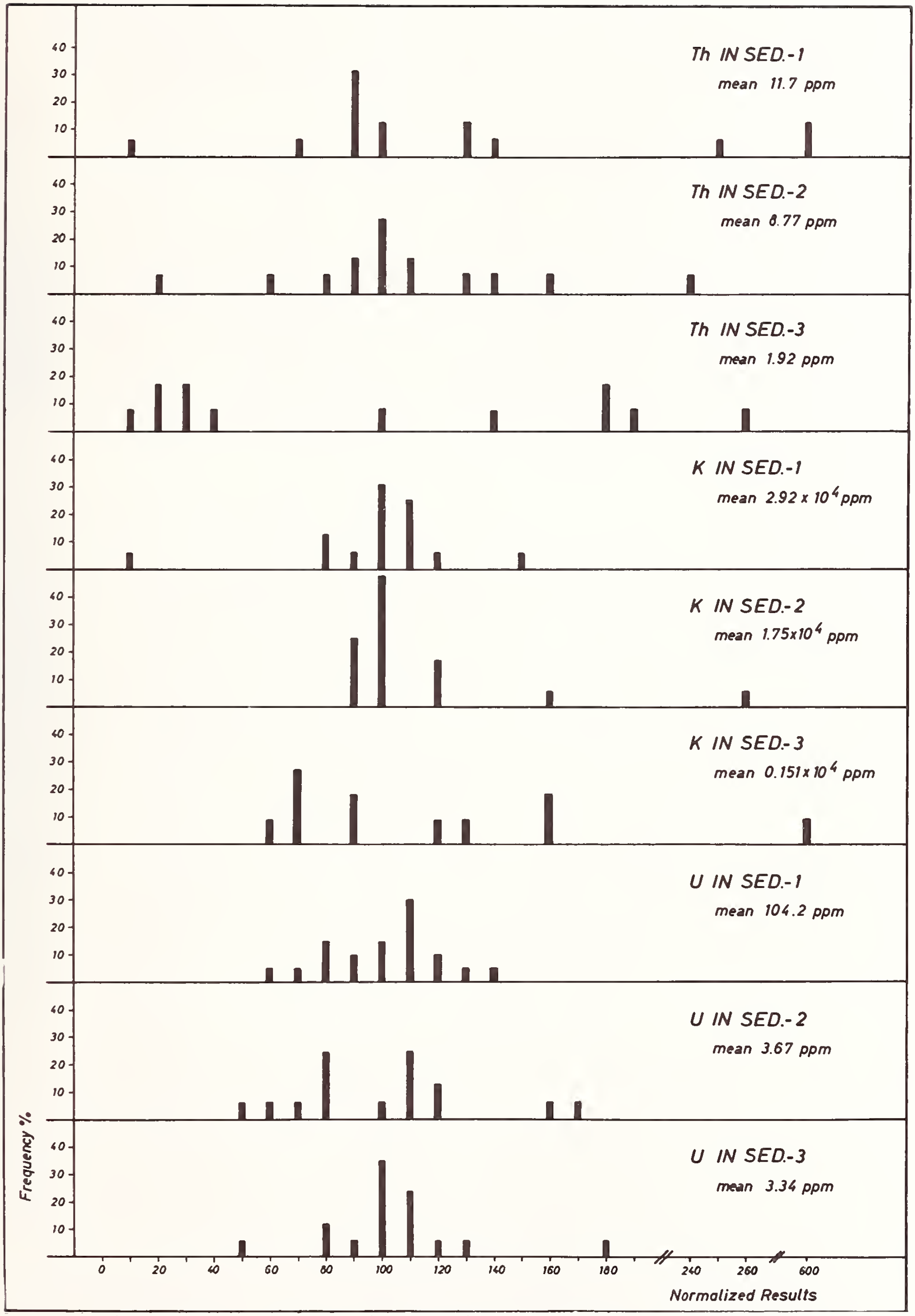

Figure 3. Normalized distribution of results of the determination of three elements in three different sediments.

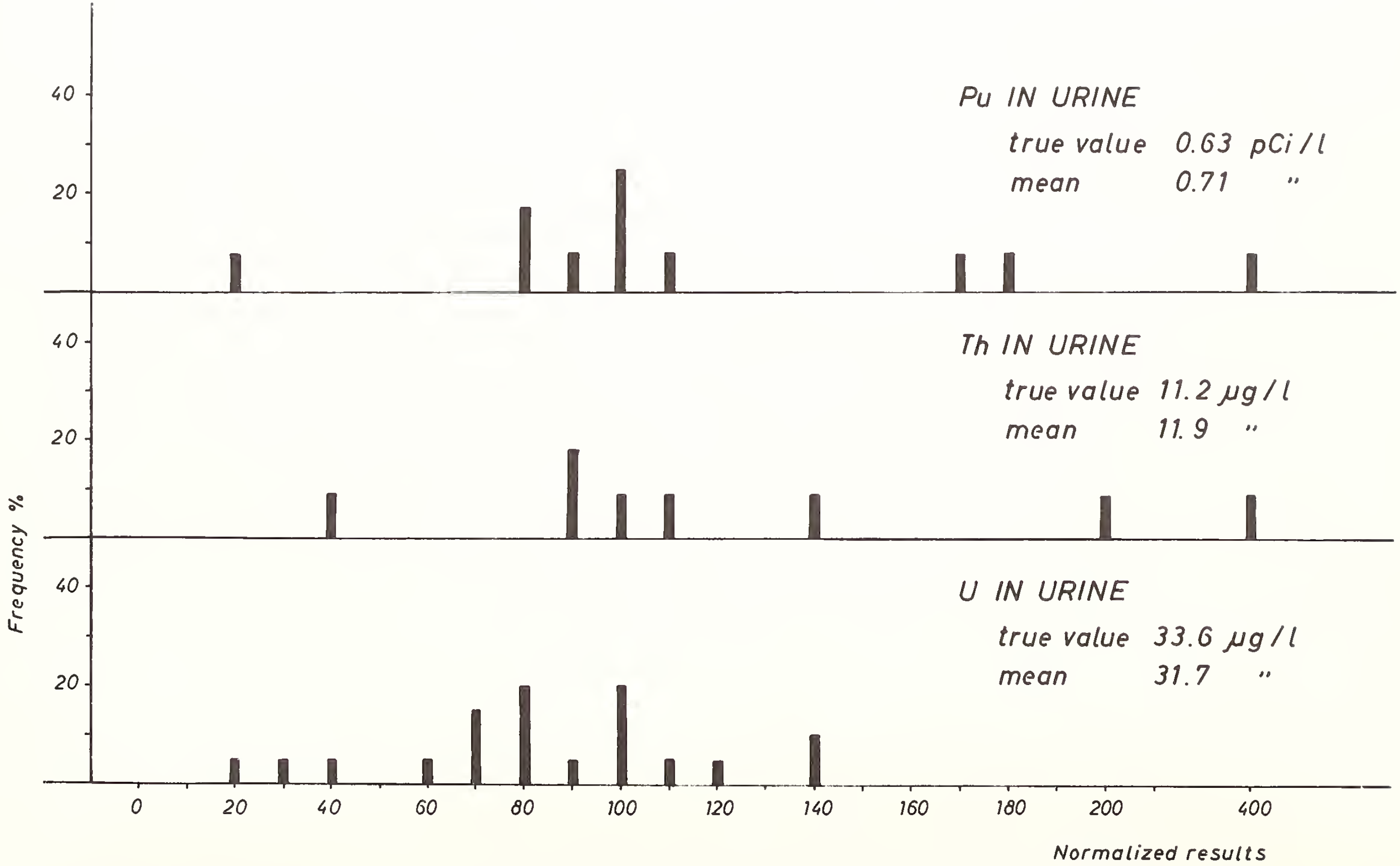

Figure 4. Normalized distribution of results of the determination of three elements in urine samples.

THE ACTIVITIES OF THE EUROPEAN ECONOMIC COMMUNITY IN THE FIELD OF REFERENCE MATERIALS AND METHODS

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Technical progress and industrial expansion are maintaining a very rapid pace while calling for high-quality production; this is reflected in an increased need for reliable methods of measurement and accordingly for reference materials (RM). Moreover, in an evolving economic and monetary community the development of certified reference materials (CRM) and the harmonization of work being done in this field constitute an important economic factor.

I. Initial Studies

A. General survey

After a number of contacts with a variety of national bodies, the Commission proposed as early as April 1969 to set up a Community Bureau of References whose staff was to assist research and industry in the field of commercial exchanges and public protection. As the result of these early discussions the Council of Ministers decided that an inquiry should be undertaken whether work in this field was of importance to the member countries.

The Ispra establishment of the Joint Research Centre was charged with the carrying out of an initial survey on the use of and demand for certified reference materials (CRM's) in the six Common Market countries. The survey was initiated with the assistance of the Consultative Group of National Experts and the active participation of the representative federations of various industries, and was carried out in the years 1970 and 1971.

Since the survey was in the nature of a pilot project, and in view of the limited resources available, it was not aimed at blanket coverage of all laboratories concerned with reference materials. Somewhat arbitrarily, various sectors of great economic, scientific, and technical importance were selected. Other sectors, by no means insignificant ones, were provisionally omitted or merely touched upon.

It was not the intention in this initial survey to draw up an exhaustive list of all requirements, replete with a catalogue of the specifications demanded, but rather to identify families of products or materials in which interest was displayed. The emphasis was laid on the demand for reference materials of certified composition and/or purity, this field being divided into six main families, RM's for: metallurgical products, inorganic chemicals, organic chemicals, pharmaceuticals, food products, and medical analysis.

Each of these families was itself divided into sub-families, and the questionnaire was designed to allow the establishment of correlations between product sub-families, the methods to be calibrated by these products, ranges of concentration of certified constituents, and annual consumption. In addition there was a section, included in view of a specific survey at a later date, on the demand for other types of reference materials (RM's for measurements of physical and mechanical properties, etc.). This part of the questionnaire was relatively general.

In order to assess the difficulties encountered by RM-users, laboratories were also asked to specify their current sources of supply, the criteria governing their choice and the shortcomings of currently available reference materials, whether quantitative or qualitative. Furthermore, as follow-up actions even on a restricted scale in this exceedingly wide field would involve the participation of a large number of laboratories, an endeavour was made to compile an initial list of bodies which, if the need arose, would be prepared to cooperate, specifying the limits of any such cooperation. The questionnaire was sent finally to 1556 addressees. An average of slightly more than one third of the laboratories consulted completed a questionnaire. Indeed, this proportion exceeded 50% in the case of the processing industries and research institutes.

It should be noted that owing to initial options the processing industries were not covered on a scale consistent with their importance in the economy of the Community countries. Their very high reply rate (53.6%) shows that this sector merits examination in greater depth. By contrast, the chemical and food industries yielded relatively few replies to our survey; however, it should be noted that here the replies received came from large-scale firms, figure 1.

Two of the interesting facts that emerged from the analysis of the replies were:

1. Sources of RM's:

   Two hundred forty-six distinct commercial sources were mentioned by the 500 RM-users identified on analysis of the returns. These sources are classified in six families, according to country of origin, in-house production being considered as a separate family, figure 2.

2. Criticism of available RM's:
   Over 50% of RM-users are not satisfied, either because the "quality" of the products available is regarded as inadequate or because the products simply to not exist. The different reasons for criticism are shown in figure 3.

No attempt will be made here to analyse the different replies and correlations given in the report on the survey. As an example we show some graphs that were given for RM's of organic chemistry. They may be considered to be representative for the other sectors analysed. This group of products is subdivided into the following 11 sub-families:

C 01 = pure substances
C 02 = solvents
C 03 = industrial dyestuffs
C 04 = petroleum products (motor spirits, additives, lubricants)
C 05 = polymers
C 06 = elastomers
C 07 = semiproducts for plastics
C 08 = organometallic compounds
C 09 = pesticides (insecticides, fungicides, herbicides)
C 10 = detergents
C 11 = pure gases and mixtures thereof
Miscellaneous organic products.

One hundred-fifty laboratories expressed a total of 436 demands for RM's for this group of products. Figure 4 shows for each product sub-family the distribution of the 257 demands for new reference substances and of the 179 demands for improvement of existing RM's. Except for solvents, the percentage of demands for new RM's always exceeds that for improved ones. Figure 4 gives details of the desired concentrations. For almost all product sub-families, there is a clear majority of demands for concentrations in the "%" range--198 demands in all.

The number of method "indications" for RM's demanded for organic chemicals is very high, 1162 (figure 5). The upper part of the figure gives the frequency of "indications" for the principal methods mentioned in this sphere. Two methods stand out conspicuously: chromatography with 281 indications and spectrophotometry (UV, IR, visible) with 239 indications. Reference substances for physical properties occupy an important position, 137 indications. Figure 5 shows also that for all product sub-families, except for polymers and gases, chromatography is the method for which the demand for

RM's is greatest.

In general, this survey aroused great interest in the scientific and industrial circles approached. By virtue of their scale, many of the sectors concerned are of great economic importance. The disparity of response rates between sectors, and a fortiori that between the percentages of RM-users, may be regarded in some cases as a test of "maturity" with regard to the use of reference materials.

An analysis of results shows that the demand for both new and improved products is considerable. Specific snap surveys (by questionnaire and by interview) undertaken later in various sectors show that after elimination of "false demands," the list of new products needed on a priority basis is still very long.

Although the number of reference materials available probably runs into thousands, very few of them are, to our knowledge, certified internationally. Yet the vast majority of users emphasize the value of being able to obtain such substances. They also state that a larger number of internationally recognized methods should be available. However, this aspect of the problem was not analysed since it does not fall within the terms of reference of this survey, but it would be worthworth while to take it up at a future date.

The complete analysis of the replies has been published in a report EUR-4886 (1973), which is available in German, Dutch, French, Italian, and English. [1]

B. Sectorial inquiries

In the light of the very positive results of the inquiry the member states of the Community concluded a one-year contract with the Commission (1972) to allow the continuation of these first inquiries and the beginning of laboratory experiments at the Ispra laboratories of the Joint Research Center (JRC). This paper does not describe the laboratory activities of the JRC in 1972 and 1973, for which separate reports are in preparation.

Because the general inquiry gave only qualitative results and lacked the needed precisions for establishing a definite programme, four additional inquiries in the fields of ferrous metallurgy, non-ferrous metallurgy, inorganic materials, and reference materials of defined physical and technological properties were launched and analysed. In September 1972 an inquiry was also launched concerning the needs of the different services of the Commission for reference methods.

Four ad hoc working groups were set up by the consultative group mentioned above. Their general task was defined to be:

1. To lay down technical specifications of reference materials;
2. To estimate the annual rate of consumption of such reference materials;
3. To examine critically and continuously the needs for reference materials;
4. To establish priority lists of the actions to be undertaken; and
5. To elaborate for each reference material considered a list of organizations or industries able and willing to cooperate.

II. EEC Research Program

As a result of all this preliminary work, the Council of Ministers of the European Economic Community decided in 1973 to launch a research program in the field of reference materials and methods (Community Bureau of References). The program of Community action is aimed at strengthening, combining, harmonizing, and complementing the national efforts.

A. Type of program

1. The object of the program is:
    a. To meet the needs of industry, research, government departments and the Commission's departments by providing: reference materials, expertise on reference materials, and measurement methods suited to the use of RM's;
    b. To align, by means of joint consultation, the efforts of organizations whose tasks are to some extent similar and concern the field of reference materials.
2. The programme dovetails into a series of activities in the Community as follows:
    a. Action at national or industrial level
    This work is financed by the governments or industries concerned.
    b. Action of the Commission's Joint Research Centre (JRC)
    This particular part of the programme includes the resources to enable the JRC to: provide the Commissions central services with technical support; take part in the joint, coordinated European-scale activities; and undertake own development work in the field. In order to implement this part of the programme, the Commission disposes until 1976 of a personnel of 39 persons and a total budget of

about $8,400,000 (US), comprising charges for infrastructure and administration. The major part of this is to be used for experimental work at the JRC.

c. Joint, coordinated European-scale actions on a cost-sharing basis:
This part of the programme on a cost-sharing basis has been specially chosen on the principle of overall joint action in which the Community countries' programmes should be harmonized and complemented by means of cooperation of national and Commission laboratories. In this type of activity all organizations, whether they are sponsored by government, industry, or the Commission, may collaborate, provided they possess laboratories, know how and/or equipment needed for this type of work. The type of action will vary from industry to industry, depending on requirements. These projects might take the form of: mutual exchange of information between national bodies, both private and public, on requirements for and availability of RM's; coordination by more rational apportionment of tasks among such bodies; financing of part of the cost of characterization and preparation in the form of a joint action; and utilization of the potential of the Joint Research Centre.

Activities over the next years will be concentrated on: listing and defining requirements for new RM's; technical specification of RM's; development and preparation of RM's; organization of intercomparisons of methods and RM's; European-wide recognition of technical characteristics of RM's; and approval of laboratories.

B. Programme Management

The programme will be implemented by a management committee, a secretariat, and the participating laboratories.

1. Management Committee
This committee is composed of national and Commission experts and its task is to keep the programme activities under review. It assists the Commission in the definition and choice of future proposals. It acts through the permanent secretariat, which it guides and advises in scientific, technical, and financial matters.
2. Secretariat
This body is responsible for: comparing and harmonizing programmes, disseminating information and analysing results; organizing and coordinating meetings of experts

in the fields concerned; maintaining contacts with other Commission departments, international organizations working in the fields covered by the programme and standardization bodies; and providing the secretarial services for the Management Committee and any necessary ad hoc working parties.

3. Participating Laboratories
   A participating laboratory is any public or private laboratory or body that actively participates in a current project at the request of the programme management bodies.

C. General principles governing organization and finances.

1. All theoretical or practical work will be carried out in laboratories administered by Member-State Governments, industry, or the Commission.
2. No new R&D laboratories will be set up. If such a need should arise, new proposals will be made.
3. The work will be carried out by teams made available temporarily for the programme by the JRC and the other participating bodies.
4. The JRC will participate in the projects adopted within the framework of its own programme and on the same footing as the national laboratories.
5. The programme will not cover the purchase, maintenance or development of research installations, the cost of which will be borne by the participating laboratories.
6. The Commission's contribution to the funding of the pilot projects, surveys, and studies will be laid down by contract.
7. Reference substances certified jointly will be sold and the unit price will be calculated on the basis of its prime cost.

D. Resources necessary

In order to implement this coordinative programme by contracting with laboratories of the member countries, the Commission is setting up the secretariat composed of six persons and will spend in total until the end of 1975 about $2,570,000 (US).

E. Status of the studies and experiments

The actual programme status of the work is as follows. Some fields and subjects have already been selected for cooperative work and are listed in tables 1-4. The work is normally being done in four phases:

1. Study phase: a very small number of specialists study

the problem;
2. Preparatory phase: a programme of work is drawn up by an *ad hoc* working party;
3. Test phase: the laboratories concerned take part in preliminary comparisons of each other's measuring methods;
4. Certification phase: the selected laboratories make the final measurements.

Surveys or studies are being prepared in other areas of industrial or economic activity in the Community (e.g., pharmaceutics, organic chemistry, petroleum chemistry, goods, clinical analysis, environment).

A simple guidebook of addresses in which users will find reference to companies and organizations selling various types of reference materials is now being printed. It is intended to follow-up this action by updating and enlarging this simple guidebook and eventually by the publication of a detailed catalogue of currently available reference materials.

Close cooperation with other organizations active outside the European Community is planned. The first contacts have been established with the European Committee for Standardization, the "Organisation Internationale de Metrologie Legale," and the US-National Bureau of Standards.

Reference

[1] Community Survey on Standard Reference Materials
EUR 4886, d,f,i,n,e. 1973

Office for Official Publications of the European Communities, Case Postale 1003, Luxembourg (Grand Duchy of Luxembourg).

Table 1. Field 1: "Ferrous Products"

Project	Sample	Description	To be Certified Element	Concentration	Remarks
1.1	1	Coke	C		Coking at different temperatures of coals of type 533 or 534 (International Coal Classification) Calibration of instruments for the analysis of coke used in blast furnaces.
	2		H	0.5 to 1.8 %	
	3		N	0.9 to 1.3 %	
			O		
			S		
			Cl		
			Ash		
			P		
			Calorific Power		

Table 2. Field 2: "Non-Ferrous Products"

Project	Sample No.	Description	To be Certified Element	Concentration	Remarks
2.1	4	Concentrated Ore I	Zn	53 - 55%	blende base (7% Fe)
	5	Concentrated Ore II	Zn	46 - 48%	blende base (15% Fe)
	6	Concentrated Ore III	Zn	51 - 53%	blende base (1% Cd)
	7	Concentrated Ore I	Pb	77 - 80%	galena base
	8	Concentrated Ore II	Pb	50 - 53%	galena base
	9	Concentrated Ore I	Sn	75 - 78%	cassiterite base
	10	Electrolytic Copper	Pb	1 - 5 ppm	chips
			As	1 - 3 ppm	
			Sb	0.5 - 2 ppm	
			Sn	1 - 5 ppm	
			Se	0.1 - 0.3 ppm	
			Te	∿0.1 - ppm	
			S	3 - 6 ppm	
			Ni	1 - 3 ppm	
			Ag	∿10 ppm	

Table 3. Field 3: "Inorganic Products"

Project	Description	To be Certified	Remarks
3.1	Antimony oxide	Impurities	Study phase
3.2	Pure mineral acids	Impurities	Study phase
3.3	Na_2CO_3/K_2CO_3	Impurities	Study phase

Table 4. Field 4: "Physical and Technological Properties"

Project	To be Certified	Materials	Remarks
4.1	Viscosity	Mineral oils	Preparatory phase
4.2	Stability of viscosity RM's		Study phase
4.3	Temperature references		Preparatory phase
4.4	Hardness		Study phase
4.5	Toughness		Study phase
4.6	Standard defects		Preparatory phase
4.7	Vapour pressure		Study phase
4.8	Thermal conductivity	fluids refractory materials fibre compounds	Preparatory phase
4.9	Tribology		Study phase
4.10	Granulometry		Study phase
4.11	Density		Study phase
4.12	Molecular weight		Study phase
4.13	Specific surface		Study phase
4.14	Thermal expansion		Study phase
4.15	Electrical conductivity		Study phase
4.16	Surface condition		Study phase
4.17	Surface tension		Study phase

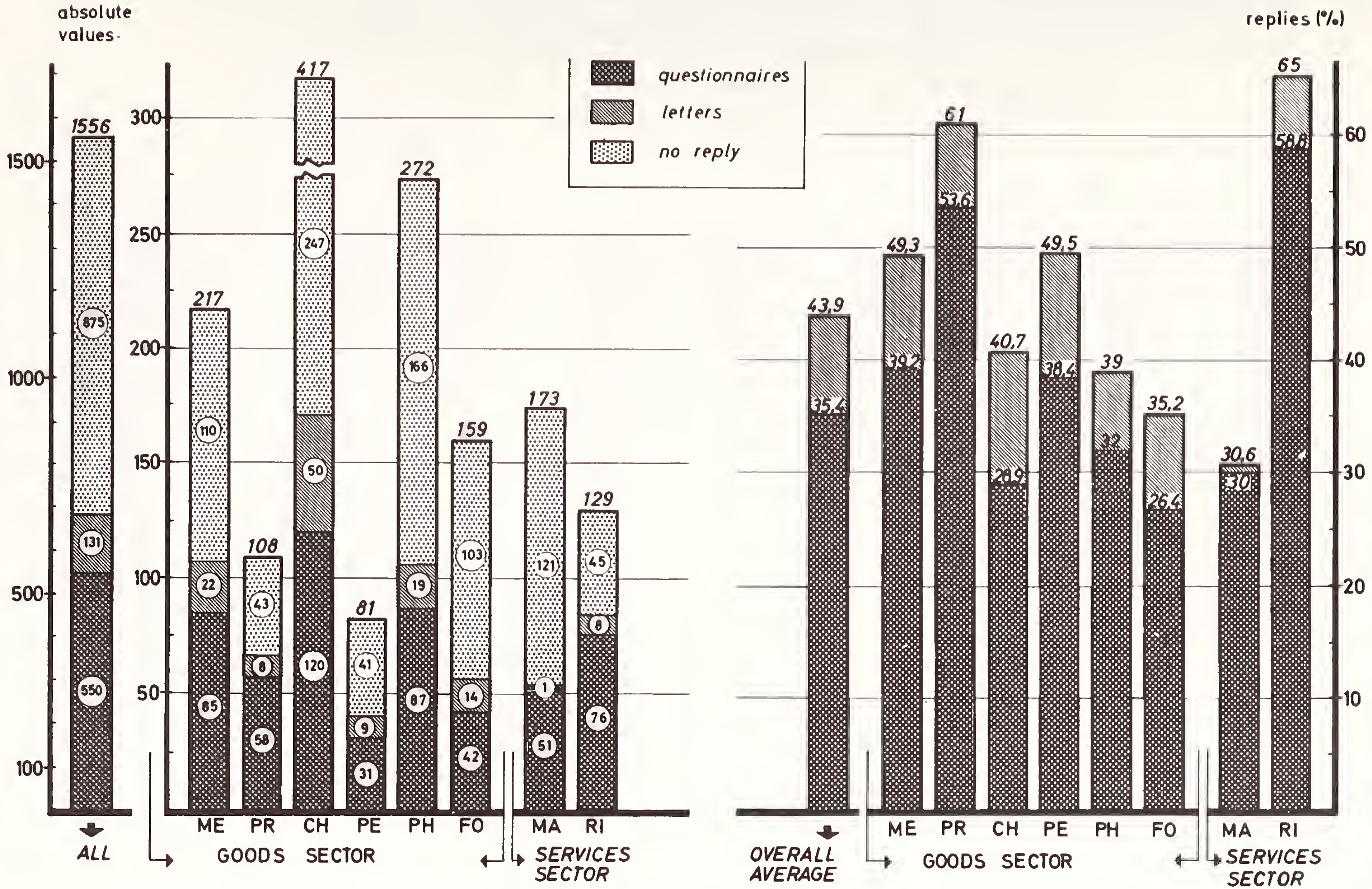

Figure 1. Organizations Consulted and Replies Received

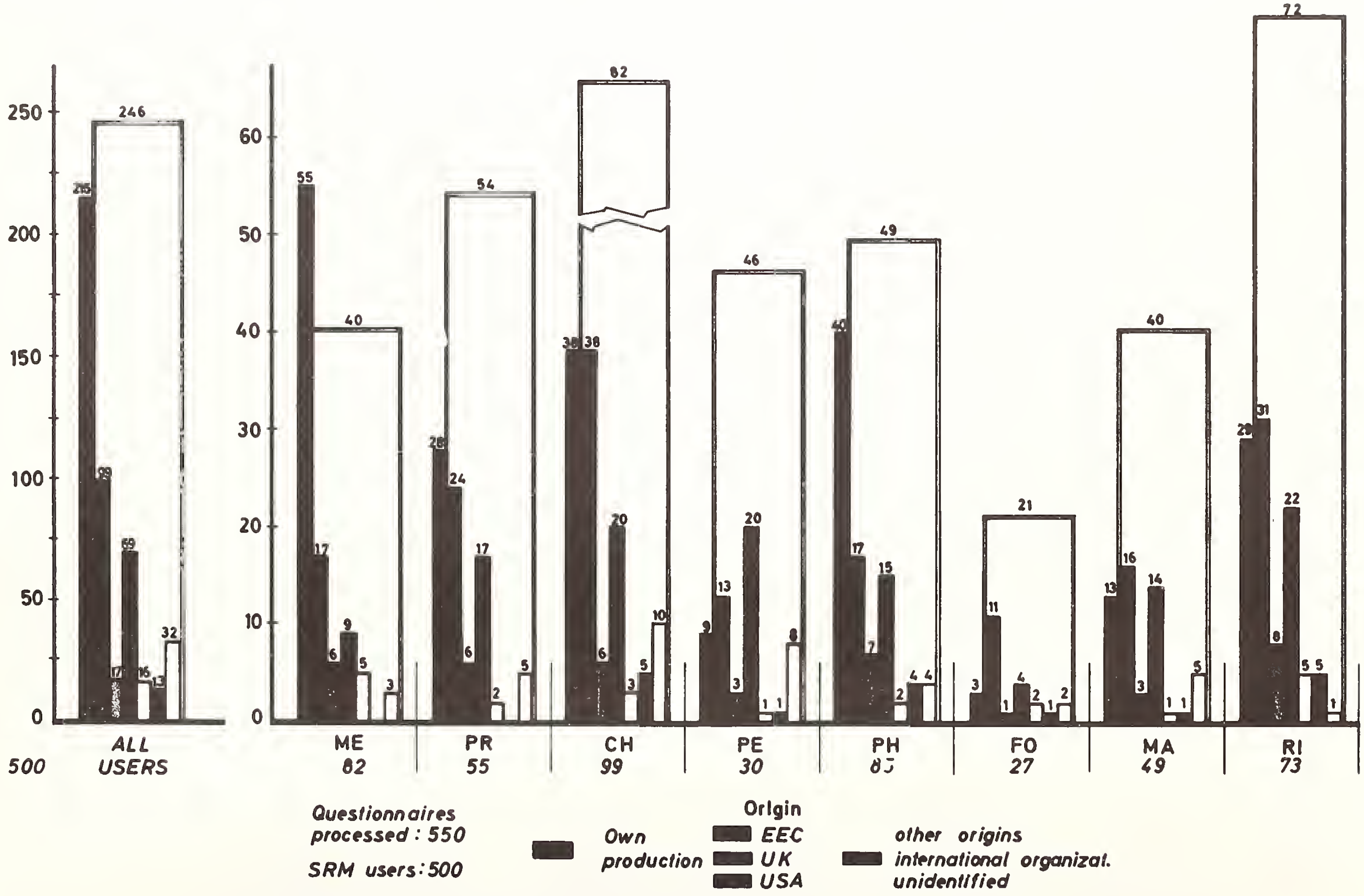

Figure 2. Sources of Supply of SRMs, Number of Different Suppliers

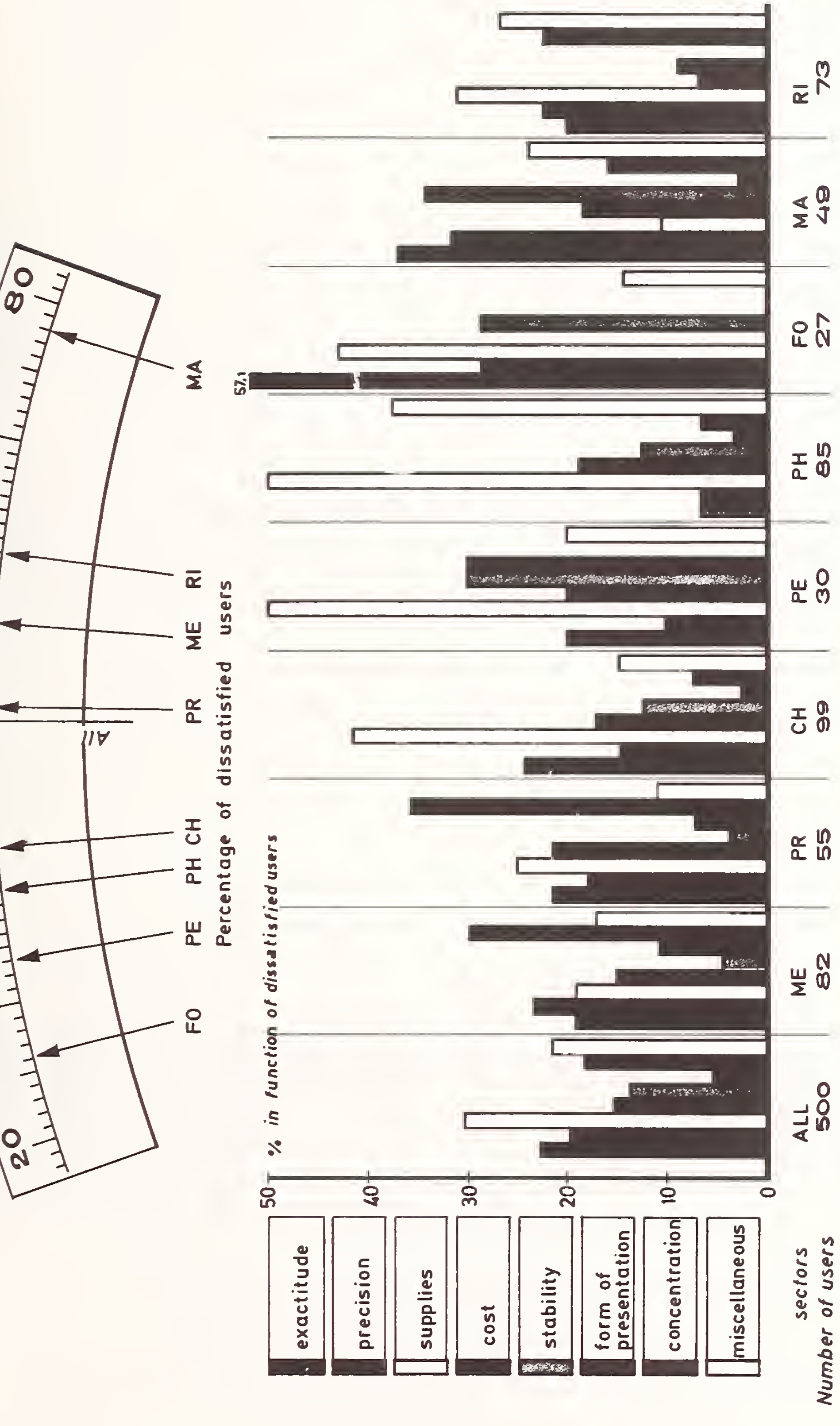

Figure 3. Criticism of Available SRMs

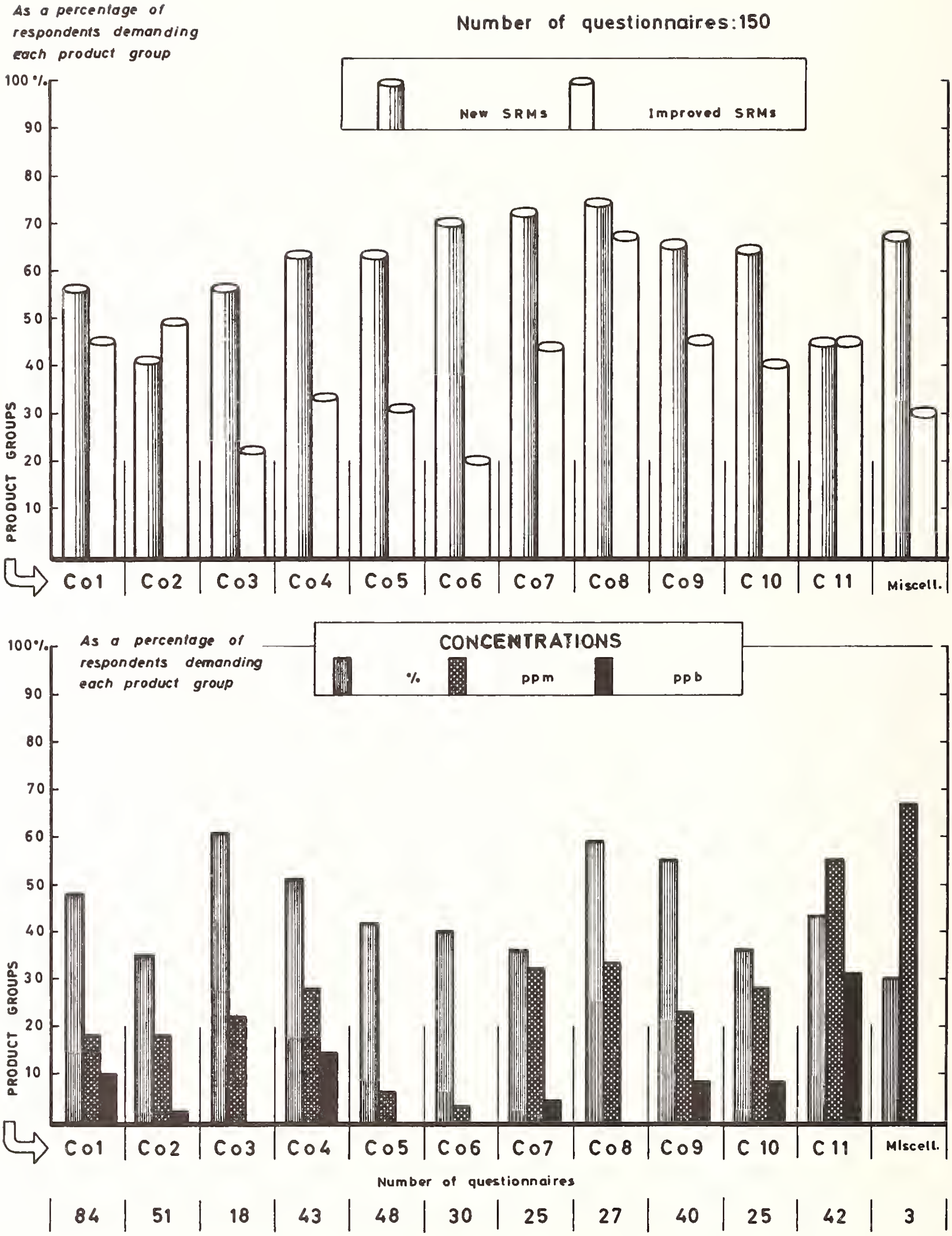

Figure 4. Demand for SRMs for Organic Chemicals

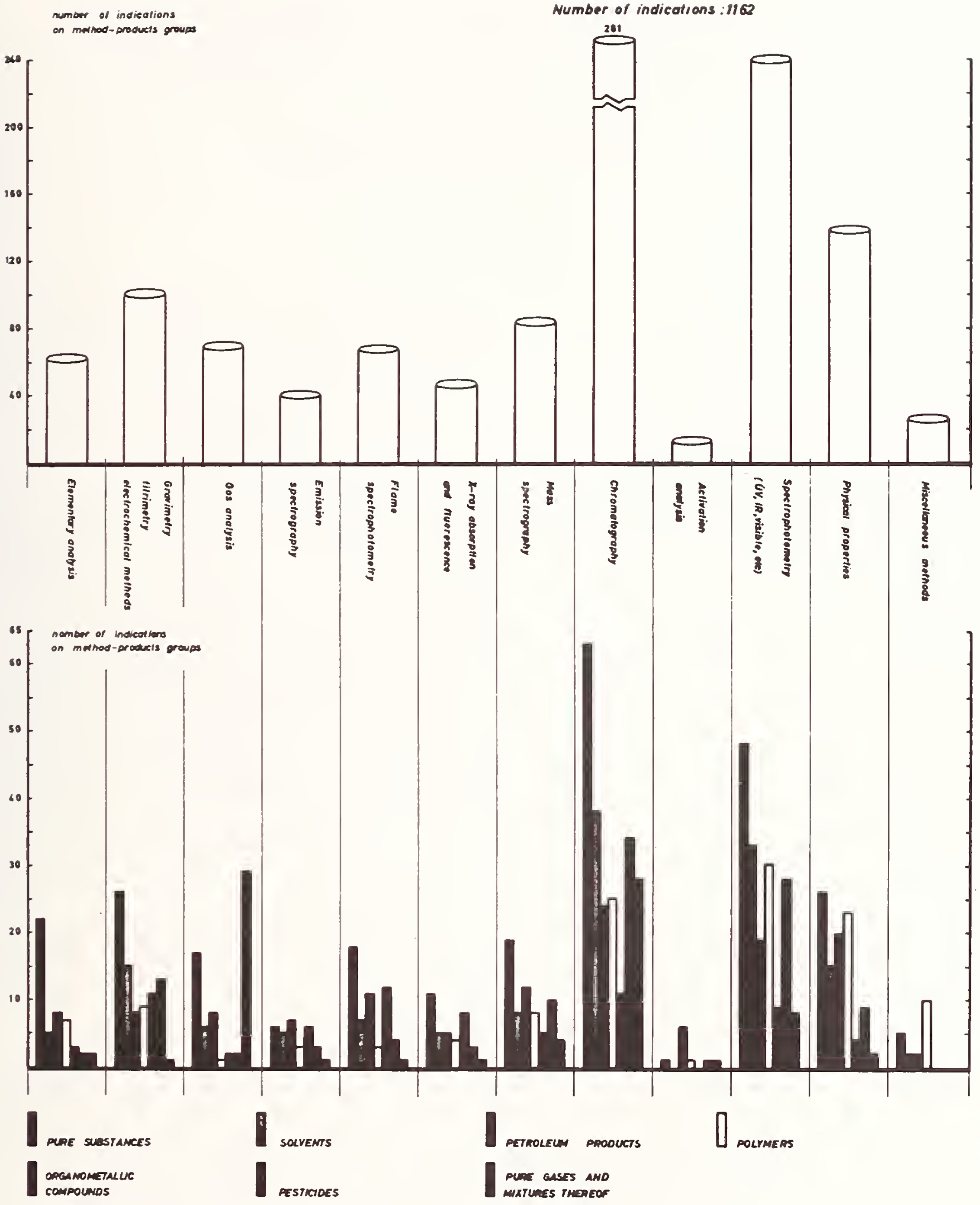

Figure 5. Methods to be Calibrated SRMs for Organic Chemicals

CALIBRATION AND TEST MATERIALS FOR PHYSICOCHEMICAL MEASUREMENTS

(REPORT ON THE WORK OF IUPAC SUB-COMMISSION I.4.1)

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I. Introduction

Knowledge concerning the chemical composition and the physical and technological properties of materials is continually required in science, industry, and commerce for the characterization, specification, and comparison of their properties and qualities. This data is required for the planning and construction of apparatus, machines and technical installations, as well as providing the basis to determine prices of industrial products in national and international trade. This knowledge is acquired not only by chemical analysis, but also by the measurement of physical properties, both of which give evidence on the purity of materials.

Physical and technological properties represented in the form of temperature and pressure dependent functions usually present an absolutely essential basis for the development of scientific apparatus and technical installations. Considerations in the field of technical application are not imaginable without the knowledge of mechanical, thermal, and thermodynamical behaviour of all the materials involved in the process, and also of all the construction materials, as well as of all the substances involved in chemical processes.

Measurements of physical and technical qualities and also determinations of qualitative and quantitative composition of materials (impurities) take place in physico-chemical and analytical laboratories, usually by means of routine methods. The accuracy demanded for these measurements and determinations is usually of the magnitude of one-tenth of a percent, occasionally even better, and is largely dependent upon and determined by the task at hand. A check of the accuracy of the numerical values of the physical and technological properties measured, or of the analytical data obtained, should be possible, in principle, in a simple manner, as a test of the quality of the measuring methods and apparatus. This gives the necessary confidence to the work of the measurement technician and helps guarantee the quality of numerical values produced for scientific and industrial purposes as well as for commercial activities.

Physical measurements may be referred to the physical base units (e.g., the SI base units) using the physical laws that are appropriate for these measurements. In most cases, referring such measurements by a direct comparison to their base units is difficult and intricate to realize. For this reason, physical property measurements are normally realized by comparison to an accurately known, internationally acknowledged reference material; this is especially so for routine measurements.

To carry out such measurements, the following procedure is usually applied: the measuring apparatus is originally calibrated with a reference material. In practical use this calibration is then checked by means of a second substance or material. A third material, the unknown, is then measured for the desired property, and this obtained value is then compared with the known (literature) value of this material. As long as a predetermined tolerance is not exceeded, measurements of these properties can be undertaken within surveyable limits of certainty on materials whose properties are to be determined.

The realization of the <u>technological</u> properties of materials must often be undertaken apart from considerations of their physical qualities or the analysis of their chemical composition. In this case, we are dealing with <u>empirically defined</u> properties of materials having special characteristics with regard to these technical properties: e.g., roughness, hardness, flash point, evaporation speed, and others. These properties can only be realized by means of reference materials, recommended by organizations for testing methods like ISO or the national institutions. It is satisfactory if reference materials and standard methods of measurement and analysis, as well as methods for the calibration of measurement and analysis apparatus, should be adopted on an international scale.

II. Reference Materials

The following types of reference materials must be distinguished with regard to the measurement of physical and technological properties, as well as for the analytical determination of the chemical composition of mixtures: (1) pure substances; (2) defined mixtures of pure substances; materials; natural or artificial products; and (3) conventional mixtures of two or more compounds that are certified by a Standard Reference Material Certificate on account of absolute measurements or comparison measurements with the primary standard.

If possible, reference materials should be chemically defined pure substances, with the property under discussion being characteristic of the substance and immanent in the substance. Reference Materials are used in: (1) measuring physico-chemical properties of materials; (2) measuring technological qualities of materials, and (3) determining the composition of materials.

Furthermore, they serve in calibrating and ascertaining apparatus quality as well as checking the correct application of measurement and analysis methods, thereby assuring the exactness of the results obtained. They should help to identify and to reduce systematic·errors.

In principle two types of Reference Materials or Substances exist in the field of physical and physico-chemical measurements: Primary Standard Substances, and Calibration and Test Substances or Materials.

A. Basic and Primary Standard Substances

These are substances required to realize measurement scales. For example, gold is one of the substances required to realize the International Practical Temperature Scale of 1968. A sample of krypton-86 is necessary to realize the meter, a sample of cesium-33 is required to realize the second. Other materials are required to realize other SI units. Still other materials are required to realize other scales, e.g., potassium hydrogen phthalate is used to define the pH scale.

B. Calibration and Test Materials or Substances

This class of reference materials includes materials or substances required to transfer measurement scales of chemico-physical measurements from a standardizing laboratory to another laboratory. Unequivocal instructions are required for the production and realization of calibration and test materials. Their composition and their purity are well-defined and can be controlled or checked by appropriate and explicit analytical instructions. Only if these conditions are accurately met and controlled will the calibration material faithfully represent the appropriate and designated physico-chemical property. Sometimes the calibration and test material can be prepared by the user according to specified instructions and including analytical control procedures. This method will be perfectly feasible for liquids and gases because of their isotropic nature, but it will not be so feasible or reliable for solid calibration and test materials. Anisotropy in the micro- or macro-structure of solid materials may influence the designated property so strongly that the determination of that physico-chemical property has to be realized by absolute measurements or comparative measurements relative to calibration materials of the same or better quality. These measurements are usually made in a governmental institution and from this institution the calibration and test material are issued with a certificate of their quality according to the definition of the physico-chemical property. In cases where a physico-chemical property cannot be represented by chemically defined substance (e.g., for measurements of high viscosities), they can be represented by materials, in most cases mixtures of several substances. Then the physico-chemical property is no more immanently a unique chemically defined substance and has to be represented by absolute measurements or comparative measurements relative to calibration materials of the same or better quality. These measurements also are usually made and certified in a government institution.

C. Classification of Reference Materials

Physical Basic Standards and Reference Materials can be subdivided in the following manner (the numbers in brackets refer to the notes).

1. Physical Basic Standards [1a]
    a. Basic Standards
    Installations (e.g., the cesium atomic clock) used for the realization and verification of basic physical scales.
    b. Basic Standard Substances [1a]
    Substances with chemically defined composition of the highest purity used for the verification of basic physical scales.
2. Reference Materials
    a. Primary and Secondary Standard Substances [1a]
    Substances of high purity with chemically defined composition for the verification of a related physical scale, especially the temperature scale.
    b. Standard Calibration and Test Material
        (1) Standard Calibration Substances [1b, 2a]
        Pure substances with chemically defined composition <u>certified</u> by National (Governmental) Laboratories as references to be used for physico-chemical measurements.
        (2) Standard Calibration Materials [1b, 2a]
        Materials with defined composition and physical structure <u>certified</u> by National (Governmental) Laboratories as references

to be used for physico-chemical measurements.

c. Calibration and Test Materials

(1) Calibration Substances [1a]
Pure substances used for the calibration of an apparatus intended for physico-chemical measurements and as such as references for physico-chemical measurements. These substances are uncertified but recommended (e.g., by the IUPAC).

(2) Test Substances [2a]
Substances for use as references in physico-chemical measurements but of lower accuracy than calibration substances.

(3) Calibration Materials [2b]
Materials with defined composition and physical structure used for the calibration of an apparatus intended for physico-chemical measurements and as such as references for physico-chemical measurements. These materials are uncertified but recommended (e.g., by the IUPAC).

(4) Test Materials [2b]
Materials used as references for physico-chemical measurements of lower accuracy than calibration materials.

NOTES:

1. The meaning of the term "standard" in this context is to define an apparatus, a substance, or a material recognized
   (a) by the International Committee of Weights and Measurements, or
   (b) by a National (Governmental) Laboratory attesting its quality.

2a. A pure substance has a chemically defined composition. The purity of this substance is better than 99.9%. The individual impurities and their concentration are known, impurities should be present in concentrations less than 1 ppm (1 in 10^6). The substance has to be stable (e.g., against decomposition in air and light) for an adequate time, say about two years. An analytical purity control cannot indicate changes higher than the double standard deviation of the analytical method.

2b. A material of the above definition is a natural or artificial product, in most of the cases a mixture of compounds whose composition or average concentration is known. The physical micro- and macrostructure of the material must be defined, known, and invariable (e.g., glass, crystalline, surface nature, etc.) The material has to be stable in all of its properties for at least two years against air and light. That is, an analytical control of the compositions cannot indicate changes higher than the standard deviation of the analytical method. Also certified calibration materials have to be checked periodically during use.

Whenever possible, substances should be used instead of materials or test materials.

The test substance or material represent the lowest grade of a reference substance or material. Calibration substances or materials will be recommended by IUPAC/I.4. for the calibration of apparatus used for physico-chemical measurements and those as reference materials for physico-chemical measurements; they are not certified by a National (Governmental) Laboratory, but can be prepared by the user, or are obtainable in the market possibly with a certificate of the manufacturer. Standard calibration substances or materials represent the next highest quality, they are produced and/or distributed by a National (Governmental) Laboratory and supplied with a certificate. In very special cases it is to be expected that a Standard Reference Substance can be considered a a Primary or Secondary Standard substance. The selection will be decided by the International Committee of Weights and Measures (CIPM).

Examples of Primary or Secondary Standard Substances are: high-purity gold to define a primary point on the International Practical Temperature Scale (IPTS)--in this instance, a certified primary gold is desirable; or carefully prepared water used to realize the triple point.

Examples of Standard Calibration Substances are: certified benzoic acid; or, certified substances or materials for measurement of viscosity.

Calibration and Test Reference Materials: This class contains by far the largest number of materials. These materials are used primarily: a) To calibrate instruments used to measure a property to insure that the property measured accurately reflects reality (within the practical limits required); b) To realize a practical scale which cannot be defined directly in terms of the basic SI units (usually because of complexity or lack of basic understanding), e.g., the definition of the standard fading hour; c) To check methods of analysis or test to insure the accuracy (sometimes only the precision) of the method; d) To provide a means whereby the quality control of an entire system of production (or some integral part) may be assured;

or e) To test some property of an apparatus or process.

Finally, attention should be drawn to the necessity of providing reference materials for the calibration of commercial instruments, especially for analytical purposes. The correctness and accuracy of measured values are only ensured by calibration materials.

The working group of the IUPAC nominated as Subcommission on Calibration and Test Materials 1972 has already commenced its activities and requests collaboration with all interested people, not necessarily only IUPAC members, institutes and organizations.

Step by step, and, if possible, according to their importance for practical use, the proposals of the working group on calibration will be completed within the next few years and will be published as international recommendations of the IUPAC for measuring reference materials in scientific, commercial, and industrial fields.

The total number of substances or materials recommended should be as small as possible. Many substances can be used as calibration standards for the measurement of various physical properties. Three different calibration materials for each type of measurement should be sufficient -- two of them for the calibration of the apparatus and the third for an independent control measurement. If the value obtained with this substance lies within a given deviation range, it is probable that measurements with other substances will also be correct. The technician who carries out the measurements is thus confident of correct values.

When comparing lists of reference materials of the national physical institutes or the national associations for testing materials, it may be seen that many of the recommended substances serve as analytical standards; numerous reference materials are also qualified for the measurement of physical constants, but many gaps still exist. There is a special lack of reference materials for troublesome measurements, e.g., for all measurements carried out under extreme conditions of temperature or pressure, and when these measurements are made, the results are often incorrect or dubious. I should like to give several examples: the density of liquified gases, the solubility of gases at low temperature or high pressure, and the density of liquids at temperatures above the boiling point.

For thermochemical calculations in the field of organic chemical reactions, a knowledge of the values of the enthalpy of combustion of the reacting components is required. Although there are standard substances for determining the enthalpy of combustion of organic substances containing carbon, hydrogen, oxygen, and chlorine, there are as yet no standards for substances containing nitrogen, fluorine, sulphur, and phosphorus.

In collaboration with colleagues of many countries 13 booklets with an introductory chapter have been compiled by IUPAC Subcommission on Calibration and Test Materials. These booklets are divided in three groups: the first group covers temperature, pressure, and molecular weight; the second, mechanical and thermal properties; and the third, optical, electrical, and electrochemical properties.

Before I give you a short report on the IUPAC work about calibration and test materials, I would like to mention the general objectives of the International Union of Pure and Applied Chemistry, (IUPAC). The IUPAC is a voluntary, non-profit association of national chemical organizations, each of which represents the chemical interests of the member country. The IUPAC belongs like the other international unions IUPAP, or IUPAB to the International Council of Scientific Unions (ICSU) which works closely with UNESCO. The objectives of IUPAC are: to promote continuing cooperation among the chemists of the member countries; to study topics of international importance to pure and applied chemistry that need regulation, standardization, or codification; to cooperate with other international organizations that deal with topics of a chemical nature; and to contribute to the advancement of pure and applied chemistry in all its aspects.

An example of the work of IUPAC is that done by the atomic weight commission. Every other year the members of Commission II.1 study the quality of the hitherto existing table of atomic weights published by IUPAC in the light of current scientific results and knowledge. The table is then revised as necessary, and a new table of the atomic weights of the natural elements is prepared. For the next two years this revision is used in science and technology. Although Commission I.4, responsible for physico-chemical measurements and standards, cannot be directly compared with the IUPAC Atomic Weight Commission in terms of the weight it carries, we intend to recommend reference materials for measurements in the scientific or technical field in accordance with IUPAC practice.

When reference materials are produced, certified and distributed by individual National (Governmental) Institutions as Standard Reference Materials they may serve as non-tariff carriers to international trade. The members of the IUPAC Commission making recommendations for international reference materials are experts from universities, industry, and governmental institutions. Their recommendations are not likely to represent parochial viewpoints.

Surveying the work of the IUPAC commission for the past few years, it can be said that the group has prepared and considered recommendations for a number of calibration and test materials in the usual ranges of measurement. However, there are gaps in these ranges, but hopefully these will be filled without major difficulties. In many cases, supporting data can be found in the literature.

These recommended calibration substances or materials are normally for use at room temperature, or, at best, from zero to one hundred degrees Celsius. Ranges of pressure are in most cases around the normal pressure of one atmosphere. For scientific purposes as well as for measurements of technical or industrial needs these ranges of measurement are by no means sufficient. It is readily apparent that there exists a lack of calibration and test substances in both the low and high temperature ranges, and in the high pressure range.

It is evident that measurements in these ranges are not easy and that the instruments required are not easy to handle. But these ranges are especially important in many cases, not only in the chemical industry, but also in planning and in constructing industrial plants. The general idea of the commission is not to collect volumes of data, but to provide the well-run laboratory with recommended calibration and test materials so that it can gather for itself, through its measurement process, all the data necessary for a given task. Finally, with a view to technology and industry, but also with regard to scientific research, we need standards and test materials to calibrate apparatus for measurements in the more extreme and troublesome ranges.

I hope this short survey of the work of IUPAC Commission I.4 is useful. Some of the ideas as to the classification and characterization of reference substances and materials that result from our discussions in the sessions of the Commission I.4 Physico-chemical Calibrations and Measurements of the Physico-Chemical Division of the IUPAC, have also been presented.

SELECTION CRITERIA OF A MATERIAL AS STANDARD REFERENCE MATERIAL AND STEPS FOR CERTIFICATION

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I. Introduction

The concepts underlying "Standard Reference Materials"* are not universally agreed on, and it is not intended to attempt this task in this paper. Rather the expression "Standard Reference Material" is defined arbitrarily so that the points made in this paper can be understood within the constraints of this specific definition.

A Standard Reference Material (SRM) in the context of this paper is a material (not necessarily a pure substance) having given properties with numerically assessed values, within given tolerances, certified by an appropriate technical body.

Before establishing any kind of SRM the question of why a certain physical or chemical property or quantity is considered worthwhile to be standardized, i.e., why an SRM is needed for this property or quantity, must be answered.

This question is not at all so obvious as it may appear at first sight, because the problem of the standardization of the considered quantity or property could eventually be solved by other means without recourse to an SRM.

The answer to the above question, whether or not an SRM is needed, requires that another preliminary condition be clarified, i.e., the purpose to be fulfilled by the SRM must be clearly fixed.

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*In accordance with the title of the Symposium, the term "Standard Reference Material" is used throughout this paper. The author thinks the simpler term "Reference Material" is better.

II. Purpose of SRM's

The purposes or goals can be broadly classified in four main groups.

Transfer of a given quantity, numerically assessed, from the standardizing laboratory to the user's laboratory. This purpose satisfies, among others, the following needs: establishment of secondary units, some special comparisons of various kinds of physical properties, and control and calibration of measuring instruments. Examples of SRM's fulfilling these needs are those for mass, length, temperature, potential difference, absorption of light, etc.

Comparison for numerical determinations and analyses (physical and/or chemical) for which no other, material-independent methods are available or for which relative methods are, for some reason, preferred. Examples of SRM's fulfilling the purposes of this second class are the materials of given certified composition for various kinds of chemical analyses, and the so-called "authentic substances" for identification and for approximate purity control by simple comparison of a certain (usually physical) property in both samples--the authentic one and the one under investigation. Typical are the spectrochemical SRM's and most pharmaceutical standards.

Checking or testing new methods or procedures. Examples of material fulfilling the purposes of this third class are the mixtures for testing accuracy and precision of new methods or procedures used in analyses of similar materials presenting particular difficulties: e.g., minerals, glasses, biological materials, clinical determinations, etc.

Assessment of properties, mostly biological, for which no exact nor reproducible numerical values of the property to be standardized can be expected for various lots of successive preparation. Examples of properties that can be standardized only this way are enzymatic activity, hematology, et. The SRM's satisfying the purposes of this fourth class are often complex, chemically not well-defined materials for which the numerical value of the considered property may vary rather extensively from one lot to another, and which serve only conventional empirical methods. Engineering and technological standards may also be considered to fall in this class.

Each time a problem arises presenting requirements falling within one of the four classes above mentioned, then an appropriate SRM is needed.

III. Steps Leading to the Selection of an Appropriate SRM

It is clear that the requirements peculiar to classes 2, 3, and 4 dictate the material to be used as an SRM and leave no choice. To perform a spectrochemical analysis of an alloy, a series of certified samples of very similar compositions is needed. To check a new procedure for a clinical determination, an SRM is needed having a composition, as far as possible, similar to that of the biological body to be investigated. To assess the enzymatic activity of an extract of natural organs, a similar extract having a certified activity is needed, even if this certification was made on the basis of empirical, conventional methods.

Practically, the selection and the choice can be considered (and must be made) only for the material candidate to fulfill one of the requirements enumerated in class 1.

Whenever the possibility of selection and choice exists for materials fulfilling the requirements of the other classes, the same criteria must be followed as for materials for the first class. Therefore, the following consideration deals primarily with the first class of SRM's. The extension to the other classes is straightforward by analogy and need not be discussed explicitly.

Once the need for an SRM for a certain quantity or property has been established, the following steps must be taken.

1. On the basis of general properties, a certain number of candidate materials is selected, as suitable to fulfill the required need.
2. Each candidate material is examined comparing the advantages and disadvantages of each so that the most favorable material is chosen that presents advantages more important than its disadvantages.
3. The experimental equipment needed to investigate the material finally selected must be carefully planned, together with a procedure designed to eliminate, as far as possible, the largest number of systematic errors and reduce the range of accidental errors.
4. Careful investigation of the remaining systematic errors is necessary to eliminate their influence either experimentally, or by knowledge of their amount, using, if possible, mathematical procedures.
5. Elimination of accidental errors and establishment of the numerical values of the quantity or property

considered (mean value, probable error of the mean value, standard deviation, etc.), using statistical procedures.

6. Certification using the results of points 4 and 5.

This enumeration of the steps of the overall procedure is in principle logical and complete, but it remains undefined for practical purposes. In fact it cannot be defined more deeply because each SRM presents different requirements and difficulties and needs different experimental equipment and measuring procedures.

It would be more appropriate, perhaps, to discuss points 1 through 6 on the basis of a practical example--an SRM for spectrometry.

Clearly an SRM for this quantity is needed to transfer the physical quantity "absorption of light as definite wave lengths" from one laboratory to another for calibration of spectrophotometers. The result of the quantitative measurement of light absorption (for characterization of a given substance, or for its quantitative analysis) is subject to a number of instrumental errors not easily found and eliminated individually, and sometimes interfering mutually. An SRM is therefore needed to ascertain that the equipment on hand and the procedure used give correct results, within the limits of errors of the instrument used. If this is not the case, then the instrument, and/or procedure, must be carefully investigated to bring to light the difficulties.

A. Preliminary Selection.

The ideal SRM for this purpose should be a material whose absorbance is constant at every wavelength considered, i.e., a neutral one. Such a material does not exist, even the materials best approximating this condition, i.e., the evaporated metals on quartz show in the UV region small deviations from constant absorbance at various wavelengths. Therefore, the dependence of the absorbance on the wavelength must always be taken into account for any material investigated. The scope being considered can be fulfilled in principle by two different groups of materials--pure substances or stable materials.

1. A pure substance must satisfy the following conditions; it must have absorption of light as one of its physical properties and it must be perfectly fixed and reproducible, provided the experimental conditions are exactly reproduced. Further, the purity of the sample must be of highest degree, approaching, as far as possible, the ideal purity, i.e., absence of any other component, absorbing or not.

2. Any kind of sufficiently stable material will be satisfactory provided its absorption is precisely and accurately measured for each individual sample.

It is clear that a pure substance must be preferred because once the numerical value of the physical property under investigation has been accurately and precisely assessed, any other sample of the same substance, of the same purity, in the same conditions will have the same value. At the limit, it would no longer be necessary that a given sample of this pure substance be certified for its physical property but its certification can be restricted to that of purity.

The materials of the second group, e.g., optical glasses or evaporated metal films, often used as light filters, do not need any preparation by the users, but they are irreproducible, each sample being a unique entity with its certified value and always dependent upon that certification. Moreover, these materials can suffer more or less considerable modification as a consequence of superficial damage caused by the laboratory atmosphere. These conditions may cause unsuspected and uncontrollable modifications of the light absorption and this is, of course, a very important drawback.

This first consideration therefore points toward a pure substance. This substance must fulfill several other conditions: it must be easily obtainable; it must be easily purifiable at the required level; it must be stable; the purity must be easily controlled; and it should be, as far as possible, easily prepared if necessary by the user. Finally, because the largest number of samples to be examined are, by far, liquids or solutions, and because the largest number of spectrophotometers are built for this kind of measurement, the SRM must be soluble in an appropriate, transparent solvent. As a consequence, instead of measuring the exact thickness of a solid sample, the thickness of one or more, appropriate containers must be measured exactly.

If possible, this substance should have more than one suitable point, maximum or minimum of absorbance, so that it can be utilized at different wavelengths. Furthermore, the maxima, and eventually also the minima, must be broad enough with rounded peaks and valleys so that the absorbance can be considered constant in a spectral region larger than that going through the exit slit of the spectrophotometer (band pass error absent or negligibly small). When this condition is also verified, small errors in wavelength setting are without consequence.

A literature search shows many substances that more or less fulfill these requirements. To limit the discussion to a practical case, the usual quartz ultraviolet wavelength region will be selected and the substances proposed for this region will be considered. The substances suggested for this task are potassium nitrate in neutral solution, sodium picrate and potassium chromate in alkaline solution, and potassium dichromate in acid solution. All these substances are, at first sight, well suited to serve as photometric standards, because they are easily found, inexpensive, easily purified, stable, and water soluble.

B. Comparison of the Initially Selected Materials

A deeper examination of these four pure substances shows that:

1. Potassium nitrate has only one broad maximum at 302 nm[1] with a molar absorptivity low enough ($\sim$7) to minimize weighing errors. But, it suffers the very important drawback that its solution is sometimes not stable enough [2].

2. Sodium picrate was thoroughly investigated, [3] it shows a broad maximum at 243.9 nm and a minimum at 227.3 nm. It must be used in alkaline solution and provides values for control at two, spectrally, rather close points. The use of an alkaline solvent is a drawback because such solvents contain OH^-, which attacks the silica walls, and because they absorb atmospheric CO_2.

3. Potassium chromate in alkaline solution has long been a favorite SRM for spectrophotometry. It was perhaps the first substance subjected to an extensive investigation. A comparison of the results by a considerable number of investigators were summarized some 20 years ago. [4] This material in alkaline solution shows two broad enough maxima at 373 and 273 nm and two broad enough minima at 312 and 229 nm. Unfortunately, the minimum at 312 is unsuitable for spectrophotometric measurements. Potassium chromate thus provides three well-spaced points for control, but the use of an alkaline solvent remains a drawback.

4. Potassium dichromate in acidic solution also has long been considered as a good SRM for this purpose, and has been subjected to various collaborative tests. [5] Like potassium chromate, it shows two broad enough maxima at 350 and 257 nm and two broad enough minima at 313 and 235 nm. All four wavelengths are very useful for spectrophotometric measurements. The acidic properties of this

solvent eliminate the disadvantage of the alkaline attack upon the silica windows and absorption of atmospheric CO_2. However, a different inconvenience is introduced, i.e., that of the equilibria between monomeric and dimeric forms. These equilibria were investigated recently at NBS [6], and apparently the experimentally measured absorbances are both concentration and pH dependent.

The conclusions that can be drawn from the comparison of the properties just discussed are the following: potassium nitrate and potassium picrate must be discarded, the first because it is sometimes not stable enough, the second because it is suitable practically for only one point in the whole ultra-violet and furthermore requires an alkaline solvent.

Between the two remaining materials, alkaline chromate and acidic dichromate solutions, a certain balance can be stated: both show more than one point suitable for control (three for chromate, four for dichromate) the alkaline chromate solution is physically better defined and constituted in solution by only one absorbing species, but suffers the drawback of the alkaline solvent. The acidic dichromate solution presents one more point suitable for calibration, does not need an alkaline solvent (and is therefore more stable), but is present in solution in more than one absorbing species, whose chemical equilibria is concentration and pH dependent.

The balance among advantages and disadvantages between chromate and dichromate would therefore seem to indicate a preference for chromate. However, the purpose of this material is the transfer of a perfectly defined physicochemical quantity from one laboratory to another; and the numerical value of the quantity to be transferred can be exactly and precisely assessed only if all experimental conditions (including concentration and pH) are rigorously fixed. Thus, the disadvantage of the acidic potassium dichromate solution being a mixture of at least two chemical species in equilibrium disappears, and the advantages become predominant.

It may be concluded that acidic potassium dichromate can be safely chosen as, at least, one of the most suitable SRM's for spectrophotometry.

C. Planning the Experimental Equipment and Procedure

To correctly plan the experimental equipment and the procedure for assessing the numerical value of the desired quantity, the possible instrumental and operational errors must be predicted and a limit of tolerance for the accidental errors must be fixed. For the case under investigation, the following premise will serve as guide in establishing the amount of the tolerated uncertainty. As the largest number of spectrophotometers (for which a SRM must be established) allows measurements to be made with an error of about $\pm(1-2) \times 10^{-2}$ absorbance units, the value of the absorbance of the SRM must be exactly assessed at the 10^{-2} absorbance unit. At this level an uncertainty not larger than $(2-3) \times 10^{-3}$ absorbance units can be considered tolerable. In general, the errors can be classified in two groups: either instrumental or operational. The influence of predictable instrumental errors must be thoroughly investigated, with each one isolated to ascertain whether they are present and, if they are, to assess their influence in such a way that the remaining systematic error does not exceed the target value. One way to ascertain this is to conduct the same measurements using different instruments or using somewhat slightly different procedures. One then determines that if a difference is found, that it lies within the target value. Then the dispersion of the results, arising from the accidental error, must be examined using well known and established statistical methods on a large number of repeated measurements, thus determining whether the resulting precision lies within the acceptable limits.

1. Instrumental errors.

In the example being considered the following instrumental errors are likely to be present: wavelength, band pass, stray light, linearity of the sensing photomultiplier (together with the connected electronics), dark current of the photomultiplier, readout, and cell thickness.

These errors were thoroughly investigated always using the same solution. The solution suggested by Vandenbelt [5c] containing 60.06 mg/l in 0.01 N sulfuric acid was chosen in order to compare the results with those given by Vandenbelt.

The optics utilized consisted of a plane grating spectrophotometer with a concave mirror focalization (800 mm), which has a linear dispersion on the exit slit of 1.6 nm/mm. Its entrance slit could be illuminated directly or by means of an auxiliary monochromator so as to realize, if desired, a stray-light-free double monochromator. Light sources used were a mercury low pressure spectral lamp and a deuterium lamp, with a stabilized electrical line input. The photometer equipment is illustrated in figure 1. It uses a selected 1P28 photomultiplier in a silica envelop with a roughened, ground entrance surface to diffuse the light to be measured on the largest possible cathodic surface. It was fed by a highly stabilized (±0.01%) high-voltage source. The photocurrent was measured:

a. Directly by a light spot microammeter (R_i = 125 Ω, scale length 200 mm, 250 divisions, 2 μA end-value, 1 division (0.8 mm) equivalent to 0.008 μA). Its linearity was determined previously and it was found to be linear within the reading error.

b. Indirectly by potentiometric measurement of the ohmic drop in a high precision resistor (205.5 kΩ, value controlled previously considering also the stability), using a differential voltmeter, which had an input impedance of 10 MΩ (relative error 1 in 10^4).

c. By direct measurements of the same ohmic drop on the same resistor as in b using a digital voltmeter (input impedance 100 MΩ, relative error 1 in 10^5.

The wavelength scale was calibrated using the line spectrum of the mercury lamp and no deviation was found at γ = 435.8 nm. The error develops linearly toward shorter wavelengths and amounts to 0.5 nm at 253.65 nm. This error was taken into account at every wavelength utilized.

The band pass error was also negligible, in fact all maxima and minima of potassium dichromate are so flat that their absorbance is practically constant ± 1 nm from the maximum or the minimum. The exit slit of the spectrophotometer was set at 0.01 mm, i.e., the utilized spectral band was 0.016 nm, or about 1/100 of the band width of the dichromate.

The next error to be considered is that of stray light. To control this error, a set of three measurements was repeated many times to avoid accidental errors. The first measurement was made at the center of the Hg-resonance line, 253.7 nm, preselected through the auxiliary monochromator. The second measurement was made using the same spectral line without premonochromatization. The third measurement was always made at precisely the same wavelength, but using the deuterium-lamp of the spectrophotometer. All other conditions (solution, cell, input energy,* photomultiplier, and

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*The input energy for all three kinds of measurements was kept approximately at the same level by appropriately choosing the distance of the mercury lamp, i.e., of the strongest light source.

reading instrument) were held constant. Using the above three different operations, the results shown in table 1 were obtained on ten different days. The measurements were always made against a distilled water blank.

Table 1. Absorbance of $K_2Cr_2O_7$ Solution, 0.060060 g/Kg in 0.01 N H_2SO_4 at 253.7 nm

Quantity	Mercury lamp		
	with premonochromator	without monochromator	deuterium lamp
Number of msmts. or	45	42	36
Mean value $\bar{A}$	0.851	0.851	0.850
Mean deviation $\Sigma(A-\bar{A})/N$	0.0037	0.0028	0.0033
Standard deviation σ $[\Sigma(A-\bar{A})^2/(N-1)]^{1/2}$	0.0046	0.0037	0.0039
Standard deviation of the mean value $[\Sigma(A-\bar{A})^2/N(N-1)]^{1/2}$	0.00069	0.00057	0.00065

Clearly, the spectrometer used at this wavelength presents a ratio of useful signal over stray-light signal that is larger than the largest value at which an absorbance measurement becomes incorrect. This conclusion obviously holds true also for longer wavelengths. If any stray light had been found, the use of double monochromator would have been compulsory.

The wavelength scale was then set at the long wavelength minimum of the potassium dichromate, i.e., at 313 nm and the linearity of response of the photomultiplier was tested by simply changing the thickness of the absorbing solution. Table 2 shows these results.

Table 2. Control of the linearity of the photomultiplier (mean value of 12 measurements)

Cell Thickness cm	Absorbance read	Absorbance computed*
4.000	1.166	
2.000	0.579	0.581
1.000	0.292	0.291_5

*The values computed for thicknesses 2.000 and 1.000 cm, respectively were obtained dividing by 2 and by 4, respectively, the value read for 4.000 cm thickness.

It is clear that the linearity of response is obeyed within the limits of reproducibility of the measurements. If this had not been verified then another photomultiplier would have been chosen, or a function $\underline{R} = \underline{f}\ (\underline{I})$, where $\underline{R}$ = photomultiplier response, and $\underline{I}$ = light intensity, would have been computed.

The next step is concerned with the influence of the residual dark current. The photomultiplier was first operated at room temperature. Relatively high values of the dark current up to 2.4×10^{-7}A with fluctuations of up to 20 percent were observed. Then, to reduce as far as possible the dark current and its influence, the photomultiplier was put in a new special housing that could be cooled to -25 °C.* The dark current was thus reduced to 1/30 of the preceding value $(2.5 - 4) \times 10^{-9}$A without significant fluctuations. The shift of this dark current during a whole day was never larger than 5×10^{-10}A, this indicated excellent current stability. Table 3 shows the influence of the residual dark current correction. The measurements were made at the shortest wavelength maximum of the potassium dichromate solution. Each entry is the mean of 12 measurements made on different days.

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*Special provision was provided to avoid condensation of atmospheric humidity.

Table 3. Comparison of the absorbance values obtained with and without residual dark current correction

Series	Digital Voltmeter		Differential Voltmeter	
	corrected	uncorrected	corrected	uncorrected
1	0.868	0.857	0.867	0.850
2	0.868	0.860	0.867	0.852
3	0.869	0.859	0.867	0.851
4	0.870	0.859	0.870	0.854
5	0.875	0.864	0.874	0.850
6	0.872	0.861	0.870	0.853
7	0.874	0.864	0.873	0.856
8	0.874	0.864	0.873	0.856

Table 3 shows that a correction is needed, even though small, and that the difference between the corresponding corrected values for both instruments is smaller than the difference between the corresponding uncorrected values.

The reliability and dispersion of results as obtained by the various reading instruments must be now examined. Table 4 shows the results obtained by means of each one of the reading instruments used.

The measurements were again carried out at 257 nm with the same solution. Five series, each consisting of twelve individual measurements or a total of sixty values of the absorbance, were evaluated statistically.

Table 4. Examination of the reading instruments. Absorbance read on dichromate solution at 257 nm

	Reading Instrument		
Quantity	Micro Ammeter	Digital Voltmeter	Differential Voltmeter
Mean value	0.862	0.864	0.863
Mean deviation	0.0101	0.0030	0.0031
Std. deviation	0.0122	0.0038	0.0041
Std. deviation of the mean value	0.0016	0.0005	0.0005

Clearly, all three instruments give the mean value at the same level of ±0.001 absorbance units, notwithstanding the very large difference of the working principle of these three instruments. This strengthens the confidence of the assessed numerical mean value of the measured absorbance. However, the values obtained using the microammeter show a dispersion of the individual measurements about three times higher than that obtained using either of the voltmeters. The values obtained with the microammeter were therefore discarded for the computation of the final values.

The next instrumental factor concerns the cell thickness. The cells used were high precision cells especially selected by the manufacturer to have nominal thicknesses equal to 1.000 cm. A series of six cells was used, one of them for the solvent. Table 5 shows the mean values obtained with each cell for a series of twelve individual measurements.

Table 5. Comparison of cell thickness. Mean value of 12 individual measurements for each cell

Cell	Absorbance
1	0.863
2	0.866
3	0.861
4	0.865
5	0.865

The deviations are always of the same order of magnitude and the conclusion can therefore be drawn that the mean value of all sixty individual measurements can really be considered as the true value of the absorbance of the used solution for 1.000 cm optical path without thickness error. This point should perhaps be confirmed by an independent measurement of the cell thickness.

The investigation of the systematic errors thus far seems to indicate that no systematic error remains at the fixed level of 0.01 absorbance units, with an uncertainty larger than ±0.002 absorbance units.

2. Operational errors

The following operational errors were considered: material purity, weighing error, pH variations, temperature variations, and the effect of different operators.

Potassium dichromate, NBS-SRM 136c, was chosen as the first starting material. It has an effective purity, assessed coulometrically, greater than 99.98 percent. [7] A difference between this purity and absolute purity cannot be detected spectrophotometrically. For comparison with this material, another material of the best commercially available quality was tested, without further purification, at exactly the same concentration and pH. The results were the same within the already established limits of uncertainty for the discussed systematic error. No difference could therefore be attributed to impurities contained in the investigated starting materials. This is obviously a consequence of the ease of purification of this material.

The weighing error can show two kinds of effects: one where a different quantity of material is really present in the solution, and the other where the concentration shifts--dependent dimer-monomer equilibrium. The first error can be completely excluded. The solutions were always prepared using a semimicro-balance sensitive to ±0.05 mg. To minimize the weighing error an amount ten times larger than that needed for the 1 liter solution, i.e., 600.6 mg was weighed. A weighing error of even 0.1 mg corresponds to a difference of 1 : 6000 with respect to the determined amount, also spectrophotometrically undetectable. The stock solution was then diluted by weight, so that errors of the volumetric flasks were avoided. The difference between the relative densities of 0.01 N sulfuric acid and of pure water is about 2×10^{-5} and therefore 1 kg 0.01 N sulfuric acid can be safely made equivalent in density to 1 liter of water without detectable error. All necessary dilutions were always made by weight.

The second kind of error caused by weighing, i.e., from the equilibrium shift, was tested by comparing the values obtained from two solutions differing by 10 percent at the considered level. The more dilute solution showed an absorbance at 257 nm equal to 0.8551, while the more concentrated solution showed an absorbance equal to 0.9385, both at the same level of about 60 mg $K_2Cr_2O_7$ in a kilogram of 0.1N H_2SO_4. Computing the absorbance for the lower concentration from that at the higher concentration, the value of 0.8527 results, which shows a difference of 0.0024 absorbance units. This difference is in the theoretically predictable direction, but remains within the given limit for systematic error. Considering that so large a weighing error must be excluded, the straightforward conclusion is that the potassium dichromate amount must be exactly weighed with an error less than 0.1 percent (which is largely possible with the actual balances used) at the level of 60 mg/kg solvent ±5 percent.

The next point considered concerns the acidity of the solution and the chemical nature of the acid used. Acidity deviation within 10 percent of pH at the 0.01N level, as used in this investigation, apparently does not change the absorbance value of solutions containing exactly the same amount of potassium dichromate: two solutions at pH 2.35 and 2.11, respectively, both gave the value of 0.855 for the measured absorbance. The pH change of 10 percent at the given value ∿2.2 therefore has no influence on the absorbance of the potassium dichromate.

Objections were raised against the use of sulfuric instead of perchloric acid, because of the possible formation of sulfur containing complexes. Even if this is a serious objection when investigating the physicochemical properties of the Cr(VI) equilibria, it is of no importance for the purpose of standardization, where the physicochemical property to be assessed and transferred, should be transferred only under rigorously stated and fixed conditions. The choice of sulfuric instead of perchloric acid is therefore without influence on the constancy of the assessed value of the absorbance of the given potassium dichromate solution, provided that always the purity and concentration of the acid used as solvent is assured and held constant. Sulfuric acid can then be given the preference because it is found more often in chemical laboratories and because it is generally less dangerous. A difference that goes beyond the limits of accuracy and precision can be noticed between the values obtained at NBS (1971) from perchloric acid solutions [6] at pH = 3 and the group of values obtained by Vandenbelt [5c] and Milazzo, as can be seen from table 6. The difference seems more likely to be attributed to a significant change of pH than to a better value of the absorbance. This point is perhaps worthy of a deeper investigation.

The temperature error was not considered here because investigations at NBS have shown that at room temperature, about 20-22 °C, the deviation of the absorbance for 1 °C is considerably smaller than the other errors.

Operator error, insofar as reading the absorbance is concerned, was also found negligible because of the use of digital and of differential (zero reading) instruments.

Finally, the influence of the accidental error as was anticipated in table 1 is completed in table 7 collecting the results obtained in this investigation together with their statistical evaluation.

Table 6. Comparison of absorbance of Cr(VI) Solutions at various wavelengths for Solutions containing 60.06 mg/kg 0.01 N H_2SO_4 at 21 °C

Source	235 nm		257 nm		313 nm		350 nm	
	A	ΔA[a]	A	ΔA[a]	A	ΔA[a]	A	ΔA[a]
1 Edisbury[b]	0.750		0.871		0.294		0.643	
2 Vandenbelt XIV[c]	0.749	+0.0007	0.865	+0.0005	0.292	+0.0004	0.641	+0.0027
3 Vandenbelt XI[d]	0.752	+0.0037	0.866	+0.0015	0.293	+0.0014	0.638	-0.0023
4 NBS 1970[e]			0.863	-0.0015			0.643	+0.0027
5 NBS 1971[b]	0.746	-0.0023	0.869	-0.0045	0.291	-0.0006	0.646	+0.0057
6 Milazzo[g]	0.744	-0.0043	0.864	-0.0005	0.290	-0.0016	0.639	-0.0013
7 Mean[h]	0.7483		0.8645		0.2916		0.6403	

a Deviation against the mean value 7

b Computed from mean absorptivity (A 1% 1 cm) values [2a] obtained from two sets of collaborative tests with concentrations considerably differing from 60.06 mg/l

c Mean value from 9 Cary XIV instruments [5c]

d Mean value from 16 Cary XI instruments [5c]

e Computed from the molar absorbance for the concentration 0.050 g/l [2b]

f Computed from the molar absorbance in $HClO_4$ solutions pH = 3

g This investigation

h Mean value computed using the most homogeneous measurements 2, 3, 4 and 6

Table 7 shows that for careful measurements the value of the absorbance of the SRM considered here is within the target uncertainty ±0.002 absorbance units.

Inspection of tables 6 and 7 suggest now some interesting conclusions. The agreement among the values obtained from the highly sophisticated instruments Cary XIV and Cary XI, those obtained at NBS in 1970 [2b] and those by Milazzo, is very satisfying. The deviation of each value against the mean value in only one case slightly exceeded 0.005 absorbance units and for the most part remained within the target value.

Table 7. Absorbance values of $K_2Cr_2O_7$ Solution (0.06006 g/Kg) in 0.01 N H_2SO_4 in 1.000 cm cell

	Wavelength			
Quantity	235	257	313	350
Absorbance	0.744	0.864	0.290	0.639
Number of measurements	70	>100	82	76
Mean deviation	±0.0043	±0.0040	±0.0028	0.0042
Standard deviation	0.005	0.0049	0.0037	0.0049
Standard deviation of the mean values	0.0006	0.0003	0.0004	0.0006

This statement perhaps suggests a proposal to adopt the mean values of the absorbance given in Table 6 as the tentative best values and to adopt the potassium dichromate solution at 0.06006 g/l in 0.01 N sulfuric acid solution as an SRM for spectrophotometry. Thus, it is recommended that this SRM and the absorbance values for this system be certified by the appropriate metrological and/or standardizing national laboratory.

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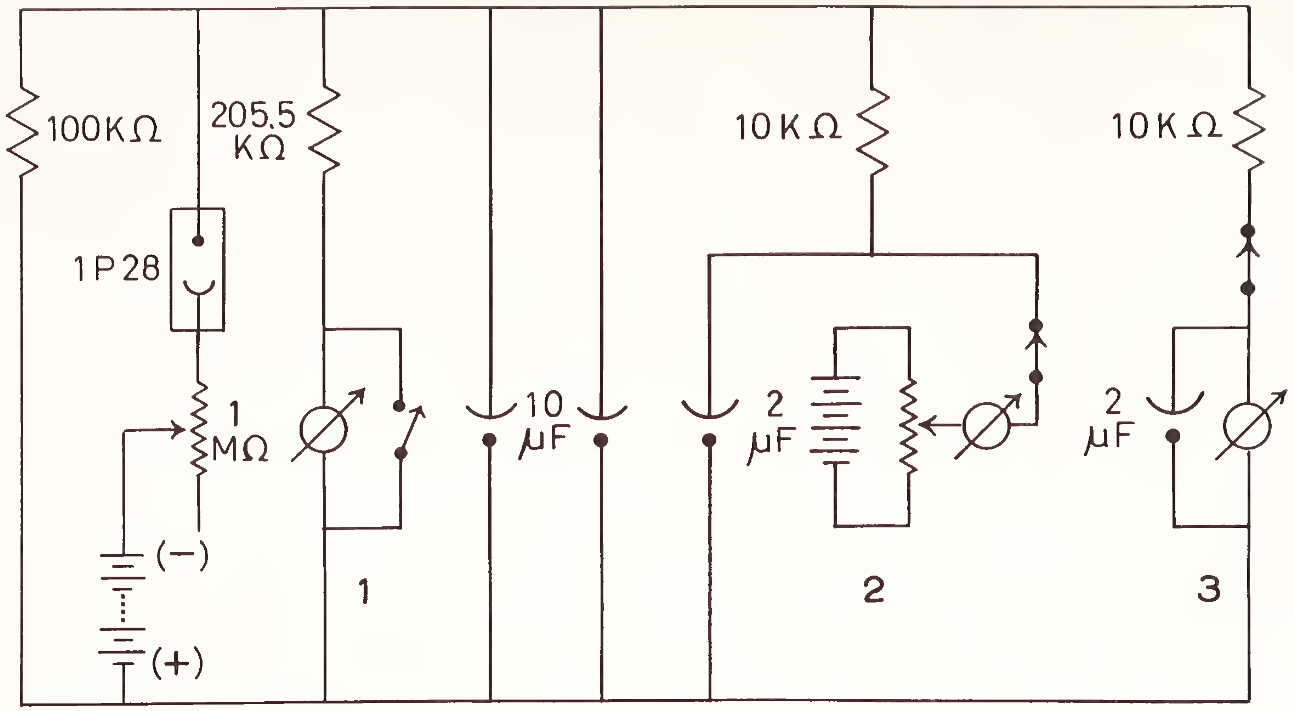

Figure 1. Photometric Measuring Circuitry: 1 = Microammeter; 2 = Differential Voltmeter; 3 = Digital Voltmeter

STATISTICS AND STANDARD REFERENCE MATERIALS

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I. Introduction

The purpose of this paper is to place the use of standard reference materials in proper perspective within the larger framework of the evaluation of measuring and testing methods. According to the dictionary, the term measurement has a dual meaning: "the act or process of measuring," and a "figure, extent, or amount obtained by measuring." The distinction is not pedantic for while we are often interested in the quality of an individual measurement result, we cannot, in general evaluate this quality except through a study of the method by which the result was obtained. The situation is presented schematically in figure 1.

II. A Statistical Model for Measuring Processes

The evaluation of methods of measurement requires the use of statistical techniques based on a general conceptual model. Such a model is presented in figure 2, in terms of the relationship between the property, P, to be measured, and the actual measurement, M, made for the determination of this property. An example will clarify this relationship. The concentration of sulfur dioxide in a sample of air can be determined by measuring spectrophotometrically the color intensity of the dye resulting from the chemical reaction between sulfur dioxide and pararosaniline. Here, P is the concentration of sulfur dioxide, M is the optical absorbance given by the spectrophotometer. Ideally, the relationship is well-defined and unique. In practice, however, it is influenced by the conditions, C, under which the measurement is made, and these conditions are subject to statistical fluctuations. The property-measurement relationship is often a linear one, or it can be linearized through the choice of an appropriate scale. Thus, the use of absorbance will generally yield linear, or close-to-linear calibration curves against concentration, whereas the related measure of transmittance would yield curvilinear relations.

A. Within and Between Laboratory Variability

Assuming that a linear relationship has been obtained between measurement and property, the effect of fluctuations in the environmental conditions is best studied by distinguishing between the variability within laboratories and that between laboratories. Indeed, the control of environmental conditions is almost always far easier to accomplish within a laboratory than between laboratories. Figure 3 illustrates this fact by showing a collection of calibration lines corresponding to different laboratories. In this particular case, the lines crisscross in an apparent random fashion, but very often simpler patterns prevail. Two important cases correspond, respectively, to a collection of _parallel_ lines, as in figure 4a, or a bundle of _concurrent_ lines, as in figure 4b. In either of these situations, considerable improvement in the precision of the method would be accomplished if it were possible to bring the lines representing the laboratories closer together. How can this be done?

Consider first the case of parallel calibration lines, and let us assume that the property and the measurement are expressed in the same scale. A simple vertical displacement of each line, to make it coincide with the bisector of the axes, would eliminate the additional variability between laboratories. This means that the results of each laboratory must be corrected for the _bias_ of that laboratory. Suppose that a standard reference material (SRM), together with a certificate giving its assigned value, is sent to all laboratories. Each laboratory can then ascertain its bias, as the difference between its own measurement of the SRM and the assigned value. In this fashion, the laboratory can actually displace its calibration line so as to compensate exactly for its bias. If this is done by all laboratories, the differences between their results due to systematic biases will clearly be eliminated and the precision of the method considerably improved. For the case of parallel calibration lines, the choice of the level at which the SRM is made is clearly immaterial: any point on the x-axis will be an appropriate choice for the SRM. This is no longer the case when the lines are concurrent rather than parallel.

Consider the case represented by figure 4b in which all calibration lines go through the origin, but have different slopes. In this case, the laboratory biases are multiplicative rather than additive, in the sense that all the values obtained by a specific laboratory are too high, or too low, by a multiplicative constant (the slope of the line). Such cases often arise from insufficiently precise instrument-calibration techniques. Here again, the judicious use of an SRM can virtually eliminate the laboratory biases. Suppose that an SRM is prepared at a level corresponding to a high value of the measured quantity (represented by a point close to the right end of the range of values plotted on the x-axis). A specific laboratory measures the SRM and divides the value it obtains by the assigned value. This represents the factor by which the laboratory is in error. Division of any measured value by this factor will yield a value corrected for the multiplicative bias of the laboratory. The same procedure is applied by all laboratories. It is seen that in the case of concurrent lines, the most advantageous choice of the level of the SRM is at a point far removed from the point of concurrence of the lines.

B. Discussion of an Example: Initial Analysis

The preceding points will now be illustrated in terms of an example dealing with the rosaniline method for the determination of sulfur dioxide in air. Contrary to a current practice, we present the original data in their entirety, to allow the reader to follow all the steps in the analysis. The data in table 1 were obtained in an interlaboratory study involving 96 laboratories (identified by the code numbers 1 to 96), and five concentrations (denoted as series A, B, C, D, and E, respectively). Each laboratory received a box containing five ampoules, each containing a measured amount of sodium sulfite mixed with mannitol. The concentrations for the five series had been determined by careful preliminary work at NBS, which also included a determination of the ampoule-to-ampoule variability within each series. Table 2 summarizes the NBS results. Comparing these results with those shown in table 1, it is apparent that the variability between laboratories was larger by an order of magnitude than can be accounted for by the variability between ampoules. To examine the nature of the laboratory biases, the first step in the analysis was to execute the algebraic counterpart of a plot of the five results of each laboratory against the corresponding NBS values. In this fashion each laboratory was represented by a straight line, fitted by the method of least squares to the five points of the plot.* This analysis revealed that four laboratories (code numbers 58, 60, 79, and 93) showed such excessive scatter about their fitted lines that their values must be suspected of containing serious blunders. These laboratories were eliminated from the data, and the subsequent analysis was confined to the remaining 92 laboratories. The 92 fitted lines can be characterized each by three parameters: height, slope, and the standard deviation measuring the scatter of the points about the fitted line. This is

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*Note that the abscissa values, $\underline{x}$, were the same for all 96 lines, namely the NBS values for the five series.

illustrated in figure 5, which is the plot corresponding to laboratory 11: the height, $\bar{H}$, is the ordinate of the fitted line at the point $\bar{X}$, where $\bar{X}$ represents the average of the five x-values. The slope, B, for this laboratory is 0.5442, and the standard deviation of scatter about the line, s, is 25.3.

Now consider the schematic plot in figure 6, representing the lines for two laboratories concurring at the origin. One of the laboratories, denoted R, is assumed to be the reference laboratory. Its height and slope are denoted by H_R and B_R. Let us calculate the percent deviation of the height of the other laboratory from H_R and the percent deviation of its slope from B_R. These percent deviations are, respectively equal to:

$$100 \frac{H-H_R}{H_R} \quad \text{and} \quad 100 \frac{B-B_R}{B_R} .$$

From figure 6, we derive at once that:

$$B = \frac{H}{\bar{X}} ; \; B_R = \frac{H_R}{\bar{X}} ;$$

therefore:

$$100 \frac{B-B_R}{B_R} = 100 \frac{\frac{H}{\bar{X}} - \frac{H_R}{\bar{X}}}{\frac{H_R}{\bar{X}}} = 100 \frac{H-H_R}{H_R} .$$

Hence, the concurrence at the origin of the lines for the two laboratories implies that the percent deviation of the height of the non-reference laboratory with respect to the reference laboratory is equal to the percent deviation of its slope. The converse is true: equality of these percent deviations implies concurrence at the origin. Table 3 lists the percent-deviation values of the heights and slopes for all 92 laboratories. It is clear that the bundle of lines corresponding to these 92 laboratories is essentially concurrent at the origin. This important conclusion regarding the structure of the data allows us to evaluate the effectiveness of an SRM.

C. Effect of SRM for the Example

In a previous section we have shown how the use of an SRM, chosen at a high level of concentration, will tend to reduce the between laboratory variability in the case of concurrent lines. We can now test this statement for our example. Assume therefore that the ampoule for Series E was used as an SRM by all laboratories. This means that in each laboratory the values for series A through D were adjusted by dividing them by the ratio:

$$\frac{\text{measured value for series E}}{\text{assigned value for series E}} .$$

Table 4 exhibits the values thus adjusted for series A through D. A comparison of this table with the corresponding values in Table 1 shows at once the considerable improvement of between laboratory precision that resulted from the adjustment procedure. This improvement of precision can be expressed quantitatively by calculating the standard deviations between laboratories for each of the series A through D, both for the original and for the adjusted data. These standard deviations are shown in Table 4b. They confirm the very real improvement that the use of an SRM would provide for this test.

D. Conclusion

Standard reference materials can play an invaluable role in the reduction of between-laboratory variability of test methods. Before deciding on the use of an SRM for achieving this purpose, a study of the nature of the laboratory biases must be made. This can be done by conducting a well-planned interlaboratory study of the test method and analyzing the data by statistical techniques that are capable of revealing the structure of the data. The example discussed in this paper illustrates a case in which the use of an SRM for calibration of the analytical procedure would result in a very considerable improvement of the between-laboratory precision. In view of the common occurrence of between-laboratory variability that far exceeds the within-laboratory variability, the use of standard reference materials for the potential improvement of precision may be a far more useful and powerful tool than is commonly recognized.

Table 1. Determination of SO_2 by Rosaniline Method
Interlaboratory Results SO_2 ($\mu g/m^3$)

Lab.	A	B	C	D	E
1	50.0	121.7	341.7	545.0	676.7
2	53.4	135.0	366.0	598.0	745.0
3	45.6	121.5	370.4	611.2	762.9
4	45.8	136.8	354.4	619.0	751.0
5	40.0	134.0	316.7	600.7	773.3
6	66.6	182.0	523.0	732.0	853.0
7	36.3	135.3	428.3	676.6	841.2
8	60.1	180.2	450.5	630.6	870.9
9	43.5	143.6	398.6	659.6	855.3
10	15.9	35.5	80.5	108.2	126.2
11	33.3	79.0	184.4	359.0	411.1
12	15.0	39.0	108.1	183.2	219.2
13	83.0	127.0	333.0	573.0	680.0
14	42.0	129.1	432.4	735.7	822.8
15	55.0	141.0	210.0	202.0	348.0
16	39.0	122.0	333.0	522.0	712.0
17	60.1	120.1	360.4	630.6	720.7
18	57.1	150.2	408.4	729.7	849.9
19	73.0	96.0	245.2	511.2	547.8
20	49.5	104.5	335.5	536.3	753.5
21	30.0	150.2	420.4	690.7	840.8
22	22.5	73.2	115.5	185.8	250.0
23	111.1	216.2	630.6	1111.1	1261.3
24	28.3	100.8	280.0	450.0	567.0
25	37.0	69.0	157.0	246.0	290.0
26	50.0	139.7	341.0	732.1	883.5
27	40.3	133.0	340.0	577.0	743.0
28	33.2	127.3	363.8	392.7	696.8
29	62.0	157.0	434.0	509.0	641.0
30	202.4	297.6	988.0	1487.9	1928.3
31	53.0	150.0	385.0	605.0	757.0
32	40.0	132.0	436.0	580.0	860.0
33	150.2	510.5	1291.3	2222.2	2582.6
34	60.1	120.1	390.4	600.6	750.8
35	30.0	120.1	390.4	390.4	450.5
36	60.1	150.2	390.4	540.5	570.6
37	10.0	90.0	306.7	563.3	610.0
38	55.2	121.3	327.2	493.3	634.2
39	50.0	133.3	413.3	676.7	866.7
40	33.2	104.0	309.8	513.4	643.1
41	39.5	117.0	324.0	521.0	640.0
42	60.1	180.2	450.5	660.7	810.8
43	4.7	11.5	32.2	50.5	62.4
44	75.2	211.0	453.0	773.0	946.0
45	25.3	65.9	130.0	142.7	146.3
46	3.0	9.0	18.0	27.0	54.1
47	42.3	140.1	393.6	623.1	773.1
48	1.3	52.0	180.7	280.7	298.7
49	53.0	212.0	483.0	711.0	742.0
50	71.7	220.0	600.0	983.3	1266.6
51	.8	2.4	5.2	102.2	125.8
52	24.1	104.2	343.5	480.9	687.2
53	30.0	150.2	360.4	510.5	660.7
54	60.1	150.2	390.4	540.5	690.7
55	39.0	112.0	638.0	7 4.3	1002.6
56	69.1	156.2	438.4	669.7	726.7
57	45.0	127.9	224.9	376.8	461.1
58	280.0	870.0	217.0	358.0	415.0
59	60.1	171.2	426.4	702.7	828.8
60	416.3	187.3	445.4	777.1	961.5
61	22.9	114.5	352.5	535.7	673.9
62	30.0	120.1	390.4	570.6	720.7
63	51.7	128.3	362.5	575.0	700.0
64	51.2	115.5	313.7	573.0	727.7
65	55.4	97.0	317.2	452.4	543.4
66	50.5	134.8	397.1	567.4	839.9
67	17.0	23.0	74.0	132.0	174.0
68	54.1	177.2	210.2	381.4	453.5
69	90.1	180.2	468.5	897.9	967.0
70	60.1	150.2	420.4	660.7	840.8
71	60.1	150.2	420.4	690.7	900.9
72	46.6	186.6	478.1	711.3	816.2
73	27.3	100.3	377.0	549.0	734.3
74	38.0	122.0	403.0	490.0	650.0
75	4.1	10.2	28.5	48.9	53.0
76	60.1	210.2	420.4	750.8	900.9
77	55.0	142.0	381.0	646.0	800.0
78	58.3	142.0	417.0	583.0	804.0
79	533.0	133.0	28.3	450.0	533.0
80	39.2	144.0	366.0	533.0	639.0
81	58.3	130.0	360.0	513.3	606.7
82	43.7	126.7	333.0	550.0	756.0
83	41.7	130.0	315.0	527.0	660.0
84	7.4	22.2	57.3	70.2	109.1
85	9.0	30.0	78.1	168.2	237.2
86	35.0	97.1	303.8	554.5	777.0
87	60.1	150.2	420.4	660.7	870.9
88	54.1	216.2	360.4	636.6	825.8
89	37.0	112.0	272.0	490.0	603.0
90	75.1	195.2	480.5	774.8	985.0
91	51.1	156.2	435.4	642.6	837.8
92	60.1	150.2	360.4	630.6	780.8
93	180.2	390.4	1891.9	2702.7	3903.9
94	42.0	114.1	201.2	402.4	585.6
95	90.0	220.0	721.0	1050.0	1400.0
96	57.0	137.0	389.0	593.0	743.0
Avg.	60.72	143.10	369.28	586.06	735.43
NBS	44.7	131.3	383.0	595.0	767.3

Table 2. Determination of SO_2 by Rosaniline Method National Bureau of Standards Results

Series	Mean Value (SO_2, $\mu g/m^3$)	Standard Deviation * (SO_2, $\mu g/m^3$)
A	44.7	6.0
B	131.3	13.3
C	383.0	23.0
D	595.0	32.3
E	767.3	31.3

* Between ampoules of the same series; based on a random sample of 20 ampoules.

Table 5. Determination of SO_2 by Rosaniline Method Standard Deviation Between Laboratories*

Series	Original Data	Adjusted Data
A	28	21
B	66	44
C	181	76
D	292	59

* For a single determination in each laboratory, in units of $\mu g/m^3$.

Table 3. Determination of SO_2 by Rosaniline Method Deviation of Height and Slope with Respect to NBS Values

Lab.	% Deviation	
	Height	Slope
1	-10	-12
2	-1	-3
3	-1	1
4	-1	-1
5	-3	1
6	23	11
7	10	13
8	14	8
9	9	12
10	-81	-85
11	-44	-46
12	-71	-71
13	-7	-13
14	13	14
15	-46	-63
16	-10	-9
17	-2	-3
18	14	14
19	-23	-28
20	-7	-3
21	11	13
22	-66	-71
23	73	68
24	-26	-25
25	-58	-64
26	12	19
27	-5	-3
28	-16	-17
29	-6	-21
30	155	145
31	1	-3
32	7	9
33	252	244
34	0	-2
35	-28	-42
36	-11	-26
37	-18	-12
38	-15	-20
39	11	14
40	-17	-15
41	-15	-16
42	13	3
43	-92	-92
44	28	20
45	-73	-84
46	-94	-94
47	3	2
48	-58	-57
49	15	-2
50	64	65
51	-88	-81
52	-15	-11
53	-11	-16
54	-5	-14
55	35	37
56	7	-4
57	-36	-44
59	14	8
61	-12	-10
62	-5	-4
63	-5	-9
64	-7	-5
65	-24	-30
66	4	5
67	-78	-78
68	-34	-49
69	36	30
70	11	9
71	16	17
72	17	8
73	-7	-2
74	-11	-17
75	-92	-93
76	22	16
77	5	5
78	4	1
80	-10	-17
81	-13	-22
82	-6	-3
83	-13	-15
84	-86	-87
85	-73	-69
86	-8	2
87	13	12
88	9	2
89	-21	-21
90	31	26
91	11	8
92	3	1
94	-30	-28
95	81	81
96	-0	-4

Table 4. Determination of SO_2 by Rosaniline Method Adjusted Data for Series A to D SO_2 ($\mu g/m^3$)

Lab.	A	B	C	D	Lab.	A	B	C	D	Lab.	A	B	C	D
1	56.7	138.0	387.4	618.0	32	35.7	117.8	389.0	517.5	65	78.2	137.0	447.9	638.8
2	55.0	139.0	377.0	615.9	33	44.6	151.7	383.7	660.2	66	46.2	123.1	362.8	518.3
3	45.8	122.2	372.6	614.6	34	61.4	122.8	399.0	613.8	67	75.0	101.4	326.3	582.1
4	46.8	139.8	362.1	632.4	35	51.2	204.6	665.0	665.0	68	91.5	299.8	355.7	645.4
5	39.7	133.0	314.2	596.0	36	80.8	201.9	525.0	726.9	69	71.5	143.0	371.7	712.5
6	59.9	163.7	470.5	658.5	37	12.6	113.2	385.7	708.6	70	54.8	137.0	383.7	602.9
7	33.1	123.4	390.7	617.2	38	66.8	146.8	395.9	596.9	71	51.2	127.9	358.1	588.3
8	52.9	158.8	396.9	555.6	39	44.3	118.0	365.9	599.1	72	43.9	175.4	449.4	668.7
9	39.0	128.8	357.6	591.7	40	39.7	124.1	369.6	612.6	73	28.5	104.8	393.9	573.7
10	96.8	215.5	489.6	657.7	41	47.4	140.3	388.5	624.6	74	44.9	144.0	475.7	578.4
11	62.2	147.5	344.2	670.0	42	56.8	170.5	426.3	625.2	75	58.7	147.8	413.0	708.6
12	52.5	136.7	378.4	641.2	43	57.5	141.4	395.7	621.1	76	51.2	179.0	358.1	639.4
13	93.7	143.3	375.8	646.6	44	61.0	171.1	367.4	627.0	77	52.8	136.2	365.4	619.6
14	39.2	120.4	403.3	686.1	45	132.6	345.7	682.0	748.3	78	55.6	135.5	398.0	556.4
15	121.3	310.9	463.0	621.8	46	42.6	127.9	255.8	383.7	80	47.1	172.9	439.5	640.0
16	42.0	131.5	358.9	562.5	47	42.0	139.0	390.6	618.4	81	73.8	164.4	455.3	649.3
17	63.9	127.9	383.7	671.4	48	3.4	133.6	464.2	721.1	82	44.3	128.6	338.0	558.2
18	51.5	135.6	368.7	658.9	49	54.8	219.2	499.5	735.2	83	48.5	151.1	366.2	612.7
19	102.3	134.5	343.5	716.1	50	43.4	133.3	363.5	595.7	84	52.3	156.1	403.0	493.7
20	50.4	106.4	341.6	546.1	51	4.8	14.4	32.0	623.4	85	29.1	97.1	252.5	543.9
21	27.4	137.0	383.7	630.3	52	26.8	116.4	383.5	537.0	86	34.6	95.9	300.0	547.6
22	69.1	224.7	354.5	570.3	53	34.9	174.4	418.5	592.9	87	52.9	132.3	370.4	582.1
23	67.6	131.5	383.7	676.0	54	66.7	166.8	433.7	600.5	88	50.2	200.9	334.8	591.5
24	38.3	136.4	378.9	609.0	55	29.9	85.7	488.3	607.9	89	47.1	142.5	346.1	623.5
25	97.9	182.6	415.4	650.9	56	72.9	164.9	462.9	707.0	90	58.5	152.1	374.3	603.6
26	43.4	121.3	296.2	635.8	57	74.9	212.8	374.3	626.9	91	46.8	143.0	398.8	588.5
27	41.6	137.4	351.1	595.9	59	55.6	158.5	394.8	650.5	92	59.0	147.6	354.1	619.7
28	36.5	140.2	400.6	432.4	61	26.1	130.4	401.4	610.0	94	55.1	149.5	263.6	527.3
29	74.2	187.9	519.5	609.3	62	32.0	127.9	415.6	607.5	95	49.3	120.6	395.2	575.5
30	80.5	118.4	393.1	592.1	63	56.6	140.7	397.4	630.3	96	58.9	141.5	401.7	612.4
31	53.7	152.0	390.2	613.2	64	54.0	121.8	330.8	604.2					
										Avg.	53.91	148.39	389.62	615.16

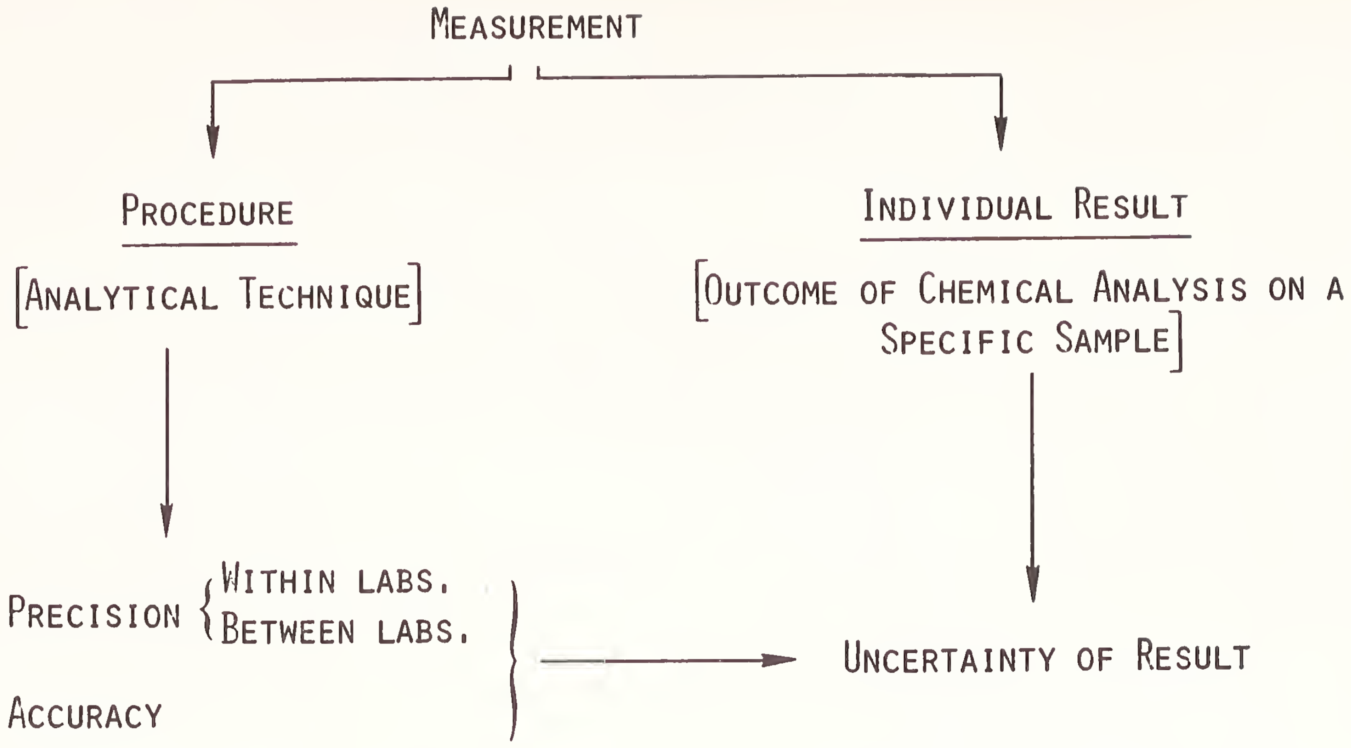


Figure 1. Schematic Diagram of a Measurement Process

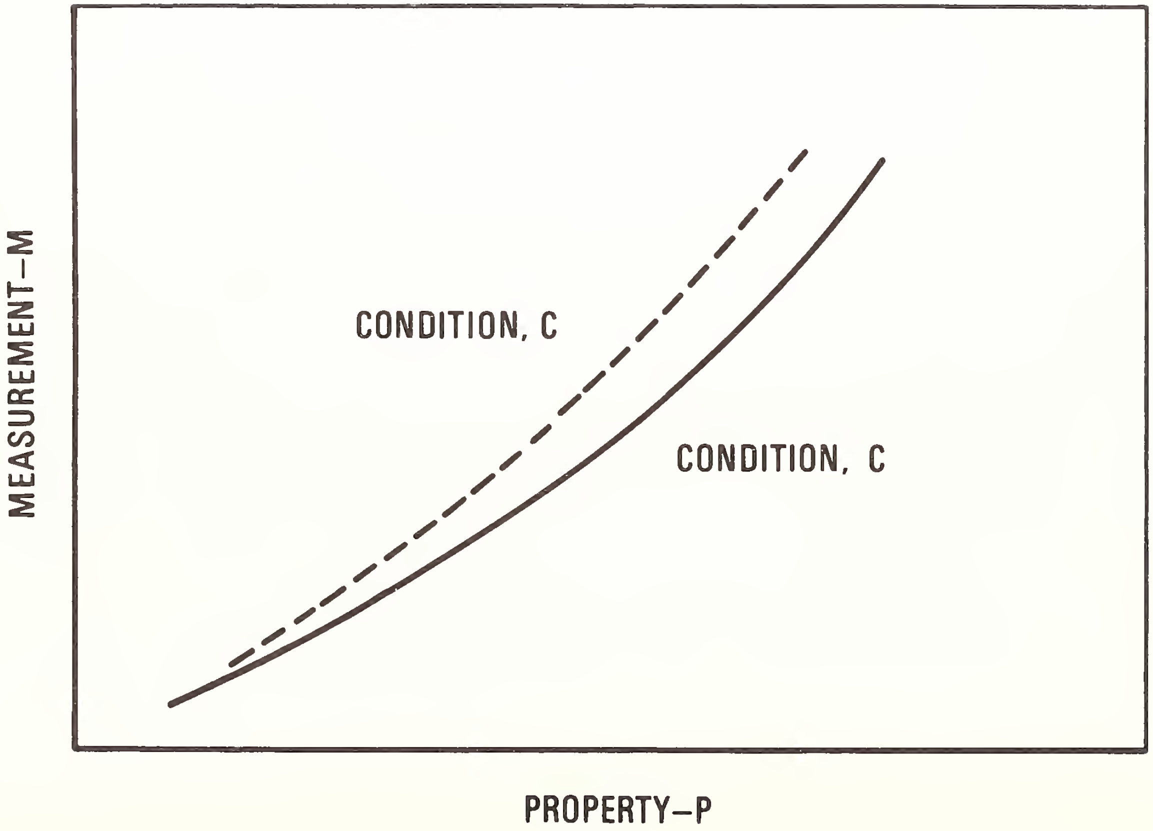


Figure 2. Conceptual Model of the Measurement Process

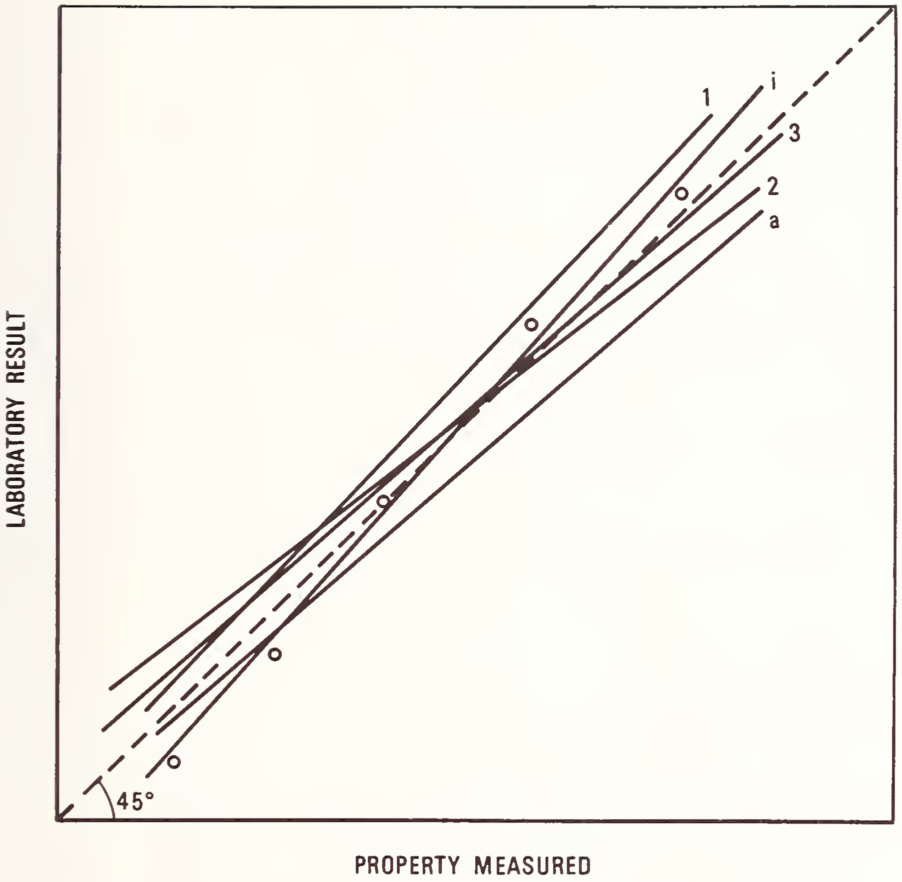


Figure 3. Graphic Display of Variations of Laboratory Calibration Curves

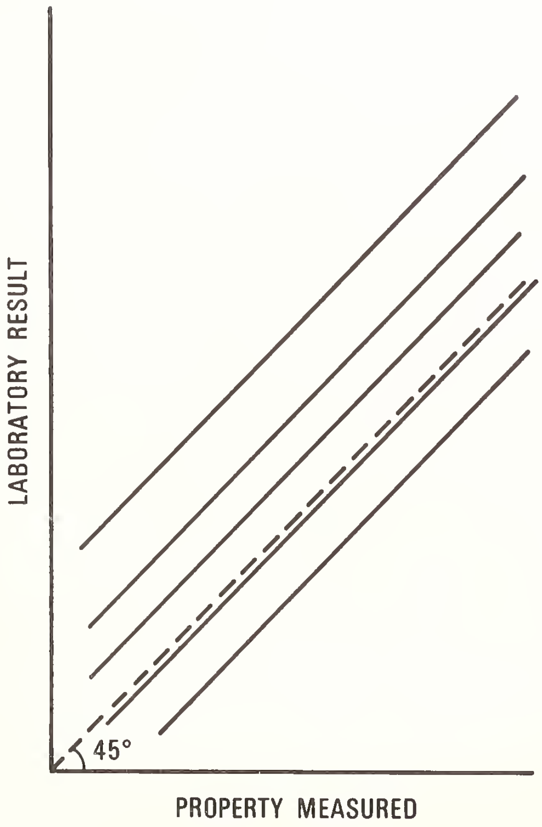


Figure 4a. Laboratory Calibration Lines - Parallel Lines

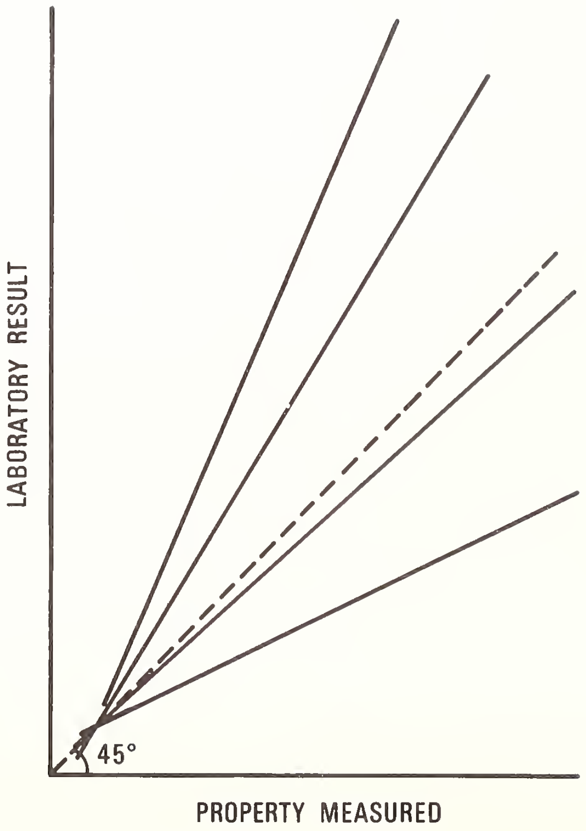


Figure 4b. Laboratory Calibration Lines - Concurrent Lines

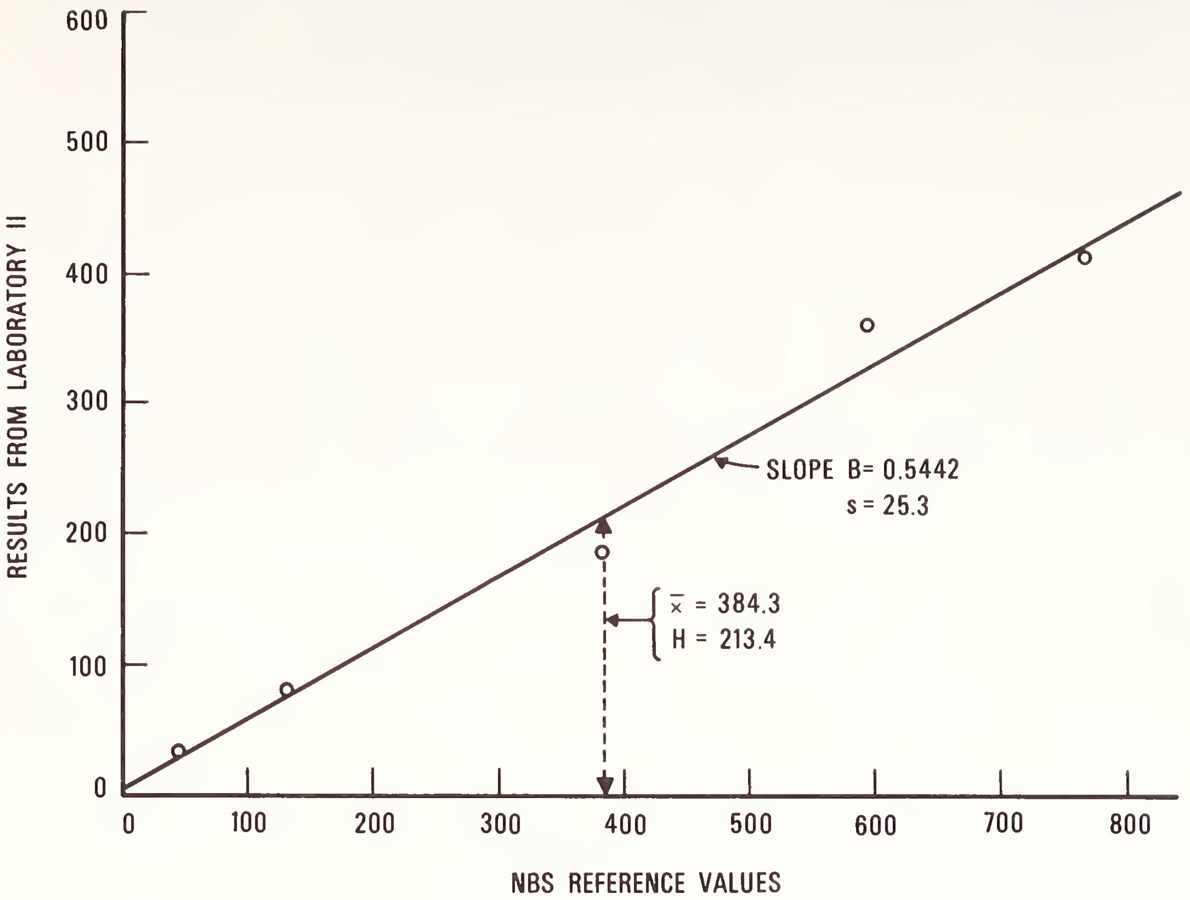
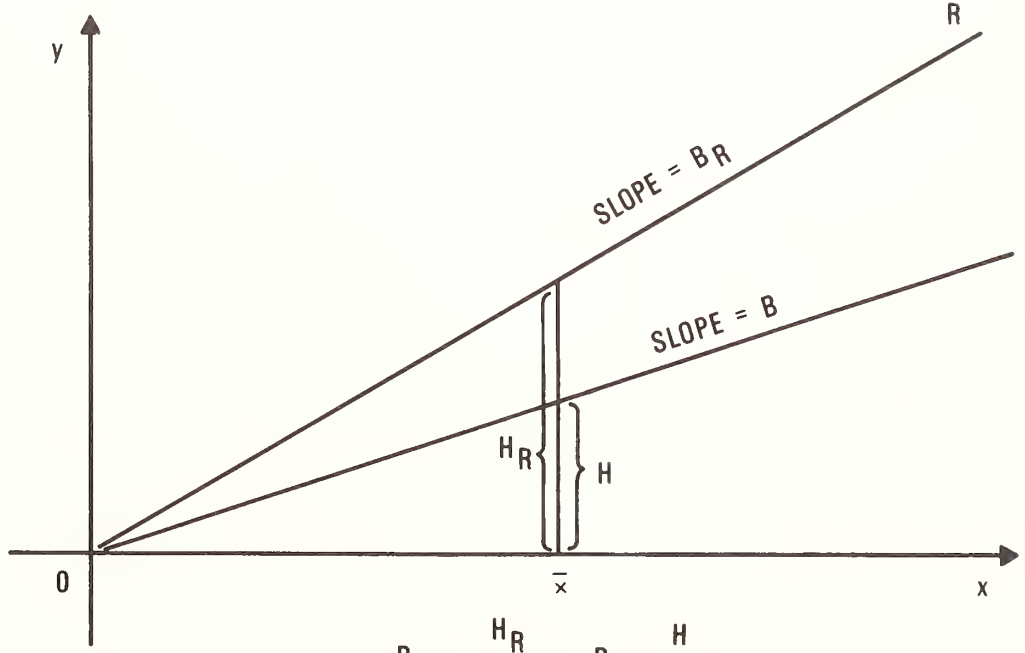


Figure 5. Results from Laboratory II as described by three parameters



$$B_R = \frac{H_R}{\bar{x}} \quad , \quad B = \frac{H}{\bar{x}}$$

$$\text{HENCE:} \quad 100 \; \frac{B - B_R}{B_R} = 100 \; \frac{H - H_R}{H_R}$$

Figure 6. Condition for Concurrent Lines Through The Origin

NATIONAL SRM PROGRAM IN FRANCE

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I. Introduction

Production, characterization, and issuing of reference materials has been carried out in France for many years in various fields. These activities were undertaken at a semi-official level, with many agencies or firms bringing their cooperation in a field characteristic of their own speciality.

It appeared necessary to coordinate the reference materials activity in France and this task has been undertaken by the Bureau National de Metrologie. This duty has been, sometimes, denied by the physicists who consider reference materials a part of chemistry. However, considering the function of reference of these materials and their use in the calibration of analytical apparatus that rely more and more on physical effects, this duty has been confirmed to the Bureau National de Metrologie. In fact, reference materials appear now very often as references for physical properties of materials, and so reference materials more and more will link physics and chemistry for their mutual benefits.

The French organization, which is being set up currently, takes into account the European Actions in the reference materials field undertaken by the Community References Bureau in Bruxelles. For example, the name of Certified Reference Substances previously used in France has been changed to "Certified Reference Materials" to comply with the designation used in other European countries and to increase the European Community spirit.

The Bureau National de Metrologie set up a national system to provide the means of coordination and development of the reference materials activity in France using a principle similar to the one used for the French calibration system for SI units. The aim is to set up a structure that will link together various high technical level laboratories to form a national reference system.

II. The Ideas on Reference Materials in France

Certification and Verification of Reference Materials

A. Reference Materials.

Determination of the physico-chemical properties of industrial materials in the various steps of production and uses, rely more and more on reference materials whose properties are well defined. To characterize a material, it is much more practical to compare it with two other materials whose properties are well known and similar enough to the tested material and then to interpolate between the values given by the two references. This kind of practice is in fact the normal one in many fields of research and industry where there is no technical capability but a real demand for absolute determination.

This state is emphasized by the development of analytical and characterization techniques using automated apparatus, which sometimes dismiss the thoughts necessary to investigate the results. Even when the method used is quite satisfactory, reference materials provide an easy, fast and cheap way of testing the apparatus and the procedures. In all cases, the possibility for analytical laboratories to be supplied with reference materials makes the work easier, makes possible the use of simple techniques, and constitutes a warranty of reliable measurements. In this field of physico-chemistry, as well as in other parts of metrology, the values of the results are directly related to the quality of the references used and of confidence acknowledged to them. The users have neither the time nor the means to test by themselves their reference materials, and this cannot be considered as part of their duty. There is then a demand for a system which can do that job with such a reliability and coherence that can only be obtained by a national system.

Such an organization must be able to offer certification or statement of the properties of the reference materials tested. This "reference materials activity" is now a program by itself within the whole French metrology program; however, to prevent confusion and misunderstanding with the activities related to the SI units, this field will be clearly differentiated in the BNM actions.

B. Certification of Reference Materials.

The "certification" of reference materials leads to an absolute need to take maximum precautions. It is necessary to call upon several laboratories whose qualifications are assured. It must be checked to insure that the analytical procedures used are well established, and that they show enough diversities to prevent systematic errors. The agreement of the results given by various laboratories must be able to give the "true" value and to determine the confidence level related to that value. It then becomes possible to "certify" the value of the parameters searched and to use that material as a reliable reference.

The long procedure that will make possible the certification by BNM of some reference materials can be summarized by the following steps:

1. Production of a sufficient quantity of a well-defined batch of material (as often as possible these materials will already exist in the stock products of firms, or will be made by various research agencies).
2. Analysis by several BNM approved analytical laboratories.
3. Investigation of the results.
4. Certification by the Bureau National de Metrologie.
5. Issuing the sample of "Certified Reference Material" composing the previously defined batch.

Thus, it is possible to certify "reference materials" with all the possible precautions and maximum strictness, with the value and the confidence level claimed being highly credible. It is evident that the precautions taken make the procedure rather laborious. The importance of the task is only justified when a highly reliable reference is needed for a special purpose. For more common reference materials it is necessary to call upon a simplified procedure called "verification."

C. Verification of Reference Materials.

In many processes of physico-chemical properties characterization, some materials or specific reagents are used as references, but are still in common use and are often consumed. These materials cannot be normal stock products because the users rely on their properties to make or test the measurement. The measurement performed, thanks to this material, is of great importance for the quality of the whole production. For example, the temperature of the melting point will be used to check the purity of a compound. The BNM procedure of "certification" is too laborious for these kinds of materials because of the work that is involved.

Such materials can be submitted to a simple procedure called "verification." This procedure consists of checking some samples by an official laboratory "approved" by BNM, and assuring that the reference materials issued by a firm are in agreement with the characteristics claimed by the manufacturer. Then, it has to be verified that these characteristics will remain satisfactory for the entire production.

The procedure of "verification" can be summarized as follows:

1. Definition of an evaluation and testing program for a reference material by a firm.
2. Analysis by a BNM "approved" laboratory of some samples of this material.
3. Investigation of the results and of the control process used by the firm.
4. Issuing a statement of "verification" by the BNM approved laboratory.
5. Issuing the reference material by the manufacturer, the current control being done by the firm's analytical laboratory "recognized" by BNM.
6. Periodical audits by BNM.

III. The Analytical Media

The system for reference materials involves two types of laboratories that are the "approved" and the "recognized" laboratories. Each type having a different task, shows structures suitable to its duty.

A. The Approved Laboratory.

This is a laboratory involved in physico-chemical characterization of materials belonging to a state or state-supervised agency. Its activities consist mainly of studying techniques, improving procedures, and practicing real analysis in the fields of materials characterization. On application for such a service, a BNM Commission investigates various criteria. Main considerations on the technical side are: methods, apparatus, staff qualification, and experience; while on a more administrative side are independent of the head, and free access to all customers. If the commission so recommends, approval is granted by BNM for a definite period. The field of characterization concerned by the approval is clearly mentioned. Any criteria usable to determine this field more precisely may be used.

The duties of an Approved Analytical Laboratory are as follows:

1. To take part in the round-robin analysis organized by BNM in view of "certifying" reference materials.
2. To proceed to test analysis for "verified reference materials," establish the statement of verification, and investigate the control program of the reference materials proposed by the manufacturer.
3. To proceed to national and international audit

analyses organized to verify the validity of the work done by the approved laboratories and to improve the mutual knowledge with foreign countires.

B. The Recognized Laboratory.

This is a private firm's analytical laboratory, which is qualified in reference materials characterization and analysis. Recognition by BNM is granted after investigation by a commission proceeding just as for an Approved Laboratory. Its duty in the system is to proceed to the systematic control of the reference material produced by its firm during production. This control is done in agreement with control specifications previously established with an Approved Laboratory. It may take part in audit analyses organized by BNM. For activities other than the verifications of the reference materials issued by its firm, the recognized laboratory is not allowed to state its recognition by BNM.

IV. The Bank for Reference Materials

The task of this office will be to centralize the BNM Certified Reference Materials, look after their storage, and deliver them to the users. It will also gather information on other reference materials available in France, their origin, and delivery conditions. It will keep current the "French Catalogue of Reference Materials": whose first edition, drawn up under a BNM grant, is being printed. It will also, in the future, gather information on analytical methods related to reference materials. The activity of this bank, coordinated with the Community References Bureau activity, will be the French part of this European action.

V. Actual Field of Interest

A. For the BNM activity, we will mention two test programs whose aims are to check the system previously described and some approvable laboratories.

1. High-purity iron and high-purity nickel. This operation started with a study to evaluate quantities of high-purity iron suitable for use and issuance as reference material. Then analyses were performed by various laboratories. The results known today indicate good chances of certifying more than ten elements in the ppm range. This iron is currently being analysed by the NBS Analytical Chemistry Division. The high-purity nickel is presently being evaluated.

2. NBS 614 and 616 glass reference materials. These analyses have been performed in 1972 and 1973 and are considered by us as a cooperation of great interest to increase the mutual knowledge of the various laboratories involved in reference material characterization.

B. In the broadest scope, we shall mention an example of present interest in France:

1. For chemical properties:
    a. Ferreous and non-ferreous metals,
    b. Organic products,
    c. High-purity gas and pollution references, and
    d. Radioactive reference materials.

2. For physical properties references:
    a. Thermal conductivity and diffusivity,
    b. Hardness,
    c. Melting point,
    d. Physical transition in solid state,
    e. Viscosimetry, and others.

VI. Conclusion

This paper is not really a scientific program stating the exact Reference Materials that are going to be evaluated and certified. The object of this paper has been to present a system that is being put into action. It will make possible the certification and the verification of various reference materials under common and well-known usage and regulations. So, it will be possible to provide the users with reference materials according to their need and characterization by well-established methods performed by reliable laboratories. The differences between certification and verification will offer solutions to various kinds of problems.

NATIONAL RM PROGRAMS IN GERMANY (FRG)

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I. Introduction

The development of science, industry, medicine, agriculture, and last but not least, the protection of our environment requires more, as well as more precise and accurate, measurements and tests. Industry manufactures many instruments and testing machines, which are easy to handle and in many cases are already automated and allow the measurement of all kinds of physical, chemical, and technological quantities. But although most of the apparatuses produce very precise results, their accuracy often cannot be established absolutely. In order to calibrate and check instruments and testing machines and in order to control the personnel, Reference Materials (RM's) are used in all areas mentioned. Sometimes there exist great difficulties in reproducing certain physical quantities because of their complexity. In these cases, SRM's are used to compare the material to be tested with them.

In a highly industrialized country like Germany the need for RM's is especially urgent in many fields of application. But the production, certification, and distribution of RM's is not centralized in Germany although the Federal Institute for Materials Testing (BAM), together with some other institutes like the Physikalisch-Technische Bundesanstalt (PTB), have a leading position in this field. Commercial firms and private institutes, founded by certain industrial branches, are participating to a great extent in the production program of RM's in Germany.

RM's produced and used in Germany may be classified according to the following three categories:

A. RM's that assist the user to reproduce certain physical quantities, which are well defined. Such well-defined physical quantities are wavelengths of certain spectral lines of certain nuclides, temperature, viscosity, activity of radioactive substances, energy of ionizing radiation, spectral radiance factor, surface colours, and colour rendering.

B. RM's that assist the user to reproduce certain physical quantities, which are of a more technological character and not easy nor even possible to define exactly. Such quantities are for instance corrosion and other types of interaction between certain oils and materials. Different types of oils as well as metal plates of certain steel and other alloys and materials (e.g., rubber) are produced as RM's for this purpose. Other quantities are hardness, wear behaviour, image quality of radiographs (which is controlled by penetrameters), several quantities tobe used in connection with the assessment of washing methods of textiles and others. For the reproduction of these quantities there exist a manifold of different RM's.

C. RM's that represent certain well-defined chemical compounds and alloys or whose chemical composition is given with very great accuracy. Sometimes only the contents of certain composites are given with very great accuracy. This category can be divided into the following branches of chemistry: metals; other inorganic substances; organic substances, among which one can differentiate between the use in industry, medicine, pharmacy, food control and production.

Besides the classification into the three groups of RM's one must distinguish between RM's that are certified by a neutral and independent authority, Certified Reference Materials (CRM's) and those for which the properties are given by the manufacturer only. In the latter case, the accuracy with which the quantity of interest is given is not necessarily worse than the values given by an independent and neutral authority, but the guarantee for accuracy cannot be so great as in the other case.

II. RM's Defining Physical Quantities

A. Length, Weight, and Volume

RM's for length, weight, and volume have been in use by mankind for thousands of years. Competent authority for the certification of these kinds of RM's in Germany is the PTB and the calibration offices in the different lands of the Federal Republic of Germany. The PTB measures and certifies length standards of the following kinds: block gauges with planparallel or spherical measuring surfaces, scales (Strichmasse) of several kinds (e.g., code or incremental scales), inside caliper gauges, cylindrical end gauges, and cadastral end meters, which are end blocks with edge-shaped extremities. In addition, PTB certifies working standards for weights and standard flasks for liquids (volume). Thread gauges are also tested and certified by the PTB.

The RM's for the definition of the wavelength are spectral lamps filled with the nuclides Kr-86, Cd-114, and Hg-198, which are produced and distributed by the PTB. The

Advisory Committee for the Meter Definition (CCDM) requires that "the radiation containing four emitted wavelengths of Cd-114 and four of Hg-198 should be produced by means of an electrodeless, high-frequency excited lamp operating at 'moderate' power and at a temperature low enough to avoid self-reversal of the green line." Because of the difficulty to comply with this regulation, the PTB developed and tested Osram type lamps with two hot cathodes, a Cd-114 lamp as well as a water-cooled Hg-198 lamp fulfilling the CCDM specifications with respect to its wavelength and line profiles. [1] The wavelengths of the four internationally recommended lines of each lamp were measured by comparison with the primary Kr-86 standard. The accuracy of the measured values of the wavelengths is about 2 or 3 x $10^{-8}\lambda$. The Cd-114 hot cathode lamp is used, e.g., for measuring end gauges.

The Fédération Européenne des Fabricants de Produits Réfractaires (PRE) produces and distributes RM's for the density (quartz sample) and expansion measurement (currently an aluminum sample, while a zirconsilicate is in preparation). They are distributed by Administratives Sekretariat der PRE, Löwenstr. 31, Postfach 3361, CH-8023 Zürich.

B. Viscosity

To calibrate viscometers, RM's with well-defined viscosities are necessary. For that purpose oils are used. The PTB certifies and sells different oils for viscosities in the range of 0.97 to 26 400 cP or 1.24 to 29 700 cSt at 20 °C. For higher viscosities polyisobutylene is used instead of oils.

Recently the PTB investigated the applicability of a standard glass produced by the Deutsche Glastechnische Gesellschaft as viscosity standard for high temperatures. This standard glass serves for the most important physical-chemical test methods in the glass technology and is of high purity and homogeneity. Its content is well defined and it was carefully degased and cooled. It was found that no deviations from the Newton behaviour occurred, and a permanent heating to 500 °C - 650 °C during 100 h and to 650 °C - 750 °C during 60 h caused no change of viscosity. Even at higher temperatures up to 1,400 °C (during 15 h) no viscosity change could be observed. [2]

C. Optical Quantities

1. Spectral Radiance Factor

Object colours are evoked when a part of the light falling on the body is reflected in the eye. The most exact method of colour identification makes use of the measurement of the reflected light. Internationally the perfect reflecting diffuser has been defined as primary standard. But this cannot be realized. Therefore, the instruments must be calibrated against a secondary standard. This standard consists, according to DIN 5033 Sh. 9 [3], of a round disk of about 5 mm thickness which was pressed in a defined manner out of $BaSO_4$ powder.

The physical quantity that is used to characterize the object colour is the spectral radiance factor, which is given by the ratio of the spectral radiance of the body to that of a perfect reflective diffuser. Erb [4] from the PTB has established a method to measure the luminance coefficient for the $BaSO_4$ standard from which the radiance factor can be calibrated, The PTB is certifying such standards within the International Standardization Organization (ISO) as well as the national institutes in Canada, England, and USA. These institutes are checking their standards against each other to establish a worldwide standardized reflexion scale.

2. Reflectance
   In order to assess the gloss of plan surfaces of paint coatings and plastics, reflectometers are used. Such a reflectometer system has been defined by DIN 67 530 [5], which corresponds to ASTM 523-67. To calibrate these instruments secondary or working standards are used that have been compared with a primary standard. BAM certified such standards that may consist of arbitrary surfaces, the reflexion properties of which must be temporarily constant.
3. Colour Rendering
   In order to investigate and identify quantitatively the color-rendering properties of light sources in the field of lighting, test colours are used that are defined by their spectral radiance factor according to DIN 6169 Sh. 2. [6] Sets of these test colours are certified and distributed by BAM (manufactured by the Munsell Corp.).
4. Surface Colours for Traffic Signs
   The German standard DIN 6171 [41] defines the colours that are used for traffic signs. These colours are red, yellow, green, orange, white, black, and grey. It is obvious that these colours must not change from sign to sign. To assist the manufacturer in the production of the traffic signs, BAM certifies and distributes colour standards for these purposes. They are painted or printed on foils with an area of 10 x 10 cm.

5. Retroreflective Colours
   Retroreflective colours are used more and more for traffic signs and number plates of cars. BAM is preparing standard colours according to DIN 67 520 [7] that will consist of coloured glass.
6. General Colour Standards
   General colour standards are in the course of preparation at BAM, which will be manufactured by printing and varnishing techniques or will be in the form of colour filter foils.
7. Gold Colours
   The Beuth Vertrieb - this is the publisher of the German Standards Institute - distributes sets of seven different gold colours which serve to define gold colours according to DIN 8238. [8, 38]
8. Grey Steps
   Other RM's that are distributed by the Beuth Vertrieb are grey steps according to DIN 16 543 [9] with 12 steps for the top view density range from 0.15 to 1.8, together with colour strip of the DIN colours according to DIN 16 545 [10] with 20 steps for transmission density from 0.15 to 3.0.

D. Radioactivity Standards

The PTB produces, certifies, and distributes several kinds of radioactivity standards for calibration purposes in radiation protection, radiochemistry, and nuclear medicine. Standard solutions of the following short-lived radiouclides are delivered at certain dates: P-32, S-35, Ca-45, Sc-46, Cr-51, Y-88, Zr-95, J-125, J-131, Ba-140, and Hg-203. Different specific activities are available: 0.1, 0.5, 1.0, and 25 µCi/g. Long-lived radionuclides of the following kinds are on stock as calibrated solutions: H-3, Na-22, Mn-54, Co-57, Co-60, Zn-65, Sr-90, Ru-106, Sb-125, Ba-133, Cs-137, Ce-144, Pm-147, Pb-210, and Am-241. In addition PTB sells calibrated standard sources of Na-22, Mn-54, Co-57, Co-60, Y-88, Ba-133, Cs-137, Ra-226, and Am-241.

E. Voltage and Resistivity Standards

The PTB certifies voltage standards and high precision resistivity standards in the range of 10^{-5} to $10^{13}\Omega$.

III. RM's Defining Technological Quantities

A. Interaction of Mineral Oil Products and Materials

A broad spectrum of cases exist within the field of industrial techniques, where mineral oil products like fuel or lubricating oil and gasoline get into contact with metals or polymere materials. Such cases are, e.g., plastic fuel oil tanks and sealings used in all kinds of engines. To test the interaction of these materials, RM's of the following types are used:

1. Metallic Test Pieces for the Investigation of the Corrosion Attack of Mineral Oil Products
   BAM certifies and distributes a great number of test pieces with different dimensions and of a great variety of materials for tests according to SAE or special manufacturer's specifications. Most of the test pieces are in the form of plates of steel, grey cast iron, Cu, brass, Pb, Zn, Al, Sn, Cd, Ag, magnesium alloys, and steel sheets with Cd-coatings. It is very important that the surface and metallurgical properties as well as the chemical composition of these materials are standardized and always the same. Well-described manufacturing methods exist for these test pieces, but it is doubted that these alone can guarantee the reproducibility of the corrosion test results. Therefore, BAM plans to perform the following additional tests and procedures of these materials: [11]
   a. Chemical analysis of the raw material,
   b. Metallographic investigations; and,
   c. Mechanical preparation in the workshop of BAM to guarantee standardized working procedure.
2. Standard Oils and Gasoline
   For testing the swelling of rubber within lubricating oil according to DIN 53 521 [12] Bam certifies and distributes three different kinds of oils (ASTM No. 1, 2, and 3). The same DIN 53 521 describes the testing of rubber and caoutchouc (india rubber) with respect to swelling in gasoline. BAM certifies and distributes two standard gasolines that can be used for this purpose.

   For testing the fuel oil resistivity of polymere materials, a materials test oil has been used since 1964 that consist of a mixture of aliphatic hydro-carbons and an aromatic component. RM's of this oil have been certified and distributed by BAM. Recently investigations were made to synthesize an oil with a more exactly defined composition, which can be produced with better reproducibility and this therefore more available. [13] These lead to a materials test oil mixture A 20/NP II consisting of about 20 wt % 1-methyl naphtalin and about 80 wt % m-paraffin II (aliphatic mixture of C_{12}- C_{18}). BAM plans to have this produced and distributed by a well-known chemical manufacturer under the control of BAM.

3. Standard Reference Elastomers (SRE)
BAM produces, certifies, and distributes SRE plates that are used to determine compatability data against oils and greases on a mineral oil basis for NBR-vulcanized rubber (Nitrile butadiene rubber) and the characterization of test liquids and greases on a mineral oil basis. DIN-standards for the production of these materials are in preparation.

   The compatibility data to be measured are relative volume change, change of shore-A-hardness according to DIN 53 505 , and the change of tensile strength properties according to DIN 53 504. The test media are additionally characterized by the relative increase of weight of the SRE sample with given dimensions after defined storage in the test medium.

B. Rubber Products for Testing Conveyor Belts, Footware, and the Structure of Road Surfaces

BAM produces and distributes several RM's that are used to test the wear of conveyor belts and footware as well as the surface properties of roads.

1. Standard rubber plates are used in connection with standard abrasive paper to establish a reference for the investigation of wear properties of rubber products. Both kinds of standards are produced and distributed by BAM. The production and test method is described in DIN 53 316. [14] The test is performed by rubbing a cylindrical rubber test piece with a thickness of at least 6 mm with constant velocity and pressure (0.33 m/s and 50 kN/m^2) on an abrasive paper (Korund with grain 60). The abrasive grade must lie between 180 mg and 220 mg. The abrasive grade is measured as loss of mass of a standard test rubber sliding along the abrasive paper. The loss of mass of the sample is determined and converted into a loss of volume after density measurement according to DIN 53 550. This test method is being discussed also with ISO/TC 45.
2. BAM produces and distributes two other RM's consisting of a combination of rubber and metal that are used for the measurement of road surface structure and non-skiddingness. To evaluate the non-skiddingness of a road surface, a pendulum instrument is used. At the end of the pendulum arm, a sliding body is mounted.

When the pendulum is swinging this body is pressed against the surface to be tested. The measure for nonskiddingness is the loss of potential energy of the pendulum. The sliding body consists of a carrier plate on to which a parallel-piped rubber is vulcanized. This sliding body is produced and distributed by BAM as an RM.

3. For the measurement of another road surface property an outflow-meter is used. [15] It consists of a glass cylinder (40 cm high and 5 cm diameter) mounted into a heavy brass ring. At the lower side of this ring, a rectangular foot ring is mounted, which consists of a brass ring on which a rubber ring is vulcanized. To measure the surface structure, the outflow-meter is set on the surface to be tested and filled with water. The time that the water needs to sink from an upper-level mark to a lower-level mark is a measure for the structure of the surface. The foot ring is produced and distributed by BAM as an RM.

C. Testing of Carpets, Vacuum Cleaners, and Gymnastic Mats

1. For testing the wear of carpets, a drum instrument is applied that makes use of a rubber buffer. This rubber buffer is produced and distributed by BAM as an RM. Another RM produced and distributed by BAM is a rubber foil that is used for the determination of the electrostatic properties of carpets.
2. The Beuth-Vertrieb distributes a collection of RM's according to DIN 44 956 Sh. 3 [16] for testing vacuum cleaners. To this collection belong carpet samples of different kinds, test strings, test fibres, standard sand, wood flour, and filter paper.
3. Standardization and testing of gymnastic mats are very important with respect to the comparability of sporting results and the safety of the athletes. To test the nonskiddingness of gymnastic mats, a sliding disk is produced and distributed by BAM as an RM.

D. Testing of the Dryness of Paintings

To test the degree of dryness of painting, rubber disks are used according to DIN 53 150. [17] These are also produced and distributed by BAM.

E. Fabrics

For the uniform dying of textiles and the testing of various washing methods, several RM's are used.

1. Standard Cotton Fabrics

   The Wäschereiforschung Krefeld, WFK Testgewebe GmbH, produces and distributes several standard cotton fabrics:
   a. A fabric for testing washing machines and washing methods;
   b. A white fabric for testing the secondary effect of washing (dirt redeposition);
   c. A green fabric for the determination of the bleaching effect of peroxides; and
   d. A standarized dirty cotton fabric that has been contaminated by a standardized procedure.
2. RM of the German Fastness Commission
   DIN 54 000 and DIN 54 072 [18, 19] described the test methods for colour fastness of textiles. The German Fastness Commission distributes the following RM's used in these tests:
   a. Grey scale for the estimation of colour changes according to DIN 54 001 [20], which corresponds to ISO R 105/I 1959 part 2;
   b. Grey scale for the estimation of staining according to DIN 54 002 [21], which corresponds to ISO R 105/I 1959 part 3;
   c. Light fastness types according to DIN 54 004; [22]
   d. Pieces of wool, cotton, polyacrylnitrile, polyamide, polyester, cellwold, and triacetate for artificial lighting;
   e. Test dyeing for the determination of humidity according to DIN 54 004; [22]
   f. Test dyeing for the test of different treatments of fibres and fabrics like bleaching and finishing according to DIN 54 031, 54 054, 54 038, 54 044, 54 045, 54 041, and 54 046. [23-29]

F. Reference Surfaces

The surface of a substance and body is not to be defined in a simple manner although it seems to be a simple physical quantity, namely that of an area. To overcome the difficulty of characterizing a surface quantitatively, RM's are used.

1. Surface Roughness
   For the determination of the finish of pieces machined by cutting, surface reference samples are used that have been machined by the different kinds of tools. They are produced and distributed by Hommelwerke GmbH, 68 Mannheim 41, Postfach 180.

   Similar surface reference samples are used for the technological determination of the surface roughness of castings (Charmille, VDI 3400 Ref and Microtechnic NAS 823). These roughness comparison specimens (Oberflächenvergleichsmuster nach DIN 4769) are used for touch and visual checking of workpiece surfaces. In addition, roughness standards for the calibration of surface measuring instruments are produced, tested, and sold by the PTB.

2. Specific Surface of Cements and Sands
   For measuring the specific surface of cements, RM's of cements and sands are used that are distributed by the Institute für Steine und Erden der TU Clausthal, 3392 Clausthal-Zellerfeld, Zehntnerstrasse 2 a.

G. Hardness

RM's for hardness measurements are calibrated and certified by the Materialprüfungsamt des Landes Nordrhein-Westfalen at Dortmund and distributed by Edelstahlwerke Buderus AG, Wetzlar.

H. RM's for Controlling Nondestrustive Testing

In this field there are two different RM's in use in Germany:

1. Penetrameters
   Penetrameters, according to DIN 54 109 [39], are used to control the quality of radiographic images. These penetrameters are produced and distributed by Richard Seifert & Co., Röntgenwerk, 207 Ahrensburg Postfach 1280 and Kowol GmbH, 4 Düsseldorf-Rath, Rather Kreuzweg 34. The penetrameters are certified by BAM.
2. Calibration Blocks for Ultrasonic Testing
   Standarized Steel calibration blocks, according to DIN 54 120 and DIN 54 122 [40,41], are used for the adjustment of ultrasonic testing instruments with special respect to the distance scale and some respect to the sensitivity scale. These kinds of RM's are distributed by the manufactureres of ultrasonic testing instruments.

I. RM's in Preparation

Different kinds of RM's are in preparation at the BAM, but are not yet available. It is planned to issue standard reference samples for the cutting-surface quality of gas-cut pieces. Other surface reference samples in the planning stage are for use with the electron scanning microscope.

There is further preparatory work on RM's as grey steps for the γ- and x-ray-radiography and for granularity standards to be used for the classification of x-ray files, In the field of nondestructive testing, there are discussions to establish other standard bodies for ultrasonic testing. They should improve the reliability and reproducibility of ultrasonic testing.

IV. RM's Defining Chemical Compositions

To control analytical procedures and to provide standardized reagents, a great variety of RM's are produced and distributed by private firms and institutes. BAM is one of the largest producers of these kinds of RM's, especially for different metals and alloys, and acts as a certifier in this field.

RM's defining chemical compositions are needed in nearly all fields of analytical chemistry. Automated analytical instruments, which use, e.g., physical effects like emission of spectral lines, x-ray fluorescence or ionizing radiation, give measurement values that are dependent on the content of the components to be determined. But it is very difficult to evaluate the measured data because the theoretical connection between the content of the component to be determined and the measured quantity is not know exactly. In these cases RM's are analyzed simultaneously with the sample, a calibration curve can be set up, and the content of the component is thus determined empirically.

A. Inorganic Materials

1. Metals

BAM produces, certifies, and distributes in cooperation with the Max-Planck-Institut für Eisenforschung, Düsseldorf, and the Staatliches Materialprüfungsamt Nordrhein-Westfalen, Dortmund, in connection with the Chemikerausschuss des Vereins Deutscher Eisenhüttenleute a great number of metallic RM's for about 50 types of steels, irons, and several special alloys, as well as ores. [30, 31]

These RM's (Analysen Kontrollproben) are needed for the control of analyses with respect to the method and to the person performing the analysis or for testing new analytical methods with respect to their reliability and practicability. Apparatuses for determining C-, S-, and 0_2- content are tested with these kinds of RM's.

These RM's should comply with the following requirements: The data given should be very accurate and precise. As the precision may differ as a function of the analytical method applied, it is necessary to give the standard deviation for all measured values. The sample should be very homogeneous and variations within it should be as small as possible. This requirement is all the more important when a small sample is used for a single analysis. The RM's should be delivered in a form that is convenient for the intended analytical method. The analyses of these RM's are performed by about 10 different laboratories according to well described methods. [32] The single analysis is performed for each sample, in each laboratory, independently for six times, and on several days. The values found by this procedure should lie within a certain given range. If this is not the case, six new determinations are made. If the new values are within the prescribed range, only these data are taken, in the other case all 12 values found are used to calculate the medium value.

By this method up to 60 values of one sample are used to determine the mean value and standard deviation. Such RM's are distributed by BAM with a certificate, an example of which is given in table 1. Another series of steel and ore RM's are commonly analysed by 16 laboratores in all countries of the European Community and distributed by BAM as EURO-RM's.

BAM also produces, certifies, and distributes RM's for non-ferrous materials. Among these are a number of light alloys and alloys of Cu, Zn, Sb, and Pb.

Especially for use in the spectral emission-analysis BAM produces, certifies, and distributes about 120 different RM's for the analysis of the following materials: steel, zinc, tin, lead, aluminium, copper and several light alloys. The RM's are offered as rods or plates and, in one case, as chips. A part of these RM's are analyzed chemically by other laboratories, too. It is very important that these RM's for testing spark-emission spectroscopy are very homogeneous. But it is difficult to produce samples by casting that comply with this requirement. BAM is making some investigations to produce these RM's by sintering methods which permits the components in a powdered form before production.

Spectral calibration standards are produced and distributed also by the Vereinigte Aluminum Werke, Bonn.

2. Other Inorganic Materials

a. Cements and Refractory Materials

BAM together with the Forschungsinstitut der Zementindustrie is preparing five different kinds of cement standards, which will be certified and distributed by BAM.

The Forschungsinstitut der Feuerfestindustrie has established RM's for 11 kinds of substances that are of interest in the refractory products industry. These RM's have been analyzed by 10 European laboratories based on a decision of the Vereinigung europäischer Hersteller von feuerfesten Erzeugnissen. The RM's are certified by the Forschungsinstitut der Feuerfestindustrie and distributed by the Administratives Sekretariat der PRE, Löwenstr. 31, Postfach 3361, CH-8023 Zürich. Three other substances are under preparations as RM's.

b. Titrimetric Standards

For the adjustment and control of volumetric solutions, titrimetric standards are needed that should correspond as closely as possible to their theoretical composition. They must be chemically pure and should not change their properties in open air. The titrimetric standard should react with the volumetric solution stoichiometrically. The equivalent mass should be great in order to hold the weighing error small. It should be soluble in water and ethanol. The titrimetric standard should have no colour. Titrimetric standards are produced and distributed by the firm E. Merck, Darmstadt, for the following analytical procedures:

(1) Alkalimetry and acidimetry
(2) Oxidimetry and cerimetry
(3) Argentometry
(4) Water analysis according to Karl Fischer
(5) Complexometry
(6) Perchloric acid titration

c. Standard Buffer Solutions

The pH-value is an important parameter for many chemical and biochemical reactions. Buffer solution have, within a certain range, a constant pH-value that is not changed very much by adding stong acids and lyes or by dilution. For the calibration of pH measuring instruments the firm E. Merck, Darmstadt, and others distribute RM's for the preparation of standard buffer solutions according to DIN

19 266. [33] These recommendations are identical with those of the NBS.

d. RM's for Physical Analyses
Besides the emission spectroscopy in the optical range, which was already mentioned, there exist the following analytical methods that are based on other physical effects: gas chromotography, infrared spectroscopy, mass spectrometry, nuclear magnetic resonance spectroscopy, and atomic absorption spectroscopy. None of these methods deliver absolute results and therefore RM's are needed to calibrate the instruments. The firm E. Merck, Darmstadt, offers a great variety of RM's for these purposes.

B. Gases

Standard mixtures of gases are needed in different fields of application especially in medicine and environmental protection. The firm Messer Griesheim GmbH, Industriegasse, Düsseldorf, offers a great number of different standard gas mixtures. BAM certifies and distributes N_2 - O_2 gas-mixtures as RM's for the O_2 trace analysis.

For the calibration of gas measuring instruments to be used in the field of environmental protection, BAM prepares the production, certification, and distribution of test gases that consist of a mean gas component and different additives that may be gaseous or in vapor form. A French-German working group is preparing recommendations for the establishment of these kinds of RM's

C. RM's for Clinical Chemistry

The reliability of a value resulting from a chemical analysis or substances stemming from the human body, e.g., blood or urine, and performed to diagnose an illness is of great importance for the medical doctor who wishes to cure a patient. The reliability can be controlled by quality control only. When the first interlaboratory analyses were made in Germany to control the accuracy and precision of analyses in clinical chemistry, about ten years ago, it was discovered that nearly half of the results were wrong to such an extent that a false diagnosis would have been made by the doctor. At this time in Germany, several medical societies had started to perform sytematic interlaboratory analyses to guarantee the quality control in clincial chemistry laboratories. For these tests, RM's are used that have been certified by certain reference laboratories. These reference laboratories have to qualify themselves every two years. At present, about 800 laboratories are participating in these interlaboratory analyses. It is expected that this number will increase to 10,000 within the next few years. It is planned that in the future only laboratories that regularly take part in interlaboratory analyses will be licensed.

When one realizes that in a single hospital each month 50-60,000 analyses are performed one can imagine the important role which RM's play in this field. These RM's are produced by private firms and as already mentioned certified by licensed reference laboratories. The interlaboratory circular analyses are now organized by the Institute for Standardization and Documentation in the Medical Laboratory (INSTAND) in Düsseldorf and by the German Society for Clinical Chemistry. [34] The analyses to be controlled are chemical analyses of organic and inorganic nature, haematological and microbiological investigations.

Another RM distributed by INSTAND is a standard reference filter for the calibration of photometers. Here some problems still remain to be solved with respect to the temperature control. RM's for grey solutions are still missing.

D. Food Control

The control of our food becomes of increasing importance because of the many possibilities by which toxic substances can get into the food. Many analyses are performed to make sure that the maximum permissible concentrations of these substances are not exceeded. In this field RM's are used too.

BAM holds on stock about 120 different organic components that are used as additives in the production of plastics. According to a recommendation of the Federal Health Office (Bundesgesundheitsamt, BGA) no toxic substances must be in household ware made out of plastic. These materials are to be tested whether this condition is met or not. The organic components mentioned serve as RM's for analyses to be performed in this field.

Pesticide residue analysis plays an important part in environmental control. In Germany, the maximum permissible quantities in food are laid down by law. RM's of high quality are required for residue analysis. The firm Riedel-de-haen AG, Seelze, offers a great variety of such RM's in the "Pestanal" program. As the quantities of pesticides to be extracted from a sample are usually extremely small the solvents have to meet very high quality standards. Therefore, these important chemicals are offered also in the "Pestanal" program. [35]

In 1949, the Deutsche Forschungsgemeinschaft (DFG) founded the Dye - Commission with the task of investigation of the principles to be observed for the use of food additives, in order to protect human health. This commission has established criteria for testing the identity of dyestuffs in food and prepared a reference-sample collection of these substances. [36]

E. Pharmaceutical Chemistry

In the field of pharmaceutical chemistry, RM's are used in Germany for testing vaccines, antibiotics, and some other drugs. The Federal Office for Sera and Vaccines (Paul-Ehrlich-Instiuit, Frankfurt) holds 15 different RM's of these kinds on stock.

RM's of antibiotics are available from the Technical Secretariat, European Pharmacopoeia Commission, Council of Europe, 67 Strasbourg, France.

The Pharmacological Institute of the University in Munich has digitalis leaves on stock as RM's, which have been compared with the international digitalis standard.

An RM for vitamin-A is prepared at the Department of Biochemical Pharmacology of the Max-Planck-Institute für Innere Medizine at Gottingen.

F. Standard Reference Water

The Federal Office of Health (BGA) is planning the preparation of RM's for water especially for the control of the waste water of nuclear power plants. [37] This standard reference water would contain well defined concentrations of certain radionuclides that occur in the waste water of nuclear power plants. It should be used by the nuclear power plant personnel for controlling their measurements of waste water. To have an independent control of these measurements, the measuring personnel in the nuclear power plants would not know the data of these standard reference waters to be included in their measuring series. They would have to send their measuring values to the BGA. This would be a reliable method of controlling the self control of the nuclear power plants with respect to waste water. This method would possibly be suitable also for the control of conventionally contaminated waste water of other industrial installations.

V. International Cooperation and Standardization

As already mentioned, Germany is cooperating in the field of RM's with other countries like France and the USA. There is already international cooperation within several European organizations like the EEC or the European Pharmacopoeia Commission. It is intended to intensify this international cooperation because the establishment of RM's for the great variety of applications cannot be solved by one country alone. Especially the smaller, but industrially-developed countries, are not able to establish all the RM's needed in their own country, but are very well able to support the work in a larger community. Nor should one forget the countries of the third world that could make use of RM's with very great benefit for the development of their science and industry.

The establishment of RM's is very strongly connected with standardization. In Germany already, many DIN-standards exist for the production of RM's. Therefore, organizations concerned with RM's and Standardization are working closely together in Germany and the same should be the case on the international level, where ISO is responsible for standardization.

VI. Conclusion

It has been shown that in Germany RM's are established and in use already in many fields. It is not sure that on the preceding pages all types of RM's existing in Germany have been mentioned. But it is hoped that no essential part has been forgotten. It is evident that the production, certification, distribution, and application of RM's is rapidly developing in Germany and that in the near future many more RM's will be needed. The institutions concerned with the establishment of RM's must prepare themselves to amplify their activities in this field.

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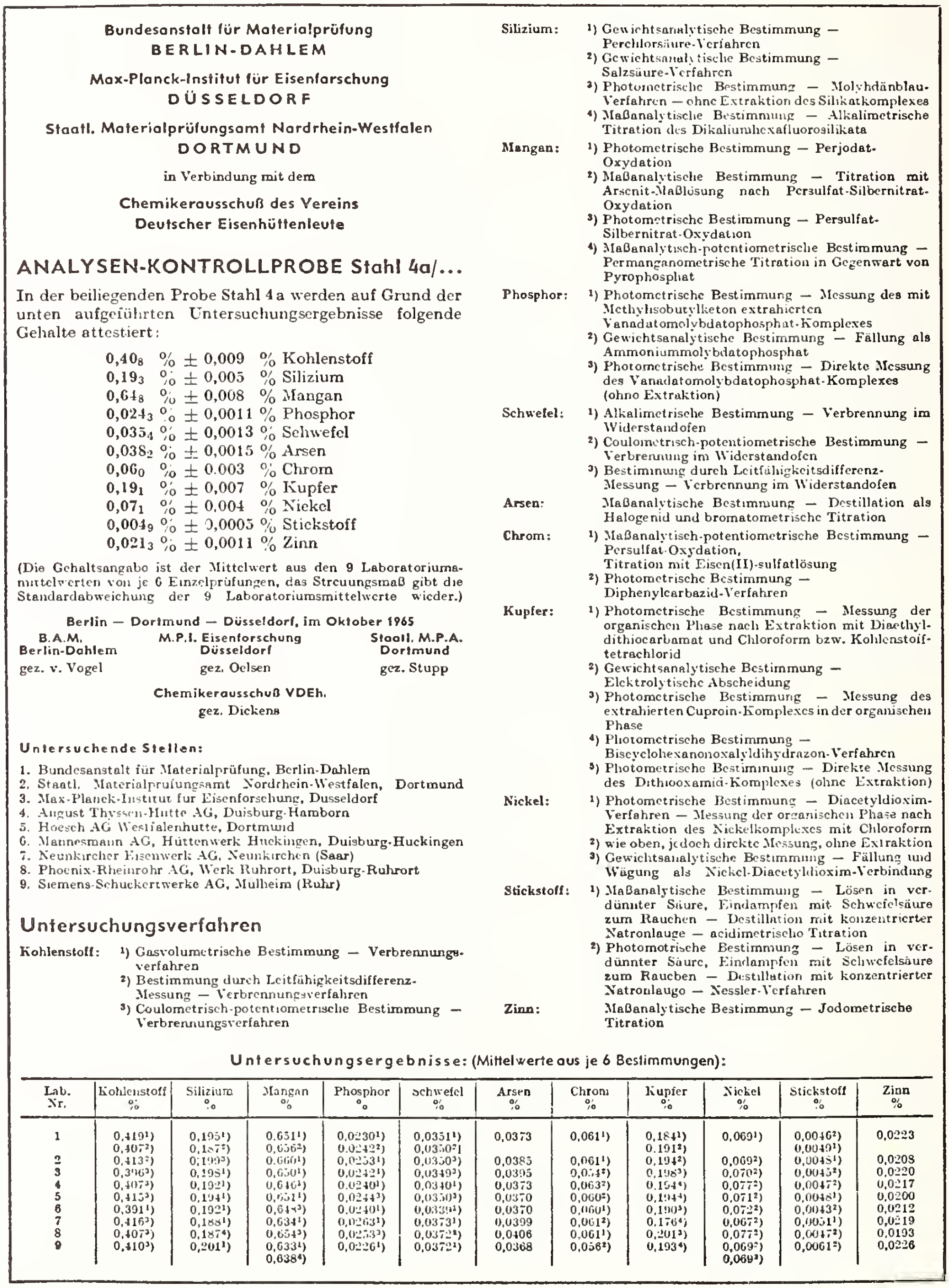
Table 1. Example of a checking certificate for metal standard specimens (in this case: steel 4a)



Bundesanstalt für Materialprüfung
BERLIN-DAHLEM

Max-Planck-Institut für Eisenforschung
DÜSSELDORF

Staatl. Materialprüfungsamt Nordrhein-Westfalen
DORTMUND

in Verbindung mit dem

Chemikerausschuß des Vereins
Deutscher Eisenhüttenleute

ANALYSEN-KONTROLLPROBE Stahl 4a/...

In der beiliegenden Probe Stahl 4a werden auf Grund der unten aufgeführten Untersuchungsergebnisse folgende Gehalte attestiert:

$0{,}40_8$ % ± 0,009 % Kohlenstoff
$0{,}19_3$ % ± 0,005 % Silizium
$0{,}64_8$ % ± 0,008 % Mangan
$0{,}024_3$ % ± 0,0011 % Phosphor
$0{,}035_4$ % ± 0,0013 % Schwefel
$0{,}038_2$ % ± 0,0015 % Arsen
$0{,}06_0$ % ± 0.003 % Chrom
$0{,}19_1$ % ± 0,007 % Kupfer
$0{,}07_1$ % ± 0,004 % Nickel
$0{,}004_9$ % ± 0,0005 % Stickstoff
$0{,}021_3$ % ± 0,0011 % Zinn

(Die Gehaltsangabe ist der Mittelwert aus den 9 Laboratoriumsmittelwerten von je 6 Einzelprüfungen, das Streuungsmaß gibt die Standardabweichung der 9 Laboratoriumsmittelwerte wieder.)

Berlin — Dortmund — Düsseldorf, im Oktober 1965

B.A.M. Berlin-Dahlem	**M.P.I. Eisenforschung Düsseldorf**	**Staatl. M.P.A. Dortmund**
gez. v. Vogel	gez. Oelsen	gez. Stupp

Chemikerausschuß VDEh.
gez. Dickens

Untersuchende Stellen:

1. Bundesanstalt für Materialprüfung, Berlin-Dahlem
2. Staatl. Materialprüfungsamt Nordrhein-Westfalen, Dortmund
3. Max-Planck-Institut für Eisenforschung, Düsseldorf
4. August Thyssen-Hütte AG, Duisburg-Hamborn
5. Hoesch AG Westfalenhütte, Dortmund
6. Mannesmann AG, Hüttenwerk Huckingen, Duisburg-Huckingen
7. Neunkircher Eisenwerk AG, Neunkirchen (Saar)
8. Phoenix-Rheinrohr AG, Werk Ruhrort, Duisburg-Ruhrort
9. Siemens-Schuckertwerke AG, Mülheim (Ruhr)

Untersuchungsverfahren

Kohlenstoff:
1) Gasvolumetrische Bestimmung — Verbrennungsverfahren
2) Bestimmung durch Leitfähigkeitsdifferenz-Messung — Verbrennungsverfahren
3) Coulometrisch-potentiometrische Bestimmung — Verbrennungsverfahren

Silizium:
1) Gewichtsanalytische Bestimmung — Perchlorsäure-Verfahren
2) Gewichtsanalytische Bestimmung — Salzsäure-Verfahren
3) Photometrische Bestimmung — Molybdänblau-Verfahren — ohne Extraktion des Silikatkomplexes
4) Maßanalytische Bestimmung — Alkalimetrische Titration des Dikaliumhexafluorosilikats

Mangan:
1) Photometrische Bestimmung — Perjodat-Oxydation
2) Maßanalytische Bestimmung — Titration mit Arsenit-Maßlösung nach Persulfat-Silbernitrat-Oxydation
3) Photometrische Bestimmung — Persulfat-Silbernitrat-Oxydation
4) Maßanalytisch-potentiometrische Bestimmung — Permanganometrische Titration in Gegenwart von Pyrophosphat

Phosphor:
1) Photometrische Bestimmung — Messung des mit Methylisobutylketon extrahierten Vanadatomolybdatophosphat-Komplexes
2) Gewichtsanalytische Bestimmung — Fällung als Ammoniummolybdatophosphat
3) Photometrische Bestimmung — Direkte Messung des Vanadatomolybdatophosphat-Komplexes (ohne Extraktion)

Schwefel:
1) Alkalimetrische Bestimmung — Verbrennung im Widerstandofen
2) Coulometrisch-potentiometrische Bestimmung — Verbrennung im Widerstandofen
3) Bestimmung durch Leitfähigkeitsdifferenz-Messung — Verbrennung im Widerstandofen

Arsen:
Maßanalytische Bestimmung — Destillation als Halogenid und bromatometrische Titration

Chrom:
1) Maßanalytisch-potentiometrische Bestimmung — Persulfat-Oxydation, Titration mit Eisen(II)-sulfatlösung
2) Photometrische Bestimmung — Diphenylcarbazid-Verfahren

Kupfer:
1) Photometrische Bestimmung — Messung der organischen Phase nach Extraktion mit Diaethyldithiocarbamat und Chloroform bzw. Kohlenstofftetrachlorid
2) Gewichtsanalytische Bestimmung — Elektrolytische Abscheidung
3) Photometrische Bestimmung — Messung des extrahierten Cuproin-Komplexes in der organischen Phase
4) Photometrische Bestimmung — Biscyclohexanonoxalyldihydrazon-Verfahren
5) Photometrische Bestimmung — Direkte Messung des Dithiooxamid-Komplexes (ohne Extraktion)

Nickel:
1) Photometrische Bestimmung — Diacetyldioxim-Verfahren — Messung der organischen Phase nach Extraktion des Nickelkomplexes mit Chloroform
2) wie oben, jedoch direkte Messung, ohne Extraktion
3) Gewichtsanalytische Bestimmung — Fällung und Wägung als Nickel-Diacetyldioxim-Verbindung

Stickstoff:
1) Maßanalytische Bestimmung — Lösen in verdünnter Säure, Eindampfen mit Schwefelsäure zum Rauchen — Destillation mit konzentrierter Natronlauge — acidimetrische Titration
2) Photometrische Bestimmung — Lösen in verdünnter Säure, Eindampfen mit Schwefelsäure zum Rauchen — Destillation mit konzentrierter Natronlauge — Nessler-Verfahren

Zinn:
Maßanalytische Bestimmung — Jodometrische Titration

Untersuchungsergebnisse: (Mittelwerte aus je 6 Bestimmungen):

Lab. Nr.	Kohlenstoff %	Silizium %	Mangan %	Phosphor %	Schwefel %	Arsen %	Chrom %	Kupfer %	Nickel %	Stickstoff %	Zinn %
1	0,419$^{1)}$ 0,407$^{2)}$	0,195$^{1)}$ 0,187$^{2)}$	0,651$^{1)}$ 0,656$^{2)}$	0,0230$^{1)}$ 0,0242$^{2)}$	0,0351$^{1)}$ 0,0350$^{2)}$	0,0373	0,061$^{1)}$	0,184$^{1)}$ 0,191$^{2)}$	0,069$^{1)}$	0,0046$^{2)}$ 0,0049$^{1)}$	0,0223
2	0,413$^{2)}$	0,199$^{3)}$	0,660$^{1)}$	0,0253$^{1)}$	0,0350$^{3)}$	0,0385	0,061$^{1)}$	0,194$^{2)}$	0,069$^{2)}$	0,0048$^{1)}$	0,0208
3	0,396$^{3)}$	0,198$^{1)}$	0,650$^{1)}$	0,0242$^{1)}$	0,0349$^{3)}$	0,0395	0,054$^{2)}$	0,198$^{3)}$	0,070$^{2)}$	0,0045$^{2)}$	0,0220
4	0,407$^{3)}$	0,192$^{1)}$	0,646$^{3)}$	0,0240$^{1)}$	0,0340$^{1)}$	0,0373	0,063$^{2)}$	0,194$^{4)}$	0,077$^{2)}$	0,0047$^{2)}$	0,0217
5	0,415$^{3)}$	0,194$^{1)}$	0,651$^{1)}$	0,0244$^{3)}$	0,0350$^{3)}$	0,0370	0,060$^{2)}$	0,194$^{4)}$	0,071$^{2)}$	0,0048$^{1)}$	0,0200
6	0,391$^{1)}$	0,192$^{1)}$	0,648$^{3)}$	0,0240$^{1)}$	0,0339$^{1)}$	0,0370	0,060$^{1)}$	0,190$^{3)}$	0,072$^{2)}$	0,0043$^{2)}$	0,0212
7	0,416$^{3)}$	0,188$^{1)}$	0,634$^{1)}$	0,0263$^{1)}$	0,0373$^{1)}$	0,0399	0,061$^{2)}$	0,176$^{4)}$	0,067$^{2)}$	0,0051$^{1)}$	0,0219
8	0,407$^{2)}$	0,187$^{4)}$	0,654$^{3)}$	0,0253$^{3)}$	0,0372$^{2)}$	0,0406	0,061$^{1)}$	0,201$^{3)}$	0,077$^{2)}$	0,0047$^{2)}$	0,0193
9	0,410$^{3)}$	0,201$^{1)}$	0,633$^{1)}$ 0,638$^{4)}$	0,0226$^{1)}$	0,0372$^{1)}$	0,0368	0,056$^{2)}$	0,193$^{4)}$	0,069$^{2)}$ 0,069$^{3)}$	0,0061$^{2)}$	0,0226

THE CURRENT STATUS OF SRM ACTIVITIES IN JAPAN

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In this report, materials for which the composition is known and certified in certain respects are all referred to as standard reference materials (SRM's). These include, primary and seconday SRM's, materials of high purity, and SRM's for composition, such as the standard granite, for use in chemical analysis or biochemical assay, and the materials for which some physical property, such as thermochemical properties in the case of benzoic acid, have been established.

I. Current Status and Prospects in Japan for Producing and Issuing SRM's From All Sources

A. Survey of the SRM situation in Japan

In Japan, SRM work has been carried on slowly, but steadily, mainly from the stand point of industry, agriculture, marine industry, and medicine, as a part of the effort to establish standards in various fields of technology and industry. Recently however, SRM activities have been promoted appreciably, mainly because of the sudden increase in the need for SRM's for use in checking environmental conditions. Nowadays, environmental pollution is getting worse. In fact, it is becoming acute and is one of the most serious problems in our everyday lives. Therefore, a pressing and very important task for us is to clarify the nature, and to determine the precise amount of the pollutants, and to check the influence of them on the basis of the data obtained. As one counter-measure, part of The Measuring and Weighing Law was revised in May, 1972, and the instruments for environmental analysis were specified as legal measuring instruments. These instruments are to be regulated, under the law, to improve and ensure the reliability of these instruments. According to the law, instruments for environmental analysis have to be legally authorized before use. To authorize these analytical instruments, i.e., to check scales and measures, appropriate SRM's are necessary. Under these curcumstances, it has become an urgent necessity to establish legal specifications (i.e., allowable inaccuracy) for SRM's and a system for supplying them.

The following instruments are scheduled to be authorized for the time being:

1. Analytical instruments based on electrochemistry.
    a. Instruments based on potentiometric titration.
    b. Instruments based on the conductance method.
    c. Polarograph.
    d. Instruments based on coulometry.
    e. Instruments based on heat of combustion measurement.
2. Analytical instruments based on photometry.
    a. Spectrophotometers.
    b. Flame photometers.
    c. Atomic absorpotion spectrophotometers.
    d. Colorimeters.
    e. Instruments based on light scattering.
    f. Non-dispersive ultraviolet analyzers.
    g. Non-dispersive infrared analyzers.
    h. Chemi-luminescence analyzers.
3. Gaschromatographs.

To carry out this task, three national laboratories, the National Chemical Laboratory for Industry (NCLI), the Geological Survey of Japan (GSJ), and the National Research Institute for Pollution and Resources (NRIPR) are going to manage the studies on SRM analyses, prepare the primary SRM's, or analyse the materials prepared by industries to certify them as the primary SRM's, and to guide in preparing or blending the SRM's, approving the primary SRM's, and in dealing with technical problems in general. Two juridical foundations, the Chemicals Inspection and Testing Institute, Japan (CITI), and the Japan Machinery and Metals Inspection Institute (JMMII) are going to perform the certification of secondary SRM's prepared by industries following the recommendation of the national laboratories mentioned above. Figure 1 shows the traceability flow between these organizations.

In the meantime, problems concerning environmental pollutants, such as PCB or organo-mercury compounds, have led to the enactment of a law governing the study and confirmation of the safety of various new chemical compounds in relation to human health, and putting the system of authorization of the quality of reagents into operation. The law and the system are now going to be enforced. With these circumstances, work on SRM's in Japan is about to be pushed forward far more actively than before.

B. Current Status in Japan

The current SRM activites in Japan can be divided into four categories:

1. Establishment of a law and system.
   The laws involving SRM's are established by the government and public agencies. Neutral organizations such as scientific societies or associations are often entrusted with the preparation of the legal draft. Sometimes the association itself prescribes a standard (specifications). These organizations form a committee that manages the business. The members of the committee are men of learning and experience in the field of science related to the SRM in question. They come from universities, national or civil laboratories, and industries. The materials satisfying the conditions of the law can be issued as an SRM in the name of the agencies or the association.*

   The industrial standardization law, established by the Ministry of International Trade and Industry (MITI), defines the Japan Industrial Standards (JIS), which establish SRM's for about 1,000 items. Another example of a national standard is the Japanese Pharmacopoeia for Medicines. The standards (specifications) for reagents prescribed by the Japan Reagent Industries Association is an example of a standard established by an association itself.

2. SRM Production and Certification
   There are three subgroups in this category.
   a. Production, survey, and certification carried out by government or other public organizations. There are few examples of this. One is the geochemical standard issued by the Geological Survey of Japan, JB-1 (titanaugite-olivine basalt) and JG-1 (biotite granodiorite), the main components determined for them are shown in table 1.
   b. Production, survey, and certification carried out by an institute or association. There are many examples of this. About 200 SRM's for metals, including iron, steel, and various light metals; for cement; for glass; for nuclear re-

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*Laws on SRM's are those concerning JIS, Japan Agricultural Standard, Japanese Pharmacopeia, etc.

actor materials; and for petroleum and LP gas are issued by appropriate associations or institutes. In obtaining the value certified, many analysts in various laboratories cooperate in analysing the sample material by various methods.

  c. Material prepared by industries and certified as an SRM by a government or other public office or by a neutral organization. Typical examples of this approach are the reagent authorized by the Industrial Manufacturers Inspection Institute. Another example is the SRM for BHC, issued by the BHC Industries Association. In most of these cases, the surveys are carried out following JIS, if there is a Japan Industrial Standard for the item in question.

3. Private SRM's

   These SRM's are produced by an industry and certified by that industry according to its private standard. Various reagents, perfumes, and cosmetics, for instance, are the samples of this.

4. Imported SRM's.

   The SRM's for the qualification of environmental pollution measuring instruments shown in figure 1 involve 1 and 2, above.

II. SRM Activities of National Laboratories

A. The production of SRM's; measurement methods; and interlaboratory planning and exchange of information on SRM's and measurement problems are activities of national laboratories. They may be divided into three classes according to the degree and nature of cooperation among the laboratories.

1. In the first class, a single national laboratory or institute performs all the SRM work.
2. In the second class, a member of a national laboratory participates, as a part of his official duties, in a cooperative analysis of SRM's; or in a committee to establish a standard (specification), such as JIS, and sometimes takes charge of experiments concerning the SRM's.

   Nearly all national laboratories are concerned with SRM's in these ways, and a few examples may be cited, as follows:

   a. Industrial materials: the National Research Laboratory of Metrology (NRLM), NCLI, the Fermentation Research Institute, GSJ, etc.
   b. Medicines: the Institute of Medical Science, the Institute of Protein Research.
   c. Agricultural chemicals: the Agricultural Chemicals Inspection Stations.

3. The third class involves studies on analytical methods.

   These studies are not necessarily concerned with SRM's directly, though in every laboratory new analytical methods are the subject of research. But, for instance, the flow of gases through a capillary is being studied in NRLM. The information obtained in the study may be used in constructing a gas-mixture generator for SRM's by the flow method.

B. Methods Used for Measurement

Measurements are carried out following JIS, Japanese Pharmacopoeia, or Japan Official Method for Agricultural Chemicals, etc., if available. When there is no prescribed standard method, another authorized method such as that of NBS, if available, is used for the time being. If necessary a new standard method will be established. Naturally, in some cooperative analyses, various methods of measurement are used to obtain an acceptable value.

C. The Interlaboratory Planning and Exchange of Information on SRM's and Measurement Problems

There is no regular meeting for these purposes. In the JIS committees, etc., interlaboratory planning of SRM's and measurements are discussed, and information about the subjects is exchanged. Symposia and meeting on SRM's sponsored by the Japan Society for Analytical Chemistry are held [1] irregularly. The articles on SRM's describing the current status and significance of SRM's and stressing the importance of them are published in various journals now and again. [2]

III. Other Institutions in Japan that Contribute to SRM Work

A. Government Institutions

Other than the institutions already described, some faculties in universities take part in cooperative analyses or in committees on SRM's. Those local public institutions that have a high potential in a familiar field cooperate in SRM work, as well as the governmental institutions. For instance, the Industrial Research Institute, and Environmental Center, both of Kanagawa Prefecture and the Kogaikenkyujo of Toyko work actively in the SRM field.

The Rikagaku Kenkyujo (The Science Research Institute), The Japan Atomic Energy Research Institute, and The Japan Analytical Laboratory, which are sponsored in part, by the Government, cooperate, too.

B. Societies, Associations

The Japan Society of Analytical Chemistry and other private associations hold meetings on SRM's. In particular, the former society organizes a technical committee that plans the drafts for some SRM's. The planning of these drafts is entrusted to this group by MITI.

Private associations and institutes work in their own fields in planning the drafts of SRM's, and in producing, surveying, and distributing SRM's. The Japan Standards Association takes an active part in SRM work as a liaison organization between those organizations and MITI in establishing JIS. CITI and JMMII, both satelite organizations of MITI, are going to start the work described in figure 1. The former will inspect the secondary SRM's for chemicals, the latter will check the pollution measurement instruments by means of blended standard gas with a gas-mixture generator. The Association for Round Table Conferences on SRM's, a branch of the Industrial Technology Council in MITI, works on organic SRM's. The names of institutes or associations in charge of each SRM are listed in table 2, which also lists the main SRM's issued in Japan.

C. Industries

Many industries produce SRM's.

D. Demand for SRM's

SRM's are required by three groups. First, MITI, the Ministry of Agriculture, and the Ministry of Public Welfare, etc., need SRM's to control, regulate, or supervise various items. Second, mainly industries and other potential or actual pollutant generating organizations demand SRM's for use in analysing pollutants in order to check them. Third, industries producing analytical instruments use SRM's for calibration.

IV. Future SRM Needs and Plans to Meet These Needs As Seen From the Japanese Point of View

As has already been mentioned, future SRM needs, especially the need for SRM's for use in the analysis of environmental pollution are and will be getting more urgent. Also, concerning environmental problems, are the needs for SRM's of petroleum, plant, soil, meat, and medical items such as human tissue and metabolites, etc., which will increase progressively.

Although the needs for SRM's are very great, some difficulties exist in supplying all of them. In Japan, it is difficult to produce and supply all SRM's on a purely governmental basis. However, at least the certifications must be issued by some governmental or neutral institution. To supply SRM's on a commercial basis, the quantity expected to be demanded will generally be too small to be profitable and consequently the price will have to be very high. The following system seems to offer a possible solution to the problem.

First, a particular country is given charge of production and distribution of a particular SRM, and that country undertakes the task as its own responsibility. Every country may undertake work on a SRM according to her own interest in it, taking her own SRM technological and production potential into account. Of course, other countries cooperate with that country in cooperative analysis, cross checking the data obtained or inspecting the quality, if necessary. Second, in order to ensure practical results, an international supervisory organization is established.

V. Cooperation Between Nations

The need for cooperation between nations has been mentioned above and has been stressed in Japan very often. [3] Japan joined ISO and IEC in 1920 and 1921, respectively. In ISO, we now have 49 participating members and would like to increase this number.

Though we do not yet have an official fund, we will participate voluntarily in cooperation between nations or through international organizations to identify and meet

SRM needs on a worldwide basis.

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[1] A symposium on "The proper use of SRM's for atomic absorption spectrometry" was held at NCLI on Sept. 26, 1973.

[2] Mashiko, Y., Measurement and Control, 10, 199 (1970).

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Table 1. Main component of JB-1 and JG-1 (%)

	JB-1	JG-1		JB-1	JG-1
SiO_2	52.27	72.37	CaO	9.30	2.18
TiO_2	1.47	0.25	Na_2O	2.87	3.37
Al_2O_3	14.75	14.35	K_2O	1.23	3.94
Fe_2O_3	2.32	0.27	P_2O_5	0.25	0.08
FeO	5.97	1.67	H_2O^+	0.68	0.43
MnO	0.16	0.07	H_2O^-	1.10	0.09
MgO	7.87	0.76	Total	100.20	99.83

JB-1: Titanaugite-olivine basalt

JG-1: Biotite granodiorite

Table 2. Important SRM's in Japan

SRM	Supplier	Use
1) Glass (Na, Ca); Ti, 3; ZrO_2; HfO_2; Zn metal 3; Cu, Ni, and Cd metals	The Japan Standard Reference Material Committee	Chemical analysis, fluorescent X-ray analysis, emission spectrochemical analysis
2) Benzoic acid	The Nat. Res. Instit. Poll. Resources	Calorimetry
3) Minerals, Granite; Basalt	The Geol. Surv. Japan	
4) SRM's of radio-active substances, 30	The Electrotechnical Lab.	
5) SRM's for volumetry Zn, Cu metals, NaCl As_2O_3, $K_2Cr_2O_7$, $Na_2C_2O_4$, Na_2CO_3, $NaIO_3$, NaF, sulfamic acid	The Industr. Manuf. Insp. Instit.	
6) Nuclear fuel and materials for nuclear reactor	The Japan Atomic Energy Res. Instit.	
Uranium oxide, 1 set, 5		Emission spectrochemical analysis
Uranium oxide, 1		Chemical analysis
Zircaloy, 1 set, 3		Emission spectrochemical analysis, fluorescent X-ray analysis
Zircaloy, 1 set, 2		Chemical analysis
Zr-Nb alloy, 1 set, 4		Fluorescent X-ray analysis

Table 2. Important SRM's in Japan (continued)

7) Iron and steel	The Iron and Steel Instit. Japan	
Carbon steel, 6; pig iron, 5; special steel, 27; steel alloy, 36; iron ore, 9		Chemical analysis
Standard sample for instrumental analysis, 7 set (1set, 6 species)		Instrumental analysis
8) Cu and Cu alloy	The Japan Brass Makers Association	Chemical analysis
Deoxidized Cu, 1; brass, 7; phosphor bronze, 1; aluminum bronze, 1		
9) Al and Al alloy	The Light Metal Rolling Association	Chemical analysis, emission spectrochemical analysis
Al metal, 8; Al-Cu, 1; Al-Mg, 1; Al-Mg-Zn, 2; Al-Mg-Si, 2; Al-Mn, 1		
10) Al alloy for casting	The Light Metal Smelters Association	
Al alloy for casting, 4		Chemical analysis
11) Mg metal	The Japan Light Metal Association	
Mg metal, 2; secondary Mg metal		Emission spectrochemical analysis
12) Cement	The Cement Association of Japan	
a) SRM of fineness		Chemical analysis
b) SRM for chemical analysis		
c) SRM of heat of hydration		

Table 2. Important SRM's in Japan (continued)

13) Coal Coke, 3	The Fuel Soc. Japan
14) Sea water 2	The Sci. Council of Japan
15) Elementary analysis 50	The Japan Soc. Anal. Chem.
16) BHC	The BHC Manufacturing Assoc.
17) Drug (Japanese pharmacopoeia) Medicine, 43 Pigment, 31	The Nat. Instit. Hygienic Sci.
18) SRM's issued by The Nat. Instit. Hygienic Sci.. 13 items including estradiol 5 items including acetanilide for measurement of melting point	
19) LP gas	3 private industries

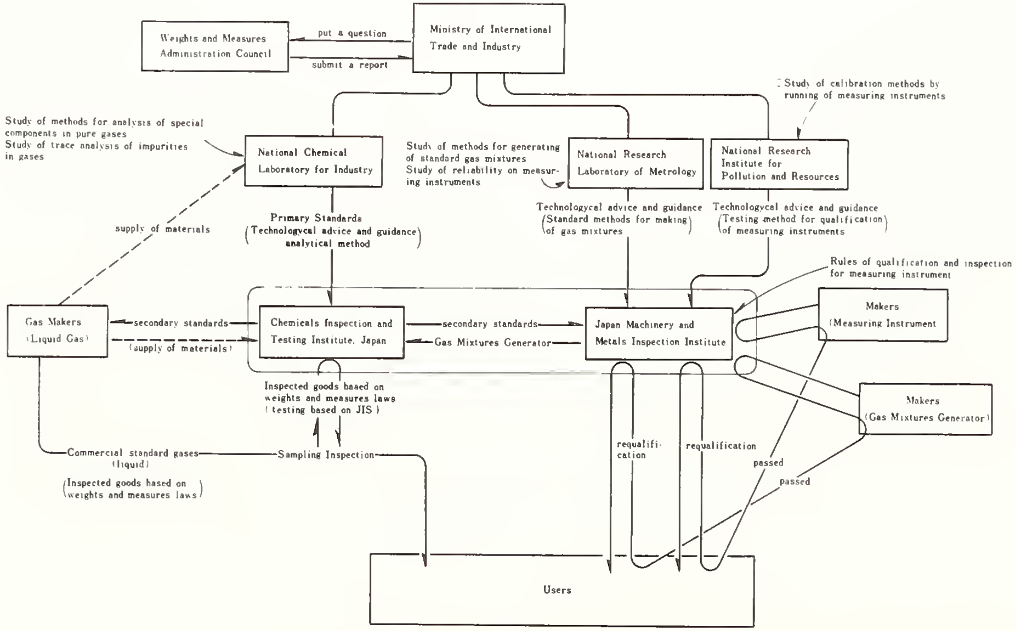

Figure 1. Traceability Flow on Qualification of Environmental Pollution Measuring Instruments and Standard Reference Gases

NATIONAL SRM PROGRAMS IN POLAND

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I. Classification, Service, and Legal Requirements

The Standard Reference Materials System is interpreted in Poland as a part of a broader System of Uniform Measurements (SUM) which consists of: [21, 23-26]

A. Unified System of Measures (USM)
  1. Nomenclature: physical quantities,
     units of measure,
     symbols
  2. Standards of SI- and derived units of measure

B. Reference Means of Measurements
  1. Reference instrumentation
  2. Reference methods
  3. Reference materials
  4. Selected reference data

Consequently, upon the decision of the Polish Committee of standardization and Measures (PKNiM), which operates national standardization laboratories, SRM's have to be responsive to general legal requirements, the same as all other reference tools of measurements. In addition, as shown in table 1, SRM's are subject to some or all of the compulsory control activities, provided by the Division of Physicochemical Metrology, which plays the role of National Standardization Laboratory in the field of SRM's.

Table 1, shows that SRM's are classified in Poland either as physical property or chemical composition standards in which four groups can be distinguished. [26] Among the physical properties SRM's are: (1) standards for calibration of measuring instruments, and (2) standards for comparative or differential measurements of physical properties of materials; while among the chemical composition SRM's are: (1) analytical SRM's of certified composition, and (2) high purity SRM's of certified content of the main component.

Table 1 clearly shows that our attention is focused on SRM's for calibration (column 1), and on the first four categories of control services, listed under points A.1, A.2., B.1., and B.2. These therefore need some kind of explanation.

Correctness versus Unified System of Measures means that all physical properties, if any, that are used to characterize SRM's, have to be expressed in legal S.I., or derived from S.I. units. In addition, they have to be determined in terms of legal standards of measures. This also means that the quality of the basic standards system determines the quality of the SRM system.

Conformity with other objectives of the System of Uniform Measurements means that SRM's have to be adequately linked in a calibration chain or analytical procedure in terms of their accuracy, precision, stability, composition, homogeneity, structure, and other properties.

The next item, licensing of import, means that each customer is responsible for getting his order for SRM's approved prior to forwarding it to the exporter. The purpose of this is to avoid introducing into the national economy unreliable references. For example, in 1972, 220 import proposals, concerning more than one thousand SRM's, were investigated and one-third were either disapproved or corrected with respect to the choice and source.

Approval of prototypes means verification of specified requirements, submitted by producers of SRM's, before starting batch production. This can also be interpreted as an act of approval of a norm that specifies properties of the given SRM, and is recognized as the most important control activity in the case of SRM's. The producer is obliged to forward a representative sample of the given SRM together with a short description of production, testing, and destination of his SRM. He should also submit a pattern certificate. In practice the work of approving SRM prototypes has turned out to be much more complicated and time-consuming than was expected, because it often involves scientific research, interlaboratory analyses, advisory needs, and international cooperation. That is why in Poland, we have only 142 approved SRM's and 278 SRM's of acceptable quality awaiting approval.

The next two items, legalization and calibration do not play any role in the case of SRM's since they either are included in a full testing procedure, or are not needed at all. Full testing, itself, concerns only SRM's produced or developed at PKNiM. From 100 to 200 full tests are provided per year.

Production is carried out at PKNiM only if there are either serious unification reasons, or national economy needs, and if the facilities are available. At present, only SRM's for calibration are produced, with a total amounting to 3,000 samples and growing by 30 percent per year. Plans were made to start in 1975-80 with production of environmental and health protection standards.

The last item on this list, teaching and training concerns physicochemical measurement techniques that are involved in testing procedures for SRM's. The Division of Physicochemical Metrology operates a 2-year technical school of physicochemical metrology, which was established in 1969 in Warsaw and issues 40 diplomas per year. This service is free of charge and supported with scholarships. Training concerns 60 university students who are granted one month summer practice.

II. National SRM Program

The perspectives were based upon recognition of users' needs [32] for a total of 1,700 different SRM's, as shown in figure 1. Not included are SRM's for dyes and nuclear materials. Of the 1,700--988 are required by more than 5 users. These 988 SRM's define the national perspective SRM program. At least half of the 988 SRM's are essential for the national economy and form the basic perspective SRM program. The SRM's that belong to this group have to be taken under permanent legal care of the PKNiM, as discussed earlier.

In comparison with these perspectives only about 50 percent of the SRM's are currently availabl , as shown in figure 2. The missing quantity of SRM's is partially imported wherever the difference in composition and structure does not affect measurement accuracy, and partially produced in small serives by non-profit industrial research institutes. Sometimes the quality of these standards is quite high, but they remain out of the system because of inaccessibility.

The distribution of the 483 SRM's forming the basic perspective national program is shown in figure 3. Thirty percent are standards for calibration, 10 percent are standards for comparative measurements, 40 percent are analytical standards, and 20 percent are high-purity materials. These figures are presented in more detail in table 2.

As shown in table 2, the most important SRM's from the point of view of standardization are physical property SRM's, which play an essential role in assuring uniformity of measurements, and SRM's for environmental and health protection, which are areas of national concern. Therefore, these programs are either in current plans [10,27] or have to be in future plans of the National Standardization Laboratories. It can also be seen that our national effort is heavily focused on metallurgy [1-9, 12, 17, 36-43, 47] and organic chemicals

[45,46], and to a lesser degree on glass [22] ceramics, and polymer SRM's. Considerable achievements are noticed in radioactive materials for instruments calibration. [11,48] Plans have been made to improve the availability of SRM's for minerals, high-purity inorganic materials, and gases, while specific needs of highly-developed mechanical, electromechanical, and chemical engineering industries are primarily presumed to be solved within their own scientific activities. A non-comprehensive list of sources of SRM's in Poland is given as Appendix 1. Also, indications exist that PKNiM's legal care over SRM's may be expanded from 483 to 760 SRM's due to the new facilities under construction. NOTE: footnote (z) to table 2.

The following figures help to show the national interest in SRM's. Currently 87 Polish industrial or scientific units are registered on our mailing list as being interested in SRM's. Among them are 37 laboratories directly involved in SRM production or interanalyses programs. On that list we also have 105 family names, with 63 holding Ph.D. degrees.

III. Actual research program of the Division of Physicchemical Metrology by the Polish Committee of Standardization and Measures

The internal program of the Division of Physicochemical Metrology may be divided in two parts: part one, includes both research and production of SRM's for calibration, which is explained in table 3; and part two, concerns evaluation of methods for testing SRM's produced by other organizations, which will be described below.

Table 3, which outlines the "Physical Properties-Calibration" SRM's of table 2, shows the current activity in 9 fields of physicochemical measurements with a total production of 62 SRM,s. [10, 13-15, 18-20, 29, 30, 33, 44] We assume that a high level of quality can be ascribed to at least 60 percent of these SRM's. Our basis of meaningful measurements in four fields, namely in humidity, pH, refractometry and IR-spectrophotometry is derived directly from absolute standards. In other areas, our measurements are referred to internationally compared reference standards of measures, and research is underway to improve their reliability by establishing absolute standards. Sometimes, however, by establishing absolute measurement systems one discovers discrepancies with international reference standards, and in that case (like pH), we might unjustly ascribe to them lower quality by assuming the difference as being possible systematic error.

As regards studies on methods for testing SRM's, which are submitted primarily for prototype approval by other organizations the following subjects can be listed:

A. Comparison of chemical and spectral methods
B. Calibration curves for chemical composition vs. physical properties
C. Comparison of corresponding SRM's and series of SRM's from various sources [16]
D. Homogeneity of chemical composition in macro- and micro-scale
E. Homogeneity of structure - defectoscopy and metallography
F. Specific applications of mathematical statistics [3, 31]

An example of such a study is presented in figure4. Two duralumin SRM's were tested using a reference. [16] In case A, the manganese content has been found in satisfactory coincidence, while in case B, the titanium content has shown considerable disagreement although points were correctly located on line. As a consequence the SRM's in question were subjected to additional chemical testing in an outside laboratory.

Another example, presented in figures 5a and 5b, is a copper determination in 5 different aluminum-magnesium-manganese series of SRM's. [16] By using arc excitation a complete disagreement of analytical curves were found (figure 5a). However, as shown, in figure 5b, this does not mean that the standards were incorrect; by using low-voltage spark excitation we obtained perfect conncidence of all five lines. In this case users were warned against inappropriate application of the given SRM's. This is also an example that very good SRM's, if incorrectly used, may lead to completely false results.

Figure 6 shows another example. This concerns recommendations developed regarding maximum admissible relative error in Polish standards for metals and alloys. [3, 31] For example, for an element content of 1 percent, the error should not exceed 0.05 percent, but for a content of 0.001 percent it may be 0.0004 percent. Based on this recommendation our standards are tentatively classifed either in class 1 or class 2. First class standards should follow the 0.01 significance level, while second class standards are admitted on the 0.05 significance level. While there are, of course, several exceptions, this curve well suits our present purposes.

Finally, it should be stressed that SRM's have gained considerable attention in Poland, especially within the activities of the Polish Academy of Sciences, which has established two permanent non-laboratory groups dealing with SRM's. These groups are: The Subcommission on SRM's by the Analytical Chemistry Commission, which is directly involved in chemical aspects of SRM programs; and the Committee on Metrology and Data for Science and Technology, which operates in a much broader field of interest and has among others the general responsibility for strengthening scientific activities involving SRM's throughout the country.

Neither the standardization nor scientific work described above will create a completely suitable SRM Program in Poland. Consequently, there must be strong international cooperation on SRM's comparable to that provided by the BIPM for basic standards of measures. [28] Therefore, Poland participates in IUPAC Commission 1.4, and ISO and other organizations that, at least partially, touch SRM questions. In addition, Poland supports each step undertaken for introducing SRM's into the activities of international metrological organizations.

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Produkcji i Dystrybucji Izotopow, Swierk k/Otwocka, exporter: METRONEX, Polish Foreign Trade Enterprise, Warszawa 1, Al. Jerozolimskie 44

Table 1. Role of National Standardization Laboratories (PkNiM) within the Legal SRM System

X - operational
0 - need not yet operational

Subject of control or service	Physical Properties SRM's		Chemical Composition SRM's	
	1 SRM's - calibration	2 SRM's - comparative measurements	3 Analytical SRM's	4 High purity SRM's
A. <u>General legal requirements</u>				
1. Correctness vs. USM	X	0	X	0
2. Conformity vs. SUM	X	0	0	0
B. <u>Compulsory control & service</u>				
1. Licensing import	X	X	X	0
2. Approval of prototypes	X	0	X	X
3. Legalization	X			
4. Calibration				
5. Full testing & certification	X			
C. <u>On-demand Service</u>				
1. Production	X	0		
2. Advisory & information	X	X	X	X
3. Teaching & Training	X	0	X	0

Table 2. STATUS OF SRM's IN POLAND[1]

Industry or Field of Application	Produced to 1972		Planned for Production 1975-80	
	Total	Under PKNiM Control	Total	Under PKNiM Control
Organic Chemicals	50	26	153	56
(analytical & high purity)				
Monomers & Polymers	-	-	20	4
Glass & Ceramics	36	-	66	9
Ferrous Metallurgy	101	28	186	71
Non-Ferrous Metallurgy	76	18	105	52

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[1] See Appendix 1 for sources of availability

Table 2. STATUS OF SRM's IN POLAND (continued)

Industry of Field of Application	Produced to 1972		Planned for Production 1975-80	
	Total	Under PKNiM Control	Total	Under PKNiM Control
Ores & Minerals	16	2	49	29
High purity metals & inorganic substances	11	1	63	17
Specific - for mechanical & electromechanical industry	5	-	28	-
Specific - for chemical engineering & catalysis	-	-	22	-
Gases	-	-	26	10
Radioactivity z)	40	-	45	10

Table 2. STATUS OF SRM's IN POLAND (continued)

Industry or Field of Application	Produced to 1972		Planned for Production 1975-80	
	Total	Under PKNiM Control	Total	Under PKNiM Control
Environmental Protection	-	-	15	15
Health Protection-Clinical	-	-	20	20
Physical Properties-Calibration	62	62	140	140
Physical Properties-Comparative Measurements	23	5	50	40
Total x)	420	142	988	483 Y)

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x) Except dyes and pigments (more than 600), and nuclear SRM's

y) 483 means minimum that may mount up to 760

z) After presenting this report, author has received a catalog [48] which essentially corrects the given figure of 40 radioactive SRM's to the total of 126 SRM's. This perfectly proves the notice under y)

Table 3. Division of Physicochemical Metrology Polish Committee of Standardization and Measures

Production & Research SRM Categories	Number of SRM's	Quality = world level ≈ slightly below < below	Meaningful Measurements basis
1. Density	8	=	Comp. vs. H_2O, Hg (search for absolute)
2. Viscosity	18	=	Comp. vs. H_2O
3. Humidity	7	≈	Absolute Gravimetric (search > 90% & < 10%
4. pH	7	<	Absolute (H_2-electrode (search: electrodes)
5. Conductivity	4	≈	Comp. vs. KCl
6. Refractometry	8	=	Absolute - Goniometric
7. Polarimetry	1	<	Comp. vs. quartz (search for absolute)
8. UV & VIS spectrophotometry	4	<	Comp. vs. lamps, filters (search for absolute high resolution)
9. IR - spectrophotometry	5	=	Absolute A scale: rotating sectors Comp. λ scale
TOTAL	62		4 Absolute Bases

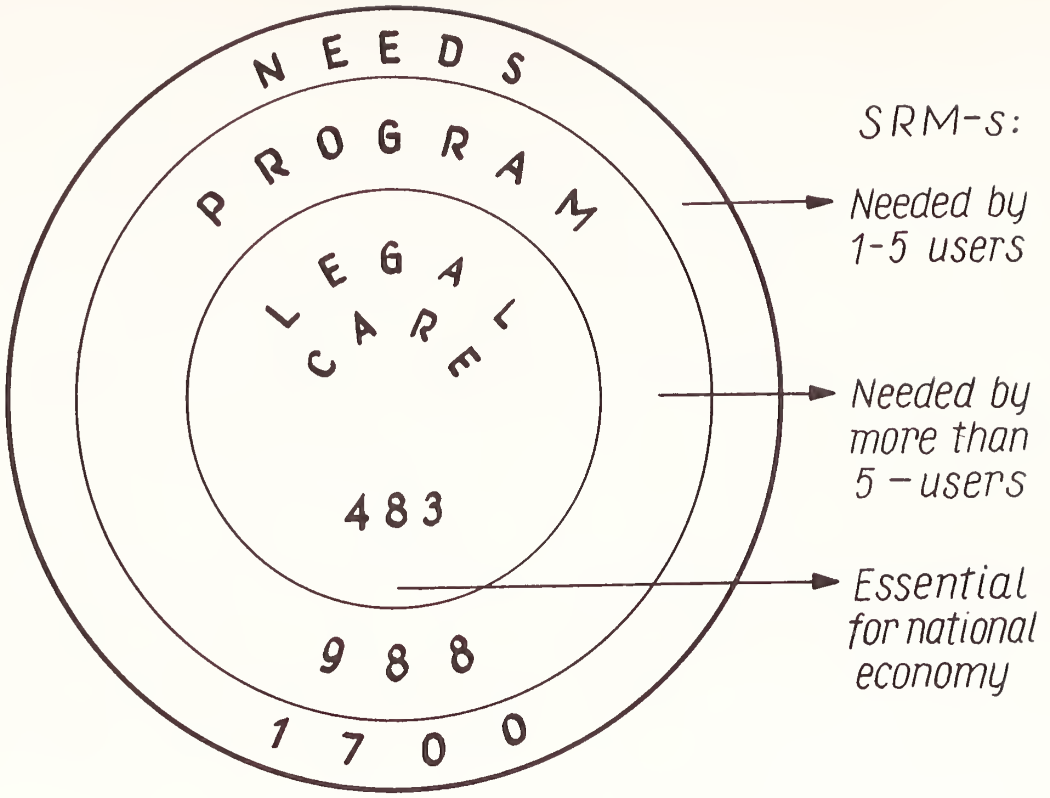


Figure 1. Perspective SRM Program

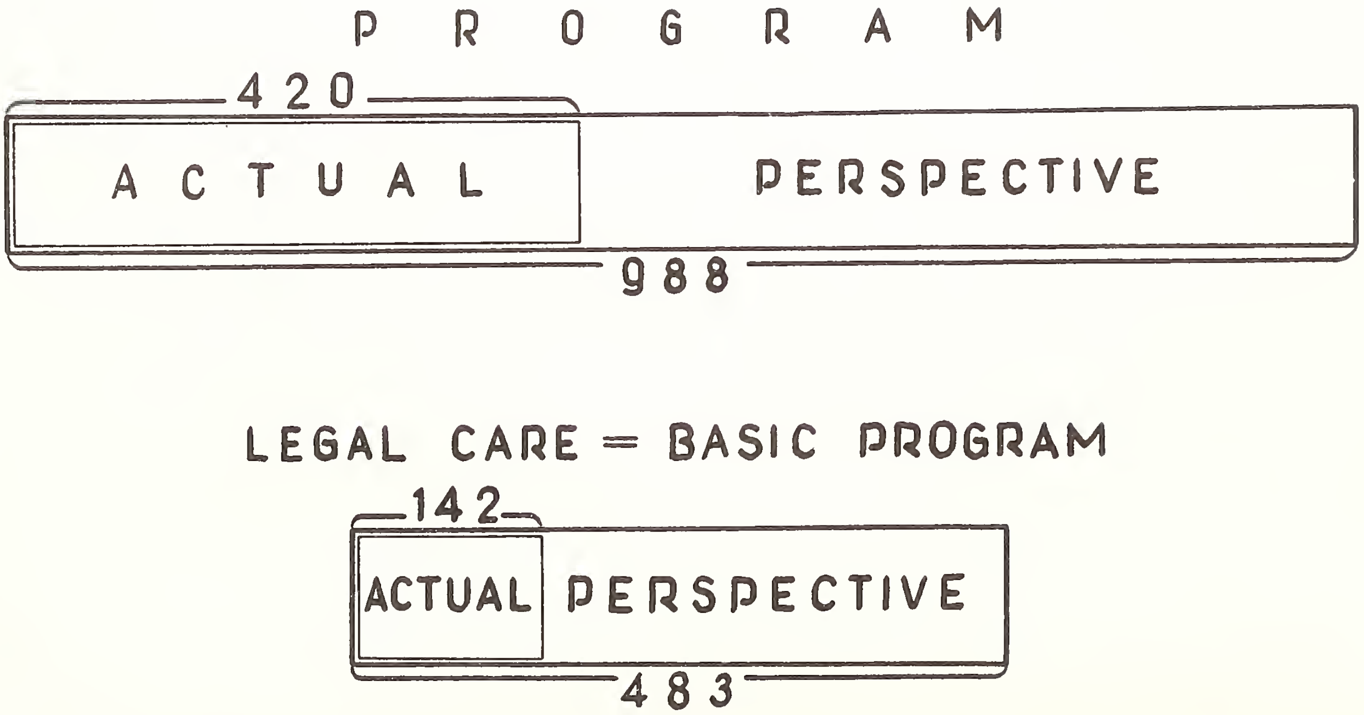


Figure 2. Actual SRM Program

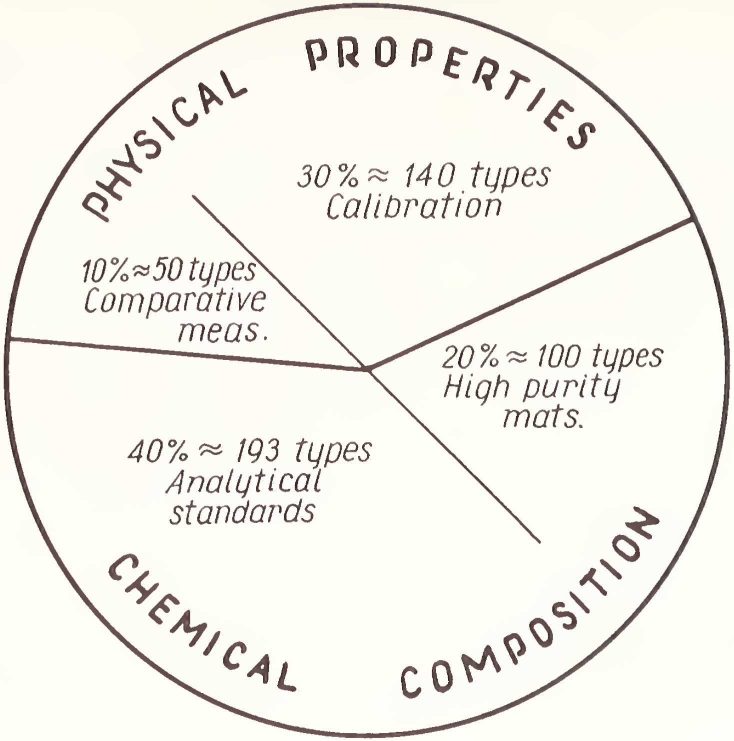


Figure 3. Classification and Distribution of SRMs in the Basic Program

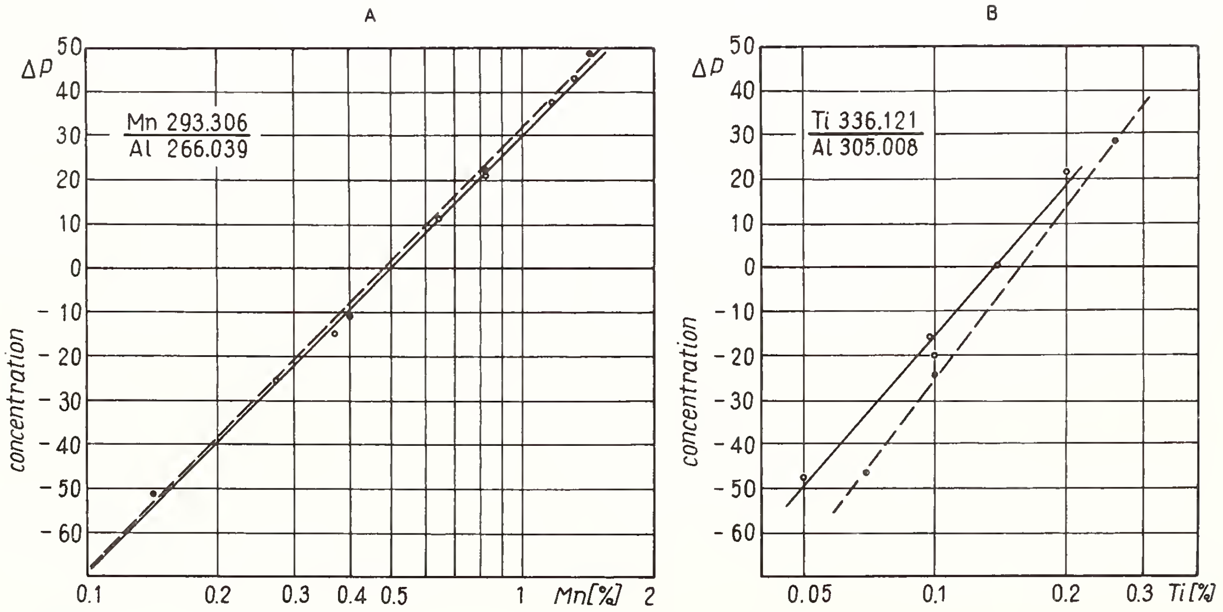


Figure 4. Spectrographic analytical curves of two (• ∘) various series of duralumin standards: example of (A) coincidence, and (B) discrepancy

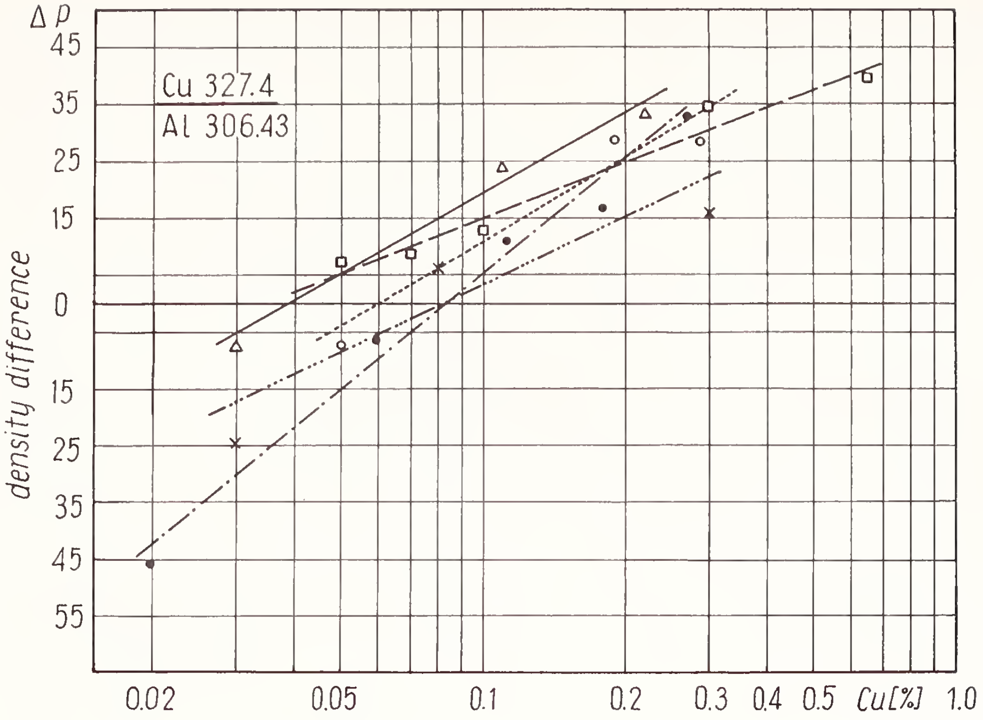


Figure 5a. Cu determination in 5 different series of Al-Mg-Mn standards. Spectrographic analytical curves, obtained in arc excitation, disagree with each other. (Compare next figure.)

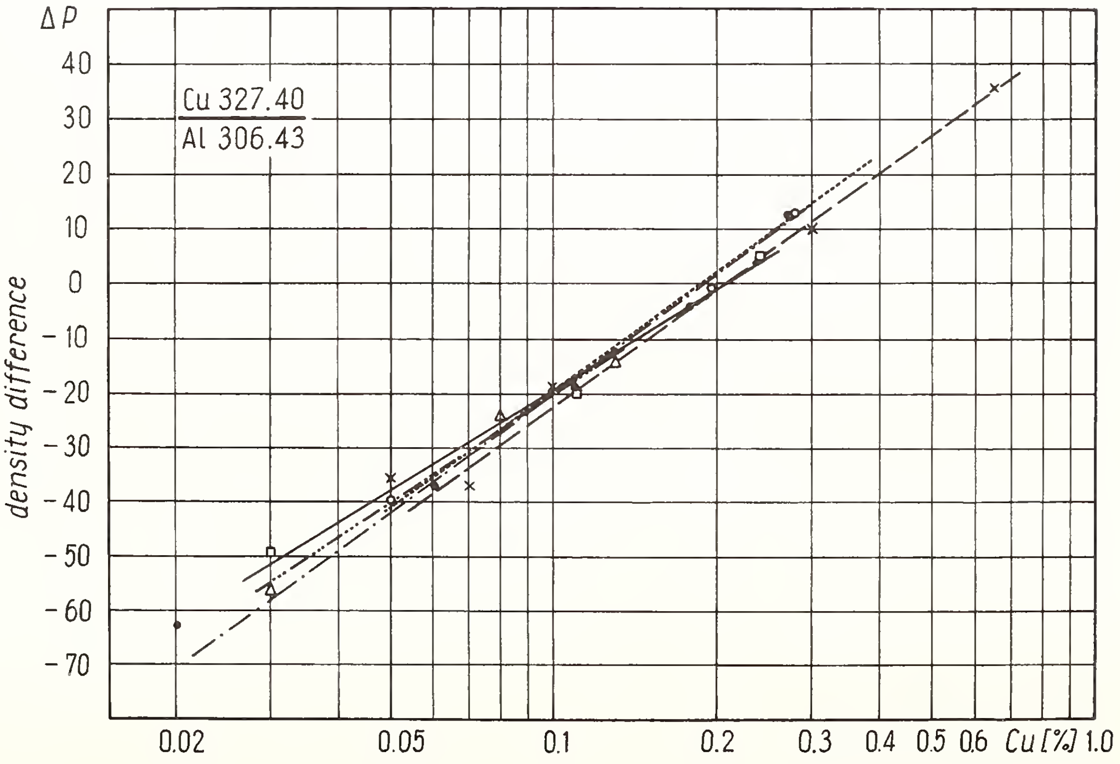
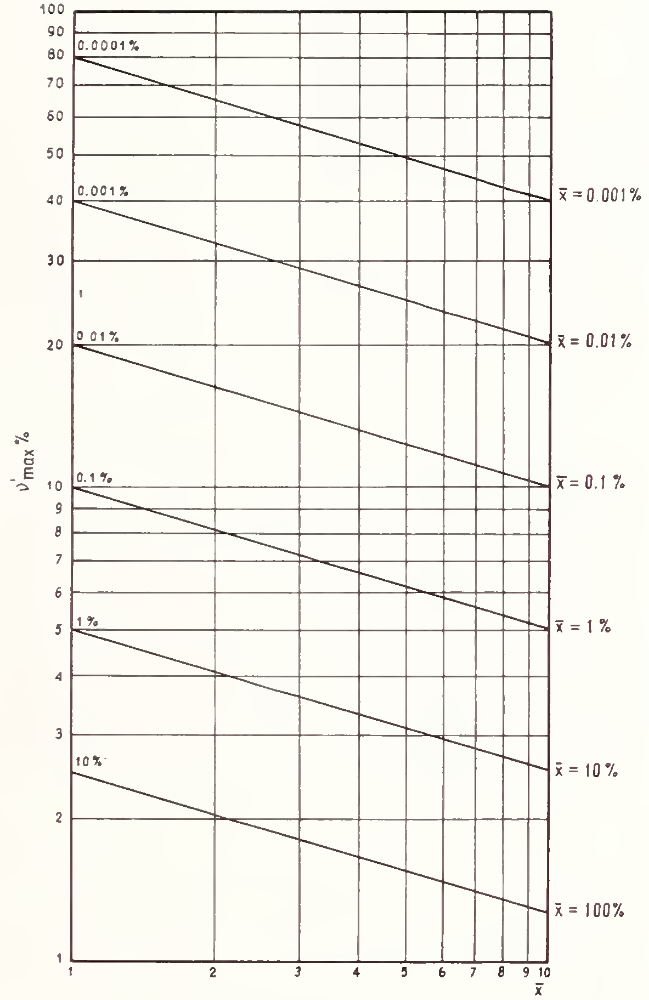


Figure 5b. Cu determination in the same alloys as shown in the preceding figure. Spectrographic analytical curves obtained in low voltage spark excitation, fully coincide with each other.



$$\nu' = \frac{t_{\alpha\varphi} \cdot s}{\bar{x} \sqrt{n}} \cdot 100$$

$t_{\alpha\varphi}$ – Student's coefficient for probability α and degree of freedon φ.

s – Standard deviation.

n = Number of experiments.

Figure 6. Recommendations concerning maximum admissible relative error ν'_{max} % vs. weight concentration % $\bar{x}$ of any given component in Polish standards of metals and alloys.

Appendix: Sources of Information and Availability of Standard Reference Materials (SRM's) in Poland. Non-comprehensive list.

No	Standard Reference Materials	Source of availability: for information please write to the director of:	Scientists involved in production or testing procedures
1	Physical properties SRM's - calibration (also called "Legal Physicochemical Standards of Measures)	Zakład Metrologiczny Fizykochemii Polski Komitet Normalizacji i Miar ul. Elektoralna 2 00-139 Warszawa This is the governmental organization for standardization and measures which, among other responsibility, takes legal care of all Polish SRM's	Prof. T. Plebański - supervision Dr. A. Kozdoń - density Mrs. E. Milewska - viscosity Dr. K. Kostyrko - humidity & moisture Dr. J. Buława - pH & conductivity Dr. M. Tarasiuk - refractive index Mr. W. Wnukowski - polarimetry Dr. J. Wacławik - spectrography & spectrometry Prof. J. Gałązka - mathematical statistics Dr. N. Sobczak - spectrochemical SRM's Dr. Z. Łukasiewicz - IR - spectrophotometry Mrs. A. Michalik - UV - spectrophotometry
2	Analytical SRM's (certified for various composition)	P. P. H. Polskie Odczynniki Chemiczne ul. Sowińskiego 11 Gliwice 44-101 This is a commercial Company for Chemical Reagents	
3	Ferrous Metallurgy Materials & Ores (spectrochemical and chemical SRM's)	Instytut Metalurgii Żelaza ul. Karola Miarki 12 Gliwice	Prof. J. Inglot Mrs. H. Biernacka
4.	Non-Ferrous Metallurgy Materials & Ores	Instytut Metali Nieżelaznych ul. Sobieskiego 11 Gliwice	Dr. M. Koźlicka Mr. S. Studencki Mrs. S. Witkowska
5	Cast & pig iron	Instytut Odlewnictwa ul. Zakopiańska 73 Kraków	Prof. R. Krzeszewski Prof. J. Buciewicz Dr. & Mrs. Z. Dolinski (gases in metals)

Appendix: Sources of Information and Availability of Standard Reference Materials (SRM's) in Poland. Non-comprehensive list. (continued)

No	Standard Reference Materials	Source of availability: for information please write to the director of:	Scientists involved in production or testing procedures
6	Geology, rocks	Instytut Geologiczny ul. Rakowiecka 4 Warszawa	Dr. W. Bitmsr Dr. A. Jedliński
7	Organic chemicals (analytical & high purity). Among them: SRM's for gas chromatography	Instytut Chemii Fizycznej PAN ul. Kasprzaka 44 Warszawa	Prof. A. Bylicki Dr. A. Mączyński Dr. J. Małczyński
8.	Radioactive materials for instruments calibration	Ośrodek Produkcji i Dystrybucji Izotopów Instytut Badań Jądrowych Swierk k/Otwocka	Dr. T. Radoszewski
9	Pesticides	Instytut Przemysłu Organicznego Żerań Wsch., ul. Noworzemysłowa 4 Warszawa	Dr. A. Kotarski
10	Glas, and related raw materials (limited availability)	Instytut Przemysłu Szkła i Ceramiki ul. Postępu 9 Warszawa	Mrs. J. Ahrends Mrs. H. Pawłowska (retired)

Attn: Most of the producers as listed above are scientific non-profit organizations. Production and sale depends on Director's decision.

REFERENCE MATERIALS IN THE UNITED KINGDOM

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I. Introduction

The theme of this symposium is "Standard Reference Materials and Meaningful Measurements" and my task is to relate the theme to the current situation in the United Kingdom. I propose to begin with a discussion of the significance of the expressions "reference materials" note the omission of the word "standard" (see part II), and "meaningful measurements," seen from the viewpoint of a chemist working in the National Physical Laboratory, the British organization most nearly akin to the National Bureau of Standards.

What are "reference materials?" Within the context of this symposium, I consider them to be substances or artifacts used for reference purposes in science, technology, and commerce. By "reference purposes" I imply that reference materials are credited with properties that make them suitable for calibrating a measuring instrument, and/or suitable for checking an existing calibration, and for cognate uses* in measurement science (and I include chemical analysis in the generic term "measurement science"). Since a reference material is to be used for <u>in situ</u> establishment of scales of measurement, it must obviously be procurable and transportable without difficulty. Now of course one measuring instrument can be used to calibrate another, and such calibrations have traditionally been an important feature of instrumental science, especially in the higher regions dignified by the word "metrology." Indeed in the UK we have a well developed system operated by the British Calibration Service, whereby instruments of certain types can be calibrated by certificated test centres, the calibration of those instruments is traceable to the National Physical Laboratory. Evidently in physically larger countries such as the USSR [2] it is more difficult to build up a network of test centres, and more appropriate to rely on reference

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*A good statement of the uses of reference materials is to be found on p. 5 of the "Community Survey on Standard Reference Materials." [1] In brief, these uses are said to be in monitoring the efficiency of industrial processes, in verifying manufacturers' specifications and conformity with regulations, and in cross-checking results between different laboratories.

materials for disseminating scales of measurement. The reference-material approach is certainly preferred in the field of chemical analysis, where it would be considered quite absurd to send, say, an emission spectrometer for calibration, when reference specimens are available for calibrating *in situ*.

So reference materials permit calibration, checking and testing of instruments (and sometimes of procedures) without the need to move the instruments. But how can one be sure that a given reference material is suited for the purpose and that the property-value credited to it is trustworthy? The answer to these questions is bound up with the answer to the question "What is a meaningful measurement?" An example may throw light on the latter question. Suppose we ponder the more specific question: "How does one make a meaningful measurement of electrical resistance?" Any answer must surely begin with the words, "It depends how accurately one needs to know resistance." If one's need is for a resistor in an electronic circuit, it may well be acceptable merely to note the coloured rings on the resistor and refer to the code relating the markings to resistance; a check of the resistance value can be made with the aid of a simple, cheap test-meter. At the other extreme one may need to know temperature on the International Practical Temperature Scale to 0.001 K, requiring measurement of the resistance of a platinum resistance thermometer to, say, $\pm 10^{-4}\Omega$. In this latter circumstance one must obviously select a resistance bridge plus auxiliary equipment of a sensitivity of better than $10^{-4}\Omega$. Furthermore, to ensure that the *precision* of a series of resistance measurements will be commensurate with the *accuracy* sought (i.e., that persistent errors, or bias, are not predominant), one must make careful checks of the instrument's performance, using calibrated resistances, and perhaps have the bridge itself recalibrated. Clearly, to use a sensitive resistance-bridge to make a time-consuming determination of the value of resistance in the first case would not be a meaningful measurement, nor would the use of a simple test-meter in the second case; moreover, a precise measurement could not properly be described as meaningful unless supported by proof of the insignificance of persistent errors. Hence, to achieve meaningful measurement one must select a measurement system appropriate to the needed accuracy, and one must ensure the overall efficacy of the measurement system: it is in connection with *efficacy* that reference materials--as aids to calibration, checking and test--find their real use.

II. Certified Reference Materials and Standard Reference Materials

It is now important to return to the question as to how a user of reference materials can trust the property values credited to the specimens he has procured. In later paragraphs I give details of reference materials available in the United Kingdom from over 30 sources, some in the private sector, and some in the public sector. One problem I had was where to draw a line between reference materials within the ambit of this symposium and the gamut of available materials that could, if one wished, be employed for reference purposes. Eventually, I decided to include reference materials that were certified as suitable for their purpose, or were offered to the public specifically for reference purposes, though not formally certified--all other reference materials have been excluded.

Ideally, all reference materials should be certified by trusted organizations, and the instrument calibrations in these organizations should be traceable to national standardizing laboratories. In the USSR and probably in other states of eastern Europe, the operation of reference materials schemes is centrally controlled in this way: thus, methods for certifying reference materials in the USSR have been elaborated, and appear to have the force of law. [3] In other countries one generally finds a mixture of public and private enterprise in the operation of schemes for the provision of reference materials--certainly this is so in the United Kingdom. Though the <u>provision</u> of reference materials may be satisfactoily undertaken in the private sector, there are grounds for thinking that the <u>certification</u> of reference materials is best carried out in the public sector, or, if not, at least by a co-operative test procedure. Such Certified Reference Materials, CRM's, stand the best chance of commanding public trust, when used for the purposes discussed in part I.

I must now briefly refer to my non-use of the word "standard" in relation to reference materials (cf. part I): I avoid this word in the reference materials context partly because it is grossly overworked in science generally, but more particularly because I do not know what meaning the word is intended to convey. If it is intended to mean "certified," why not use the latter word directly? If it is intended to mean "of superior quality" who is to judge quality and by what criteria? If it is intended to mean "issued by national laboratories" then the word must necessarily have differing levels of usage in differing countries, since the activities of the various national laboratories differ widely in the reference-materials field. If it is intended to mean "for use with published standards (specifications) only" then the word is frequently misused. So I regard "standard" as expletive, and prefer not to use it at all.

III. The Provision of Reference Materials* In The United Kingdom

To turn the detailed information, now to be presented, into a reasonably digestible form, I have categorized it as follows:

A. Reference materials for compositional analysis,
B. Reference materials of high purity,
C. Reference materials for well-defined physical properties, and
D. Reference materials for technological properties.

Of course these categories are not to be regarded as rigid or mutually exclusive. For example, one and the same sample of benzoic acid might well be used as a pure chemical in acid-base titrimetry (B), or as a physicochemical-property standard (C). It should be noted that category C contains reference materials credited with properties whose definition is clear-cut within the realm of physics, while category D contains reference materials credited with properties whose definition requires citation of a test method. A similar categorization was used in an article [4] describing certified reference materials available in Western Europe.

I have tried to make the information up-to-date, but errors and omissions are definitely expected. Moreover, the mention of a particular organization or product is not to be taken as an endorsement of that organization or product by the National Physical Laboratory.

In the paragraphs that follow, named organizations are accompanied by identifying numbers, in parenthesis; the addresses of the organizations can be found by reference to the corresponding numbers in the Appendix.

A. Reference Materials for Compositional Analysis.

Reference materials to aid the determination of chemical composition have been in use for a long time. Thus schemes

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*The word "materials" is used in a broad sense, and therefore includes shaped specimens and simple devices.

for the supply of compositional reference materials have been running in the USA since 1906, [5] in Germany since 1912, and in the United Kingdom since 1916--indeed these schemes were the foundations upon which wider schemes for the supply of reference materials, notably that the National Bureau of Standards, have been built.

Compositional reference materials are specimens for which the proportions of some or all of the contained elements or compounds are authoritatively stated; mostly such specimens have been deliberately made homogeneous (e.g., as powders, turnings, or solutions), but in a few instances composition is stated as a function of position in the specimen. Compositional reference materials are used by analysts: 1. to calibrate instruments for chemical analysis, or 2. to develop, prove, test, or practice procedures for chemical analysis. Examples of analytical instruments that may advantageously be calibrated by reference materials are those dependent on emission or absorption spectroscopy, mass spectrometry, and chromatography in its many forms. Absolute quantitative measurement is often difficult by such techniques, so relative quantitative measurement, utilizing a reference material, is usually preferred. The certification of the composition of a reference material used in this mode will often depend on exhaustive chemical analysis, or on a programme of clinical analysis organized on a cooperative basis, the results of which are treated statistically.

A United Kingdom organization that has long specialized in the supply of composition reference materials is the Bureau of Analysed Samples, Ltd. (1) "Spectroscopic Standards" of many types of steel, and some nickel-base and aluminium alloys, and "British Chemical Standards" of steels, cast irons, ferro-alloys, non-ferrous alloys, ores, slags, ceramic materials and cement are supplied. A new line is represented by oxygen-in-steel standards. The Bureau of Analysed Samples, Ltd. also serves as a retail outlet for hydrogen-in-steel standards [6] prepared by the Welding Institute (2), and for various iron standards prepared by the British Cast Iron Research Association (3).

Other United Kingdom sources for spectroscopic standards are: the British Non-Ferrous Metals Research Association (4) which offeres brasses, bronzes, gunmetals, nickel-silvers and cupro-nickels; Johnson Matthey Chemicals, Ltd. (5), which offers copper, aluminium, and lead standards; Henry Wiggin & Co., Ltd. (6), which offers nickel-base alloy standards; and G. L. Willan, Ltd. (7), which offers steels and copper-, nickel-, and cobalt-base standards. The latter firm also undertakes preparation of spectrographic standards according to customers' requirements.

Other United Kingdom sources of compositional standards for chemical analysis are: the British Glass Industry Research Association (8), which supplies glasses of various compositions; Hopkin and Williams (9), which supplies oil-soluble standard solutions of non-ferrous metals; the National Physical Laboratory (10), which supplies "British Standardised Steel Samples;" the Water Research Association (11), which supplies water samples containing various named impurities; and the British Oxygen Co., Ltd. (12), which supplies gas mixtures for calibrating chromatography and other instruments.

Uranium oxide compositional standards, containing stated concentrations of the ^{235}U isotope in the range 0.2--4% of the uranium content, are available from British Nuclear Fuels Ltd. (33).

B. Reference Materials of High Purity.

This class of reference material relates to substances of a specified high purity, that is >99% purity. Although the purity specification relates to the major component present, the actual methods of determining purity generally relate to the minor components, and it might therefore be more logical to speak of "0.05% impure anthracene" rather than 99.95% pure anthracene." Methods of determining residual impurities may give a value for the sum total of impurities, e.g., as derived from cryoscopic methods, or values for the individual impurities, e.g., as derived from chemical or spectroscopic analysis.

The uses of reference materials of high purity are many and varied. They are important as standards in quantitative chemical analysis (cf. A), but additionally they serve as physical-property standards. It can be argued (cf. C) that the ideal physical-property reference material is certified with respect to the property value of a given specimen or of a sample from a homogeneous large batch. Many users of reference materials, however, are prepared to utilize a reference material of high purity in the calibration or test of an instrument or measurement system, taking the needed physical-property value from a reliable published source--examples are the use of highly pure indium metal as a reference material for checking the temperature and energy calibration of a differential scanning calorimeter, or the use of purified water to determine the volume of a pycnometer.

Many chemical supply houses in the United Kingdom offer ranges of chemicals that are said to be "pure," with or without an additional epithet or quantitative description. It is a moot point whether all such materials truly qualify as reference materials, and the samples that follow are limited to: 1. reference materials certified as to purity; and 2. materials of indicated purity, which are intended to be used for reference purposes. This, Kock-Light Laboratories, Ltd. (13) offers a range of amino-acids and steriods ("purissimum", homogeneous by either paper or thin-layer chromatography) that are offered as chromatographic standards, and a number of highly pure metals. BDH Chemicals, Ltd. (14) offers highly pure "Analar" and ultra-pure "Aristar" laboratory chemicals, substances such as amino-acids and fatty acids intended as chromatographic standards, organic analytical standards, and a range of high-purity gases, which are marketed in collaboration with Air Products, Ltd. (15) The British Oxygen Co., Ltd. (12) offers high-purity "Grade X" gases. Hopkin and Williams (9) offer highly pure "Analar" and reference-standard "Purified for Volumetric Standardisation") analytical reagents, and micro-analytical reagents ("M.A.R."). Johnson Matthey Chemicals, Ltd. (5) provides spectrographically standardised substances ("Specpure") in both solid and solution form. Metals Research, Ltd. (16) offers high-purity single crystals of metals and alloys, which are classified in terms of their structural perfection. The Bureau of Analysed Samples, Ltd. (1) also supplies high-purity metals.

Westfield College (17) supplies samples from the Steriod Reference Collection, formed in 1954 at the request of the Medical Research Council. The National Physical Laboratory (10) supplies highly pure specimens of organic compounds, [7] some of which are pesticides and related substances, provided by arrangement with the Collaborative International Pesticides Analytical Council, Ltd. [8] The British Pharmacopeia Commission (18) supplies two grades of reference materials needed for pharmaceutical assays, namely "British Pharmacopeia Authentic Specimens" and "British Chemical Reference Substances." Development of the range of substances of the latter type is not intended, but work on samples of the former type continues to develop. The National Institute for Biological Standards and Control (32) assists with this programme, when biological assay is called for.

C. Reference Materials for Well-defined Physical Properties.

Reference materials of this type find use for calibrating and testing instruments for physical measurement. The physical properties in question are usually easy to define and to relate to the Système International d'Unités (SI), yet the realization of the definitions in the average laboratory may be inconvenient or even deterringly difficult. In these circumstances the reference materials serve to transfer a scale of measurement (or perhaps a point on a scale of measurement) from a laboratory with a standardizing capability into the user's own laboratory. Other instances occur where a reference material is needed to establish a scale of measurement that is not provided for by the SI: the scale of pH of solutions is an example.

It is worth noting that many end-uses of physical-property reference materials involve the destruction of the specimen. Thus, benzoic acid used to calibrate a combustion calorimeter is converted into carbon dioxide and water in the calibration process. An assured supply of such reference materials must obviously be available to users on a continuing basis.

A range of physical-property reference materials in the United Kingdom is available from the National Physical Laboratory (10). Aside from reference materials certified as to physical property by NPL but marketed, or used in-house, by other organizations, NPL supplies sets of 12 coloured ceramic tiles certified as to diffuse reflectance [9] of each tile at wavelengths in the range 200 - 2000 nm, fine powders [10] certified as to specific surface area in the range 11 - 286 m^2g^{-1}, samples of organic compounds certified as to freezing or melting point, samples of polypropylene certified as to number-average and weight-average molecular weight, and a range of radionuclides certified as to activity; the radionuclidic reference materials are both long-lived (available from stock) and shorter-lived, the latter being available either to order or to a pre-published timetable. A wide range of radionuclides certified for radioactivity is also available from The Radiochemical Centre (19), which additionally offers calibrated neutron-emission sources.

Benzoic acid certified (by the NPL as to energy of combustion is available from the Bureau of Analysed Samples, Ltd. (1) and from BDH Chemicals, Ltd. (14) The latter firm also supplies potassium hydrogen phthalate certified (by NPL) as to its suitability for establishing a scale of pH, according to the relevant British Standard [11]; it should be noted that the British pH scale differs from the American. [12]

Oils certified as to viscosity in the range 0.05 - 20 $N \cdot s \cdot m^{-2}$ are available from the Paint Research Association (20), and an oil and various solid specimens certified as to thermal conductivity in the range 0.15 - 2 $W \cdot m^{-1} \cdot K^{-1}$ are available from the Explosives Research and Development

Establishment (21). Samples of quartz characterized as to particle size, 0.5 - 5 μm, are available from the Safety in Mines Research Establishment (22), while cement samples characterized as to specific surface area are available from the Building Research Establishment (23). Fluorimetric specimens suitable for checking wavelength calabrations of fluorimeters are available from Koch-Light Laboratories, Ltd. (13).

Triple-point water cells suitable for use in realizing the International Practical Temperature Scale, 1968, are available from Sembly, Ltd. (24).

The rubber and plastics Research Association of Great Britain (25) issues through its Polymer Supply and Characterisation Centre various types of Standard Polymer (polystyrene, polyvinyl chloride, polyethylene, polyoxymethylene, nylon 66, polycarbonate, and polymethylmethacrylate), described as materials "each sample of which over a substantial period of time has the same properties, within known limits, as any other sample and which is procurable in realistic sample sizes for a number of years." Additionally, the Centre issues a CRM grade of polystyrene, described as "a material with certified properties as measured by defined methods." Both grades of polymer issued by the Centre (i.e., "Standard", and "CRM") are characterized by a combination of molecular-weight and physical-property measurements (See D.)

D. Reference Materials for Technological Properties.

It is often convenient to make a distinction between "well-defined physical properties" and "technological properties" (which is a fairer discription than "ill-defined physical properties"). The former are definable and realisable without great difficulty, the latter require specification of a test method for their proper definition and realisation, e.g., a method of the ISO, the British Standards Institution, the American Society for Testing and Materials, or the Institute of Petroleum. Hence, reference materials for technological properties are used to calibrate and check instruments for technological measurement, used in conjunction with written methods of test, destructive or non-destructive.

The National Engineering Laboratory (26) supplies steel balls used for rolling-contact fatigue tests, oils used for various lubrication tests, and calcium carbonate abrasive used in a standard test for dentifrices. W. and T. Avery, Ltd. (27) supply steel blocks calibrated for use in hardness tests. The British Standards Institution (28) supplies cotton felt for calibration of dust-index machines, lead dioxide, and tapestry cloth for use in SO_2 detection devices, flannelette for use in fireguard tests, aluminium bar for testing industrial helmets, and hexagonal steel bars for testing the abrasion-resistance of seat-belt webbing; these tests, like many others in the United Kingdom, are specified in British Standards, Shirley Developments, Ltd. (29) and The Society of Dyers and Colourists (30) both supply fabrics used in technological tests in the textile industry.

Pira, the Research Association for the Paper and Board, Printing and Packaging Industries (31), supply paper and board test pieces for a variety of tests (thickness, grammage, bursting strength, tensile strength, elongation-to-break, air permeability, surface smoothness, tearing resistance, stiffness, puncture resistance, crush resistance, folding endurance, ink absorbency, etc.) and aluminium foil and spring-steel strip for testing bursting strength and stiffness, respectively. Many of Pira's specimens are suitable for tests specified by ISO or other standardizing bodies outside the United Kingdom.

RAPRA (25) offers standard rubber samples for abrasion tests and standard fabricated thermoplastic samples for a variety of end-uses; additionally they provide CRM rubber hardness-blocks for the calibration of durometers, according to British Standard or other procedures. (See C. RAPRA's definitions of "Standard" and "CRM").

IV. A Forward Look

Anyone who has read paragraphs A through D, part III, must have been struck by the diversity of the reference material situation in the United Kingdom. If he deduced that this situation had developed in an unplanned way, he would be right. There never has been any attempt to coordinate reference material work in Britain overall, though there may well have been some coordination in certain sectors. The situation as it exists today has resulted from the laws of demand and supply. The National Physical Laboratory, for example, has various activities in the supply and certification of reference materials (see above), which have resulted from demands in diverse subject areas. These demands have been met by work in the particular NPL Division having the necessary expertise, and no coalescence of these activities has yet occurred.

But what of reference materials in the future? This question must be answered in relation to a scenario that will include better consumer protection, harmonization of trade and safety regulations, husbanding of resources, preservation of the environment, protection of health, and so on. Legislation will have a part to play in attempts to reach these goals, and inevitably much of this legislation will refer to written standards. The latter, in turn, are likely to require certified reference materials for their implementation. The future, therefore, will require provision of certified reference materials on a bigger scale, and in a more planned way, than hitherto. The necessary increased effort may in some instances require an international endeavour, and it is noteworthy that the European Economic Community has set up a Bureau Communautaire de Référence to take action in meeting some unsatisfied demands for reference materials in its nine member states. Hopefully, also, this symposium will point the way to meeting unfilled needs on an internationally agreed basis.

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Appendix

(1) Bureau of Analysed Samples, Ltd.
Newham Hall
Newby
Middlesbrough
Teesside, TS8 9EA, UK

(2) The Welding Institute
Research Laboratory
Abington Hall
Abington
Cambridge, CB1 6AL, UK

(3) British Cast Iron Research Association
Alvechurch
Birmingham B48 7QB, UK

(4) British Non-Ferrous Metals Research Association
Euston Street
London, NW1 2EU, UK

(5) Johnson Matthey Chemicals, Ltd.
74 Hatton Garden
London, EC1P 1AE, UK

(6) Henry Wiggin & Co., Ltd.
Holmer Road
Hereford, HR4 9SL, UK

(7) G. L. Willan., Ltd.
Sheffield Works
Sheffield Lane
Catcliffe
Rotherham, S60 5RL
Yorkshire, UK

(8) British Glass Industry Research Association
Northumberland Road
Sheffield, S10 2UA, UK

(9) Hopkin and Williams
P. O. Box 1
Romford, RM 1HA, UK

(10) National Physical Laboratory
Teddington
Middlesex, TW11 0LW, UK

(11) The Water Research Association
Medmenham
Marlow
Buckinghamshire, SL7 2ND, UK

(12) British Oxygen Co., Ltd.
Special Gases Department
Deer Park Road
London, SW19, UK

(13) Koch-Light Laboratories, Ltd.
Poyle Trading Estate
Colnbrook
Buckinghamshire, UK

(14) BDH Chemicals, Ltd.
Poole
Dorset, BH12 4NN, UK

(15) Air Products, Ltd.
(Head Office)
St. Georges Sq.
New Malden
Surrey, UK

(16) Metals Research, Ltd.
Melbourn
Royston
Hertfordshire, SG8 6EJ
UK

(17) Westfield College
Chemistry Department
MRC Steroid Reference Collection
London, NW3 7St, UK

(18) British Pharmacopoeia Commission
8 Bulstrode Street
London, W1M 5FT, UK

(19) The Radiochemical Centre
Amersham
Buckinghamshire, UK

(20) Paint Research Association
Waldegrave Road
Teddington
Middlesex, UK

(21) Explosives Research and Development Establishment
Powdermill Lane
Waltham Abbey
Essex, UK

(22) Safety in Mines Research Establishment
Off Broad Lane
Sheffield, S3 7HQ, UK

(23) Building Research Establishment
Bucknalls Lane
Garston
Watford
Hertfordshire, UK

(24) Spembly, Ltd.
Newbury Road
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(25) The Rubber and Plastics Research Association
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Shrewsbury, SY4 4NR, UK

(26) The National Engineering Laboratory
East Kilbride
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(27) W. and T. Avery, Ltd.
181 Kings Road
Reading
Berkshire, UK

(28) The British Standards Institution
Maylands Avenue
Hemel Hempstead
Hertfordshire, UK

(29) Shirley Developments, Ltd.
Didsbury
Manchester, M20 8RX, UK

(30) The Society of Dyers & Colourists
Perkin House
P. O. Box 244
Grattan Road
Bradford
Yorkshire, UK

(31) Pira
Randalls Road
Leatherhead
Surrey, UK

(32) National Institute for Biological Standards & Control
Holly Hill
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(33) British Nuclear Fuels, Ltd.
Capenhurst Works
Chester
Cheshire, CH1 6ER, UK

THE NATIONAL STANDARD REFERENCE MATERIALS PROGRAM IN THE U. S. A.

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I. Introduction

For Standard Reference Materials (SRM's) to be effective in helping to produce meaningful measurements, they cannot stand in isolation. Standard Reference Materials need to be viewed and used in terms of a complete measurement system to insure optimum results. This paper describes that segment of the U.S. measurement system that depends in large part on Standard Reference Materials. The philosophy, management, and current efforts at the National Bureau of Standards (NBS) to strengthen the system is also discussed.

II. The SRM Measurement System in the U.S.

An important segment of the U.S. measurement system that is dependent on Standard Reference Materials is shown in figure 1. Base and derived units, which form the first link in the SRM measurement system, are also a common foundation for most quantitative measurement systems. Fortunately, the base and derived units have been agreed upon internationally with the latest revisions and agreement being between forty countries at the General Conference of Weights and Measures held in 1960. The modernized metric system that resulted from this meeting is called the International Systemé of Units (SI).

The next link in the U.S.-SRM measurement system involves the production, certification, and distribution of SRM's on a national basis. In the United States this is mainly the job of the National Bureau of Standards as has been prescribed by Congressional legislation. It should be pointed out, however, that other U.S. organizations do, in a particular field of science or technology, produce calibration materials. An example of such a specialized case are the geological samples available from the U.S. Coast and Geological Survey.

Reference methods of measurement, a parallel link with SRM's in the system, are defined at NBS as methods of known and demonstrated accuracy. In addition, the accuracy inherent in the methods has been shown to be transferable by interlaboratory testing. The first two parts of the SRM Measurement System, base and derived units and SRM's, are the direct responsibility of NBS in the United States. This is not the case for reference methods, however. In most cases, NBS only becomes involved in reference methods when outside organizations have not or cannot develop reference methods by themselves. NBS is fortunate that many collaborative efforts exist between NBS and professional societies, standards bodies, trade associations, industry, universities, and other Government agencies to provide SRM's and reference methods.

Primary SRM's and reference methods, in general, do not find wide-spread daily use in measurement laboratories, but link directly to the next part of the measurement system. This part of the measurement system, which is concerned with the ultimate user, consists of field methods of test and working or everyday calibration standards. Reference methods and NBS-SRM's used together in the U.S. provide industry, professional societies, standards bodies, other Government agencies, and commercial producers of working standards with the means to evaluate their working standards and field methods of test, and where appropriate to place measurements on the basis of accuracy.

From this network, or system, measurements are produced that are meaningful in terms of accuracy, precision, and specificity. However, one more part is needed to insure that the system works smoothly and produces the desired results over a long period of time. A quality control assurance program involving interlaboratory testing with unknown samples and analysis of the results as evaluated against SRM's and reference methods fulfills this need. Quality control assurance programs are sponsored in the U.S. by many different organizations. However, they are not always based on SRM's and reference methods. The quality assurance programs that are not based on SRM's and reference methods only give a measure of between-laboratory precision, not accuracy.

The remainder of this paper will be devoted to describing in more detail three of the areas of the measurement chain: SRM's, referee methods, and quality control assurance programs. Examples of current NBS involvement for each area are given.

At NBS, an SRM is defined as a well-characterized material, produced in quantity, and certified to help: calibrate instruments, develop reference methods of measurement; and provide long-term quality control in a measurement system. One of the most important facets of most NBS-SRM's is certification at a stated level of accuracy. This is generally established through one or more of the following three modes in order of preference: reference method; two independent methods; or interlaboratory comparison.

In the first case, a reference method is a method of known and demonstrated accuracy, and its use assures the accuracy of the determination if personal bias is eliminated. This is why the measurements must be made, if possible, by two or more analysts. An example of a reference method relative to the NBS definition would be gravimetry for chemical analysis of selected elements.

The second mode of certification, used when a reference method is not available, consists of using two or more independent methods of analysis. Each of these independent methods must have estimated systematic biases that are small relative to the accuracy goal set for certification.

The first two modes of certification of NBS-SRM's are subject to critical scientific review through statistical analysis of the data obtained. This, however, is not the case for the interlaboratory comparison or round-robin mode where data is determined in several different laboratories. Interlaboratory data is subject to a somewhat less rigorous analysis. The proof that this mode is valid is that in a system under good quality control, it works.

There are many steps in the production and distribution of a NBS-SRM as shown in table 1, which contains the steps that the average NBS-SRM goes through on its way to the user. The first stage, which includes the first four steps, takes place before final production of the SRM can start. Information on needs is collected by NBS from a wide spectra of contacts including industry, standards bodies, Government agencies, and individuals. Secondly, because needs always far outrun NBS resources to provide new SRM's, a priority assessment is essential to select those SRM's that will be produced in a given year. And then, the third step is the development required before production can begin, source and specification of material, statistical sampling, homogeneity testing, limits of accuracy, methods and kind of certification test to be used. In the fourth step any research and development that may be necessary is completed.

The second stage of producing a NBS-SRM includes all the actual production steps from procurement of material to measurement of certified properties and, certification of the data. The last stage of production includes packaging, storage, distribution, answering technical inquiries, distributing technical information, and notices of availability.

In general, research and development costs for NBS-SRM's are funded either from general NBS funds appropriated by the U.S. Congress or from transferred funds from other U.S. Government agencies. Once a prototype SRM has been made, the total production cost and distribution cost of the SRM cooperation with the American Association of Clinical Chemists (AACC), the College of American Pathologists (CAP), and the Center for Disease Control (CDC) set out in May of 1970 to develop a reference method of analysis for calcium in serum. The approach used was to recruit an outside group of experts who picked a "candidate" method, atomic absorption, for development into a reference method. In addition, the experts group developed a "protocol" for the method. The procedure for testing and establishing the reference method consisted of providing eight cooperating clinical laboratories with the details or protocol of the candidate method and with samples of calcium in serum. This was repeated in five consecutive exercises. The true value of the calcium in serum was determined at NBS using isotope dilution mass spectrometry, a method that has been highly refined at the Bureau for use in absolute determination of atomic weights. The uncertainties in the determination of calcium in serum by this method are less than ± 1/2 percent. The results obtained by the eight laboratories were analyzed by NBS statisticians and analytical chemists and improvements on the procedure were introduced as the successive exercises were completed. Figure 2 illustrates the results of the last exercise involving the cooperating clinical laboratories. Line "A" represents the true value of calcium in the serum as determined by isotope dilution mass spectrometry. Line "B" represents the limit of inaccuracy of the reference method, which is about ± 2 percent, while line "C" represents the desired medical limit of uncertainty, ± 4 percent.

Calcium in serum samples from this same exercise were sent blind to hospital and commercial laboratories producing the results shown on the right in figure 2. It should be emphasized that no firm conclusions should be drawn from such a small sampling. However, deviations greater than ± 8 percent (line "D") might possibly result in an incorrect medical decision. The level of line "D" and its interpretation was provided to NBS by a knowledgeable physician and clinical chemist. Additional reference methods are currently under development at NBS for lead in blood and various other electrolytes in serum.

Quality assurance programs, the last link in the measurement system are needed to assure long term reliability in the system. These programs are not primarily the responsibility of the NBS. However, in cases where problems occur, NBS will assist other groups in setting up or improving their quality control programs. The ongoing effort to improve the quality control programs for the production of radiopharmaceuticals and commercial radioactivity standards is an example of NBS assistance in this link of the measurement system. NBS and the Atomic Industrial Forum initiated is funded from an NBS revolving fund and the fund is repaid from sales of the SRM.

There are currently over 850 different SRM's in stock with annual sales of about 30,000 units. Approximately 20 percent of the sales go directly to customers outside the U.S. with perhaps another five to ten percent being used outside the U.S., but sold in the U.S. In the industrial area, NBS has a very heavy concentration of SRM's for the ferrous and non-ferrous metals producers and users. Rubbers, cements, ores, and glasses are also well covered. Over the past several years, there has been a rapidly expanding number of SRM's important to both the health and environmental fields. Included are SRM's for clinical analytical chemistry, nuclear medicine, and pollution monitoring, both chemical and radioactive. The list of SRM's for use in metrology has been growing slowly but steadily and includes SRM's for heat, optics, and density measurements.

SRM's available for the scientific community include standards for Mossbauer spectroscopy, magnetic susceptibility, vapor pressure, and permittivity. Several fertilizers, bovine liver, and orchard leaves are presently available for agricultural interest. A wide range of chemical and isotopic composition SRM's of uranium and plutonium to help meet the measurement needs of the nuclear energy field are also available. More detailed information concerning the available NBS-SRM's is published in NBS Special Publication 260, Standard Reference Materials 1973 Catalog, and NBS Special Publication 260-Supplement, 1974 SRM Price List.

Current NBS efforts to develop and produce new SRM's are focused heavily in the health and environmental areas. This presents somewhat of a dilemma as NBS is lacking the resources to also move ahead as rapidly as needed in developing and producing new SRM's for industry. Fortunately, mechanisms do exist and are currently being used to help NBS develop and produce new NBS-SRM's for the industrial sector. These are collaborative mechanisms available to outside organizations and include: supplying materials to NBS on a gratis basis, providing industrial research associates to work at NBS on problems of mutual interest to NBS and industry, and assisting with collaborative or round-robin measurements. Additional support would certainly be welcome.

As presented earlier, reference methods of analysis are an important, parallel link with SRM's in the total system. In this light, it became apparent several years ago that the clinical analytical chemistry measurement system required more than just SRM's to reach the state of quality control that the professional societies felt was needed. NBS in this effort in the spring of 1972 and it has resulted in the formation of a Standards Committee on Radioactivity Measurement. The goals of the Committee, which has widespread industrial and Government participation, are:

1. Uniformity in reporting the accuracy of measurements of radioactive standards;
2. Initiation of a Quality Assurance Program for manufacturers, including a round-robin calibration program under the sponsorship of NBS; and,
3. Developing and publishing recommended procedures for measuring radioactivity.

III. Conclusions

This paper has described a portion of the total measurement system in the U.S. that is based on SRM's. Variations of this system are, of course, possible and are most likely being utilized both in the U.S. and in other countries.

It should be emphasized that the measurement system just described cannot be truly effective until it is immersed in a viable international SRM effort.

Table 1. Producing an NBS-SRM

PLANNING AND RESEARCH

- INFORMATION GATHERING
- PRIORITY ASSESSMENT
- TECHNICAL PLANNING
- RESEARCH AND DEVELOPMENT

PRODUCTION AND CERTIFICATION

- PROCUREMENT OF MATERIAL
- PROCESSING OF MATERIAL
- ACCEPTANCE AND HOMOGENEITY TESTING
- MEASUREMENT OF PROPERTIES
- CERTIFICATION

DISTRIBUTION

- PACKAGING
- STORAGE
- SHIPPING AND BILLING
- CUSTOMER LIAISON
- PUBLICITY

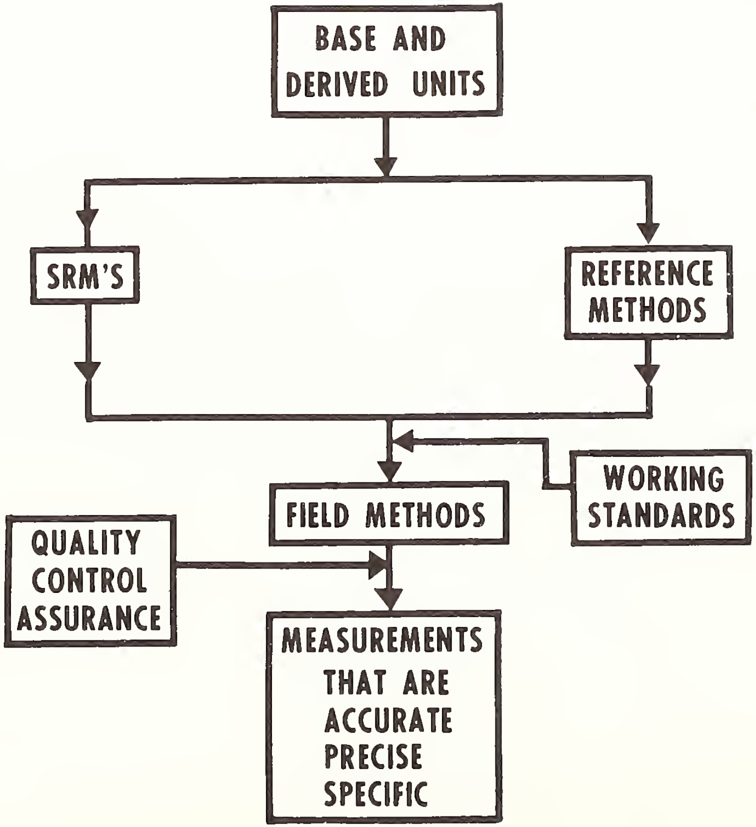

Figure 1. Meaningful Measurement System in the U.S.A.

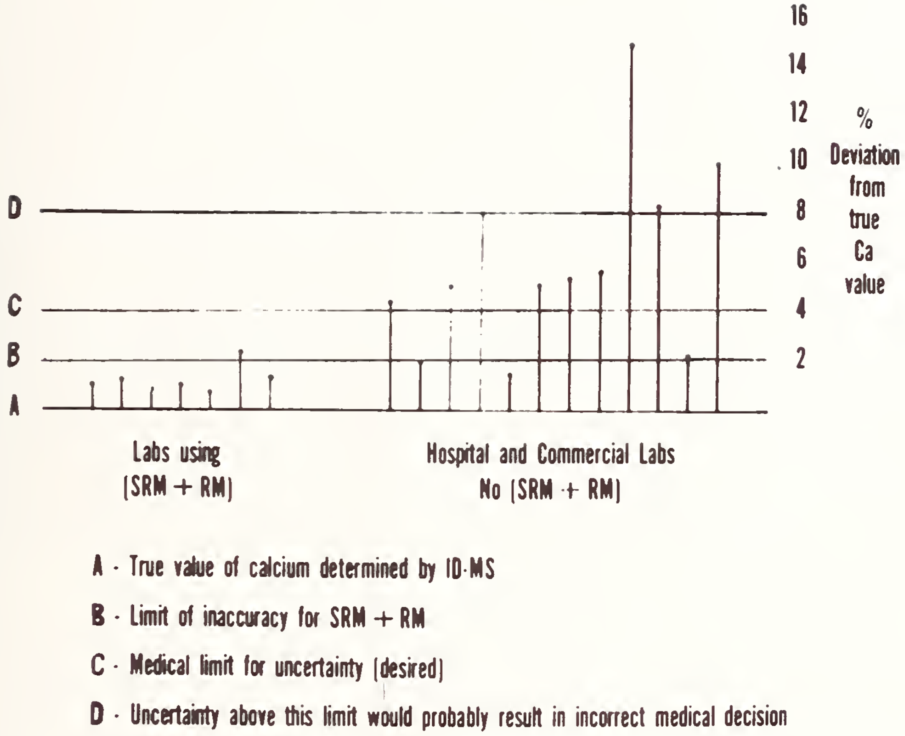

Figure 2. Calcium in Human Serum

THE SRM STORY AT NBS

R. E. Michaelis

I. Introduction

In today's technologically advanced world, standardization is an absolute necessity. The application of meaningful measurement must be applied to every dimension and to every property of materials. One of the main ways NBS assists science and industry in the achievement of meaningful measurement is through the production, certification, and issuance of Standard Reference Materials (SRM's.) NBS defines an SRM as a well-characterized material produced in quantity that can be used to calibrate a measurement system or to produce scientific data that can be readily referred to a common base. An NBS-SRM is the vehicle for transmission of measurement science and technology, through channels of industry and commerce, to the country at large. The principal goals of SRM's in the national measurement system are to facilitate the exchange of goods, strengthen quality control, help determine performance characteristics and encourage development at scientific frontiers. SRM's are used in companies and organizations concerned with aerospace, oceanography, pollution control, nuclear energy, clinical medicine, as well as the steel, brass, aluminum, rubber, glass, cement, petroleum, automotive, clinical, plastic, pharmaceutical, and transportation industries. SRM's contribute to progress in almost every area of national concern such as health, environment, and energy.

SRM's currently available from NBS are only a small fraction of the total number used by science and industry, but they do provide the essential benchmarks to which secondary industrial standards are related. As America's continuing technological revolution proceeds unabated, pressing demands for new SRM's increase and further widen the gap between those that are available and those that are urgently needed. By necessity then, NBS must exercise a thorough and continuous process of judging which new materials should be prepared. In short, establish a priority list that will serve the best overall interests of the nation. This task is performed only after extensive consultation with standardizing bodies, industry representatives, and other interested groups. SRM's now in production at NBS have been selected because they meet one or more of the following major criteria:

1. The attainment of the needed accuracy of analysis or the measurement of characteristics for SRM's is not economically or technically feasible elsewhere;

2. Industry-wide standards for commerce are needed from a neutral supplier not otherwise available; and

3. The continuing availability of highly characterized material from a common source is important to science or industry in our nation.

Other factors that enter into the consideration are: the impact on areas of national concern (health, environment, energy, etc.), the status of supporting research, material availability, cost of production, and sales potential.

Not only has the need for various types of SRM's grown in unprecedented manner, but also the requirements have become correspondingly more exacting and complex. For example, standards certified for a half dozen elements to a few parts in one hundred were sufficient to meet the steel industry's needs in the 1920's. Today, however, the uranium content in fuel rods used in nuclear power plants, must be certified to one part in ten thousand. In addition, the specifications for the chemical composition of materials have reduced allowable tolerances in recent years and this trend is almost certain to continue in the future. These specifications are established to ensure that the material will fulfill all of the performance requirements of the material's end use. A classic example is high-temperature alloys used in turbine blades of jet engines. Not only is close control necessary for major and minor constituent elements, but also for certain tramp elements, such as lead and bismuth, which have been proven to be deleterious in the performance of these materials. Recently proposed specifications limit the maximum content of lead to 5 parts per million and bismuth to 1/2 part per million. For applications where material failure could be catastrophic, the close scrutiny of almost every element in the periodic table will soon be necessary. Similar examples can be found for almost all segments of science and industry.

II. Seven Decades of Growth

The NBS-SRM story began over 65 years ago when the American Foundrymen's Association turned over to NBS the Association's work of preparing and distributing samples of standardized irons to member companies. These were gray cast irons certified for their chemical composition. Although the compositions have shifted somewhat over the intervening years and additional elements have been included in the certification, similar SRM's still are available today. This is not surprising as the tonnage production of gray iron exceeds that of all other cast metals combined. It is estimated that more than 1/2 million units of these gray iron standards have been distributed from NBS and that they certainly have aided industry in standardization.

The lead of the American Foundrymen's Association was followed by the Association of American Steel Manufacturers which requested that NBS prepare a series of 17 steel standards. The high quality of the resulting standards led to similar requests for the certification of other basic materials under the Bureau's statutory function of determining "Physical constants and properties of materials."

In response to growing demands from many areas of industry, the NBS Standard Sample program, as it was then called, grew to include standards of chemical composition for an increasing variety of materials and for materials certified for their chemical purity or for some physical or chemical property. Although some standards were certified for such properties as acidity, viscosity, freezing point, density, index of refraction, and heat of combustion, most of the standards were certified for chemical composition. The needs in this area grew tremendously with the advent of spectroscopic methods of analysis in the 1940's. Figure 1 shows the growth of the SRM program with respect to the number of SRM's available from its beginning to the present. The dramatic growth between 1940 and 1950 resulted from urgent needs for standardization of products during World War II, and the acceptance of relative types of measurements (spectrochemical analyses) that were both rapid and precise. The figure shows the almost exponential growth in the availability of SRM's that parallels the dynamic growth of U. S. Industry in the 20th century. Until 1964, the SRM program was generally considered an adjunct operation of the old Chemistry Division, now the Analytical Chemistry Division. The program was small-scale operation with less than 20% of the SRM's measured and certified outside the Chemistry Division. In 1964 the OSRM was established to consolidate the SRM activities. The present SRM program is Bureau-wide with some 14 technical divisions involved in the production and certification of SRM's that now number nearly 1000.

III. Industry - Government Cooperation

It has been stated that one of the main ways NBS assists science and industry in the achievement of meaningful measurement is through the SRM program. Obviously this is a two-way street. At its inception it was a cooperative program between industry and the government. With this start the U.S. became the first country to have a national standard reference materials program. Indeed, the history of the program, is a history of industry-government working hand in hand towards standardization. In the most crucial areas of need, NBS must necessarily cooperate with many industrial groups to provide the SRM's most urgently demanded.

In managing the NBS-SRM program, the Office of Standard Reference Materials (OSRM) evaluates the requirements of science and industry for carefully characterized reference materials and directs their production and distribution. To accomplish this task, it is absolutely essential that interactions take place at all levels among all interested standardizing bodies to ensure that the SRM's most urgently needed are prepared, and that they are characterized to fulfill their ultimate end use. Some of these standardizing bodies include such groups as: American Society for Testing and Materials, College of American Pathologists, American Association of Clinical Chemists, and Association of Official Analytical Chemists. Within the government the following agencies are involved: Environmental Protection Agency; Atomic Energy Commission; U.S. Customs; and the Departments of Health, Education, and Welfare; Housing and Urban Development; Defense; and Transportation.

Such interactions and collective efforts are absolutely essential if SRM's are to serve as essential benchmarks in such areas as health and medicine, air and water pollution, power generation and transmission, biology, botany, agriculture, metrology, instrument calibration, etc.

Despite needs in new areas, the NBS program cannot forsake the industrial SRM's that started the entire program. It should be emphasized that as the SRM program moves into the new areas, NBS will not discontinue any SRM the utility and need for which is current and in reasonable demand. We must, however, continuously evaluate the needs in the industrial areas to ensure that those that are required are produced. For example, NBS for many years provided a wide range of SRM's for raw material analysis and control, especially ores, minerals, and steel-making alloys. NBS is currently reevaluating its position in this field to determine present and future national needs for SRM's. The polymers and plastics industries have shown interest in achieving quality control of their products and processes on a nationwide basis. These needs are being explored. Some interest has been expressed for oil-shale SRM's. Several new and important inorganic compounds including glasses and ceramics undoubtedly will find their way into this program. NBS also must be continuously alert to needs for high-purity materials be they metal, inorganic, or organic.

The cooperative nature of the SRM program is illustrated by eight SRM's of ingot iron and low-alloy steel that were prepared for calibration in spectrochemical methods of analysis.

In September 1952, an NBS proposal was sent to members of the steel industry in response to an ASTM questionnaire that had established the need for steel SRM's in solid form. The chemical compositions of the eight proposed SRM's were agreed upon by industry representatives and NBS. Melting and casting were done by the Naval Research Laboratory, and fabrication from ingot to final size was performed by the Republic Steel Corporation. The raw materials were donated by Armco and U.S. Steel Corporation, while Bethlehem Steel Corporation provided some of the master alloys. The American Iron and Steel Institute aided with grants for preparing these SRM's. Following homogeneity testing and acceptance of the material, each material was analyzed in an extensive cooperative program, which involved many laboratories in the steel industry and NBS. These eight SRM's were first issued in 1957, five years after their planning was initiated. Called the "1100" series, they were enthusiastically accepted throughout all steel producing nations. It has been estimated that the 1100 series, either directly or indirectly, controlled the production of 90% of all the ingot iron and low-alloy steel produced in the world. These SRM's were designed primarily for use in calibration of optical emission spectrometers, although later they were found to be useful for calibrating x-ray spectrometers as well. The recently completed "1200" series replaces the 1100 series, and is a good example of SRM's made specifically for industry. The 1200 series further emphasizes the fact that NBS will not discontinue the preparation of SRM's when utility and need are current. The 1200 series consists of 4 low-alloy steels and an electrolytic iron for optical emission and x-ray spectrometric methods of analysis. In addition, these same materials have been issued in three other forms - chips for chemical analysis, rods for microchemical analysis, and rods for the determination of gases in metals. The electrolytic iron material is also being issued as a thermal conductivity SRM. The basic considerations in the preparation of the 1200 series were no different from those of the 1100 series, nor for that matter, the preparation of any SRM.

IV. Making an SRM

The first criteria in making an SRM must be a demonstrated need. Once justified and a priority established (in competition with all other SRM's that are needed), then production can begin. When any SRM is made, several major stages are involved: planning, preparation, acceptance and homogeneity testing, measurement characterization and certification, and applicability and distribution. Each stage must be successfully completed to ensure that an SRM will provide the ultimate goal of service toward meaningful measurement. The 1200 series serves as an example in describing these stages.

A. Planning and Setting of Specifications.

In the planning stage the following questions are asked and answered:

(1) What properties are to be measured and certified?

(2) What limit of accuracy is required for the intended use?

(3) Is material of requisite purity, form, and composition readily available?

(4) What measurement methods are to be used to test and assure the homogeneity of the material and also to measure the properties to be certified?

The planning stage is actually the most important, and indeed it continues and overlaps all of the following stages.

In the preliminary planning for the replacement of the 1100 series, the first step was to establish the proposed compositions of the new 1200 series. This was accomplished through a cooperative effort within the iron and steel industry, and through Committees E-2 and E-3 of the ASTM. To ensure that the new SRM's would provide maximum applicability, 68 individuals in industry were requested to participate in planning the compositions. The result was a proposal for a set of five compositions. This proposal was accepted in September 1967.

B. Material Specification and Procurement

Generally, NBS does not make or fabricate the materials from which SRM's are produced. Rather, U.S. industry and scientific groups cooperate fully in supplying special lots of materials or having them prepared to meet NBS specifications.

NBS expended considerable effort in an attempt to find a firm that would be willing to prepare the material for the 1200 series. By 1968 it became clear that no one firm could underwrite the cost of preparing the entire set. As with the 1100 series, a grant was sought and received from the American Iron and Steel Institute that enabled NBS to solicit bids for the material. A contract was placed in September 1968 to the Carpenter Technology Corporation, Reading, Pa., to prepare the materials. Specifications were carefully written and documented to ensure that the materials were prepared to meet the most exacting needs for composition and homogeneity. The material for each SRM was vacuum melted and cast in lots of 7 1/2-tons (about 6750 kg). In the planning stage, provision was made to include 40 elements over a graded concentration range for the 1200 series. (The 1100 series contained 25 elements). Also in the planning stage, the decision was made to produce two ingots from each melt, a 5-ton (about 4500 kg) ingot and a 2 1/2-ton (about 2250 kg) ingot. The 5-ton ingots were to be processed to form the solid SRM's. These were: disks, 1 1/4 in (32 mm) in diameter, for optical emission and x-ray spectrometric methods of analysis (SRM's 1261 through 1265); rods, 1/4 in (6.4 mm) in diameter, for determining gases in metals by vacuum fusion and neutron activation methods of analysis (SRM's 1095 through 1099); and smaller rods, 1/8 in (3.2 mm) in diameter, for microanalysis and spark source mass spectrometric analysis (SRM's 661 through 665). The 2 1/2-ton-ingots were to be processed to rounds 5 in (127 mm) in diameter and subsequently converted to chips at NBS for use in chemical methods of analysis (SRM's 361 through 365).

C. Acceptance and Homogeneity Testing

The composition of each melt had to be determined. Samples for acceptance testing were obtained between casting of the 2 1/2-ton ingots and the 5-ton ingots. The sample for each melt was analyzed completely at NBS and only when found acceptable was a subsequent heat made. This ensured that each material would fulfill its contribution towards providing the analytical range needed for each of the 40 contained elements.

Once the compositions had been accepted, the 5-ton ingots were pressed into slabs and full cross-sections were obtained of each material for homogeneity testing. The test sections were representative of near the bottom of the original ingots, the middle, and at the top after a 15% discard. Selected positions on each cross section were tested for homogeneity. Only that material meeting a critical evaluation was further processed to the final sizes and shapes. The 2 1/2-ton-ingots, after top and bottom cropping, were processed into the rounds for chips. Both longitudinal and transverse studies were made in the homogeneity testing and only the material of suitable homogeneity was subsequently lathe cut to chips.

The homogeneity testing stage is crucial in the preparation of an SRM. It is useless to perform highly accurate characterization of materials that eventually exhibit high variability. Actually, the homogeniety testing stage is a continuation of the planning stage in that tests are made to determine if all the specifications have been met with regard to uniformity of product. Although these tests differ radically with various types of materials and with the various properties to be certified, all have the same common basis in that the material must be sufficiently uniform to completely satisfy the end use. This ensures that tests made in different laboratories will produce the same number; also that tests made in one laboratory on one date will be the same as that made at some later date. Thus we have a two-fold goal:

1. To ensure initial homogeneity; and
2. To ensure that the material is stable and does not change over a period of time.

In the planning stage every precaution is taken to ensure that specifications are written for the production of a material that will yield the highest possible homogeneity. It is akin to the design of a bridge where safety factors allow a margin of error of perhaps several hundred percent. In specifying homogeneity, the same is true: every effort is made to ensure the highest possible homogeneity, although it may not be required for the end use of the specific material. In most instances far more measurements are made to test the homogeneity than are involved in the final certification. Homogeneity testing therefore can be a very costly and time-consuming task.

Two points should be emphasized. First a statistical plan for sampling should be established that will enable full evaluation of the material under study. When the production process is orderly and known, discrete selection of a relatively few test samples will often provide sufficient information to represent the extremes of the material lot. When the production process is not known, a relatively large number of random test samples must be taken and this increases the complexity by several orders of magnitude. Second, methods of test should be applied that are rapid and are of high precision - accuracy is relatively unimportant in homogeneity testing under normal circumstances.

The 1200 series presented a most complex problem with respect to homogeneity testing. Each material was prepared in large lot sizes and each contained 40 elements. For the most part, both optical emission and x-ray fluorescence methods of analysis were used. These are rapid and precise methods and are widely used in homogeneity testing programs. However, some elements could not be determined by these techniques and necessitated the employment of specialized chemical methods of analysis.

In the fabrication process, material of suspect homogeneity (based on previous work) was discarded prior to testing. Only the material that was believed to be uniform was tested to observe both longitudinal and transverse homogeneity, and then only the material that met the strict requirements (developed in the planning and setting of specifications) was accepted and fabricated to the final sizes and shapes. Fortunately, it was not necessary to include all 40 elements in the homogeneity test program. As is often the case, several elements were known to behave in a similar manner and could be tested as a group.

The elements were grouped depending upon whether they were: volatile or nonvolatile; carbide formers or non-carbide formers; in solid solution in the matrix or in the form of intermetallic compounds. Another consideration was the question of how the elements partition in the various microconstituent structures observed in this material.

In evaluating the test data, it is important to consider how the homogeneity may be affected by subsequent working and fabrication procedures. Also it must be emphasized that homogeneity characterization is relative to the type of method used in the analyses. For chemical analysis, sample sizes are on the order of a few tenths of a gram; for spectrochemical analysis--a few milligrams; and for electron-probe microanalysis--a few micrograms. The finding of inhomogeneity on the microscale is not at all uncommon. The important point is that quantitative evaluations of the homogeneity are necessary in the characterization--how uniform is the material and what sample sizes must be used to achieve uniformity. Only when satisfactory homogeneity has been demonstrated is it possible to move on to the next stage.

D. Measurement of Properties and Certification

In this stage, great skill and diversity of methodology must be used to full advantage. Physical properties measured and certified for SRM's range from micrometer size particle distribution, through density, viscosity, dielectric properties, to extreme complex property measurements, e.g., thermal emittance or specular spectral reflectance. Certification for chemical composition SRM's ranges from steels, where only the carbon content is measured; through primary chemicals, where accuracy on the order of a few parts per hundred thousand is required; to the complex chemistry of such materials as bilirubin or cholesterol; and on to very high-purity materials such as zinc, where more than 20 elements are measured--some at the parts-per-billion level.

Fourteen of the Bureau's technical divisions, which involve more than 200 distinct scientific competences, contribute toward this work. In many instances it is possible to perform homogeneity testing and measurement of the properties simultaneously. Significantly, it is often possible to utilize a planned cooperative program to aid in the measurement of these properties.

In the 1200 series, a comprehensive plan was developed to measure the chemical composition of the 40 added elements. Each of the 5 SRM's required a separate master plan, depending on the composition and on the accuracy required for each of the elements. In this stage, results of the measurement process were obtained by one or more of the following routes:

1. A reference method (every possible bias examined and does not exist or has been evaluated fully) run independently by two or more analysts.

2. Two or more reliable and independent methods.

3. Intralaboratory comparison systems - hopefully utilizing several independent methods.

In certifying the 1200 series, all three of these routes were used. For the elements normally certified in steel--carbon, manganese, phosphorus, sulfur, silicon, copper, nickel, chromium, vanadium and molybdenum--the third route was used. For tungsten, cobalt, titanium, arsenic, tin, aluminum, niobium, tantalum - a combination of routes 2 and 3 were used. Route 2 was used for zirconium, antimony, bismuth, silver, selenium, tellurium, cerium, lanthanum, and neodynium. Two reference methods (route 1) were used for the determination of boron. The first was isotopic-dilution mass spectrometry (IDMS), the second was nuclear track technique. For lead, the IDMS reference method was used, with polarography as a backup method. Statistical evaluations were applied to establish uncertainty values. The uncertainty values usually report a combination of both material variability and method imprecision.

As SRM's are intended as calibrants for measurement systems, each laboratory utilizing SRM's is expected to "anchor" on the certified values. All laboratories can thus be standardized, at least within the uncertainty levels.

E. Applicability and Distribution

The applicability by the user of an SRM to a particular measurement system may be critical. This is true because many, if not most, measurement systems rely on comparative type data between the SRM (or SRM's) and the "unknown" sample (or samples) to be measured. The reliability and limitations of an SRM in its application to the intended measurement system, along with any precautions that should be observed in its use, are explicitly stated on the certificate that accompanies each SRM. Obvious information appearing on the certificate would include the specific chemical composition or the physical or chemical properties that are certified, the size of samples that should be used to ensure homogeneity, avoidance of contamination, storage problems, etc. Not so obvious, but highly critical, would be the inclusion of any precautions that should be observed in the use of an SRM to achieve meaningful measurement. For example, on the 1100 series Iron and Steel SRM's, the certificate states: "Caution: Because these standards contain a graded composition for more than 20 elements, care must be observed in their use to make certain that element lines and internal standard lines are free from interference. All of the analytical points certified have been made to fit a smooth analytical curve at the National Bureau of Standards." For SRM 1264, one of the 1200 series replacements, the certificate states: "Caution: This standard has been found generally satisfactory for application in x-ray spectrometric analysis with the analytical points fitting curves established by use of the 1100 series. However, in preliminary application testing for optical emission spectrometric analysis with conventional air-spark excitation, some biases were observed relative to curves from the 1100 series--particularly for the carbide-forming elements (Ti, Nb, Zr). This may be due to metallurgical structure differences in this standard (more and different carbides) or composition interferences (higher carbon, molybdenum, and titanium). In any event, the user is cautioned in application of this standard to test its comparability with other available SRM's."

It is important to note that a series of NBS Special Publications called the "260 Series," is dedicated to the dissemination of information on the preparation, testing, measurement, certification, and applicability of NBS-SRM's. The 260 Series, which now numbers about 50, provides additional information not found on the certificate so that the user will be able to gain a greater in-depth understanding of the application of SRM's to measurement systems.

The preparation, packaging, and storage of SRM's is not a simple problem. Materials vary markedly in size and shape--from just a few milligrams for electron microprobe SRM's, to many kilograms for rubber SRM's. Some SRM's have properties that may be subject to changes with respect to time and/or storage conditions. If so, these facts must be known by the user. The user receives not only a positively identified material, clearly labeled, but also the appropriate certificate that details the characterization of the material--exactly what is being certified and the uncertainty limitations.

All SRM's produced and certified by NBS are distributed throughout the U. S. and other countries of the world by the NBS Office of Standard Reference Materials. This Office maintains the overall responsibility for the entire NBS-SRM program including dissemination of information describing the SRM's, such as catalogs, price lists, brochures, and announcements of new Standard Reference Materials.

<u>This then, is the SRM Story at NBS</u>.

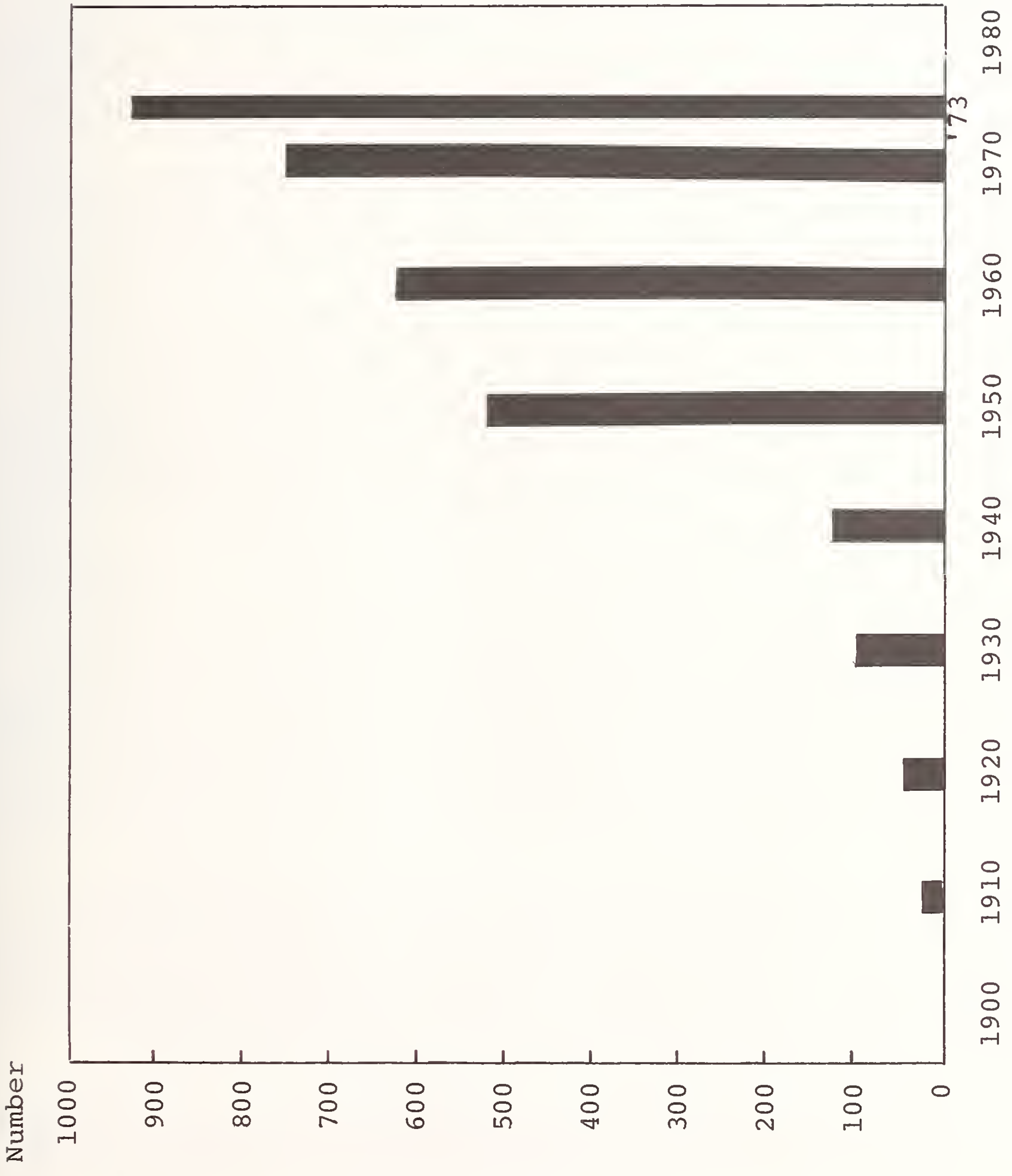

Figure 1. Growth of the SRM Program

THE ROLE OF THE AMERICAN NATIONAL STANDARDS INSTITUTE IN NATIONAL AND INTERNATIONAL CONSENSUS STANDARDS PROGRAMS

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In the past decade more legislation has been enacted requiring mandatory standards than in the entire history of the United States. Occupational safety and health, environmental protection, product safety, consumer protection--in these and other areas new laws have given the federal government a clear-cut responsibility for safeguarding the public and a clear-cut order to specify limits and methods.

All this will require a multitude of standards for products, for components, for processes, for testing, for inspection, for performance. Where are these standards to come from?

Many of them already exist in the private sector, available for government agencies to adopt either directly or by reference. Others need developing or improving. In some cases the agencies of government that are responsible for the standards are authorized to work with the private sector in developing them; in other cases the agencies have mandates--or think they have mandates--to develop the standards themselves.

Some government agencies are experienced in developing standards. Some are not. The Environmental Protection Agency, for example, has developed a whole series of documents largely by contract with various research and development organizations. Many of these have been found by experts in such fields as water quality, air quality, and solid waste disposal to be less than satisfactory in meeting the objectives of the environmental protection acts. Some, in fact, are felt to be counterproductive.

If this trend continues, there is real danger that American industry will find itself producing and purchasing to a host of mandatory standards that vary widely both in technical soundness and in their acceptability to the broad spectrum of producer, user, consumer, and public interests involved. As never before we need a strong, consistent national standards policy that will, so to speak, set standards for standards.

For an audience such as this there is no need to belabor the importance of standardization. The term standardization, of course, does not refer to any attempt to impose uniformity on products, processes, or procedures. Rather, it means an attempt to promote the use in industry of carefully conceived and nationally agreed upon normalizing factors--and the French word normalisation is somehow much less ambiguous than the English work standardization. These normalizing factors become an integral part of the goods and services that industry markets and the methods by which it produces and distributes.

Traditionally, standards have been thought of primarily as a means of documenting and expressing certain rather narrowly defined areas of technical agreement between engineers or between companies in a given industry or between industries or--more and more often nowadays--between nations. Standards enable people to agree upon certain levels of performance in products and on specifications for materials as well as on requirements for construction and installation of utilities and appliances. Reaching and documenting such agreements save a great deal of time--and money--that would otherwise be spent reinventing the wheel--renegotiating, respecifying, redesigning.

Our present massive array of goods and services would be far more costly were it not for the sound use of nationally recognized and accepted standards by industry. Mass production was built on the system of interchangeable parts. Standardization of components has lowered unit manufacturing costs. Packaging and shipping costs have been reduced through use of containerized cargo and modern physical distribution techniques based on national and international standards.

For industry, standardization means lower engineering, labor, and capital costs; greater dependability of parts; more sources of supply; interchangeability of parts. For the consumer, standardization means that products are more adaptable, more consistent in quality (particularly if standardization is combined with certification), safer, more durable, and less costly.

Because standards enable a customer to specify and a producer to satisfy on a competitive basis, they are the basic language of commerce. Without standards we would have products that not only would be far more expensive but also would provide far less in the way of performance and safety.

Those of us who attended the recent worldwide meeting in Washington of the International Organization for Standardization heard some graphic descriptions of the problem's lack of standardization can create. The deputy director of the Standards Association of Australia, for example, presented this picture of the situation of the automobile industry in that country:

Three American companies have more than half the Australian automobile market, with vehicles of virtually 100 percent local manufacture. A British company has a significant share of the market, partly with local manufacture and partly with local assembly. Japanese cars enjoy a growing market share, with some local content and assembly and finish. European cars from several countries also have a sizable share, mostly with some local assembly and finish. Many firms with overseas principals supply automotive parts. All these companies--in purchasing--tend to specify the standards of their own countries.

The result is, the speaker said, that "Australian manufacturers of raw materials such as steel sheet, forgings, castings, and the like and of components such as fasteners and of finishes such as vinyl fabrics and electroplating and enamels find themselves faced with a bewildering array of specifications, leading to fragmented production runs, to high inventories, to diversity in inspection and testing, including differing laboratory conditions and testing equipment, and so on. Many basic industries are affected in this way--the metals industry, the metal finishing industry, the rubber and plastics industries insofar as they supply the Australian automotive industry--all these industries operate less efficiently than they would if confronted with common standards."

Any manufacturer that produces for export has this problem of differing national standards. For developing countries, in particular, this requires difficult decisions--either to hitch their wagons to a particular star--Europe, the United States, the former British Empire--or produce the same item to a multitude of standards, thus sacrificing the advantages of product simplification and pushing up production costs.

It is significant that horrible examples of the costs and consequences of nonstandardization are much easier to find in the international field than in the domestic. There is a good reason. The United States has built one of the strongest standards system in the world on the consensus principle--and the key to that system is the organization I represent, the American National Standards Institute.

ANSI is the national coordinator for the private sector of voluntary standards development and the national clearinghouse for information on both national and international standards. ANSI is not a trade or professional association but rather a federation of such groups (with representation of other interests as well). It is not itself a standards-developing organization but rather a coordinator of the standards-developing efforts of others and a forum in which disagreements can be threshed out before a standard is finally awarded the status of an American National Standard.

In a voluntary standards development system, consensus is, of course, the heart of the matter. National consensus implies general recognition of a standard and its acceptance for use. It assures that parties having a substantial interest in the scope or provisions of a given standard have been afforded an opportunity to participate in its development or to comment on its content. All comments and negative positions must be given full and complete consideration and the issues resolved to the satisfaction of our independent Board of Standards Review, which, under the ANSI structure, is responsible for approval of all American National Standards as well as for revisions, reaffirmations, or withdrawals.

Although the judicial function of the Board of Standards Review is ANSI's single most important responsibility, the association does not play a passive part in standards development. When there is need for a standard and no competent group appears to be writing one, ANSI can persuade a group to do so. Or ANSI can assist in forming a committee of representatives of substantially affected groups and recruit a competent organization to provide the secretariat. Through its councils, boards, and committees ANSI has the technical capability to identify needs for standards, to encourage and support their development by competent organizations, to provide effective procedures for use by standards-developing groups, to coordinate and provide management services to ensure efficient use of resources and avoid unnecessary duplication, and to organize competence for standards development where no existing group possesses it.

The talent to write the standards is recruited on a voluntary, unpaid basis from industry, the professions, organized labor, consumer organizations, and government. Those who work on standards need not be members of ANSI, nor need the organizations that employ them. ANSI's procedures and participation are completely open.

In terms of policy making, ANSI is so organized that approximately one-third of its input is from the various sectors of commerce and industry that use standards, one-third is specifically representative of public (including governmental) and consumer interests; and one-third is from the standards-developing organizations themselves.

There now exist some 5600 American National Standards in categories ranging from construction to dental materials. About seven percent of these are classified as safety standards. One of the newest ANSI-approved standards, published this fall, is titled "Safe Use of Lasers." Hundreds of safety-related standards are being developed each year under ANSI's new nuclear program.

Safety was one of the primary reasons for the formation of ANSI's predecessor organization by five professional societies and three agencies of govenment during World War I, and safety has always remained one of its primary purposes. Hundreds of American National Standards are utilized in such fields as pipeline safety, automotive safety, every facet of the American distribution system, and building codes and regulations. There are thousands of standards bearing on product safety. The strength and performance of a nut and bolt, for example, are critical in mechanical product safety.

In recent years however, safety has become an even more important part of the ANSI program with the passage of so much federal legislation aimed at safeguarding the health and safety of workers, consumers, and the general public. Both the Williams-Steiger Occupational Safety and Health Act of 1970 and the even newer Consumer Product Safety Act specifically provide that the regulatory commissions responsible for enforcing them have the power to adopt existing voluntary standards where they are deemed satisfactory and to utilize the existing voluntary standards system to develop standards where none exist or where existing ones are inadequate.

OSHA, the Occupational Safety and Health Administration, already utilizes more than 100 ANSI-approved national consensus standards and is in the process of adopting many others. OSHA also has been turning to ANSI and its federated organizations for new and revised standards. The Consumer Product Safety Commission is just getting started, but we anticipate a similar working relationship with it.

Another area of ANSI activity that has been growing in importance in recent years is international standardization. On a truly global basis, there are only two nongovernmental groups whose sole purpose is the development of voluntary international standards. These are the International Organization for Standardization, commonly called ISO, and its electrotechnical counterpart, the International Electrotechnical Commission or IEC. ISO and IEC work with the national standards organizations of most countries to provide standards or standards recommendations having international recognition and acceptance. They also operate in liaison with hundreds of international organizations, mostly intergovernmental in nature, and with a multiplicity of regional groups to promote the cause of international standardization.

ANSI provides the total U.S. financial and administrative support for both ISO and IEC--to ISO directly and to IEC through the U.S. National Committee for the International Electrotechnical Commission, which is affiliated with ANSI. ANSI is a permanent member of ISO's governing council and a member of its executive committee and planning committee.

Until a few years ago the international standards approved by ISO and IEC had only limited acceptance, but that situation is changing rapidly. More and more countries are now adopting the international standards, and we can expect the pace to accelerate.

This is partly because of the worldwide rush to adopt the new international metric system, which is replacing traditional British units in what used to be the British Empire and replacing older versions of the metric system in Europe. This is also partly because, in the current atmosphere of reciprocal tariff reduction, nontariff barriers--including national standards unique to particular importing countries--are looming ever larger as hindrances to the free flow of international trade.

American industry has always tended to assume its products were irrestible, whether they fit with those of other countries or not. Americans generally, too, have always regarded the international market as a minor one compared with the gigantic opportunities at home.

The world economic climate has changed, however. The economies of other countries are now growing as fast as--or sometimes faster than--ours. The world is becoming a single market with competition from producers everywhere. The United States no longer has a clear-cut technological edge over other countries. Our share of world trade (as an export nation) has declined by nearly 25 percent in the past fifteen years. That fact, and our recent balance of payment problems, suggest that American industry could not fail to benefit by increased adoption of international standards where they exist and by increased participation in their development.

ANSI expenditures for international standardization, have been rising by between 20 and 25 percent a year. ANSI now has a full-time office in Geneva to work in the closest possible liaison with ISO, IEC, the various European standards organizations, and the European Economic Commission in Brussels.

American working participation in international standardization also has increased dramatically. The U.S. now is active in 200--about half--of IEC's committees and has 29 secretariats, a substantial increase over even two years ago. In ISO, ANSI holds participating status in 102 technical committees, nearly double the number of six years ago; holds 16 committee secretariats, compared to 10 in 1967; and holds 44 subcommittee secretariats, a whopping 238 percent increase over 1967. The United States, through ANSI, participates in 600 ISO technical committees, subcommittees, and working groups, three times the total of six years ago.

ANSI's international participation would benefit by more generous funding and by a substantial increase in the number of American personnel participating in the actual standards development process.

The same is true, of course, of ANSI's domestic activities. The Board of Standards Review is currently approving some 1000 standards a year, double the rate of eight years ago. This increase in productivity is partly the result of a greatly accelerated demand for standards, partly of an improved ANSI organizational and procedural structure that has made for greater efficiency.

But much more is needed if the private sector is to rise to the standardization challenges and opportunities that now confront it. To ensure that there continues to be a viable alternative to standardization by fiat, ANSI needs much more support from industry and from a much broader spectrum of industry. Currently ANSI's 835 company members tend to be concentrated in a few industries that expend most of the funds and do most of the work required to develop standards that benefit all of American industry.

From the federal government also we need more support--manpower, of course, but--much more important--official recognition of ANSI's role as the coordinator of voluntary standards development. All the national standards organizations with which we deal in international work have official status as <u>the</u> standardization bodies of their countries; only ANSI stands in a sort of limbo between government and public.

At present neither the government nor all standards-making organizations are willing to recognize an authoritative central core standards organization. They continue to circumvent the nominal central organization (ANSI) by establishing cross communication between industry and individual technical organizations on matters that should be coordinated on a national basis through one central organization. This is even true internationally to some degree; there is relatively little input by the private sector of the United States to international standards work or to the standards-making activities of the treaty-type organizations in which U.S. government departments and agencies participate.

With the spate of standards setting that is going on now, the United States more than ever needs a national approach to standardization. It needs an approach that would provide a means for distilling the composite opinion of government and the private sector instead of the continuing adversary relationship that exists between them and within them against the rest of the world.

Such a national approach to standardization should have as its cornerstone the designation of a single central standards organization--ANSI--whether by federal charter, by congressional declaration of intent, by use of model legislation, or by some other means.

The benefits that would flow from such recognition were listed by my predecessor as ANSI President, Mr. Francis L. LaQue, in a speech nearly three years ago. They include these:

(a) Greatly increased financial support of ANSI by all segments of industry and government;
(b) Routine submission by all standards-developing organizations of their standards to ANSI for recognition as national standards;
(c) Wider use of standards approved by ANSI as American National Standards by government agencies for the implementation of regulations and for procurement;
(d) Use of ANSI, through its organizational members, for the development of recognized national standards required for the implementation of regulations; and
(e) Recognition of ANSI by foreign standardization bodies and governments as the focal point for USA participation in international standardization and certification programs.

The cause of American voluntary consensus standardization desperately needs a focal point of unquestioned and unquestionable authority. ANSI is the only conceivable candidate for such status. ANSI needs this designation if the voluntary consensus system is to survive and grow.

ANSI has support from and participation by government, but it needs more. It has support from industry, but on a spotty and inequitable basis; it needs more.

ANSI and the private sector it represents cannot--and should not--do the whole job alone, but they can and should do much more than they have been doing. We need to be given the opportunity.

ASTM IN THE U. S. MEASUREMENT SYSTEM

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Knowing Roy Trowbridge as I do and realizing that he would present, as he has, an excellent overview of the voluntary standards system in the United States, and anticipating the great sophistication in standards knowledge of this audience, I will not this morning say the parochial ASTM things you might expect; rather I want to use these few moments of your time to present, with a degree of candor I have rarely found in meetings of this kind, an overview of major problems facing this system. In my view, these problems are all the more dangerous and difficult because until now they have not been fully described in any consistent way.

Before I press on, let me state a few assumptions and make a couple of personal references only to justify your listening to me at all and perhaps, later, lending a bit of credence to what will be said.

I assume you know that ASTM is the largest, and certainly one of the most respected and most comprehensive (in its involvement) nongovernmental standards-developing organization on earth.

I assume you have heard (even if you do not agree) that in most respects ASTM is a very healthy, vigorous organization. It knows where it has been and where it ought to go in terms of service to the expanding and new standards needs of our nation. ASTM listens well.

I assume you know that since their beginnings ASTM and the National Bureau of Standards have had a mutually productive relationship second to none. Both organizations have recently celebrated their 75th anniversary of service to the standards community. By way of interesting coincidence, the Bureau and ASTM are also at some point in the next few years observing their 50th anniversary of joint cooperation in the development of Standard Reference Materials. It was in the mid '20's that this activity started around the problem of refractories. This early and continuing SRM work helped solidify close cooperation and a working cameraderie between ASTM and NBS that has grown more fruitful and prolific over the years. Now at the end of fifty years we are facing a new revolution in measurement--the change from specifications defining chemical content and physical properties to specifications defining performance. At any rate, our relationship with the Bureau has been a model of such--unmatched. It improves constantly and we in ASTM are very proud of it.

I assume you know that ASTM is not a kindly old lady who lives at 1916 Race Street in Philadelphia, but a youngish swinger whom you'd be well advised to think of as Ms. ASTM's free-wheeling experimentation and probes beginning some years ago in the area of real-life standards development for consumer products and product safety, its new and to some extent daring programs concerned with accelerated procedures, the nation's first and only subsidy program for consumer input, and working consumer sounding boards are, for the moment, evidence enough of this spirit. We are even in the process of giving the word "consumer" back to the end-use marketplace where it rightfully belongs. Industry consumers will from now on, in our lexicon at least, be "users."

My personal orientation to all of this is that of a concerned manager with a little more exposure than some have to the institutional structure of our country--government agencies, corporations, societies, standards organizations--and how they work and interact; a manager responsible to a very knowledgeable, active, sophisticated Board of Directors for the development and implementation of the organization's affairs. My background contains no formal technology whatever. I am, in short, simply a person who for years has insisted that organizations answer the question: "What business are we in?", and having achieved an answer, helped devise procedures to achieve it efficiently, responsibly, and, if possible, with a smile.

The first and major problem is that most of us in and out of government professionally charged with the management of the system, presumably for maximum service and productivity, have ourselves not reached agreement on what the problems are--mostly because there has been, and is, no forum where the responsible management of the system, both in and out of government, can agree or, for that matter, even discuss such things.

There really are not <u>many</u> problems facing the managers, government and otherwise, of the standards system in the United States today. They are few but extremely difficult--indeed perhaps impossible of solution within the system's total problem-solving mechanism. The reason is that such a mechanism--literally--does not even exist. If we can agree that one of the principal purposes of this system is to provide for the continuing blending of public need and private knowledge, and vice-versa, in a variety of ways and using a variety of well-understood mechanisms in pursuit of the reasonable fulfillment of public policy, then I believe my position to be valid as a management assessment of the current state of affairs. We may really be faced with the need to invent something organizationally unprecedented. In my view, the major obvious gaps are between the nongovernmental elements and the management of the governmental enterprises that are potentially and theoretically becoming, as a disorganized group, a major constituency of the system as never before. It has often been said that--in a political sense--the standards bodies have "no constituency." (By constituency in this context I mean individuals and organizations who care and can say so.) The constituency in government is certainly there in the form of extrapolating needs by government for standards for many purposes. It's just not organized in a way that can provide guidance in crucial matters to those of us outside of government who are responsible for interaction and results.

This lack of organization is most awkward at the management level of the concerned agencies. From our point of view, without an organized constituency in government, we don't have a real status. To function without status is at times futile and, we are now learning, can be dangerous.

In 1971, the Stanford Research Institute published a report entitled "Industrial Standards" following a couple of years of studies of various standards organizations in the United States. Almost three years later, the following excerpts from their Executive Summary seem, at this moment, eerily prophetic:

"Consumer unrest, stemming largely from incomprehension of the function of industrial standards and stringent expectations for product performance, has stimulated growing government involvement in the standards process. Legislators and federal, state, and local agencies are proposing mandatory standards that go beyond the traditional issues of public health and safety to include criteria for product value, performance, and composition. Many of these efforts have direct impact on corporate activities.

"In response to these pressures, three movements will broaden industrial standards during the 1970's. These are: a growing user orientation in product design; development of standards for the whole product, rather than for just its parts; and accelerating use of performance criteria to supplement materials specifications....

"...Top management will develop a standards plan similar to other business plans to formulate goals and strategies, and to implement action plans. One important result will be an alteration of the design process to make it more multidisciplinary and more responsive to customer needs....

"Trends in legal activity--both antitrust and liability--will spur procedural changes by manufacturers and standards organizations...."

This language was aimed at top industrial leadership. However, it is equally applicable to top government management, who need to formulate goals and strategies to implement action plans and thereby to ensure, accelerate, and obtain maximum value from the enormous potential that exists in the so-called voluntary standards system and in fact exits nowhere else. As I understand it, one of the objectives of the Administrative Procedures Act was to achieve consistency and fairness in the handling of administrative elements of public affairs. It would seem we need some osrt of parallel and similar system for the handling of technical elements in public affairs, especially now since so many of these involve what we can characterize as high technologies. It seems, for example, that all concerned agree that publication in the Federal Register is a very poor way to elicit total response to complicated technical questions. They usually add, "but it's the only ballgame we have." Perhaps we need a different ballgame. At the very least, it deserves discussion at the highest levels in government--but where?

Let me try to provide, for a few moments, some insights from a management point of view of the real-world consequences of these vacuums.

Right now, ASTM has day-to-day working and thinking involvements with about 25 federal agencies--bureaus, departments--and who knows how many subsidiary groups of various hierarchial levels in these organizations. The attitude of every one of these agencies toward the standards system is different, both from a policy and operations point of view. Basic attitudes vary all the way from chilly detachment to all-enveloping warmth.

Now I'm enough of a public lawyer to know that every agency--regulatory or otherwise--has a different statute and style--and is entitled thereto. But there are many basic--indeed crucial--problems in our current and future operations that could yield even to a commonality of communication and generic goals.

Rattling around in various filing cabinets, I am told, in our Nation's Capitol is an overall official position. To paraphrase, it tells us--meaning all federal agencies and private ones in the standards business--to work well together.

I am also aware that the inter-agency committee device has been attempted in pursuit, presumably, of a higher degree of understanding and coordination. While conceding that both of these devices have helped all of us work better together, my position is that our overall public-private standards system is devoid of substantive policy and an organized constituency and is, therefore, essentially directionless. This situation is really not new. Nowadays it's important.

As the responsible manager of the largest quasi-public element of the standards system in the United States, I feel the compelling need--in the glare of obvious demands of today and tomorrow--to really get organized; together. I am sure we can all agree that the development and use of standard metrology (which really means little laws used as the measurement base of public policy) has, in an overall sense, an importance no longer obscure and no longer the quiet domain only of concerned and knowledgeable technologists.

Let me for a few moments be specific again from a management point of view, concerning some problems facing us today. These will not by any means be discussed in what I would consider to be their order of importance.

As some of you know, ASTM has, since last May, been involved in a complaint against it by the Federal Trade Commission. I have no intention here of getting into the merits of the situation. It does occur to me, however, that this may be the best recent example of what can occur in the absence of an organized constituency. Let me conjecture for just a moment whether or not this situation involving ASTM would have been handled by this regulatory agency in the way it has been handled, if instead of ASTM, it had involved another nonprofit, quasi-public organization such as the National Academy of Sciences or the National Academy of Engineering. Perhaps before the first pebble was thrown into the pond there would have been more in-depth consideration of its consequences. In this case, the consequences obviously include the possibility that we have here the germ of the destruction not only of ASTM but of all quasi-public and nongovernmental standards developing organizations. Some of you may not know that the publicity attendant on the FTC complaint has set in motion a series of so-called private suits in which ASTM is now a defendant. It is obvious that the situation must be defended by ASTM not only on behalf of ASTM but of the system. If the courts establish that organizations developing standards are liable for the use to which their product is put in the marketplace, that will in all likelihood end it all. De Toqueville may very well be spinning in his grave.

Apart from this hideous possibility is the very practical matter that, even if successful in defense, ASTM will have expended what in its terms is an enormous amount of money--money which could have been used in the further development of programs of which we have been the initiators to help crack some of the major problems now facing the system.

I have to ask the question: was this action against ASTM necessary? -- or better yet: was it set in motion by those competent to judge <u>really</u> whether or not the government of the United States wants to imperil and burden the voluntary standards system in this way? Who knows? Who can we ask?

This concern could very soon have negative impact on things we do or do not do while these problems are being adjudicated. Let me tell you about CHETAH as an example. CHETAH is an acronym for "Computer Program for Chemical Thermodynamic Data and Hazard Appraisal," a marvelous computer-based data system developed in our Committee E-27 by the nation's experts on the hazards of chemicals. Without getting into technical detail, there is little question that this system, the result of years of effort and hundreds of thousands of dollars worth of technology, could, if used properly, save lives and property. Basically, CHETAH suggests ahead of time how chemicals will react in large bulk in an infinite variety of storage, use, and transportation situations. In layman's language CHETAH helps determine way ahead of time what will go boom. If CHETAH is used in "accordance with the intent" untold harm can be avoided.

If CHETAH is used improperly or as the sole tool in judging the hazard potential of a chemical compound in transportation, for example, the results, as in the misuse of any tool, can be disastrous. If ASTM is to be liable for the latter, what do we do with CHETAH? It appears at the moment that CHETAH is going to be put in a cage.

Let me turn to another matter of great import. Perhaps we could agree that it should be possible to achieve a government-wide attitude concerning the posture of regulatory agencies' participation in the nongovernmental standards organizations involved in developing the base metrology for various regulatory programs. Some participate fully, some participate symbolically, some refuse to participate either symbolically or otherwise and explain that participation in the development of metrology might commit the agency to something in the future to which it would not then want to be committed.

Does the latter attitude tell us that it is a fundamental mistake of legislation to combine enforcement and metrology responsibilities in the same agency? Does this suggest to those of us who feel that the science of metrology should not be fragmented as it is currently and will probably continue to be, but should be concentrated where for years it has been done well--in the National Bureau of Standards? When laws are being written concerning the establishment of new regulatory bodies, does the subject of the difference between measurement methods and regulatory activities based on measurement methods even get discussed? Are we in the situation where we may be inviting rubber rulers in the metrology area?

I have no viewpoint on any of these questions and neither does ASTM, for the moment; but they are questions that need very, very badly to be discussed. But where?

Perhaps someone has noticed that until now the word "consensus" has not been used in these remarks. I am beginning to suspect that the word has been bandied about to such an extent that it has very little "standards" meaning left. If we can agree that standards are little laws that achieve impact either through contract or regulation--both of which by their legal nature deprive someone of something--then perhaps we should be talking about "due process." Is the 14th Amendment really the legal base of our standards system? As you will recall, it forbids government to do various things without "due process of law." In our standards procedures, is "due process" the real core element? If so, why not say so and thus consciously endow our procedures with the core element of Anglo-Saxon law and freedom. But whom do we talk to about this? This is the important question--for now.

Is a standard test method a standard test method before validation--before, in short, its authors have data to prove the facts of its repeatability and reproducibility? There's an ASTM attitude here which says, no. But there is no overall policy. I am reliably informed that both kinds are in regulatory use today. Can we discuss this?--where?

Our system, so the folklore goes, is very, very slow. Earlier this year we achieved a due process analysis of great use to a large regulatory agency of a quality control sampling plan--our Committee E-11 on Statistical Methods was involved--in less than 90 days. As a result, the agency withdrew its intent in this area.

We are in process of doing the same thing again. We are learning that the period of standards gestation can be remarkably shortened, given certain attitudes on both sides but, like the clergyman who made a hole in one during a solo, bootlegged round of golf on Sunday, whom can we tell?

Hope springs eternal. I have every justification for assuming that these ideas will, like many things, be lost in the spongy fabric of private and public bureaucracy, which can absorb and attenuate all but the most energetic, persistent, and resourceful. I draw great hope, however, from the fact that "there's a new kid on the block," the Consumer Product Safety Commission, which is doing some very, very provocative and, in our view, sensible things. You will not, for example, hear the CPSC talking about consensus. They talk about due process. You will find that to them a standard method of test is worthless without data validation and reproducibility and a sampling plan. You will find that they have separated out for consideration something that we have assumed as part of our standards system--an economic analysis of the impact of the standard. To us, although these are specific policies of only one of the many regulatory agencies with which we are pleased to deal, they may be the lightening rods that will be the beacons as we struggle forward to improve what it is we try to do.

CHEMICAL COMPOSITION CONTROL PROBLEMS AND SOLUTIONS RELATED TO METALS AND ALLOYS

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I. Background

We live in an age of rapid economic and technological change. The ability to respond to these changes will be a necessity for some time to come. Present projections of market trends for the steel industry enable us to forecast trends in steel manufacturing and processing. Substantial rates of increased steel shipments forecast for full alloy, low alloy, and stainless steels, as well as superalloys indicate the need for definite growth in tons melted. The steel industry's ability to greatly improve yield performance in the next 10 or 20 years will, to a large degree, depend on providing the optimum process and fabricating methods or modifications for existing installations or anticipated new capital installations.

One important trend is the upgrading of tonnage steel specifications because of new safety legislation (OSHA), and general reliability improvements required by the rapidly growing automation market. In short, then, any analysis of melting equipment must place high on the list the ability to be versatile with regard to type of melting and grades that can be made within a given system. The use of the term "system" implies that no one universal melting method exists that is capable of handling the full range of the above considerations--that is, tonnage melting, small lot melting, high purity, high reliability, high yield, low cost, low maintenance, etc. Certain processes are combined to optimize desirable features.

II. Melting for Wrought Products

Let's consider, briefly, the various melting requirements as a function of alloy grade. [1] The BOF process accounts for highest tonnages of low alloy and plain carbon steels. A rapidly growing tonnage method of manufacturing involves vacuum-carbon deoxidation. We do not wish to enter into a discussion of the merits of vacuum-carbon deoxidation versus argon-oxygen in this particular paper. However, most industry technologists recognize argon-oxygen as relatively limited in terms of types of alloys that can be treated, as well as requiring significant tonnages in order to be competitive. Vacuum-carbon deoxidation steelmaking, on the other hand, has much less limitation in this respect.

The next largest tonnage of steels is melted by the electric furnace, perhaps combined with one or more types of vacuum degassing. These types of melting would include the stainless steels, electrical steels, and certain of the tool and die steels. The balance of steels as far as tonnage is concerned is made by straight air melting. While we have no figures to support the claim, a qualitative observation of the industry shows that there is less and less straight air melting, along with a general growth of all types of vacuum melting including vacuum degassing.

Table 1 outlines the major superalloy grades in terms of vacuum induction melting, vacuum arc remelting, electroslag remelting, and combinations thereof. [1] Vacuum induction melting followed by vacuum arc remelting accounts for the largest tonnage of high performance Ni, Fe, and Co base alloys. However, ESR is making strong inroads because of the promise of improved yields, greater simplicity, and comparatively low costs.

Table 1. Contemporary Production Melting Processes and Typical Alloys to which they are Routinely Applied

PROCESS	TYPICAL ALLOYS	REMARKS
VIM + VAR	Wasp., R-41, U-500, U-700, I-718 I-901, D-979, A-286, I-600, R-41	
VIM	B-1900, I-713C, MM246, MM302, A-215, R-41, I-718, R-41	MOSTLY REMELT FOR CASTINGS-SOME SHEET PRODUCT VIM CAST INTO SLAB INGOT
AAM + VAR	A-286, I-718, Maraging Steels D6AC, Chromalloy, S-816, HX, L-605, N-155, I-625, H-188	
ESR + VAR	A-286, I-718, HX, H-188	PRIMARILY FOR SHEET PRODUCT FROM SLAB MOLDS

III. Metallurgical and Product Design Needs

In this section we will summarize some of the needs of large scale metals production. [2] To begin with, melters try to lower the cost of charge materials by using as much alloy revert scrap or other low cost raw material (ferroalloys) as possible. Techniques such as selective carbon deoxidation through argon-oxygen or vacuum-oxygen were motivated by the desire to conserve expensive charge materials (chromium). Another factor of prime concern to the melter is the lowering of meltdown time through ultra high performance transformers and/or the use of oxygen blowing. It is desirable to limit or lower the degree of oxidation of alloying elements. This can be accomplished by selective thermal spike treatments over short times, using higher amounts of oxygen in a short period of time, or through improved decarburization by mixing oxygen with an inert gas. Desulfurizing, of course, is a prime consideration, especially in large melts.

IV. Safety and Reliability

Factors regarding safety and reliability indicate an even added importance to the improvement of cleanliness and the ability to mix uniformly or homogenize the melts to determine the bath chemistry properly. In conjunction with this, the use of "in-place" continuous measurements of oxygen, etc., offers new opportunities for automatic control of melts. Of course, degassing treatments would be a first choice for improvement in air-melt cleanliness, plus the use of stirring either by induction coil or argon bubbling in the ladle.

Concurrent with the reduction of melt cycle time is the sometimes confounding factor of having to meet very close analysis ranges. Therefore, new equipment considerations must involve the ability to make either slight or massive alloy additions with satisfactory uniform yield and sufficient homogeneous mixing in the melt within the vacuum unit itself.

Lowering of hydrogen and oxygen contents per se are advantages to be achieved by nearly any properly conducted vacuum degassing or vacuum melting treatments. Melters are concerned with the removal of undesirable metallic contents having high partial pressures. For example, the lowering of lead to a fraction of its original value is possible within the vacuum unit. Another attribute that melters look for in equipment is the ability to limit the amount of temperature loss during the degassing cycle, especially in smaller heat sizes. This factor brings forth the desirability of adding heat either by resistance, arc, plasma, induction, or whatever technique best enhances the melt system under consideration.

Finally, another factor that is being given more consideration is vacuum treatment of the charge prior to vacuum melting. Some melters have found that preheating the charge in vacuum results in more efficient reduction of certain gasses that can be achieved during melting. Certain furnace configurations automatically offer the potential of this sort of advantage, since the charge remains under vacuum during vacuum treatment.

V. Processing Interactions With Environment

Historically, melters have tended to view vacuum melting environments and their effects on melt chemistry and melt behavior in terms of eliminating certain interaction factors. For example, in the electric furnace we generally speak of the melt interacting with the air, the crucible, and the slag. By going to vacuum induction melting we generally eliminate the undesirable aspects of air contamination, as well as slag interactions. The ultimate is the vacuum consumable electrode remelting, or vacuum arc remelting, where even the crucible interaction is eliminated. Unfortunately, the interactions with the melt are more complex.

As shown in figure 1, melters today have to consider many other factors. First of all, variations in outputs from the virgin charge materials themselves are to be evaluated. Secondly, variations in scrap chemistry, scrap configurations, and inputs therefrom must be evaluated. Refractories remain an area of very important influence over the melt, and this is perhaps the area in which there is the most ignorance as far as melt interactions are concerned. Finally, in recent times we speak of certain refining and ppm (parts per million) additions. In this respect, we speak primarily of those that are beneficial; however, it is well recognized by melters that there are ppm residuals that can be extremely harmful. The entire matter of ppm additions has recently been discussed. [3]

From this discussion, it is evident that the optimum melting system must give the melter a wide latitude of control. It is also clear that different alloys and products therefrom require different combinations of melting methods, as shown for example in table 1.

The following section proceeds with a discussion of various melting techniques, both singly and in combination.

VI. Combined Methods of Melting for Wrought Products

The purpose of this section is to delineate various processing methods, their advantages and disadvantages when they are combined to fulfill the needs of the final product (figure 2 and table 2). [4-9]

The workhorse duplexing method, in wide use today for advanced alloys, involves the combination in vacuum arc remelting using vacuum induction cast electrodes as VIR. The melt interactions here still involve a refractory, and those factors associated with the virgin and scrap charge material, as well as interactions that involve the addition of refining elements or ppm's. The advantages of this process are very close chemistry control, low residual gas content, and excellent control over ingot structure. The disadvantages involve the aforementioned inability to control certain elements such as sulfur and nitrogen, high cost, and generally poor yields, especially associated with larger furnaces.

The electroslag process (ESR) is generally practiced in combination with air melt electrodes. In this case we have interactions with refractories, air melt slags, charge materials, and the ESR slags, in addition to other factors considered in the air melt step. The presence of ESR slags can be an advantage or a disadvantage. For example, ESR slags are of such a nature as to naturally result in efficient desulfurization. On the other hand, this makes the process unsuitable for free machining grades requiring high sulfur.

Considering the highest strength superalloys, the general opinion in the U.S. is that high titanium and aluminum contents are difficult to control in the electroslag process. However, many other alloys are suitable to ESR melting and the combination of air melted electrodes plus electroslag has a number of advantages, such as generally improved soundness, uniformity of structure, and workability. Probably the most pronounced advantage of electroslag remelting is its ability to directly produce various shaped ingots. As a matter of fact, one of the most frequent applications of this process is the direct casting of slab ingots for subsequent rolling to sheet. The disadvantages primarily involve a rather low receptivity in certain critical parts specifications. It is expected that this particular factor will change with more frequent use of this growing, popular melting technique.

The ESR process allows the application of structure refinement to production in semicontinuous modes. This factor alone should add much to the popularity of ESR melting in the coming years.

EVR is the duplexing of vacuum induction melted electrodes with electroslag remelting. While at first glance this might appear to be an unlikely combination, many complex alloys have been melted by this duplexing technqiue to great advantage. The principal attribute of this combination is the ability to retain high aluminum and titanium contents in the initial electrode, and optimum second phase disbursement. The principal difficulty is the controlling transition of the high aluminum and titanium content of the slag melted ingot. Melt interactions involve the VIM refractories, the virgin and scrap charges, as well as the ESR slag.

Plasma melting is currently being reevaluated in the U.S. and Europe. PMR involves plasma melting in a refractory crucible. In this case, we still have interaction with refractories, scrap and virgin charge, as well as binders, if these are used to fabricate the consumable electrode. In most cases, however, binders are not used. Because of the relatively modest use of this process, we will refrain from commenting on advantages and disadvantages except to say that currently there are development programs taking an intensive look at this type of melting.

Beginning with this brief discussion of plasma melting and those that follow, we are essentially covering potential technqiues that exist today, most of which are being practiced only on a developmental basis.

PMS involves plasma melting into a continuous or semicontinuous casting mode with skull crucible. In this paricular case the contaminations are drastically reduced to those involving the virgin and scrap charges.

PMV is a logical evolution involving plasma melting of electrodes which are subsequently vacuum arc remelted. With this combination one could reasonably reduce the number of interactions to those involving the original charge.

EBM is the drip remelting mode of electron beam melting where the interactions involved are primarily those of the charge. VEB is the Airco-Temescal electron beam unit where VIM molten metal is fed onto a cascading electron beam hearth directly from a vacuum induction furnace. In this case, the interactions are those of the virgin charge, scrap, the refractories in the vacuum induction mode, and perhaps even ppm's used to refine in the VIM mode. It is interesting to note that even with this exotic process, which offers an unprecedented degree of flexibility, optimum refining is not achieved. For example, sulfur is not removed by the high localized heating of the electron beam.

NAR is a relatively new method of melting involving nonconsumable rotating arc melting in a refractory crucible. Depending on charge make-up, we still have interactions from the virgin charge, refractories, scrap (if used), plus the potential of contamination from the nonconsumable electrode. Using a skull crucible, this same mode is duplexed into a semicontinuous casting mode called NAS. In this case, the skull eliminates refractory interaction. NAV is a logical evolution by duplexing with vacuum arc remelting. This limits the melt interactions to those of the charge materials.

NER is the duplexing of nonconsumable melt electrode into ESR either directly, which is quite possible if one considers the rates of casting on both of these machines, or indirectly in a two-step process. In this case we would have the interactions of the original charge plus that of the electroslag material.

NEV combines the nonconsumable electrode and the cascading hearth electron beam processes. This offers the unique possibility of limiting contamination strictly to that of the charge or feed material.

Thus we can see that there are many possible combinations of contemporary methods of melting to fulfill the needs of the final product.

Table 2. Melting Methods

Melt Type	Description
AAM	Air Arc Melted (electric furnace)
AIM	Air Induction Melted
VIM	Vacuum Induction Melted
VAR	Vacuum Arc Remelting of Air Melted Electrode
VIR	Vacuum Arc Remelting of Vacuum Induction Melted Electrode
ESR	Electroslag Remelting of Air Melted Electrode
EVR	Electroslag Remelting of Vacuum Induction Melted Electrode
PMR	Plasma Melted in Refractory Crucible
PMS	Plasma Melted in a Skull Lined Crucible
PMV	Plasma Melted Electrode Plus Vacuum Arc Remelting
NAR	Nonconsumable Arc Melted into Refractory Mold
NAS	Nonconsumable Arc Melted into Skull Lined Crucible
NAV	Nonconsumable Arc Melted Electrodes Plus Vacuum Arc Remelting
NER	Nonconsumable Arc Melted Electrodes Plus Electroslag Remelting

Table 2. Melting Methods (continued)

Melt Type	Description
EBM	Electron Beam Melted (Drip Melt plus Sintered Electrode)
VEB	Vacuum Induction Melted plus Cascading EB Hearth
NEB	Nonconsumable Electrode Melting
NEV	Nonconsumable Melt and EN Refine Prerefined Alloy Feed Stock plus VAR

VII. Processes for Tonnage Alloy Products

Figure 3 represents a montage of the more frequently used tonnage vacuum treatment techniques. A recent newcomer to the field, known as vacuum-oxygen refining (VOR) combines the best of many features of those previously mentioned. VOR processing allows vacuum-oxygen blowing, alloy additions or the additions of certain refining agents, bubbling with argon, and - by duplexing with a swing roof with heating elements - allows the addition of heat. This unit also utilizes a slide gate nozzle design that permits the ladle to be used as the reaction vessel.

The above demonstrates that melting combinations now available on a commercial basis are potentially suitable to be applied to a wider range of alloys. Table 3 (a,b) demonstrates the advantages known to most of us in regard to removal of hydrogen and oxygen as well as improved cleanliness, which attributes suggest improved reliability and quality. In addition, the time for annealing vacuum treated metal is substantially less than in the case of air melted carbon steels. Less heating time in annealing can be directly translated to improved process economy. [10]

Table 3a. Hydrogen, Oxygen, and Nonmetallic Content of Vacuum Deoxidized Heats

Grade	Hydrogen Removed, Percent	Oxygen Removed, Percent	Nonmetallic Count	Normal Elec. Furnace Count at Gauge
1016	36	81	1000	14000
1030	53	78	8150	15000
1070	37	66	9480	9500
1050	51	63	--	---
1010	35	--	--	---

Table 3b. Vacuum Degassed vs Normal Expected Count for Undegassed

Grade	Nonmetallic Count, Vacuum Degassed	Normal Nonmetallic Count, Undegassed
1045-9	10600	23750
1045-9	8400	23750
1045-9	6500	23750
1065-5	14400	15800
1065-5	10500	15800
1046-5	10800	23750
1095-8	2700	19100

As shown in figure 4, any ideal process must consider the attributes of the final product that is going to be cast. From a processing viewpoint, the ideal melting process should be able to accept a wide range of melting stock, be it virgin stock, scrap, powder, ferroalloys, low grade ores, etc. It must have the ability to allow treatment of the molten baths for certain refinements without undue processing complexity, and it must pour into a wide variety of forms such as static cast ingots, withdrawn ingots or electrodes, remelt stock, powder, or specialty shapes for extrusion or reforging.

What we have attempted to do, therefore, is to point out the numerous possibilities open to the metals processer and the growing indications of vacuum melting in a wide range of today's metals and alloys. Concurrent throughout have been the need and desire for optimum flexibility in a given melting system in order that manufacturing and inventory costs may be minimized by providing for order change during dynamic production conditions. While some of these techniques may seem far-fetched to us in these times, we might well remember that less than fifteen years ago the viable combination of vacuum induction melting plus vacuum arc remelting was considered only a mere possibility on a high production basis. Thus, we see that our initial prediction of growing use of vacuum in even tonnage products can be justified.

VIII. Metal and Alloy Forming Processes

The 1960's and 1970's will probably be remembered for the proliferation of new or renewed metal forming processes. Driven by the need for cost reduction, designers are calling for closer development of final net part shape with an absolute minimum of material yield loss. Carrying this further, it is fundamental that all companies, if they are to survive, must face and meet the challenges of cost reduction and competition. For these reasons, melting techniques, casting methods, prealloyed powder production, hot-isostatic pressing of prealloyed powders, and all forming techniques must be carefully evaluated, not only as to their individual merits, but also as to what effects there will be in combining these various technologies.

It is not possible in the scope of this paper to review all of the new, or renewed, processes and show the interaction of processes on costs or final part performance. Therefore, the sections that follow will only highlight some interactions of a few contemporary processes.

IX. Extrusion

Steel extrusions are not unknown throughout the world, but until recently production has been concentrated on stainless and high alloy grades. Now, new contemporary developments make practicable the combining of technology into cost-competitive mini-tube mills.

Specifically, new techniques can be built around a combination of the Ugine-Sejournet (CEFILAC) hot extrusion process, the use of continuous cast billets, and a hot stretch reducing mill. [11] The Spanish company, Tubacex, has recently issued a report on its successful combination of these contemporary processes.

A schematic sequence of the Tubacex operation is shown in figure 5. The billets are cut to proper length by sawing, and then induction heated, pierced, extruded, stretch reduced, and finished.

It is an interesting and important economic criterion of the process to emphasize that the Tubacex plant extruded tubes up to about 100 feet in length. These long lengths could not be obtained if it were not for the Ugine-Sejournet process, which reduces the friction forces through the use of glass as a lubricant.

Thus, innovations make it possible for this combination of processes at Tubacex to be cost competitive with the older, more conventional methods of producing carbon steel tubes. Also, when a mini-tube mill complex based on the Tubacex experience is compared to other production techniques, capital costs are much lower for the complex using extrusion. Furthermore, the combination results in a flexibility of product line that could not be achieved with any other single installation of a more conventional tube making process.

Size changes take hours to make on the older presses; they take minutes to make when using the extrusion process. This permits a pattern of order acceptance that could only be duplicated by a company with a large variety of tube making facilities, and therefore one with a very high capital equipment investment.

The Tubacex plant averages about 300 size changes per month. This is indeed a large number of size changes; yet the average production for 1972 at Tubacex was about 12 tons per hour. This year, as a result of additional heating capacity, the production rate will approach 18 tons per hour, or approximately 75,000 tons per year.

An important result arising from this proper and well-managed combination of contemporary processes at Tubacex is profitability. A mini-mill tube complex based on the Tubacex experience would require an investment of about $25-million; $7-million for the steel melt shop and continuous caster, and $18-million for the extrusion and finishing shop. It has been estimated that such a mini-tube mill complex could provide a return on investment of about 15 percent. Obviously, this makes it an attractive investment for consideration, and has led to some predictions that the mini-mill tube concept is on the threshold of worldwide expansion.

X. An Example of Trace Element Chemical Process Effects on Product Performance

To show how processes can affect product performance, let us consider some recent work by Ugine Aciers on bearing steels. [12]

Ugine Aciers noticed that loaded bearings often contained "butterflies," figure 6a and b, which develop around discontinuities of the material, especially nonmetallic inclusions.

When butterflies are well developed, microcracks are located on the edges of the wings. These microcracks progressively spread, finally reaching the surface, and lead to spalling.

Continuing work indicated that butterflies were never noticed on sulfide inclusions. In the same way, butterflies were not seen on oxide inclusions completely surrounded by sulfide. Figure 7 illustrates a one-winged butterfly on an inclusion formed by the juxtaposition of an oxide and a sulfide. Note that the wing corresponds to the oxide, not the sulfide.

The butterfly observations led to a study of the influence of steel making practice on types of inclusions and their effects. Subtle adjustments of sulfur (and oxygen) contents were directly involved.

The steelmaking processes were as follows:

(a) The basic electric arc furnace,

(b) Acid induction,

(c) Vacuum degassing, and

(d) Consumable vacuum remelting.

Each process imparts its own particular metallurgical characteristics to the final product. In relation to fatigue, it can be seen in figure 8 that vacuum remelting and vacuum degassing resulted in superior properties in these experiments. We hasten to point out that this should not be taken as a condemnation of any of these processes, but rather that process parameters can be adjusted to optimize a given part requirement.

As mentioned above, the explanation herein lies in the modification of nonmetallic inclusions in such a manner as to eliminate the butterfly phenomenon. This leads to an improved and even more reliable product.

XI. Chemical Analysis

Other papers will deal more thoroughly with chemical analysis techniques per se. It is sufficient for purposes of this paper to acknowledge that many good methods of chemical analysis exist today. And for major elements it appears that sufficient standard reference materials (SRM's) are either available or contemplated at the National Bureau of Standards. The two areas that seem in need of attention are:

1- Reproducibility between laboratories

2- Trace or Residual Elements

The perennial problem of variable results from the same sample sent to different laboratories has been discussed for many years. It is disconcerting that in the melting industry we still have problems with consistency of results in such familiar elements as sulfur, aluminum, oxygen, hydrogen, and nitrogen. Part of the problem has to do with sampling, still other problems are associated with technique, and in some cases variable working standards are involved. While various technical societies are looking at one or more of these problems, the pressures of product liability legislation and other forces will make it mandatory that everyday control analyses be closer to "absolute" than we enjoy today. The National Bureau of Standards with its SRM Program could prove to be a potent force in this respect.

With regard to trace elements, the industry is already undertaking various studies related to high performance equipment. [13] Trace element effects need not all be considered bad. For example, see figure 9, an addition of magnesium in the ppm range can dramatically improve hot-ductility and workability. [14] Boron, zirconium, hafnium, yttrium, and lanthanum, are now well known additions to superalloys to enhance high temperature properties. On the other side of the coin, however, contaminants such as Pb, Zn, Cu, and Bi are exerting very bad effects at very low ppm levels. For example, Bi must be controlled so as not to exceed 0.3 ppm in certain superalloys, and Bi contents can be measured with assurance at this level using atomic absorption techniques. Atomic absorption spectroscopy is of course, the last word in in analyzing elements at the ppm level. Beyond any question we are in need of standards at these levels and the time to develop them is now. NBS is working with certain industry groups to develop ppm standards for nickel base superalloys, but progress will be slow and cost very high. Titanium levels are already creeping up in high strength steels and tool steels resulting in heat treatment problems. Phosphorus is well known to stainless steel melters as an element that cannot be tolerated in stainless steels for welding rod applications.

Unfortunately, many of these harmful alloys cannot be refined out of the metal (P, N_2, and in vacuum melting, Sulfur) so sources must be found and levels accurately controlled. This problem should receive closer attention across the board. The NBS once again will be a potent force and has already shown concern by participating in programs. [16-19]

XII. Closure

There is a saying, "We learn from physics that one eye, no matter how sharp, cannot see in perspective." In this same context, we share the opinion that chemical analysis needs of the future will require more of a systems approach. This is true not only for the selection of the materials, but also for the choice of processes used to produce the material. In addition, it is crucial that we establish "fix-points" through adequate standards and using these, we should undertake to even further increase the accuracy and reproducibility of chemical analyses in the metals industries. Once this is achieved, there are untold improvements in products and processes we can enjoy using new melting technology.

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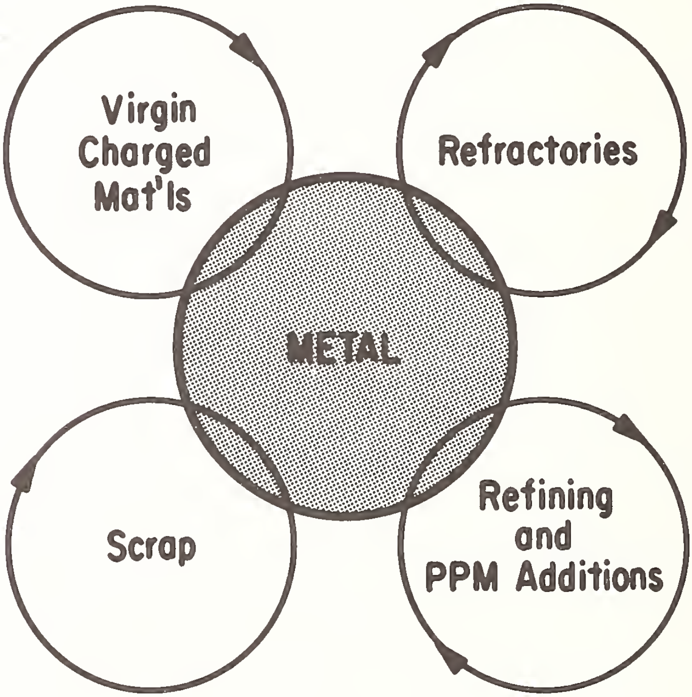

Figure 1. A More Critical Analysis of Melting Interactions

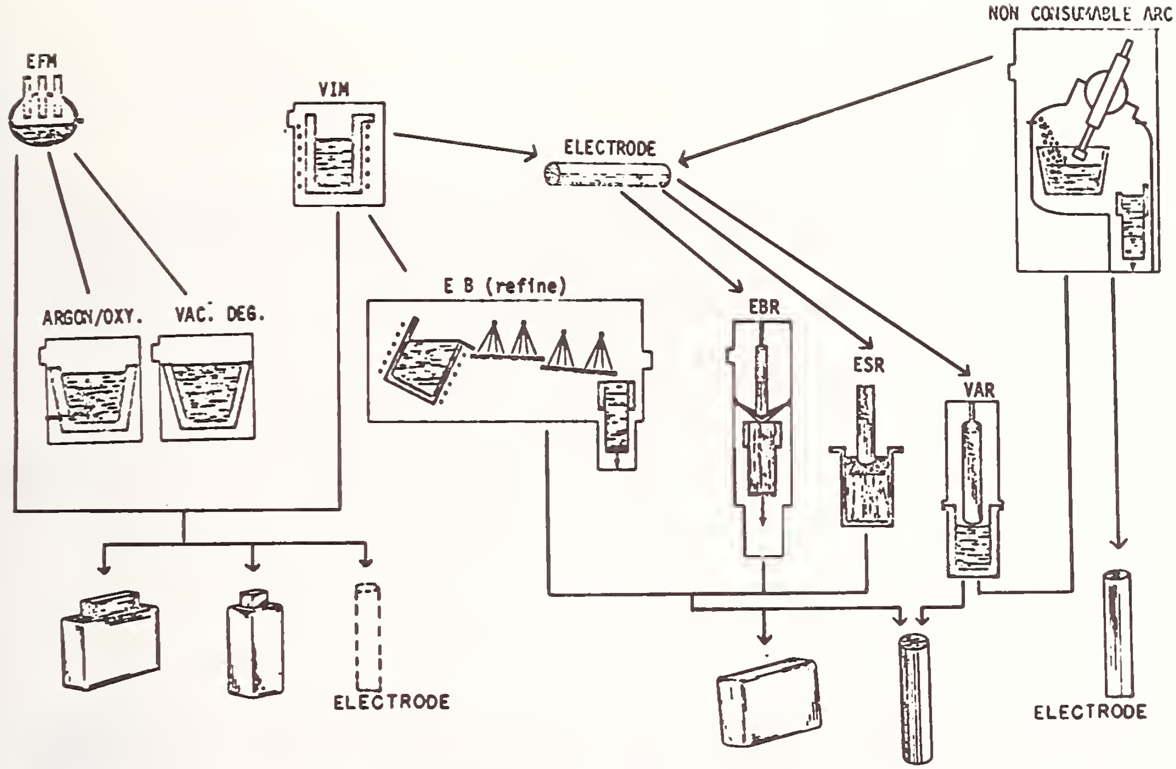

Figure 2. Existing and Potential Routes for Processing Superalloys

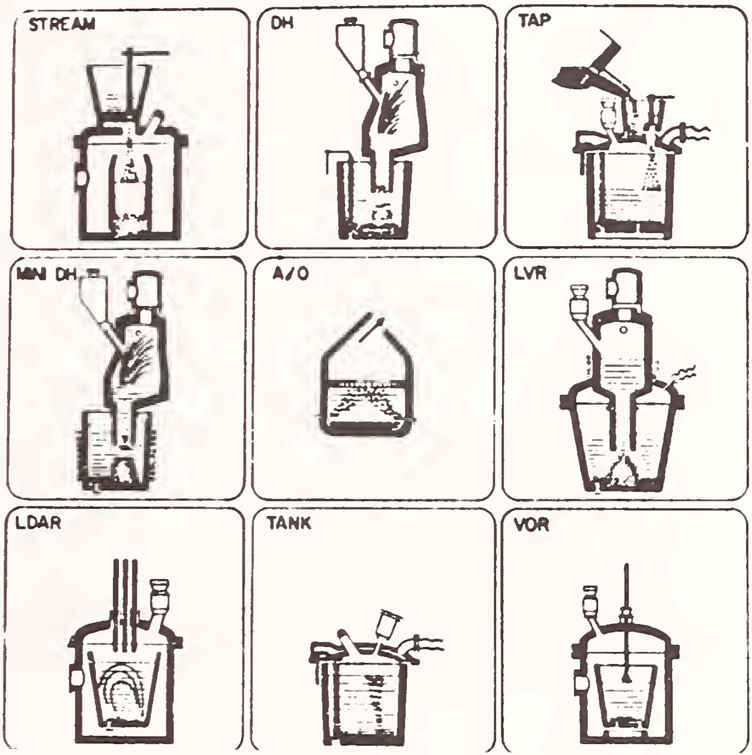

Figure 3. Advanced degassing methods for steelmaking which might be adapted for producing VAR electrodes for improved economy of superalloy melting in the future

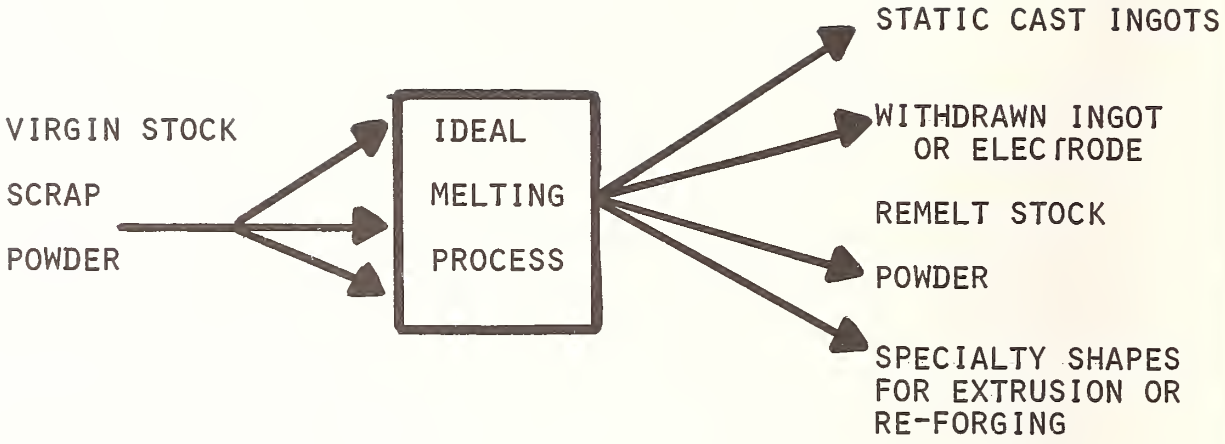

Figure 4. Ideal Melting Process

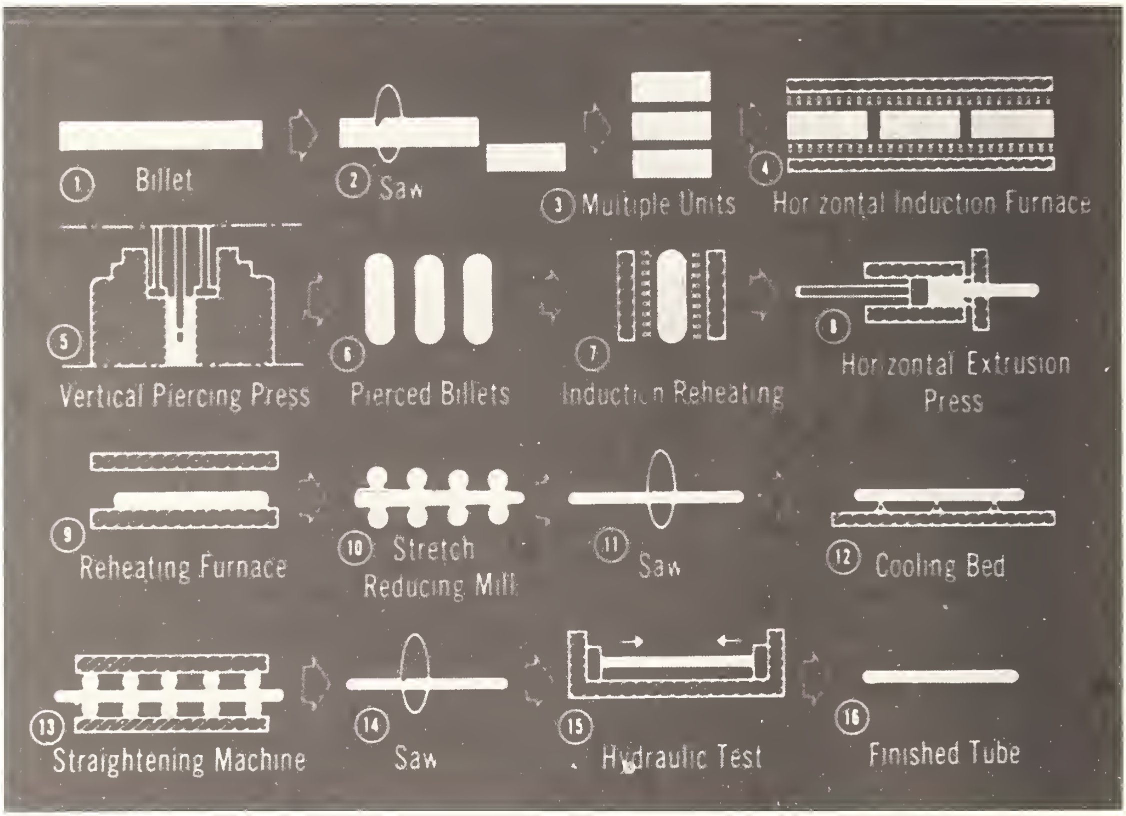

Figure 5. Sequence of Hot Extruding Operations

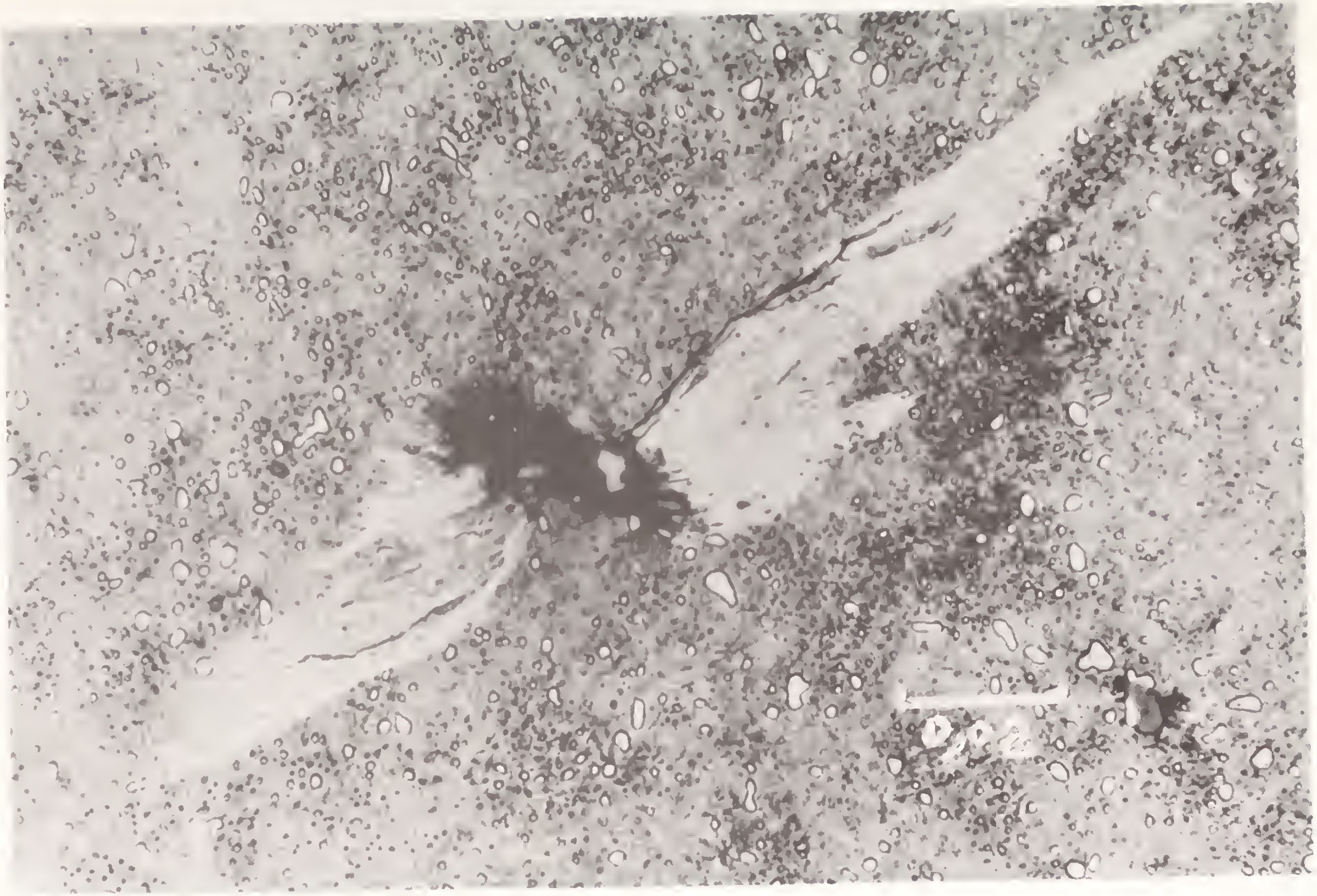

Figure 6a. Single "Butterfly" on an Oxide Inclusion (606X). Courtesy of Ugine Aciers, France

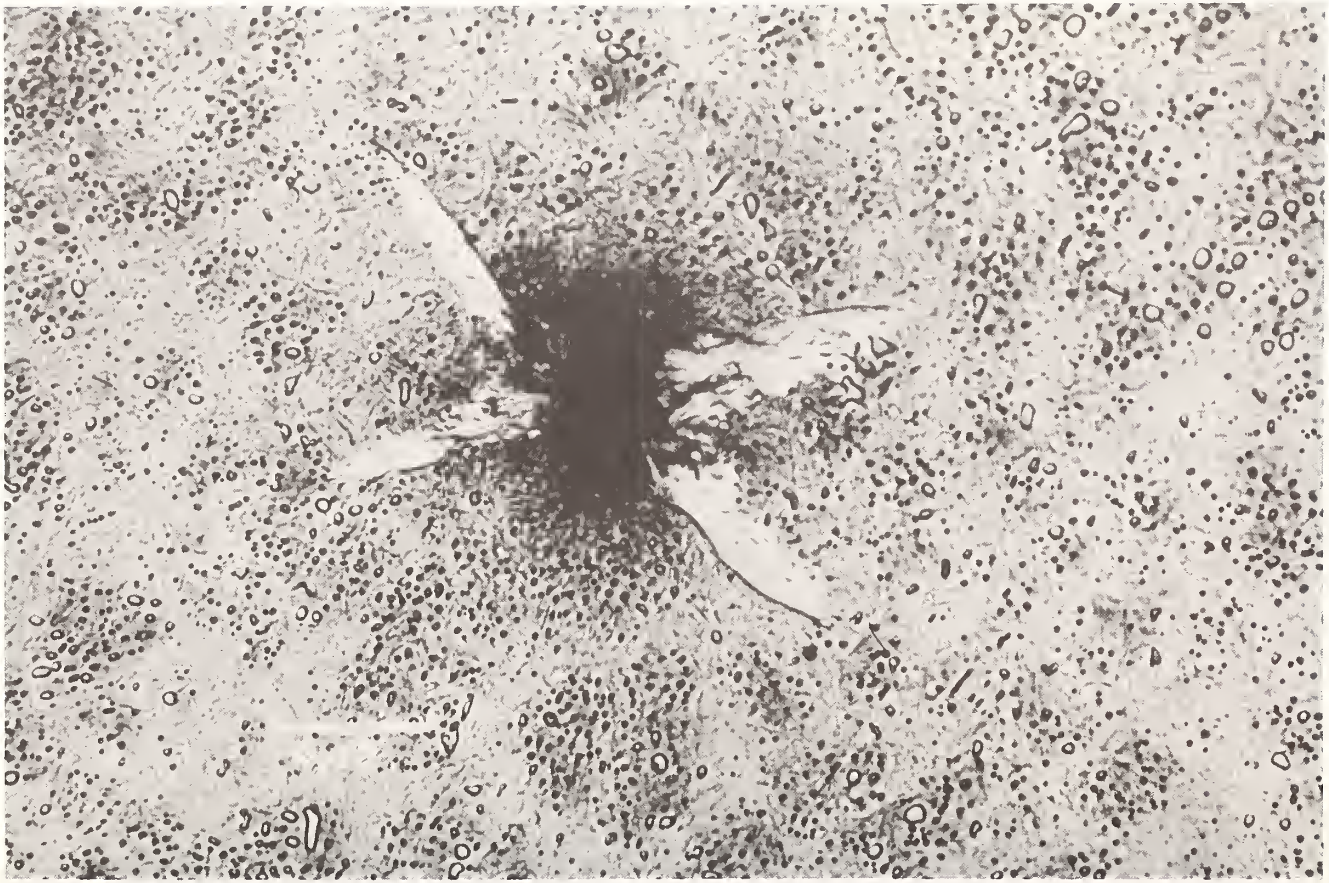

Figure 6b. Double "Butterfly" after Rotating in both Directions (606X). Courtesy of Ugine Aciers, France

Figure 7. One-Winged "Butterfly" Associated with Sulfide-Oxide Inclusion in Stressed Region (828X). Courtesy of Ugine Aciers, France

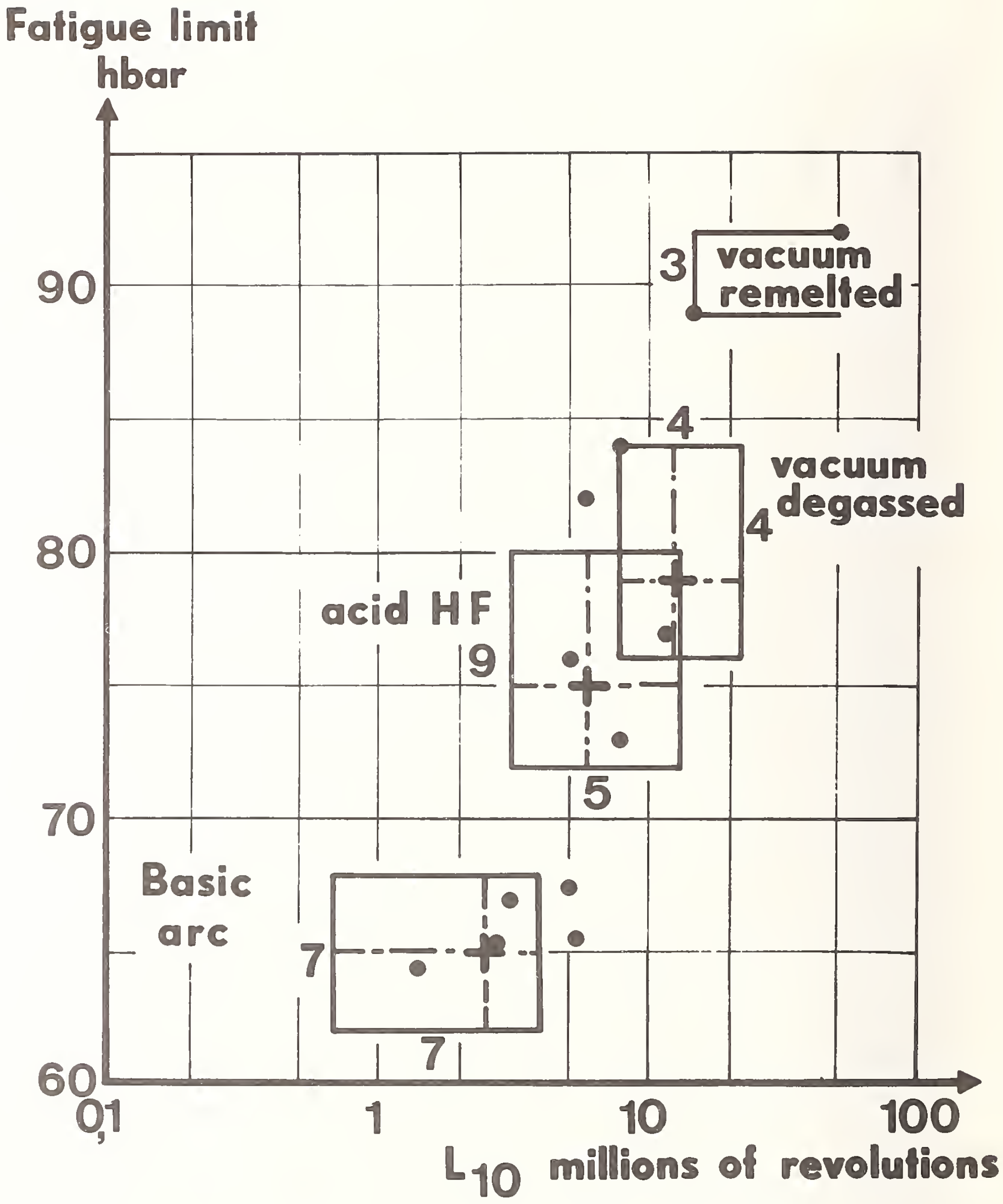

Figure 8. Correlation Between Fatigue Limit and Life of 6309-Type Bearings. Courtesy of Ugine Aciers, France

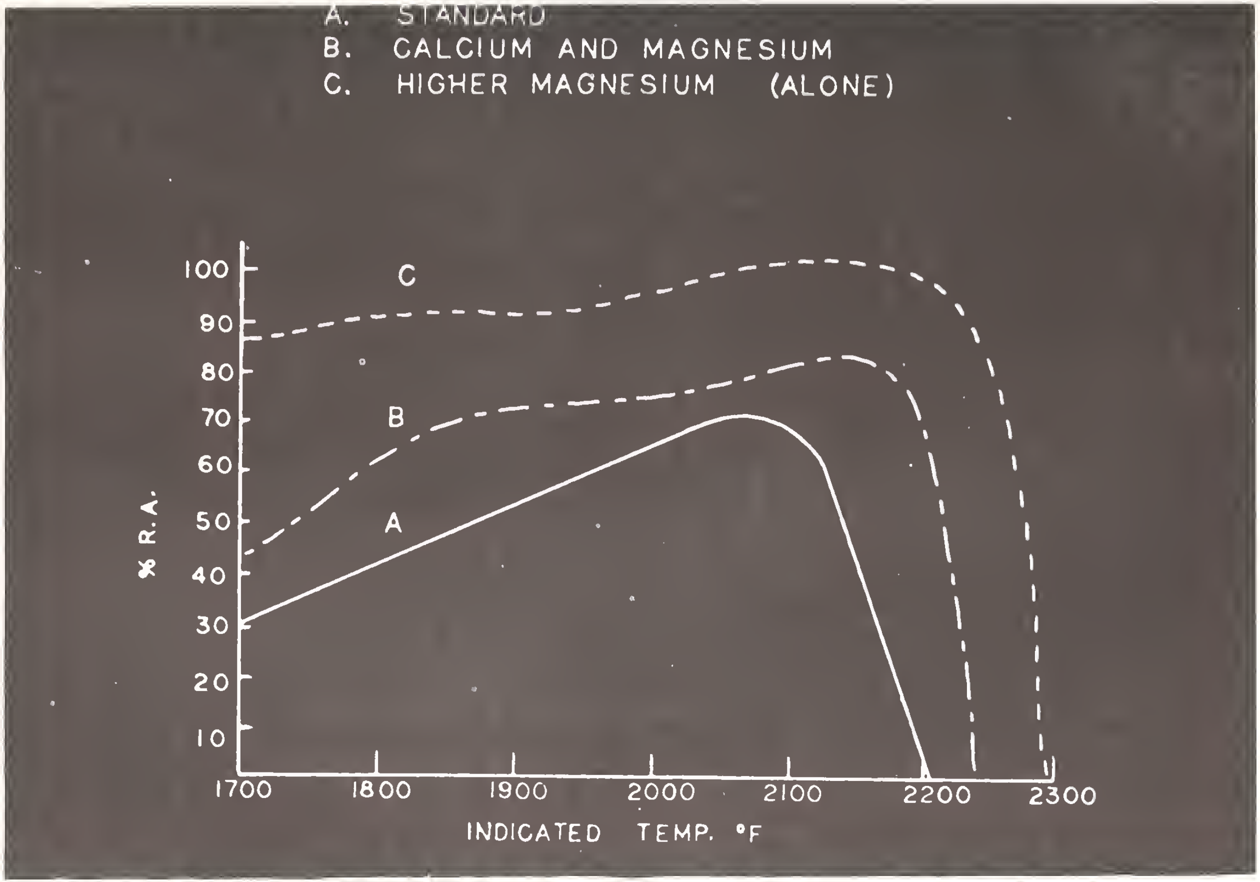

Figure 9. Not all trace element effects are bad, adding magnesium in the ppm range to superalloys can improve hot-ductility and workability

MEASUREMENT PROBLEMS IN PHYSICAL AND MECHANICAL PROPERTIES OF INDUSTRIAL METALS AND THE USE OF SRM'S

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I. Introduction

The title of this paper covers a large spectrum of disciplines connected with fundamental and applied metals research, as well as the metallurgical evaluation of industrial-metal products. It would be a formidable task to attempt a discussion of all the usual and unusual test methods used in controlling product quality and of the performance criteria for the great variety of metals and their alloys that are essential in meeting the rapidly growing demands of modern technology. It could certainly not be done in a short paper and, therefore, the scope of this presentation has to be limited to a summary discussion of some of those properties and measuring techniques that are used in the industrial applications of metals.

In metals research investigations SRM's are seldom used other than for the calibration of instruments, and where the absolute determination of properties is preferred. Methods for the measurement of basic physical properties (optical, thermal, electrical, magnetic, acoustic, etc.) are well-established and various SRM's are used. Their industrial application is especially important in the non-destructive methods of quality control evaluation of metal products. No SRM's are used in measuring mechanical properties, except for hardness determination and the calibration of testing equipment.

Much more difficult to define and measure are the more complex engineering properties encountered in industrial fabricating processes (castability, formability, machinability, weldability, etc.) or severe service conditions (e.g., wear, extreme temperatures). It seems that with the increasing requirements for assured high-product quality and more demanding performance as well as safety considerations for modern machinery and construction, new or improved methods of property measurement will have to be developed for better accuracy, higher speed, lower cost, and adaptability to automation and computerization of quality control testing.

It is rather difficult to organize and arrange the somewhat unrelated topics in a reasonably systematic fashion. To avoid repetition I propose to discuss the subject of metal properties grouped according to actual applications in the quality control of industrial products and the evaluation of metallurgical defects and service failures.

II. Physical Properties

The description of all measuring methods of physical properties used in metals research and industrial applications would require a few volumes. In this short presentation I propose to list or discuss only those measuring methods that are important in industrial quality control evaluation and/or the use of Standard Reference Materials.

Conventional methods for the measurement of basic physical properties are well-established and there are no significant measuring problems encountered, if recommended techniques and properly calibrated apparatus are used. In fundamental metals research, very often novel or even exotic methods have to be developed and tailored to specific applications, but they are -- at least for the time being -- not practical for industrial use.

Many of the methods of measurement important for industrial quality control assessment are used in non-destructive testing or in metallographic examinations; both of these areas will be discussed separately.

The wide variety of conventional measurements of physical properties includes elastic, optical, acoustic, thermal, electrical, magnetic, electromagnetic, and nuclear methods. Standard Reference Materials are used in most methods for the calibration of apparatus, the verification of techniques, or for the comparison of results.

The best known SRM's (either solid metal samples or reference charts, photographs, radiographs, etc.) used outside the fields of metallography and industrial non-destructive testing are those for the measurement of:

Thermal expansion (dilatometry)--especially for thermal analysis of metallic materials and for design data on equipment for high-temperature service.

Thermal conductivity--important in the aerospace and nuclear fields, and in heat treating and casting operations.

Heat capacity and enthalpy--if available, could be useful for heat treating and casting operations.

Vapour pressure as a function of temperature (e.g., Cd, Ag, and Au SRM's available for NBS).

Thermoelectric properties--used in temperature measurements, in studies of alloy systems, and plastic deformation. Some of the practical problems encountered in thermocouples in long-time creep tests are mentioned later. SRM's are available for calibrating thermocouple wires.

Freezing and boiling points--used for defining fixed points for the calibration of temperature measuring devices (according to IPTS-68).

Cryogenic temperatures--by the use of a superconductive thermometric fixed-point device. This NBS device contains five cylinders made of high-purity elements (Pb, In, Al, Zn, and Cd), providing thermometric fixed points, used for high-precision calibration of cryogenic temperature measurements between 0.5K and 7.2K.

Reflectance--SRM's for the calibration of reflectometers used in the evaluation of metal surfaces and thermal radiation properties.

Magnetic susceptibility--for the calibration of instruments.

Surface coating thickness--SRM's are available in considerable number for use in calibrating various magnetic and eddy-current type coating thickness gauges or as a comparison reference sample for use in other measuring methods.

High-purity metals--important industrially because alloys based on high-purity components show significantly higher strengths and ductility, better formability, and corrosion resistance.

Other SRM's are used or proposed for measurements of dimensional accuracy, elastic constants, density, radioactivity, electric and dielectric properties, surface roughness, wear resistance, calibration of x-ray diffraction equipment, particle size distribution and particle counts, etc.

Special remarks seem to be necessary for the assessment of the surface properties of industrial metal products. Technical development has increased the efficiency of machinery by not only more exacting design considerations, but also by increases in speed, operating temperature, and specific loading, as well as by more severe requirements for accuracy and durability. The correct functioning and reliability of machines depends to a large extent on the accuracy of the component parts and on the quality of their processed surfaces.

Evaluation of the surface finish in earlier metal work was only qualitative and depended on its reflectivity. Today it is necessary to understand better the relationship between the surface condition and the functional characteristics, and to request quantitative assessment methods rather than personal opinions.

Parameters affecting the surface condition include surface geometry and some metallurgical aspects, such as hardness and structure of the surface layer, and residual stresses in the surface layer.

Surface roughness (roughness height rating) is measured by a number of non-destructive testing methods employing optical, acoustic, mechanical, and pneumatic principles, but most of the devices in use are very accurate tracer-type instruments using stylus tracers and electrical amplifiers. Precision reference standards are used to check the performance of the instruments.

Texture comparison specimens, having the characteristics of typical machined surfaces, are used for visual or tactile comparison with surfaces under examination. Other important parameters of surface texture are flatness, roundness, waviness, lay (direction of predominant surface pattern), etc., which are sometimes important in industrial applications.

Two problems were recently mentioned at international conferences relating to the measurements of electrical conductivity and density.

The electrical conductivity of metals is usually specified in comparison with the international annealed copper standard (IACS). This standard was established in 1913 and in recent ISO committee discussions it was agreed that the density value used for the IACS should be updated and, as British investigations show, increased (probably from 8.89 to 8.91). This change would, of course, affect the values of conductivity (weight basis) of all metals, which are defined as a percentage of the established IACS conductivity. Electrical resistivity measurements require the use of a stable reference standard, usually a manganin resistor.

Electrical resistance measurements are also a very important and extremely sensitive tool in studies of plastic deformation, order-disorder transitions and age-hardening processes, as well as in the non-destructive testing of industrial-metal products; consequently, SRM's are necessary.

Electrical resistivity measurements (weight basis) depend upon accurate density determination, which is based on the density of water. Water density data were established many decades ago and, as requested at recent international conferences, should be re-examined.

III. Mechanical Properties

Traditionally, the mechanical test methods most commonly employed in the evaluation of metallic materials are those for determining tensile and compression strengths, hardness, impact, fatigue, and creep properties. The interchange of data derived from these tests is primarily based on the use of national and international test method standards. The value of Standard Reference Materials, to verify testing techniques and apparatus and to enable this interchange of data, is recognized, but the development of SRM's is costly and time consuming, and at the present time they are available for only a few types of mechanical tests.

Probably the most common reference materials in the field of mechanical testing are standardized hardness test blocks for the calibration of hardness testers. These test blocks are particularly important in facilitating the exchange of hardness test data since hardness is not a fundamental property of a material. Standardized test blocks used in Europe and Japan are traceable to their national standardizing bodies. In North America these controlling test blocks are prepared and distributed by the manufacturers of the various hardness testers and not necessarily coordinated. The creation of a national standardizing authority for hardness testing in the United States would allow more meaningful discussions on the feasibility of international hardness conversion tables.

Other examples of available reference materials are the standard Charpy impact specimens for the verification of Charpy impact testers, provided for the ASTM by the U.S. Army Materials and Mechanics Research Center, Watertown, Mass., and the Bank of Calibrated Type 304 stainless steel stress-rupture specimens maintained by the ASTM-ASME-MPC Joint Committee on the Effect of Temperature on the Properties of Metals, and marketed through the ASTM.

A. Static test

Static (or rather quasi-static) tests are the most universally used methods for measuring the mechanical properties of metals. They are considered as one of the cornerstones of engineering design and metal science generally.

Tension tests are the most common general source of mechanical property data; some other static methods, although less frequently used, are the compression, torsion, and bending tests. The engineering tension test provides basic design information on the strength and ductility of a metal, and is used generally as an important industrial acceptance test. All of these tests can be performed at elevated or low temperatures.

The most important factors in obtaining reliable and repeatable test results are the careful preparation and dimensional measurements of the test specimen, the speed of testing and proper alignment in the testing machine, and the verification of extensometers.

An extensive set of standards on the different test procedures, requirements for proper testing equipment, and calibration methods of testing machines and extensometers, etc., is available, and in most cases internationally accepted (ISO).

B. Hardness

Hardness is not a fundamental or even a well-defined property of a material. Nevertheless, hardness tests are the simplest, fastest, relatively non-destructive, and most commonly used means of checking the strength and heat treatment of metal. Hardness implies resistance to indentation deformation. Hardness numbers, although they are empirical values, are useful because of their relationship with many important engineering and physical properties of metals. For some steels, hardness tests are used for practical, although not accurate, estimation of tensile strength and even the endurance limit. Testing arrangements for hardness determination at elevated or low temperatures are available.

There are three general types of hardness measurements; these are the indentation, dynamic (or rebound), and scratch hardness tests.

The most commonly used and standardized indentation hardness methods are the Brinell, Rockwell, and Vickers (or diamond-pyramid) tests for macrohardness, and the Vickers and Knoop tests for microhardness determinations. Unfortunately, each of these tests uses different indentors (steel balls, or diamond penetrators of different shapes) and different loading systems. It is therefore not surprising that no universal hardness-conversion relationship has been found. Existing conversion tables for particular materials (e.g., various steels, cartridge brass) are accumulations of empirical results on industrial metals and alloys. Although they are included in ASTM standards, they are only approximations and may be inaccurate for specific applications.

The dynamic (or rebound) hardness tester, the scleroscope, measures the impact resilience of the material. The method is standardized by ASTM, but its use is generally limited to some hardened steel products.

Scratch hardness methods measure the width and depth of the scratch, and are used very rarely for metals, but are useful in microhardness tests.

Microhardness testing is a very useful tool in metallographic research for the determination of alloy constituents, small inclusions, segregations, bond and thickness of surface coatings, etc.

Standard Reference Materials (calibration blocks) must be used with all hardness testers; they are prepared and distributed by the manufacturers of the particular machine and are generally not interchangeable for use with other hardness testers. National standardization of these blocks seems to be necessary.

Another difficulty in international hardness conversions arises from the small variations in testing techniques and equipment (such as small differences in the shape of the diamond indentor) recommended in national standards of various countries, in spite of agreements reached in ISO.

C. Creep and Creep Rupture Tests

The creep test measures the dimensional changes of metal specimens that occur under constant load at long-time elevated-temperature exposure, while the stress-rupture test measures the effect of temperature on long-time load-bearing characteristics. Other elevated temperature tests are used to measure special properties such as thermal shock resistance and stress relaxation.

Some high-temperature applications (e.g., gas turbines, jet aircraft engines) require operation under extreme conditions of temperature and stress, but their service life is comparatively short and permissible deformations of the part are not highly critical. For the evaluation of such materials the stress-rupture test rather than the long-time creep test is used. Stress-rupture tests measure the time of fracture of the specimen, when sufficient load is applied at a given temperature. The two tests supplement each other in defining the load-carrying ability at elevated service temperatures.

ASTM standards for creep and creep-rupture testing procedures, apparatus and its calibration, are available. For the calibration of creep-rupture testing machines, unmachined blanks of material with calibrated rupture properties (SRM's) are available from the ASTM.

The results of creep and creep-rupture measurements are subject to wide scatter due to the inhomogeneity of commercial materials and to inherent or inadequately controlled testing techniques and instrumentation. National and international interlaboratory programs of creep-rupture testing, recently undertaken on controlled material for AGARD (NATO), showed significant variations in reported results. A British evaluation of all the test data revealed that the major sources of error were associated with temperature measurement and control. Recommendations were made on further studies to improve temperature measurement and control techniques.

Inhomogeneities in the thermocouples develop during service due to straining, oxidation, aging, and contamination (e.g., rhodium on platinum). This is especially significant at long exposure times (during the AGARD test programs, testing times up to 20,000 hours were used). It was found that chromel-alumel thermocouples should be stabilized by heating to the test temperature for 200 hours before calibration, while the Pt/PtRh thermocouples should be annealed at 1300 °C (2370 °F) for two or three minutes. All working thermocouples should be frequently calibrated against standard reference thermocouples.

Other sources of variations in creep-rupture testing results are connected with load application and control, specimen design and surface conditions, and extensometer design and control.

D. Fatigue Strength

Fatigue strength and toughness characteristics are probably the most quality-sensitive of all engineering properties. They are greatly affected by the thermo-mechanical history of the material, including the inhomogeneity of industrial alloys (solidification, heat treatments), all the shortcomings of fabrication processes (residual stresses, surface properties), and imperfections of product design (stress concentration). Small local metallurgical defects, such as surface or sub-surface inclusions, voids, microsegregation of hard particles, may be significant causes of fatigue failures. Another problem in assessing the fatigue life of metal products is the inability to predict completely the actual service (overload, misuses) and environmental (temperature, corrosion) conditions.

Fatigue failures generally start as minute surface cracks that grow under the action of a fluctuating stress until a dominant crack attains a critical size, causing failure. There are two stages in the fatigue process: (a) the crack initiation phase (microcrack), and (b) the crack propagation phase (macrocracking). Monitoring of the development of fatigue damage may be conducted by visual-manual techniques or use of strain gauges (wire grids), and various methods of non-destructive testing (ultrasonic, electrical potential, microwaves, eddy-currents, acoustic emission).

Fatigue tests are performed for a wide variety of purposes, mostly on small test specimens designed for the variety of fatigue testing machines (rotating bending, axial or torsion loading), but also on full scale components and complete structures to simulate actual service performance. Very careful preparation of the test specimens is of the greatest importance in regard to dimensional accuracy and surface integrity, especially the avoidance of surface stresses due to cold work.

Several standardized methods of fatigue testing have been published recently amd more recommended practices are in preparation, including axial fatigue, elevated temperature and low-cycle fatigue, calibration of machines, and specimen preparation procedures.

E. Notch Toughness

The notch toughness of a material is a measure of its ability to absorb energy in the plastic range and to yield plastically under high localized stresses such as might occur at the root of a notch. Toughness is a parameter that comprises both strength and ductility.

The notch toughness of a face-centered cubic metals, comprising a large group of non-ferrous alloys and the austenitic steels, can be judged by their room-temperature tensile properties; if they are ductile in tension they will show ductile fractures and low temperatures do not change this. In contrast, the behaviour of body-centered-cubic or ferritic alloys cannot be predicted from conventional tensile properties and they show a significant change in notch-fracture characteristics. At elevated temperatures, impact specimens fracture by a shear mechanism absorbing large amounts of energy; at low temperatures they fracture in a brittle manner by a cleavage mechanism absorbing little or no energy. In the latter case, fracture is frequently sudden and may be catastrophic.

The importance of the notch toughness of structural steels for products subject to low temperatures is self-evident, especially in view of the growing interest in the development of industrial activities in artic or sub-artic regions where temperatures may drop to -75 °C (-100 °F). The determination of the lowest transition temperature, acceptable for a particular application, is therefore of crucial importance to the designer and producer of engineering structures, such as pipelines, transmission towers, etc.

The ductile-to-brittle transition temperature is that defined as corresponding to:

1. a specified energy level;
2. the appearance of the fracture of a broken impact specimen, or a measurement of the proportion of ductile or fibrous shear vs. brittle or crystalline cleavage (comparison charts for fracture appearance--shear fracture comparator--are available in ASTM Standard A370-72; or
3. a specific amount of lateral expansion of the broken specimen, measured by a lateral expansion gauge.

The simplest and most commonly-used test for assessing the notch-toughness of steels, and therefore the one from which most data are available, is the impact test on notched specimens. There are two methods standardized, the Charpy simple-beam test using V- or keyhole-notches, and the Izod cantilever-beam test, used mainly in Great Britain. In North America the Charpy V-notch test is in general use. Notched-bar impact tests are subject to considerable scatter, particularly in the region of the transition temperature. Most of the scatter is due to local variations in the properties of steel, while some is due to difficulties in preparing perfectly reproducible notches. Both notch shape and depth are critical variables, as is the proper placement of the specimen in the impact machine.

Various empirical impact tests, such as the Charpy V-notch test, give a first approximation of the dynamic toughness of materials. Some materials, most notably structural steels, can have a dynamic toughness that is very much lower than the quasi-static toughness. In fact the critical defect sizes can differ by an order of magnitude. Yet, it is often the dynamic toughness that correlates with a service failure under quasi-static loading. The reason for this is that an increment of fracture, at a local region of impaired ductility, can give rise to local dynamic loading. Tests on instrumented, pre-cracked specimens indicate that dynamic toughness can be measured quantitatively.

Larger scale dynamic tests are becoming more widely used because in larger specimens the fracture may run several thickness lengths and thus a better appreciation of the properties is obtained. The Naval Research Laboratory (NRL) dynamic tear test and the Battelle Drop-Weight Tear Test are the most widely used. Both fracture strength and fracture ductility are important. Fracture strength can be measured for static and dynamic loading rates in terms of the stress-intensity factor. In many cases, a simple dynamic ductility sorting test, such as the Nil-Ductility Drop Weight Test, may give an adequate basis for assessing safely.

Non-destructive testing methods for the measuring of crack propagation include such electrical potential measurement, displacement gauges, exoelectron and acoustic emission methods. A most useful instrument in fracture evaluation (fractography) studies is the scanning electron microscope because of its great depth of focus.

F. Stress Analysis

Design is frequently a major factor in the service failures of metals. The proper distribution of stresses, of paramount importance in eliminating mechanical failures, is obtainable largely through the physical shape and position of the part to be loaded. Factors of stress concentration may be determined in various ways, including mathematical analysis, strain gauges, photoelasticity, and brittle coatings.

Experimental measurements of stress are actually based on measured strains. The most universal strain-measuring device is the bond-wire resistance gauge, which is attached to the surface of the examined part. After deformation, the wires of the gauge are strained and their electrical resistance is altered and can be accurately measured. The high sensitivity, stability, comparative ruggedness, and ease of application make the strain gauge a very useful tool for quantitative stress evaluation.

Photoelastic coatings are bonded to the surface of the examined part. When the part is loaded, the strains in the part are directly transmitted into the coating. The optical fringe pattern obtained is related to the strain distribution in the part and may be measured and evaluated. Sometimes prototype models are prepared from photoelastic material and used with a transmission polaroscope to assess the design. Brittle coating tests are based on the use of brittle lacquers and the strain distribution can be measured qualitatively by the crack pattern of the coating.

Proper evaluation of prototype products (castings, forgings, assembled machine components) by stress analysis is of great importance in the economic development of new designs.

G. Residual Stresses

Residual stresses are stresses existing in a component or structure free from actual load. They are set up within a metal as the result of non-uniform plastic deformation caused by cold working or machining, or by drastic gradients of temperature from quenching or welding. Residual stresses are a dangerous factor in stress-corrosion failures of metals.

Residual stresses may be measured by x-ray diffraction, strain gauges, the Sachs boring method, bending-deflection method, or cutting techniques. The quantitative measurements of residual stresses are reasonably reliable in determining stress values and give a rough idea of their distribution. X-ray diffraction has so far been the only non-destructive way of measuring residual stresses, but is limited to surface stresses only. Residual stress relief may be obtained by proper heat treating operations.

In view of the growing number of industrial acceptance tests and the necessity for the elimination of human error in visual observations or manual operations, a strong effort is being made toward automated production testing with computer data logging and machine control. Computerization allows better data evaluation and output, a real-time test control, selective data acquisition, and the ability to run complete tests that are not possible with manual control.

Some automated equipment is already available in the fields of tension, creep, and low-cycle fatigue testing. Another area of interest is the computer-control of fatigue testing of entire structures (structural testing).

Another way of speeding up quality control procedures is the mechanization of machining of test specimens by using tracer-lathes for round test bars and the simultaneous milling of stacked flat specimens. Speeding up test bar preparation is important because of time and cost economics, but it should not affect the care for dimensional accuracy and suitable surface properties--especially the avoidance of residual stresses.

IV. Metallography

Metallography is one of the most important methods of evaluating metals, both in research and in the determination of service failures. Most of the physical and mechanical properties of metals depend on their structure and the effect of internal defects (e.g., inclusions, porosity, segregation). During the last two decades considerable progress has been made in the field of light microscopy, e.g., improved optical systems and special illumination techniques for better image quality and brightness; hot stage attachments for the study of elevated temperature phase changes and similar arrangements for low-temperature investigations; enlarged viewing screens; micrometer eyepieces; and more refined photographic equipment.

More important was the introduction of the electron microscope, which increased the limited resolving power of the light microscope by well over two orders of magnitude. The electron microscope has permitted the determination of microstructures of many alloys with very fine details, previously unknown, such as those in quenched and tempered steels, age-hardening aluminum alloys and heavily deformed metals.

There are precise methods available for the direct measurement of metallographic features, but for faster--although less accurate--quality control evaluation, comparison standards are used. These comparison standards are either metallographic reference charts, showing a series of standard photomicrographs, or suitable equivalent transparencies inserted in the eyepiece of the microscope. Some of these reference charts are included in national standards (e.g., ASTM), others are distributed by metal producers; standard microstructures are also contained in various published metallographic atlasas (e.g., vol. 7 of the ASM Metals Handbook 8 ed.).

Reference charts are available for the estimation of average grain size; the determination of the number, size, shape, appearance, and distribution of non-metallic inclusions in steel; oxygen content in copper; porosity rating, pearlite precipitate, and massive compound in cast magnesium alloys; graphite size, form and distribution in cast iron; and others. Assessing grain size (or other metallographic features) by visual examination and comparison with a standard chart is not very reliable or reproducible, but the more accurate determination by intercept or planimetric procedures is too slow and tedious for use in routine quality control testing.

Another important development is the commercial introduction of the scanning electron microscope. The most significant application of this instrument is in the study of fractured surfaces. The great depth of focus allows all irregularities of the rough fracture surfaces to be in focus at once and relief can be measured by stereo-effects or by shadowing. The scanning microscope has been particularly useful in studies of crack initiation and propagation caused by fatigue or stress-corrosion, determining surface texture, examination of surface blistering, and in studies of metal powders. New experiments have been aimed at determining the amount of plastic deformation in metal surfaces.

Present trends in x-ray diffraction studies are towards the absolute determination of such parameters as retained austenite in steels, internal stresses, amount of cold work, and preferred orientation. However, many of the determinations involve computer analysis that may be too complicated or expensive, especially in industrial conditions. Often a measurement is required to determine not actual values, but only whether or not a certain value has been obtained, or even whether a certain phase is present or absent. In such cases, provided other parameters do not interfere, standard reference materials, charts, or films can be used, first to calibrate the instrument and then as routine measuring criteria. The best example of this is the ASTM index of powder diffraction lines, listing standard reference patterns for thousands of crystalline materials. A series of standard reference materials is available to measure the accuracy and reproducibility of x-ray diffraction equipment, for example to determine the relative amounts of retained austenite or of spheroidized iron carbide in steel. Except in laboratories devoted to measuring unknown structures, most materials are identified from standard reference cards. Recently computer programs have become available, using ASTM standard data to process the results of x-ray diffraction measurements on materials containing several "unknown" components.

A most valuable advance in metallography is the recent introduction of computerized television screening microscopes, which automatically count, measure, and classify selected features in images produced directly in the light microscope or from photographic reproductions of electron micrographs. This complete image analysis system is being used for the quantitative assessment of grain or particle size, inclusions, alloy phase distribution, porosity or segregation in welds or castings (from examination of radiographs), size analysis of metal powders, or any other parameter that can be made to show up as an appropriate change in contrast. For absolute measurements, data must be processed to take account of the way the sample was sectioned or otherwise prepared, the shape of the phases in three dimensions, the contrast mechanisms, and the size limits. For many purposes, processing of the information can be avoided by using a working graph from which the readings of the machine can be interpreted directly.

The obvious advantages of automated metallography are speed and reliability of computerized determinations and the elimination of human error in visual observations and comparisons with reference charts.

V. Industrial Non-Destructive Testing

Non-destructive testing (NDT) has been used for years in industrial quality control of metal products and components. Its purpose is to detect and evaluate, without damage to the examined part, any inhomogeneity, structural change, geometrical variation, surface or internal defect, or stress concentration, which may affect the serviceability of the product. In the past, non-destructive testing methods have been limited to meet specific problems and, except for radiography, were not developed for general use. Recently, these earlier methods and procedures have been considerably improved and made more sensitive and reliable, leading to more general application. New and sometimes exotic tests are being developed to satisfy the requirements of modern production engineering. Most of these new developments have been at first directed to meet the close quality control specifications in areospace, nuclear, and defence industries, but now they are used more generally.

The different non-destructive tests have many features in common; however, each has certain characteristics that make it the best test to use for a given material under a specific set of conditions. No single test is suitable for all materials nor for the detection of all kinds of discontinuities and other imperfections. The tests should complement each other and the best results are obtained when this is done. The test method should be selected in accordance with the material to be inspected, the degree of inspection required and the economy of time and money involved where high-product quality is required, such as in the case with high-pressure vessels or nuclear equipment, several test methods may be necessary.

Non-destructive tests are indirect measurements of various physical properties, which permit an assessment of imperfections in the inspected product. Considerable experience in quality control testing and evaluation of actual service failures is essential for proper and correct interpretation of NDT indications, and their correlation with product quality and service requirements.

Some of the more common NDT methods are described below.

A. Industrial Radiography

Industrial radiography is a long established and accepted NDT method. Unfortunately, its limitations are not fully recognized. It is often required in standards or industrial specifications simply because the authors are not aware of other proven non-destructive tests suitable for a particular application; it tends to be used indiscriminately. However, it is the most reliable of all non-destructive tests, if it is used by qualified personnel.

Reference radiographs are available to identify the character and grade of a variety of flaws suitable for use as standards for most metals and alloys. However, they are often not used to the best advantage; in many inspection laboratories, although they are available, they are not fully exploited. This is deplorable because of the great amount of tedious work necessary for the preparation and the high cost of these reference standards.

New developments in radiography include high voltage units, new low-energy isotopes, better film quality, the introduction of radiographic paper as a cheaper substitute for films, stereo-radiography, and neutron radiography.

B. Fluoroscopy

Fluoroscopy makes use of a fluorescent screen and x- or gamma-ray radiation to produce an image of the examined product. The advent of image intensifiers has brought about a resurgence in the interest in fluoroscopy that is now generally used with television monitoring. It allows high screen brightness levels, good resolution, contrast, and permanent image recording on film or video-tape. Much work is being done on new and improved applications of this method. Its use in examining moving systems (cine-fluorography) is becoming a very important tool in R&D investigations. One of these applications is the observation of the pouring of liquid metal into a casting mould to study the flow of metal through the gating, the filling of the mould cavity, and the formation of casting defects during solidification.

Improvements in optical systems, television tubes, electronic circuitry, and image recording will undoubtedly lead to an increased use of this test method. Standard reference radiographs or photographs may be useful for proper assessment by comparison.

C. Ultrasonic Inspection

Ultrasonic inspection makes use of the passage of sound waves through various materials; as the name implies the frequencies are beyond the audible range, travel at different speeds through different media, and can be directed towards a definite area. The reflection or absorption response from that area can be measured and recorded on a cathode-ray screen. The use and application of this test appears to have had the greatest growth of all NDT methods in recent years.

Because ultrasonic testing is quicker and more economical, for many applications, than radiography, it is tending to replace it. Although it is ideally suited for certain applications, it has not yet proven itself in others. Unfortunately, the new method is being used in some areas as a substitute for, rather than in conjunction with, radiography and other tests.

Standards for the various ultrasonic test methods and the preparation of calibration blocks (SRM's) are already well established and test procedures should be constantly checked.

Ultrasonic testing is generally considered the best method for detecting fine internal cracks or separations of the "two-dimensional" type, but only when used and evaluated by a skilled operator, who can detect small imperfections beyond the resolution of radiography.

D. Acoustic Emission

Acoustic emission is an integrity monitoring method capable of detecting crack formation or movement at the time it occurs. This method constitutes a powerful tool for both structural integrity surveillance and for the basic study of material failure mechanism (crack initiation and growth rate). Full utilization of the technique will require considerable additional development work.

E. Eddy Currents

Eddy currents are created in the metal by electromagnetic induction, when a coil carrying alternating current is brought near a metal sample. The magnitude of the induced eddy current depends upon the magnitude and frequency of the alternating current and the properties of the specimen, including conductivity, permeability, geometry, presence of discontinuities, or other imhomogeneities. Eddy currents are used in many applications and usually the test results are compared against a standard reference sample (SRM). Test procedures are standardized, but there is often a difficulty in preparing a comparative reference specimen (SRM) with properties suited to maintaining the desired sample properties within the tolerance specified.

F. Electric Current

Electric current tests are used for detection of cracks, laminations or faulty bonding surfaces, and wall thickness measurements. This test uses electrical resistance and potential drop to locate and measure defects. The electrical resistivity in the area of a defect differs from that in solid metal. The presence of a defect changes the potential difference between chosen points on a specimen. Measurements on the unknown specimen are compared with results obtained on a standard specimen (SRM) with simulated defects or other faults.

G. Infrared Testing

Infrared testing is based on the principle of applying heat to the test specimen and measuring or observing the resulting temperature distribution by infrared optics. Flaws or voids in or on the specimen can alter the temperature distribution. The main advantage of observing the specimen by infrared radiation is the ability to sense remotely and to detect very small changes in surface temperature. One of the problems is the providing of standards (SRM's) to interpret the surface temperature variations in terms of specimen voids or other characteristic defects.

H. Holography

Both optical and ultrasonic test methods based on holography are still under development and awaiting proper assessment as NDT tools. The apparatus necessary to carry out this at present exotic method is very expensive. So far its use has been limited, although it seems that the many unique characteristics of holography will be very useful in practical applications of NDT.

I. Liquid Penetrant

Liquid penetrant inspection is one of the oldest and probably most practical of the non-destructive tests. It is used only for the detection of surface defects, on both magnetic and non-magnetic materials. It is widely used because of its low cost and speed of application. Reference photographs are used for comparison.

J. Magnetic Particle

Magnetic particle inspection is a widely used and accepted method of detecting surface and sub-surface discontinuities on ferromagnetic materials, especially in the inspection of welds. The test is relatively simple and inexpensive, giving immediate visual results. Reference photographs are used for comparison.

There are, of course, many other NDT methods, using the measurement of optical, acoustic, magnetic, electrical, electromagnetic, thermal, or nuclear properties for the detection and evaluation of metallurgical defects, wall thickness, surface coatings, leak (pressure tightness) testing, friction, or wear damage, etc.

The future of non-destructive testing seems to be very bright, because some of the NDT methods may be easily adapted to automation and computerized monitoring, and in many cases the apparatus is, or could be made portable, for use in remote service locations (bridges, pipelines, etc.). The use of standard reference materials is essential in many NDT methods, but more standardization of SRM's on a national scale is necessary, followed by international coordination.

It is to be hoped that in the near future new and improved NDT methods will be the most important inspection tools for monitoring and maintaining standards of materials quality, reliability of components, and safety of systems.

VI. Industrial Engineering Properties

It is premature to attempt to describe measuring methods of such industrial engineering properties as castability, formability, machinability, wear resistance, etc. From the point of view of product engineering, these complex properties, or rather groups of properties, are very important both for obtaining satisfactory product quality and for assuring production efficiency and costs. To illustrate the problems encountered, a few examples are given.

A. Castability

Castability or casting fluidity (not to be confused with the physicist's term of "fluidity" meaning the inverse of viscosity) is a complex property, controlling the ability of molten metals to fill a complicated mould cavity and to penetrate into sharp corners and thin sections. Alloy composition, heat content, heat transfer, hydraulic variables, mould material characteristics, and mode of solidifications are the major factors affecting casting fluidity, while surface tension of the molten metal becomes important in ultra-thin sections. Unfortunately, to date no consensus has been obtained on a standard test mould design and procedure. A modern approach to the study of metal flow in gates and mould cavities is the use of cine-fluoroscopy monitored by television, already mentioned.

For most practical purposes the ideal casting is one that is sound (freedom from porosity), has a fine structure (grain size, dendritic cell size, and alloy constituents), and is free from segregation. However, the factors that the foundryman has to consider to accomplish this ideal, such as gating, risering, chilling, section thickness, complexity of shape, etc., cannot be taken independently because they affect more basic variables, such as cooling rate, direction of heat flow, and thermal gradients at various sections of the casting. In broad terms, the cooling rate determines the fineness of the structure, and the other variables affect the soundness of the casting.

B. Formability

Formability (or workability) of metals relates to the ability of industrial metals and alloys to be deformed under the influence of an applied state of stress. This force can be applied by rolling, extruding, forging, various sheet metal shaping methods, or any other forming operation. Due to the great variation in the applied stress (compression, tension, hydrostatic, etc.), the temperature, the strain, and the strain rate, a general parameter of formability has not been found.

When applied to a particular forming process, formability is both the ability of the metal to be strained into a desired shape without failure (ductility factor), and the ability of the forming machine to exert a force sufficient to overcome the material strength (flow stress factor). The parameter concerning ductility determines when fracture will initiate. Before a general value of formability can be developed, a clear concise parameter, defining when fracture will occur under a triaxial strain state must be found. It is important to realize that both flow stress and ductility are functions of temperature and strain rate.

Tension, compression, and torsion tests have been used to determine general formability data. The tension test is useful for cold formability testing of sheet metal; the torsion test is probably the most widely used test for hot forming. Compression tests are very useful for obtaining flow stress data for all temperature ranges and strain rates. A variety of machines is used, but the most suitable is the Cam Plastometer, which is used for hot deformation studies. An important feature of the plastometer is that it deforms the cylindrical specimen at a constant true strain rate. The compressive mode of deformation is similar to many forming processes such as rolling and forging.

Apart from the above tests, which can be applied more or less to any forming process, there are many specialized tests for particular applications; for example, in sheet forming there is a variety of qualitative laboratory tests such as the various cupping tests, bending and reverse bending, etc.

A useful concept has been developed recently for the description of fracture during sheet forming operations and its presentation in forming limit diagrams. It has been shown that the principal surface strains at fracture, when plotted as minor strain versus major strain, define a distinct limiting band separating safe from unsafe strain combinations. These diagrams are now being extended to bulk forming. With the use of this type of data it should be possible in the future to determine if a part will fracture during forming, if the strain field within the material is known.

C. Machinability

Machinability is another complex engineering property. It defines the ability of industrial metals and alloys to be shaped by partial removal of material by sharp tools. There are many kinds of machining operations, such as turning, drilling, milling, broaching, threading, reaming, sawing, or grinding, and each of these processes produces different machinability criteria. Factors affecting machinability are: the material being cut (composition, structure, shape and size); the cutting speed, size and shape of cut; the cutting tool (material and treatment, shape, size, surface quality); the condition of the machine tool; the cutting process involved; rigidity of the tool and work holding device; and characteristics of the cutting fluid used. If any one of these factors is changed, different results will be obtained. It seems, therefore impossible to have a set of cutting conditions that will utilize all factors equally and ideally, and some compromise has to be found by combining the various factors.

Machinability is evaluated in different ways, depending on the objective. Machinability may be measured by tool wear and life, tool-chip interface-temperature, cutting force and power requirement, surface finish quality and dimensional accuracy of the machined part, and by characteristics of the swarf produced. Values of machinability are usually comparative ratings and represent the material only under established condition of measurements.

In view of the considerable interest in additional standardized machinability evaluation, ASTM is working at present on this problem and as a start is considering proposals for a test procedure to compare machinability of bar stocks used in the production of metal parts in automatic screw machines. There would be a possibility of using standard reference bars (SRM's) for this comparison.

D. Wear Resistance

Wear resistance is another engineering property that is difficult to define or to measure. The problem of wear metals is of vital concern to the industry, because everything that moves causes and is exposed to wear.

Wear resistance is not an inherent property of a metal and cannot be determined apart from the specific service application. Wear depends on a combination of characteristics of the moving parts in contact and of the service conditions. Wear may be considered essentially a surface phenomenon, and consists of the gradual mechanical deterioration of contacting surfaces, such as tearing off particles through friction. There are different types of wear, such as metallic wear, abrasion, or erosion (by liquids or gases), frequently combined with some kind of corrosion.

The complexity of the problem can be indicated by considering the major factors influencing wear: (a) metallurgical factors such as the composition, hardness, toughness, constitution, and structure of the metal; (b) service variables including contacting material, pressure, speed, temperature, and surface finish; and (c) other contributing factors such as lubrication and corrosion.

There can never be a universal wear test, because there are too many different types of wear. Equipment for wear testing must be designed to simulate actual service conditions. There are many commercial wear testing machines and others designed and built in individual laboratories, but they are directed to evaluate a specific wear problem. There are also some empirical comparison charts relating some type of wear to hardness, tempering temperature, or carbon content in steels or cast iron.

Most important is the protection against wear by adequate lubrication, careful surface preparation, elimination of corrosive conditions, and--in some cases--the application of surface coatings. Serious considerations have to be given to the establishment of allowable wear limits and the development of methods for wear failure detection.

VII. Conclusions

Future progress in product engineering depends on further mechanization and full automation of fabricating processes and servicing operations to eliminate faulty workmanship, the largest single cause of poor product quality, and the availability of assured high-quality metal products and components. Automation and computerization of quality testing by nondestructive methods throughout all production phases would further eliminate human errors and ensure interchangeability of components and consistent performance characteristics of industrial products.

"Premium-quality" guarantees, "Zero-defect" and other quality assurance programs are already successfully used in some industries. Computer-controlled automatic quality testing machines are even now in use in the petroleum, automotive, electric components, and die casting industries.

International standardization (or at least better harmonization) of testing methods and apparatus, introduction of internationally approved SRM's and, finally, conversion to metric (or rather SI) units in North America, would enable closer correlation of test data from R&D work throughout the world and, at the same time, facilitate international trade.

HIGH-PURITY COMPOUNDS: AN OVERVIEW

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I. Introduction

If high-purity metals can be said to have come of age by the 1960's, then high-purity compounds still represent challenges for the 1970's. In the framework of a symposium on meaningful measurements, high-purity chemicals deserve consideration since compounds of adequate purity, or their dilutions or mixtures, represent a key apprrach to calibration standards and other reference materials.

The term "high purity" is a relative one. Some workers have elected to define a high-purity compound as having an overall purity or assay of 99.95 percent (w/w) or greater and a <u>total</u> impurity content of 0.05 percent or less, that is of 500 parts per million maximum. (Some authors prefer the term ultrapurity.) This definition is a limiting one. Chemicals with far smaller impurity content are needed and can be prepared. For many organic compounds, it may be noted, this definition is too restrictive because it is difficult to attain a purity of 99.9 percent for them.

This paper draws on the experience of one corporate team that has been attacking high-purity problems since 1967*. So far the production of over 95 high-purity chemicals has been achieved in lot sizes ranging from 1 to 250 kilograms. The team is sharing information and findings with interested groups and individuals, rather than working in secrecy. This commitment is indicated by the fact, that for high-purity chemicals, team members as of late 1973 had published or had in press 13 technical papers, 3 monographs, and 11 general papers and reviews, and had made over 17 major technical presentations.

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* The Advanced Materials (ULTREX^R) Team of the J. T. Baker Chemical Company as of April 1974 consisted of: F. W. Michelotti and C. A. McMenamy (Administration), M. K. Brandt, M. Zief, and J. Horvath (Purification), and A. J. Barnard, Jr., E. F. Joy, J. D. Brooks, N. A. Kershner, K. Little, and J. D. Bonn (Analytical Studies). The team was a 1970 winner of an <u>Industrial Research</u> Award for Technological Innovation.

The rationale of the team is that high-purity chemicals have diverse and increasing applications and that many findings may have spin-off value in the purification and the assessment of chemicals of either lower purity or special purity. Some of the early efforts were catalyzed by the reagent needs for the study of lunar samples in the Apollo programs, by the requirements of the National Bureau of Standards in its Standard Reference Materials program, and by some laboratory needs both for new standards and special reagents.

The three key parameters for high-purity chemicals are delineated in figure 1. In our view, there must be an interaction between preparation and analysis. When preliminary analysis indicates that the desired purity has been achieved, the product must be appropriately contained and stored so that its purity is protected. For some products, such as acids and other corrosives, it is imperative that the final analysis of a lot be undertaken only after final packaging. As pictured in figure 1, the success of the operation rests on the pivot of analysis.

Some of the purification techniques that have been applied successfully by the team are listed in Table 1. This aspect of our programs will not be elaborated on in this paper. However, attention is directed to the three monographs on purification and other techniques associated with high-purity substances edited by M. Zief. [1,2,3]

Table 1. Some Purification Approaches for High-Purity Chemical Programs

Complexation

Crystallization

Electrolysis

Fractional Distillation

Fractional Solidification:
   Column Crystallization
   Progressive Freezing
   Zone Refining

Ignition

Ion Exchange

Liquid Chromatography

Membrane (Pressure) Filtration

Precipitation

Preparative Gas Chromatography

Quartz Still Distillation

Solvent Extraction

Sublimation

Clean-Air Operations
   (Class 100)

II. Analysis of High-Purity Compounds

The assessment of a high-purity chemical, whether inorganic or organic, should not be based on a single analytical technique or on the determination of a limited group of impurities. Rather the assessment should be as broad based as feasible. In our view, the higher the purity of a chemical produced by a batch process, the more imperative is the evaluation of each discrete lot.

A. Parameters

The four parameters for the broad-based practical analysis of a high-purity chemical may be listed:

1. Conduct of general tests
2. Determination of the major constituent or the overall assessment of purity
3. Measurement of physical properties, and
4. Determination of minor and trace constituents

Some of the methods and techniques that fall within these classes are mentioned below.

The adjective "practical" should be stressed in the phrase "the practical analysis of high-purity compounds" to emphasize the economic factors that can influence the analytical approaches and strategies adopted.

B. General Tests

Our corporate analytical efforts are grounded on years of experience with the lot characterization of numerous laboratory-use and industrial chemicals. Many conventional tests and procedures can be readily adopted to high-purity chemicals by close attention to sample size and solution conditions and by minor modification.

This situation can be demonstrated by the general tests highlighted in Table 2. Here for various tests the limit of detection commonly realized in our work is listed with the associated sample size. [4-9] Note that the limits refer to the isolated compound and not to its solution. In brief, most of the detection limits for these relatively general tests are in the range of 0.5 to 5 parts per million (μg/g).

Our work toward an improved photometric determination of trace bromide in alkali metal chlorides is noteworthy. Advan-

Table 2. Detection Limits for Some General Tests (revised from ref. [7])

Determination	Sample size g	Detection limit µg/g (or µg/ml)
Ammonium (NH_4)[a]	1	5
Arsenic (As)[b]	5	0.05
Bromide (Br)[c]	2	0.2
Halide (as Cl)[d]	5	1
Iodide (I)[e]	2	0.02
Nitrogen compounds (as N)[f]	2.5	10
Phosphate (PO_4)[g]	5	1
Silicate (SiO_2)[g]	5	1
Sulfur Compounds (as SO_4)[h]	8	0.5
Acidity[i]	15	0.5[l]
Alkalinity[i]	15	0.5[l]
Ash (sulfated)[i]	5	20
Iodine-consuming substances[i]	5	0.5[l]
Loss on drying[i]	5	10
Particulate matter[j]	10	5
Residue after evaporation[k]	25	4
Residue after ignition[k]	10	2
Substances reducing permanganate[k]	5	5[l]

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[a] Direct nesslerization of solution of compound; visual comparison.

[b] Evolution of arsine and silver diethyldithiocarbamate photometry.

[c] Hypochlorite oxidation; bromination of rosaniline; photometry [8].

[d] Visual comparison of silver chloride turbidity.

[e] Kinetic analysis, cerate(IV)/arsenite system; photometry.

[f] Reduction with aluminum and sodium hydroxide: distillation; nesslerization of distillate; visual comparison.

[g] Heteropoly blue formation; visual comparison.

[h] Oxidation, methanol addition; visual comparison of barium sulfate turbidity.

[i] Ref. [9].

[j] Membrane filtration and gravimetry.

[k] [9].

[l] Values in microequivalents of acid, base, reductant, or oxidant per gram of sample.

tage is taken of the enhancement by chloride of the color development in the bromination of rosaniline. The range from 0.2 to 200 parts per million of bromide can be covered with a total sample size of 2 grams of the salt. [8]

C. Determination of Major Constituent or General Assessment of Purity

A direct determination of the major constituent in a high-purity chemical, that is, a compound with a purity of 99.95% or higher, requires a method reliable to about one part in 5,000 parts or better. At this level of reliability assay techniques are severely taxed. Some of the relevant approaches are listed in Table 3.

Table 3. Approaches for the Determination of the Major Constituent for High-Purity Compounds or the Overall Assessment of Purity

Coulometry

Differential scanning calorimetry (DSC)

Elemental organic analysis

Functional group analysis

Gas chromatography (GC)

Gravimetry

Liquid chromatography (LC)

Phase solubility analysis (PSA)

Titrimetry

Spectrophotometry

Of gravimetric procedures for assay purposes, those based on silver chloride precipitation are the most used. K. Little [10] has published full details of a highly reliable gravimetric determination of chloride that we have now applied to the assay of chloride salts and to the standardization of hydrochloric acid solutions. When all precautions are followed, the agreement between replicates can be within one part in five thousand or better.

To the art of <u>weight</u> titrimetry, we have added compleximetric titrations to a photometric end point. Details were published in a 1970 paper [4] concerning the purification and characterization of the important chelating agent (ethylenedinitrilo) tetraacetic acid (EDTA). Such titrations are applicable to the assay of high-purity forms of salts of multivalent metals. [11]

Another group of approaches to the assessment of purity involves measurement of a property of the major constituent that undergoes a change proportional to the mole fraction of impurities. The use of calorimetric measurements for this purpose became more practical with the introduction of differential scanning calorimetry (DSC). In the DSC technique, as the weighed samples (a few milligrams) undergoes a thermal transition, the instrument records the heat required as a function of the scanning temperature. The DSC curve (calories vs. time) can be analyzed in terms of the Van't Hoff equation and thereby a value for the molar impurity content can be derived. [12]

Our work on the extension of the DSC technique to high-purity compounds was reported in 1971. [13] Good agreement has been secured in favorable cases for polycyclic hydrocarbons between DSC purity values and gas chromatographic assay values. For some halogenated benzoic acids, used as microanalytical reference standards, good agreement has been obtained between DSC purity values and acid-base titration results. [13,14] The limitation of the DSC technique is its blindness, or at least partial blindness, to equilibrium solid solution formation; consequently the use of differential scanning calorimetry is not recommended [13] as the <u>sole</u> criteria of the purity of organic compounds purified by zone refining.

Elemental analysis of an organic compound by conventional techniques does not provide sufficient reliability to allow expression of a result as a precision assay value. The situation is pressing for nitrogen since many nitrogen compounds of biochemical importance are not sufficiently acidic or basic to allow their titration. Additionally, many of them melt, if at all, with decomposition, thereby ruling out differential scanning calorimetry. We have followed up on an idea of R. Paulson of the National Bureau of Standards and have developed a <u>precision</u> Kjeldahl procedure. [14] The precision achieved is improved by a factor of two to five over that by the conventional semimicro procedure. In this precision technique a sample corresponding to 25 mg of nitrogen is digested in a 30-ml Kjeldahl flask and steam distillation is initiated. The distillate for the first 10 minutes is collected in a known volume of standard hydrochloric acid, which is chilled. Then the absorber is changed to one containing boric acid solution and the distillation is continued for 6 more minutes. The first absorber is swept with air to remove carbon dioxide and a back-titration is performed with equal increments of standard sodium hydroxide solution. pH values are recorded and the end point is calculated from second differences. (The acid and base used are compared under conditions identical to that in the first absorber in the titration of samples of primary standard 2-amino-2-(hydroxymethyl)-1,3-propanediol(tris) corresponding to 25 mg of nitrogen.) Any residual ammonia caught in the second absorber is titrated with sodium hydroxide using a mixed indicator. The amount of ammonia in the second absorber seldom exceeds one-five hundreth of the total and is usually less than one thousandth. We are applying the technique to a variety of high-purity standards and the findings for a few compounds are summarized in Table 4. Note that for these samples the standard deviation of the mean for the assay ranges from ± 0.03 to ± 0.07 percent.

Table 4. Assay of High-Purity Nitrogen Compounds via Precision Kjeldahl Nitrogen Determination (5 determinations each sample)

Compound and Sample Description	% Nitrogen, mean ± S.D. of mean	% Assay, mean ± S.D. of mean
Urea, Ultrex, UCS 209	46.643 ± 0.031	99.99 ± 0.07
Urea, exptl., AK-47-1	46.630 ± 0.016	99.97 ± 0.03
Creatinine, Ultrex UCS 210	37.111 ± 0.015	99.90 ± 0.04
Amm. Phosphate, Monobasic, Ultrex, UMO 477	12.135 ± 0.006	99.97 ± 0.05

D. Measurement of Physical Tests

Some of the physical properties that we view [4,6,7] as useful in the assessment of one or more high-purity chemicals are listed in Table 5. In general, the use of physical properties is more valuable for organic compounds. Most of the properties listed have been used by one or more companies or compendia in the assessment of conventional products and little additional advance has been secured.

Table 5. Physical Properties Useful in the Assessment of High-Purity Chemicals

Boiling point
Critical solution temperature
Density
Electrical conductivity
Half-wave potential
Heat of fusion
Melting point
Molecular weight
Optcal and X-ray crystallography
Osmolality (of solutions)
Particle size
Refractive index
Solubility
Solvent partition ratio
Specific rotation
Spectra (fluorescence, infrared, NMR, uv/vis)
Spectral maxima and absorptivities
Surface area
Reaction temperatures

For organic liquids, low-level electrical conductivity measurements have proved valuable. Some hydrocarbons prepared by either preparative gas chromatography or fractional freezing [3] appear purer than previously offered as standards. Additionally the moisture can be brought to extremely low level and be maintained so by dry-box operations. Since literature values for the electrical conductivity of a given liquid can range over one or more orders of magnitude and since in our hands lower conductivity values than previously reported have been secured, we have used the technique largely for the specification of minimum purity and to assure that some blunder has not occurred.

Early in our program 8-quinolinol was needed for trace metal enrichment procedures. A reagent extremely low in multivalent metal content was required. We were studying the purification of this compound, when a paper by Eckschlager and coworkers [15] came to our attention. On purification by both zone refining and sublimation, absorbance in ethanolic solution in the region 410 to 600 nm was found to be decreased markedly. This is a region in which many chelates of 8-quinolinol show strong absorbance. We have confirmed Eckschlager's findings and have established that the decrease in absorbance does parallel a reduction in the content of key multivalent metals established by wet ashing and emission spectrography. Absorbance measurements at several wavelengths have therefore afforded a simple and reliable index to purification. Lots of 8-quinolinol have now been achieved with a total multivalent element content at or below a few parts per million.

E. Determination of Minor and Trace Impurities

Approaches to the determination of minor and trace constituents are listed in Table 6. We believe that the listed techniques can be valuable in the practical assessment of impurities in one or more inorganic or organic compounds of high purity.

Table 6. Approaches for the Detection and Determination of Minor and Trace Constituents of High-Purity Chemicals

- Activation analysis
- Atomic fluorescence
- Chromatography:
  - column
  - gas
  - liquid
  - paper
  - thin-layer
- Emission spectrography
- Fluorimetry
- Kinetic analysis
- Mass spectrometry
- Nuclear magnetic resonance
- Paper electrophoresis
- Photometry:
  - atomic absorption
  - cold-vapor atomic
  - flame emission
  - infrared
  - solution
- Polarography
- Ring-oven techniques
- Spot & other identification tests
- Stripping analysis
- Turbidimetry
- X-ray fluorescence spectrometry

A few remarks on the assessment of trace element contents is appropriate. In high-purity forms of compounds, trace elements must be detected or determined below the parts per million level. In such trace analysis, close attention to blanks is imperative to reduce their magnitude and, especially, their variability. Clean-air conditions must be considered for all transfers and virtually closed systems for many operations. Specially purified reagents are often required and their preparation is an important part of our high-purity program. [3,4] Laminar flow chambers and laminar flow fume hoods are appropriate for may operations and for transfers.

Many chemists have overlooked the merits of the Thiers assembly [16] illustrated in figure 2. It might be termed the poor man's clean room. By passage of a high-purity gas through a membrane filter into the side arm, the sample preparation is maintained in a clean-air environment. Heat is supplied from above by infrared radiation and from below by a hot plate. The use of this simple expedient can reduce blanks substantially in such operations as wet digestion, evaporation, and pre-ashing. Where hydrofluoric acid is involved, the assembly can be fashioned from plastic. [17]

In our hands, emission spectrography has proved to be the single most important method for the evaluation of trace elements. By use of the recently introduced five-level standards with an internal standard up to 40 elements can often be determined with modest investment of staff time. To improve the spectrographic detection limits, we resort to various enrichment techniques, including collection, extraction, volatilization, and crystallization. [18,19] For such enrichment procedures, sample sizes of 1 to 10 grams are often appropriate.

III. Uses of High-Purity Compounds Other Than as Standards

A variety of uses have been realized for the high-purity compounds developed in our programs. Some applications, other than as standards, are delineated in Table 7 with examples. It will be noted that the uses cover the spectrum of the laboratory and extend to advanced technologies and to materials research.

Table 7. Uses of High-Purity Chemicals
Other Than as Standards

Reagents

Acids: HCl, $HClO_4$, HF, HNO_3, HOAc, H_2SO_4, P_2O_5

Bases: Li_2CO_3, Na_2CO_3

Fluxes: $CaCO_3$, Li_2CO_3, Na_2CO_3, P_2O_{55}

Buffers: HOAc, K Biphthalate, KH_2PO_4, K Citrate, Na_2CO_3, $NH_4H_2PO_4$, NH_4OAc

Others: EDTA, 8-Quinolinol

Biochemical & Nutritional Research

Trace Element Research: KH_2PO_4, KBr, KCl, NaCl

Others: Cholesterol, EDTA, Glycine, Sugars, Urea

Electronics & Materials Science

Semiconductor Dopants: BBr_3, CrO_3, $POCl_3$, P_2O_5, PCl_3

For "Laser Glasses": B_2O_3, $CaCO_3$, Li_2CO_3, Na_2CO_3, SiO_2

For Single Crystals: Zone-refined Hydrocarbons

Others: KBr, KCl, Metal Oxides & Carbonates, NaCl

Optical fiber communication is an area of extremely active research. For long-distance application, the glass from which the fiber is drawn must be virtually free of elements absorbing significantly in the wavelength region of the laser or other source. This requirement implies that each of the transition elements (Cr, Co, Cu, Fe, Mn, Ni, V) should be present, if at all, at a maximum of 10 to 50 parts per billion (ng/g) and that the total transition metal content should be less than 100 parts per billion. Our team has been working with advanced groups in the communication field toward the synthesis of high-purity and special purity compounds that can be fused to form such low-attenuation glasses. For most of the proposed glasses, silicon dioxide is a major component. In late 1973, a general offering was announced by J. T. Baker of silicon dioxide of extreme purity and in a granular form. The text of the certificate of analysis of a typical lot appears in Table 8.

A direct chemical assay is achievable for silica, only with difficulty; consequently, the overall assessment of purity is based on the loss of ignition and the residue after volatilization with hydrofluoric acid. To define the impurity content in the terminology of the electronics industry, the purity has also been expressed conservatively as "5N" in terms of the spectrographically detectable elements, less boron.

It will be seen that lot values are provided for 25 elements. Boron is determined by direct d.c.-arc emission spectrography. Sodium is determined by atomic absorption spectrometry after hydrofluoric acid volatilization of silica. For the remaining metals, silica is volatilized in a laminar flow fume hood using ultrapure hydrofluoric acid, prepared by subboiling distillation in Teflon, and high-purity perchloric acid, prepared by quartz still vacuum distillation. In the evaporation, graphite is added as a carrier and matrix. Sodium chloride is also added and the resulting sodium content serves to enhance the emission lines of the transition metals and certain other elements. The residue is subjected to d.c.-arc emission spectrography under total burn conditions and the plate is read against a multielement standard in graphite. [19] The sample and blank determination are run in at least duplicate. Since transition elements are of special importance in the use of this produce, it is noteworthy that their total content is below 50 parts per billion.

The product is offered in acid-leached borosilicate containers packaged under argon. The product is intended to be opened and to be used under clean-air conditions.

This recent product addition serves as an excellent example of what can be achieved for a high-purity compound, namely, a high degree of purification supported by broad-

Table 8. Actual Analysis for a lot of Silicon Dioxide for Preparation of Low-Attenuation Glasses for Optical Fiber Communication

(ULTREX Lot 329183)

Assay (SiO_2) based on loss on ignition and nonvolatile with hydrofluoric acid)	> 99.0 %
Purity (based on spectrochemically detectable impurities)	5 N[a]
Loss on ignition at 1150 °C for 1 Hour	0.94 %
Nonvolatile with Hydrofluoric Acid	0.001 %

NON-METALLIC IMPURITIES - in parts per million (ppm)

Boron (B)[b]	< 5	Sulfate (SO_4)	< 1
Chloride (Cl)[c]	2		

METALLIC IMPURITIES[b] - in parts per million (ppm)

Aluminum (Al)	0.02	Manganese (Mn)	0.003
Barium (Ba)	< 1	Molybdenum (Mo)	< 0.001
Bismuth (Bi)	< 0.001	Nickel (Ni)	0.002
Cadmium (Cd)	< 0.01	Niobium (Nb)	< 0.001
Calcium (Ca)	0.05	Potassium (K)	< 0.05
Chromium (Cr)	0.02	Silver (Ag)	< 0.0005
Cobalt (Co)	< 0.001	Sodium (Na)[d]	8
Copper (Cu)	0.002	Strontium (Sr)	< 0.01
Iron (Fe)	0.02	Titanium (Ti)	< 0.001
Lead (Pb)	0.001	Vanadium (V)	< 0.001
Lithium (Li)	< 0.1	Zinc (Zn)	0.02
Magnesium (Mg)	0.02	Zirconium (Zr)	< 0.005

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[a] In terms of spectrochemically detectable impurities, disregarding boron, purity is 99.999%, that is, 5N or 5-9s.

[b] Average value for duplicate samples analyzed by DC-arc spectrography (boron directly reading against standards in graphite; other elements after concentration by evaporation with addition of water, graphite, sodium chloride, and hydrofluoric acid); against commercial standards in graphite with added sodium chloride, reading of lines in 2450-3875 A region; elements found at or below a significant blank value are reported as < (equal to or less than) one-third of the blank; elements found at or below a blank value near the detection limit are reported as < (less than) the detection limit.

[c] By AgCl turbidimetry of water leachate of finely ground product.

[d] By atomic absorption spectrometry.

NOTE: Due to the method of preparation, this product is granular and may contain occasional black specks, which are pure carbon and do not contribute to the metallic impurity content.

based analysis of each lot, and the use of suitable, non-contaminating containers.

IV. Use of High-Purity Compounds as Standards

Most analytically defined high-purity compounds can find use as standards. Table 9 lists such applications for constitutional analysis and cites examples drawn from our team efforts. Some of our work in this area has been in support of the efforts of the National Bureau of Standards and of various professional groups that have defined needs for added and improved standards.

Table 9. Some Uses of High-Purity Chemicals as Standards

For Spectral Methods: $CaCO_3$, KCl, Li_2CO_3, LiCl, Na_2CO_3, NaCl, other Metal Salts

For Organic Elemental Analysis:
- for C/H: Anthracene, Benzoic Acid, Biphenyl
- for C/H, Halogen: *m*-Cl-, *p*-F-, *o*-I- Benzoic Acids
- for N: $(NH_4)_2H_2PO_4$, 8-Quinolinol, Sulfamic Acid, Urea
- for P: Diphenylphosphinic Acid
- for S: Benzyl Disulfide, Sulfamic Acid

For Titrimetry: Benzoic Acid, $CaCO_3$, EDTA, Na_2CO_3, K Biphthalate, NaCl, Sulfamic Acid, tris

For Clinical Lab.: $CaCO_3$, Cholesterol, Creatinine, Dextrose, Glycine, KCl, KH_2PO_4, Li_2CO_3, $Mg(OAc)_2$, Mg Gluconate, $(NH_4)_2SO_4$, NaBr, NaCl, Urea, Uric Acid

For Gas Chromatography: Various Organic Compounds

In the offering of a standard, the limitations of the user are sometimes overlooked. He must be provided with adequate information as to the handling and use of a standard and he must have adequate training to apply that information. These considerations can be pressing when a standard is to be applied by persons with limited appreciation of the art of weighing, diluting, and transferring a standard quantitatively. Our experience in the offering of high-purity compounds for use as clinical laboratory standards is revealing. We found it necessary to make available a bulletin on the preparation of stock and working standards for about 10 key clinical laboratory standards that presented procedures in such minute detail that little previous knowledge is required of precision weighing and volumetric techniques. [20] The implications of this example to other disciplines should be obvious.

The user should also be considered in the selection and recommendation of a standard. An example from clinical analysis is instructive. For the determination of serum magnesium, a variety of standards have been recommended. All in common use have limitations for application in the clinical laboratory. Magnesium metal must be acid washed to remove the oxide film, be water rinsed and dried, and then be dissolved in acid without losses. Magnesium oxide of high assay requires extreme precautions in its weighing and transfer due to its pickup of moisture and carbon dioxide. Magnesium acetate trihydrate is difficult to obtain in exact stoichiometry; however, it undergoes increase in weight on exposure to moist air at such a rate that some precautions must be taken in its weighing and transfer. Zief and Varnard of J. T. Baker and Rains of the National Bureau of Standards have recently proposed [21] magnesium gluconate as the standard for the atomic absorption determiation of serum magnesium. This salt has a favorable weighing factor ($FW_{Mg}/FW_{compd.}$ = 0.05393) and is preparable with exact stoichiometry, high assay ($\geq$ 99.9 percent) and low impurity content (e.g., calcium, <45 ppm). This salt takes on moisture only slowly (ca. 0.2 percent over 40 minutes at 50 percent relative humidity), and has a favorable solubility in water and in the presence of acids or bases up to pH 11. The gluconate anion has no influence on the flame characteristics of magnesium. These combined properties make magnesium gluconate dihydrate extremely promising for use in the clinical laboratory. Introduction of a high-purity form of this compound as a NBS Standard Reference Material for serum magnesium is planned.

V. References

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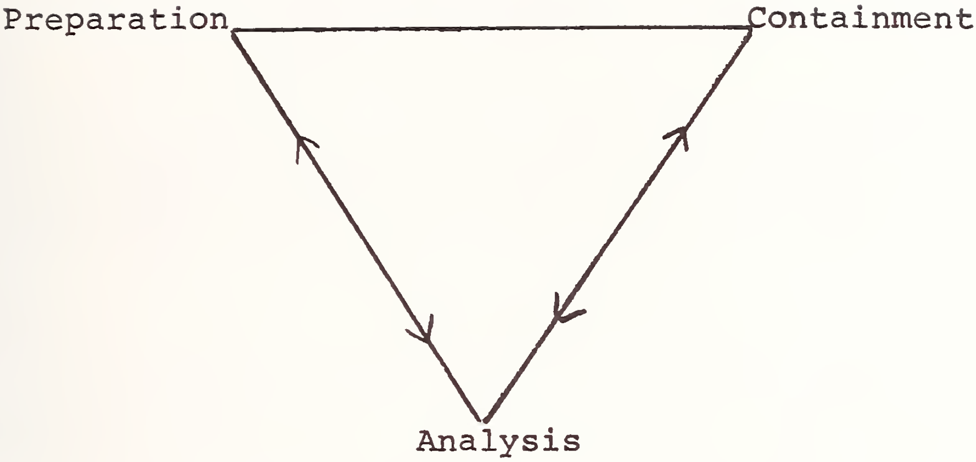

Figure 1. Interrelation of Key Parameters for High-Purity Chemicals

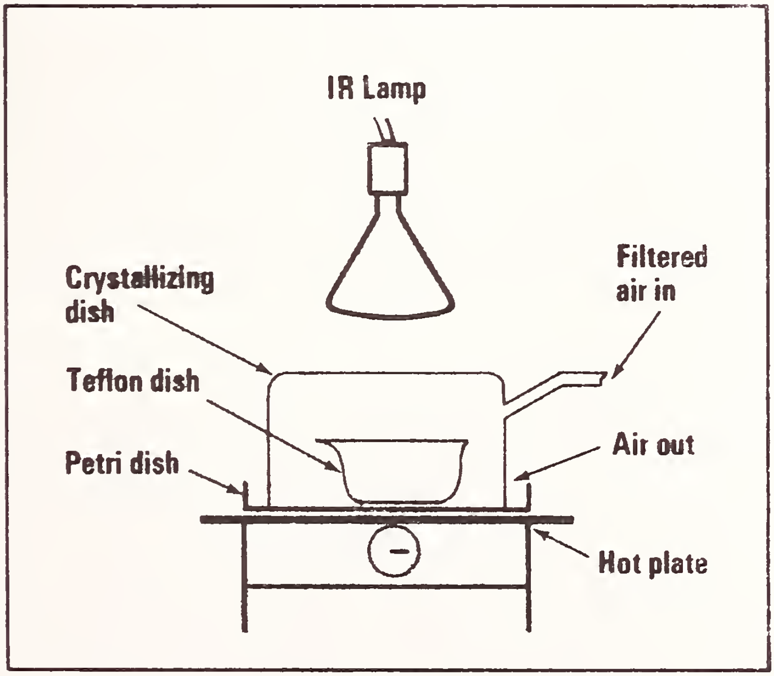

Figure 2. Chamber for Drying or Pre-ashing after Thiers

INDUSTRIAL SRM NEEDS AND MEASUREMENT PROBLEMS IN INORGANIC MATERIALS: CHEMICAL PROPERTIES

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Introduction

The purpose of this paper is to survey needs for standard reference materials (SRM's) in the inorganic chemical industry, especially as such needs are related to the chemical properties of raw materials, intermediates, and final products of the industry. Metals and ultra-pure substances, which are covered elsewhere in this symposium, will not be included except for illustrative purposes. The need for SRM's will be discussed in terms of the changing requirements and qualifications of SRM users, the development of instrumental analysis, and the economic ability of the industry to support a standards program.

Under a given set of physical and chemical conditions the chemical properties of a pure element or compound are constant and are based upon the capacity of the substance to participate in, or to resist, chemical change. Chemical change is a concept that is not clearly defined in elementary textbooks; it involves the interaction of atoms or molecules in other than a simple physical way, such that the species produced are chemically different from those originally present.

The chemical properties of an impure substance or of a mixture are functions of its chemical composition and the physical states of its components. For example, lead containing a trace of elemental magnesium is much more rapidly oxidized by air than pure lead. On the other hand, zinc alloyed with a little magnesium becomes more stable. Hydrochloric acid containing dissolved arsenous oxide is less corrosive to iron or steel than pure acid. Glasses vary widely in resistance toward leaching by water, depending upon their chemical compositions, but in any case the leaching of a glass proceeds more rapidly on finely ground particles than on a solid mass.

The chemical composition of a material depends upon the substances from which it was formed and the reactions involved in its preparation or later treatments. The physical state depends upon both its chemical nature and the conditions to which it has been subjected up to the time of testing or use.

For the above reasons, measurement problems related to chemical properties usually occur in connection with the study of chemical composition, the latter including also the physical states of the components. This field, the precise specification and determination of chemical composition in its broadest sense, is the province of the analytical chemist. In considering the need for standard reference materials in the inorganic chemical industry, then, one must be concerned with the needs of industrial inorganic analytical chemists.

The Need for Standard Reference Materials

The uses of, and consequent necessity for, standard reference materials in general have been ably presented by a number of authors. [1-9] Their views may be summarized in the following statements: Accurate information about any chemical or physical system can be presented only in quantitative, numerical, terms under a consistent system of units. Fundamentally the data should be referable back to primary units of mass, length, time, and temperature. [9] In the case of chemical composition, information is expressed as concentrations, in terms of the mass of a component per unit total mass, or in terms of mass or volume per a derived unit of volume (L^3). Here it is not necessary to relate back to the primary units in each analysis, if a suitable reference material is available for standardization of the measuring method employed.

A distinction may be made between pure standard substances and reference materials, which are actually mixtures, of certified composition. Pure elements and compounds are needed as standards for testing physical properties and for the preparation of standard solutions to be used in various types of analysis. Such solutions can be used for reference both in classical analysis (gravimetric and titrimetric) and in various kinds of instrumental analysis (spectrophotometric, potentiometric, polarographic, radiometric, etc.). This kind of standardization is indispensible in the laboratory, but it does not necessarily indicate how a method of analysis will perform when applied to a mixture of substances. A material other than the one being determined may cause either direct interference, by being included in the measurement, or a matrix interference, in which it may either hinder or enhance the response of the measuring method to the substance sought.

Both direct and matrix interference may be tested for by using mixtures of pure compounds. In practice, however, this might require testing the purity of a number of materials for a single analysis. It is much more economical to have available a reference material of certified composition similar to the sample under examination. The needs of the inorganic chemical industry for such certified materials (SRM's) will be elaborated further in subsequent sections. Ultimately, however, the need for standards depends upon the need for accurate information about chemical composition, which in turn rests upon the needs of consumers for products, whether for food, shelter, transportation, information, comfort, convenience, or recreation, that perform as they should.

The Changing Qualifications of Analytical Chemists

When the senior author was an undergraduate student some 45 years ago, one of the popular courses in chemical engineering included a series of trips to inspect industrial plants. It was apparent in many of the establishments of those days that the laboratory was in charge of a man who had begun his career as a sample boy or lab helper and whose only analytical training had been received from his predecessors in the organization. He was skilled in the performance of particular routine analyses but was not likely to have a ready answer to a previously unasked question. Such advances as were made in his art were usually incorporated slowly, diffusing from one lab to another. Under those conditions there was a real need for standards by which to check the performance of personnel and the reliability of new procedures. Sample No. 1 in the list of SRM's issued by the National Bureau of Standards was an argillaceous limestone, probably prepared initially for use in the metallurgical and cement industries.

Through the years there have been marked changes in the training of analytical chemists. High levels were reached at several stages. Perhaps the first and most significant one was brought about by a realization that the methods employed in analytical chemistry are based upon the principles of physical chemistry. A person who had studied chemistry because of his interest in chemicals, who had mastered the practical skills necessary in volumetric and gravimetric analysis, and who then acquired a strong fundamental background in physico-chemical principles, became best qualified for either teaching or contributing to the industrial development of analytical chemistry. This led to a great emphasis on the study of physical chemistry courses by students of analytical and inorganic chemistry.

High points for training in inorganic analysis were stimulated by the renaissance in inorganic chemistry associated with nuclear energy, the space program, the introduction of semi-conductors, and the corresponding need for exotic materials to be used in those fields. Parallel with these came developments in instrumental methods of analysis which offered much in the way of time-saving and in the ability to yield analytical information that could previously be obtained only with great difficulty, if at all.

Meanwhile, however, there arose a trend which now appears unfavorable. On one hand, emphasis on the importance of theoretical training reached back into high schools and students failed to become curious about chemicals themselves, thinking that chemical behavior could be predicted entirely by theoretical calculations. On the other hand, it became difficult to find time in college curricula for sufficient training in fundamental analytical practice, descriptive chemistry in all basic branches, physical chemistry, and instrumental methods. As a result, many institutions gave up the teaching of analytical chemistry except as it could be incorporated into other elementary courses or into courses on the theory of instrumental methods. Research programs were centered on fundamental phenomena, usually in terms of simple and very dilute systems, and graduates tended to become specialists in a particular technique, with little knowledge of the requirements of industrial chemistry in the real world.

Fortunately the latter trend seems to be changing. Problems with the environment are bringing academic scientists into contact with the analysis of things as they are, where interferences are the rule and accuracy depends upon representative sampling, clean separations, reliable manipulation, avoidance of contamination, and finally, meaningful measurement. A prominent professor recently told of having requests from more than a dozen institutions for doctoral graduates to teach analytical chemistry. Regrettably he did not have that many to recommend. It will take time to restore a proper balance in the curricula available to students planning to enter the analytical profession. Meanwhile, frequent reference to standard samples is necessary to improve the reliability and bolster the confidence of workers in the field.

Changing Requirements in Chemical Analysis for Industry

At one time the main tools of the analytical chemist were a balance and weights, pipets, burets (spelled with two e's and two t's), beakers, flasks, and funnels. Such trace analysis as was done required only Nessler tubes, though eventually the visual colorimeter was introduced. Most analyses involved considerable elapsed time and the results were utilized as matters of record rather than for process control.

With the advent of larger scale production and continuous processes, much pressure was placed upon industrial chemists to obtain results more quickly. Manual methods of considerable speed were developed in the iron and steel industry, and pH control was provided in chemical works, sugar processing, and elsewhere. Some of the faster methods depended upon shortcuts requiring the use of calibration standards to offset inherent errors. Frequently the demand for standards was satisfied by using previously analyzed samples, but recognition of the importance of greater reliability led to the involvement of the National Bureau of Standards and the issuance of many standard samples, particularly for metallurgical industries. Most of these samples were certified after thorough analyses by both NBS and industrial chemists in cooperative programs, often arranged through ASTM committees.

Recognition of the speed and sensitivity of spectrography led to its wide adoption as the first prominent physical method of chemical alalysis. In metallurgy it enabled rapid process control and the recognition of trace metals as beneficial or harmful to certain properties of the product. Matrix effects in spectrographic analysis were noticed early [10] though not called by that name at the time. The success of spectroscopic methods, when properly calibrated, stimulated the development of other physical methods. We now have many from which to choose: x-ray diffraction, emission, absorption, and fluorescence, U.V., visible, and IR spectrometry, NMR, mass spectrometry, electrochemical methods, neutron activation analysis, and the various types of microscopy, to mention the more prominent techniques. Each has its own advantages and shortcomings, among which are direct interferences and matrix effects. Frequently the best way of deciding which technique should be used, or of correcting for errors, involves the use of an SRM. Methods of calculating matrix corrections for given cases are available, but should always be checked against known standards. For example, at least forty papers in the literature, only a few of which are cited here [11-18], deal with matrix effects in x-ray fluorescence analysis. Presumably each paper which discloses a method of calculating matrix error represents some improvement over those published earlier. However, one cannot yet be sure that accuracy is attainable in all situations. Any data obtained through a calculated correction should be confirmed experimentally by reference to materials of known composition, preferably to two SRM's that bracket the unknown.

Demands upon analytical laboratories have not been for speed alone, but also for determinations of smaller and smaller concentrations of impurities. Most industrically important inorganic chemicals have several uses, in one or more of which a certain kind of impurity may be objectionable. Specifications for the compound may differ according to the use. Thus a lot destined for shipment to a food processor likely falls under requirements of the Food Chemicals Codex, [19] while one for a pharmaceutical or drug manufacturer should meet USP specifications. [20] Many compounds are covered by specifications of ASTM and other standards organizations, and requirements for analytical reagents are published by the American Chemical Society's Committee on Analytical Reagents in its book Reagent Chemicals. [21] Furthermore, federal agencies as well as institutional and commercial purchasers frequently call for conformance to one or more of the foregoing organizations' requirements. The tendency of each specification-setting group is to establish tighter limits for impurities, either because of particular substances being found harmful or as part of a general quality improvement objective. The overall result is that analytical chemists in the industry have to use more sensitive methods and be able to handle a wider variety of problems. In order to be assured that the methods and conclusions of the chemists are reliable, quality control inspectors are likely to call for tests on SRM's.

Commensurate with the general need for determining and minimizing undesirable trace impurities is the more specific need in many cases for controlling additions of desirable substances. Such substances may be trace elements beneficial in fertilizers or foods, or they may be required as inhibitors, catalysts, or other property modifiers. Probably the extreme example is that of electronic components, where "doping" may be done at levels too low to determine by any method except testing for the property involved. In some instances a limiting factor in analyzing for trace additives may be the purity of reagents used for dissolving the samples. Preparation of ultrapure acids for such purposes has been described by NBS workers. [22] The Bureau is also active in developing SRM's that are very useful for comparison purposes in trace analysis. Those already available are glasses of the 600 series and biological standards of the 1570 series. [23]

Environmental considerations have led many industrial as well as government and academic laboratories into new analytical areas as well as into new demands upon the sensitivity of their testing methods. Not only manufacturers, but also users of inorganic chemicals are faced with reducing pollution from certain elements as more knowledge becomes available about their effects in water, marine life, soils, plants, land animals, and birds. The problem arises from the fact of an increasing population coupled with limited water and air resources, and involves also the economics of pollution control versus possible changes in the utilization of chemicals. Whatever course is followed in a particular case should be based upon dependable analytical data as well as reliable information concerning the bio-accumulation tendency and toxicity of the element in question. Elements of current or potential concern as water or soil pollutants include lead, copper, cadmium, chromium, mercury, arsenic, antimony, selenium, phosphorus, and radioactive isotopes of several others. Inorganic substances of concern in air include most of those mentioned plus sulfur dioxide, nitrogen oxides, beryllium compounds, asbestos, and silica dust.

In a number of cases it is not sufficient merely to determine that an element is present in a certain concentration, because the hazard which it presents may depend upon the form in which it occurs. For example, methyl mercury in a food is considerably more toxic than elemental mercury or mercurous chloride. Chromate is more objectionable in water than trivalent chromium, which is easily coprecipitated with iron or aluminum and becomes inert in sediments. Beryllium oxide which has been heated to a very high temperature is relatively harmless if inhaled as a dust, while unignited oxide is extremely damaging in the lungs. Presumably different varieties of asbestos differ in their biological effects, and in any case it is important to be able to distinguish between asbestos and diatomaceous materials that appear similar under the microscope. Such factors must lead analytical chemists and biochemists into studies in terms of the concentration of each individual or mineral subspecies rather than the total concentration of an element or mineral regardless of its condition.

Moreover, laboratories in the inorganic industry are expected to be qualified to handle samples of much wider variety now than in former years. It is not uncommon to receive samples of urine, blood, milk, oils, fats, muscle tissue, or organs to analyze for trace elements. Almost any conceivable type of SRM that might be issued by the Bureau of

Standards is likely to find a use in a modern laboratory at some time. The more unusual a sample may be to an analyst, the greater is his need for a corresponding reference material.

The trend toward automation of analyses calls for a somewhat different application of SRM's. Because SRM's are expensive and are generally furnished in rather small quantities, they are not practical for use in on-line calibration. It is best, when analyzing solutions, to prepare a large quantity of solution from a compound of known purity and to employ this for the routine standardization of the instrument. Assurance that both the standardization and the application of the instrument to a certain type of sample are satisfactory can then be gained by analysis of an appropriate SRM at infrequent intervals. Linearity of response can be checked by using various quantities of the standard solution or by preparing dilutions of it.

Ability of the Industry to Support a Standards Program

According to the U.S. Census of Manufacturers, [24] the value of industrial chemicals produced domestically in 1971 was $17.8 billion. Approximately 40 percent of this, or $7.1 billion, could be attributed to inorganic materials. Tables 1-5 give data, obtained from the U.S. Bureau of Mines, [25] Chemical and Engineering News, [26] or other sources, on the magnitude and value of annual production of various inorganics. The figures have been rounded off and in some cases recalculated in order to harmonize the units.

As a rough rule of thumb, one may consider that the cost of analysis in the inorganic chemical industry is about one percent of the value of the product. This is admittedly an uncertain average, for the percentage may well vary somewhat inversely with the volume of production. Furthermore, it would not include the cost of analyses made in connection with research on new products. However, if the figure can be used, it would indicate annual analytical costs of well over $71 million in 1973, which was a much better year for inorganic production than the two years preceding.

One may further consider that a three percent fraction of the cost of analysis would not be an unreasonable price to pay for standards designed to assure that the analytical results are reliable. At this rate, an investment of over $2 million per year, nationally, for development of reference standards for use in the inorganic chemical industry would appear justified. Cali [27] has estimated that the cost of preparing and certifying one SRM may exceed $100,000 for some of the more complicated materials. Probably most others could be processed for less than $100,000 each. Hence it would seem likely that at least 20 new inorganic standards could be issued per year without straining the resources of the industry. If the supply of each standard is planned to last for 10 years, a stock of at least 200 inorganic SRM's could be maintained.

Considerations of this kind may not tell the entire story, for the data used are not necessarily complete and some assumptions may be questionable. For example, imports of several of the listed raw materials far exceed the domestic production, and analyses of the imports are needed too. Again, the figure of $7.1 billion for all inorganic chemicals does not include the value of metals and alloys. Many of the inorganic standards are useful in metal analysis, and vice versa. If a conclusion can be drawn from this section, it is that industry can well afford to pay for the costs of certifying the standards that it needs, and that the certifying body is justified in charging for the standards at rates that will fully recover the costs.

The Availability of SRM's, and Additional Needs

Tables 1-5 also indicate whether or not NBS SRM's corresponding to the various commodities are available. Examination of the tables reveals that more emphasis has been placed on issuing standards for raw materials than for finished chemicals. This was probably logical in view of the generally greater complexity of analyzing raw materials in the past. It is also apparent, with some exceptions, that the major effort has been to supply standards for the industries having the largest production rates. Since metals and alloys are not covered in this paper, the numerous SRM's available for their control are not included in the tables.

NBS Special Publications 260 and 260-30 [references 23 and 8] present complete lists of the standards issued by NBS and by the metrological institutes of the USSR, respectively. Several other countries have institutions that offer analyzed or certified samples and that will furnish lists upon request. NBS, ASTM, and perhaps other organizations have started projects that hopefully will lead to consolidated lists, cooperation to avoid duplication of effort, and a more complete selection of reference materials in the future. A catalog of physicochemical standard substances available in nine reporting countries has been compiled by an IUPAC committee. [28]

Analyzed rock samples are frequently useful as standards for inorganic analysis. Complete lists of available samples, analyses, and sources have been published by F. J. Flanagan of the U.S. Geological Survey. [29-31]

The lack of standard samples corresponding to many of the chemicals listed in tables 3-5 indicates the possibility of unmet needs in those areas. Emphasis on some specific needs is given in the appendix to the NRC-NAS report on reference materials. [4] In the absence of standards, personnel of industrial laboratories frequently resort to the use of collaborative samples developed and analyzed among themselves. The existence of ACS reagent grade chemicals and a few ultrapure reagents is helpful in preparing such samples. Unfortunately the results of the work are seldom published and the samples are usually prepared in quantities too small for general distribution.

Chlorine is one element that would likely stand out in any listing of inorganic substances for which standards and both reagent and ultrapure grades are lacking. It is widely used in industrial syntheses and bleaching, as well as for water purification and sewage sterilization. A proposed specification of the Food Chemicals Codex would allow a non-volatile residue of 150 ppm, but most commercial chlorine should be well under that limit. Consideration by NBS of the need for a standard with identified typical impurities would seem to be justified.

A general need in the chemical industry is for standards that correspond to corrosion products of metal alloys commonly used in piping and equipment. Frequently it is necessary to identify the source of such materials when they are found in plant streams or final products, as trace impurities. SRM's containing oxides or chlorides of the various metals, usually high in iron, would be useful in emission spectroscopy, atomic absorption, x-ray diffraction and fluorescence, and microprobe analysis.

Two widely used compounds shown above as lacking standards are sodium chloride and hydroxide. The former is commercially used as a raw material in the form of rock salt or solutions thereof, produced by hydraulic mining. It would be desirable to have a typical rock salt analyzed for impurities and certified as an SRM. Results of a thorough study would also be important inasmuch as rock salt is commonly employed for the regeneration of ion exchange media in water softeners, where there is a probability of impurities entering the water supply. Availability of a table salt certified for iodide content should also be useful. Industrial sodium hydroxide is sold in several solid forms and also in solutions of various concentrations, the impurity contents varying with the methods of preparation and treatment. Typical impurities might be chloride, chlorate, sulfate, and organic matter in products from diaphragm cells and traces of mercury in products from mercury cells. While sodium hydroxide is not a stable enough compound for use as a standard, it should be possible to prepare a sodium carbonate with known impurities to serve the same purpose.

Natural limestone used as calcium carbonate for addition to foods and drugs contains several impurities including fluoride. It would be convenient to have a fluoride analysis certified for one or more of the NBS limestone SRM's, for corroboration of results obtained with fluoride-selective electrodes.

With the increasing importance of low grade iron ores, an SRM such as taconite would seem to be desirable.

A good start has been made on supplying SRM needs in environmental analysis, with the trace element standards in both glasses and biological media, mercury and sulfur in coal, sulfur in fuel oils, lead in paint, three levels of carbon dioxide in nitrogen, six levels of oxygen in nitrogen, and permeation tubes for sulfur dioxide. A need may arise for carbon monoxide in air or nitrogen at several levels. Nitrogen oxides present a difficult problem because of their reactivity, but if atmospheric limits are to be tightened and enforced, calibration procedures and reference materials will be necessary. In water analysis, a standard siliceous-type sediment material analyzed for trace elements would be helpful.

In air analyses for particulate matter (aerosols), where the solids are collected on filter papers or other membranes and analyzed by either classical or physical methods; SRM's consisting of known micro quantities of inorganic materials on individual membranes would be especially useful.

Conclusions

The authors hope the thoughts in this paper will serve to convince readers that standard reference materials have an important place in laboratories associated with the inorganic chemical industry, that those standards that are already available are being used, and that needs exist for many others. It should also be clear that the economic base of the industry is capable of supporting a broader standards program.

It would be inappropriate to conclude the paper without expressing the gratitude of industrial chemists to all those workers at the National Bureau of Standards who have contributed to the development of SRM's. Their painstaking efforts have resulted in exceptional analytical accuracy and have contributed much toward improving the accuracy and precision of the rest of us. We should also take note of the valuable information gained and disclosed by Bureau scientists in the course of their studies. Long ago one of us pointed out [32] that in using standard substances, the conditions under which they are applied demand as much consideration as their purity. One example given was the titration of sodium oxalate in acid solution with potassium permanganate. This titration is reliable only if carried out under conditions established by chemists at the Bureau who had collaborated on the development of sodium oxalate as a standard. Through the years the published papers of Bureau workers have added a great deal to our knowledge, as each standard substance issued has usually been accompanied by a full report of the studies, including an evaluation of error sources.

Table 1. U.S. Raw Materials for Production of Metals, 1971

Material	Production (thousands of tons)	Value ($ million)	Standards Availability NBS-SRM
Bauxite	1,988	28	69a
Copper ores	242,656	1,583	330-332
Iron ores	80,762	891	27e
Lead ores	9,962	203	no
Mercury ore	276	5	no
Molybdenum conc.	55	165	333
Nickel ore (1970)	1,138	22	no
Silver ores	739	30	no
Ilmenite conc.	713	15	154b [1]
Tungsten ore	663	16	no
Uranium ores	6,056	159	950a
Zinc Ores	9,163	148	113a [2]
	Total	3,265	

[1] TiO_2
[2] In preparation

Table 2. U.S. Raw Materials for Production of Inorganics (Non-Metallic), 1971

Ore or Mineral	Production, 1000 tons (crude or concentrates)	Value ($ million)	Standards Availability NBS-SRM
Barite	3,899	14	no
Boron minerals	1,047	90	no (except borax)
Clays and shales	56,666	274	97a, 98a [1]
Diatomite	535	34	no
Feldspars	1,701	10	70a, 90a, 607
Fluorspar	749	20	180
Gypsum	10,418	152 (calcined)	no
Limestones	628,157	1,016	1b, 88a, 606
Phosphate rock	38,886	204	120b
Potash salts	16,117	88	no (except 99.9% KCl)
Salt	44,700	303	no (except 99.9% NaCl)
Sulfur (Frasch)	6,756	118	371f [2]
	Total	2,323	

[1] Also cements 633-639, 1011-1016.
[2] Issued for use in rubber compounding, not analyzed.

Table 3. General Chemicals Production and Value, 1972 (U.S.)

Product and Basis, %	Production (thousand tons)		Value ($ million)	Availability of Standards	
				NBS-SRM	Reagent grade
NH_3, 100	14,302		820	no	yes (NH_4OH)
NH_4NO_3, sol'n	6,872		274	no	yes
$(NH_4)_2SO_4$, 100	2,449		38	no	yes
$Al_2(SO_4)_3$, 17 as Al_2O_3	1,124		67	no	yes
CaC_2, 100	493		83	no	no
$CaHPO_4$, 100	593		43	no	yes
H_2O_2, 70	107		62	no	yes
Phosphorus, 100	547		219	no	no
$K_4P_2O_7$, 100	50		16	no	no
$Na_2Cr_2O_7$, 100	137		47	no	yes
$NaClO_3$, 100	182		25	no	yes
$Na_3(PO_3)_3$, 100	1,031		165	no	yes
Na_2SiO_3, 100	663		33	no	yes
Na_2SO_4, 100	1,363		20	no	yes
TiO_2, 100	687		89	154b	yes
		Total	2,041		

Table 4. Acids, Alkalies and Chlorine Production, 1972 (U.S.)

Product and Basis, %	Production (thousands of tons)	Value ($ million)	Standards NBS-SRM	Availability Ultra-pure
HCl, 100	2,201	88	no	yes
HF, 100	332	133	no	yes
HNO_3, 100	7,021	702	no	yes
H_3PO_4, 100 (P_2O_5)	6,263	876	no	yes
H_2SO_4, 100	30,046	900	no	yes
KOH, 88-92	178	43	no	no
NaOH, 76 (Na_2O)	10,266	820	no	no
Na_2CO_3, 58 (Na_2O)	7,461	298	192 [1]	yes
Cl_2, 100	9,868	790	no	no
	Total	4,650		

[1] Certified only for use in admixture as a pH standard.

Table 5. Industrial Gases, 1972 (U.S.)

Gas	Production and Units	Standards Availability NBS-SRM
Acetylene	11,449 mcf	no
Argon	3,752 mcf	no
Carbon dioxide (all forms)	1,345,000 tons	no
Helium	447 mcf	no
Hydrogen	58,000 mcf	no
Nitrogen	185,000 mcf	1601-1609
Oxygen	352,000 mcf	no

Total value of industrial gases in 1971 = $712 million

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INDUSTRIAL STANDARD REFERENCE MATERIAL (SRM) NEEDS: ORGANIC MATERIALS

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I. Introduction

Standard Reference Materials (SRM's) of inorganic species have been available for many years. Thus, metals of certified composition are provided by the National Bureau of Standards (NBS). These have been invaluable in developing and demonstrating acceptable industry-wide reference analytical methods for assay and for trace analysis. Equally valuable have been primary standards offered by NBS for use in microchemistry, acidimetry, and pH measurements.

Recognition of the need for international as well as national cooperation on SRM's was discussed in an American Chemical Society symposium in September, 1964.[7] Reference was made to NBS, API, IUPAC, NAS-NRC, ASTM, ISO, and ANSI activities. The NBS has been active in promoting foreign participation in certification studies, particularly in trace element work.[9] Japan is quite active in this area, [10] as are France, Germany, Poland, Canada, and the United Kingdom, the programs of which have been described by representatives from each of these countries. NBS has been highly instrumental in providing pH standards and standardization of acidity measurements.[3]

Cali and Seward [5] have published a fine survey of the NBS-SRM program. They indicate needs for additional standards in: (a) health and medicine; (b) air and water pollution; (c) biology, botany, and agriculture; (d) metrology; and (e) instrument calibration. To achieve indicated requirements, Cali and Seward stress the necessity for continued support, cooperation, and interest by industry and with organizations such as ASTM, ANSI, and AOAC. Details of the NBS programs have been described in previous talks.

II. Organic SRM'S

Organic reference materials are becoming essential in broad areas of industrial, academic, clinical, and governmental activities. These needs are complicated by the frequent requirement that a specific compound or functional group be identified, often in the presence of a related species. Much has been done in collecting repeatability and reproducibility data on a variety of chemical and instrumental analyses and on physical measurements. Much needs to be done in obtaining data on accuracy and selectivity.

Recently, the demand for organic SRM's has become more critical as our understanding of toxicological and ecological activity improves. In these areas, in particular, specificity becomes extremely important. The drive to publish, unfortunately, has resulted in a number of reports that are suspect because of erroneous identifications and incomplete analyses of the materials under study. We must recognize that some specific compounds are highly toxic while certain isomers are inert. Conclusions on such studies must be based on known composition of the test material. For example, a report that the α-form of compound x is toxic must take into account other forms as well as other compounds in the sample. A form other than α- may be highly toxic. If present, even in small amounts as a contaminant in the α-compound, false conclusions may be drawn from experimental observations.

A. Chemical and Physical Structure

Organic SRM's are needed in measurements of chemical and physical structure. Chemical structure refers to the area usually referred to as analysis, covering determinations of specific compounds, functional groups and elements. Needs vary from analysis for major to trace components. In some cases toxicological and ecological demands require specific detection of fractional parts-per-billion levels of certain species.

Analysis utilizes a wide variety of chemical and physical techniques. Table 1 lists many of these, all of which require reliable reference standards.

Physical structure and characterization provides information usually independent of chemical structure. However, many physical measurements also serve to identify substances. Table 2 notes some physical techniques broadly used in establishing properties and behavior. Some of the techniques listed are suitable for a wide variety of measurements. For example, thermal methods of analysis employ a family of techniques (table 3). They provide information on many types of thermally induced transitions as shown in table 4.

B. Organic SRM Types

A number of purified organic compounds (SRM's) are currently offered by the NBS and other organizations. These for the most part are stable, relatively low molecular weight substances listed under techniques. Examples are shown in table 5. These SRM's provide a wide variety of functional groups, many of which are useful for many more measurements than those specifically listed.

III. Polymers

A. Interlaboratory Studies

A good example of the need for organic standards and standardization is that of an International Standards Organization (ISO)-sponsored interlaboratory study of procedures for determining melting points of polyamides.[8] Laboratories in Italy, France, Germany, the Netherlands, and USA reported results. Plots of data by several widely used methods are shown in figure 1. Methods employed were Fisher-Johns, Köfler, capillary, x-ray, polarizing microscope, and differential thermal analysis (DTA). Three points were used for the DTA results; at increasing temperature these were (a) endotherm peak, (b) extrapolated end temperature, and (c) end temperature. The spread of the data even by the same method was large, pointing to the subjective nature of several of the procedures. In this case the need for standardization is obvious. The x-ray and DTA methods are the more objective and, therefore, offer the potential for best precision and accuracy. The x-ray method is based on disappearance of crystallinity, a well-defined end point. Any one of the three DTA end points could be used to provide fairly good precision. However, the extrapolated end and end temperatures would appear to be more reliable since they agree more closely with results by the x-ray method.

In collaboration with the International Confederation for Thermal Analysis (ICTA) the NBS has issued three sets of DTA standards (SRM's 758, 759, and 760) for the three temperature ranges of 125-435°, 295-675° and 570-950 °C, respectively.[12,13] These are inorganic substances well suited to instrument calibration. Other interlaboratory tests are being conducted by ICTA, ASTM, ISO, etc. [4,6,11,14]

Additional cooperative tests have been organized for establishing reliability of polymer characterization procedures. IUPAC Macromolecular Division [16] has sponsored studies on molecular weights, molecular weight distribution (MWD), viscosity index, degree of branching, and stereoregularity. Results have been collected for polystyrene, poly(vinyl chloride), and linear and branched polyethylenes. The USA Naval Air Systems Command [1] sponsored an international evaluation of gel permeation chromatography to assess the precision of the technique for MWD. Polystyrene samples served as SRM's for studies of carboxyl-terminated and hydroxyl-terminated polybutadienes.

B. Polymer Standards

High polymer standards are offered primarily as molecular weight SRM's. Polystyrene and polyethylene have been listed by NBS. Polybutadiene has been offered by Phillips Petroleum Co. Physical data on standardization are noted in table 6. It is interesting to note the $\bar{M}_n$ and $\bar{M}_w$ were obtained on the narrow MWD polystyrene samples by osmometry, light scattering, sedimentation equilibrium, and viscosity. This standard (NBS-SRM 705) had a molecular weight ratio based on fractionation, $\bar{M}_z:\bar{M}_w:\bar{M}_n = 1.12:1.07:1$. The broad MWD polystyrene (NBS-SRM 706) on the other hand, had a ratio of $\bar{M}_z:\bar{M}_w:\bar{M}_n = 2.9:2.1:1$. Data on the polyethylene standards included melt flow and density.

The polybutadiene standards offered by Phillips included quantitative infrared data on geometrical isomer ratio among cis-, trans-, and high vinyl types. Molecular weight range of five polybutadiene standards was $\bar{M}_n$ = ca. 16,000 to 285,000 and $\bar{M}_w$ = ca. 17,000 to 425,000 with $\bar{M}_w/\bar{M}_n$ of 1.06 to 1.48. The four hydrogenated polybutadiene standards were in about the same molecular weight range with $\bar{M}_w/\bar{M}_n$ of 1.16 to 2.66. Polystyrene standards also have been available from Dow Chemical Co., Pressure Chemical Co., Duke Standards Co. (very high MW), and the Polytechnic Institute of Brooklyn Polymer Sample Bank offered through Distillation Products Industries (DPI). Polyethylene standards also may be obtained from Pressure Chemical Co and DPI.

Numerous other polymers are offered as standards by other organizations, several of which are given in table 7.

Both DPI and Cellomer Associates list numerous other polymers, including cellulose, fluorine-containing polymers, polyamides, poly(phenylene oxide), polysiloxane, plus several other acrylic and vinyl homo- and copolymers. For purposes of this discussion no further identifications are necessary. The important conclusion to be drawn is that a wide variety of polymers are available as standards that have differing functional groups and physical properties with broad molecular weight ranges.

Polymers, therefore, may well provide the basis for many organic SRM's. They can be synthesized in molecular weights varying from a few hundred to several hundred thousand. Most of these materials are quite stable and are solids at room temperature. With the capability for obtaining polymers having a large number of differing functional groups (such as hydroxyl, carbonyl, peroxide, ether, carboxyl, ester) a few standard structures can be used effectively for several measurements involving chemical and physical strucure. For example, end group analysis, where applicable, serves as one of the most reliable means for determining molecular weight of polymers. Acidimetric and basimetric

SRM's having equivalent weights of 1000 to 5000 would be highly desirable for calibration and standardization purposes. Viscometric standards have been almost exclusively paraffinic in nature. There is also a real need for more polar materials as standards.

Inclusion of polymer SRM's does not preclude the continuing need for specific compounds as standards. Cali and Seward [5] refer to several of these materials. Thus, for clinical standards, NBS is adding cortisol, 4-hydroxy-3-methoxymandelic acid (VMA), mannitol, and nicotinamide adenine dinucleotide (NAD). Other aids to clinical laboratories include dyes for spectrophotometer calibration, serum albumen, respiratory gases, and particle-size standards. In defining criteria for mycotoxin standards Rodricks [15] recommended that collaborative studies of quantitative analytical methods for mycotoxins include: (a) characterization of mycotoxin reference standards as to their source and method isolation, method of purification and criteria of purity, and stability under conditions for dispensing and use; and (b) a method for checking concentration and purity of mycotoxin reference standards. These recommendations may well serve as criteria for other chemical standards.

The need for standards and standard procedures in environmental quality studies is widely recognized. In addition to specific trace metal analyses there is a critical demand for specific trace determinations of polynuclear aromatic compounds including possible carcinogens and pesticide residues. Both high-purity organic standards and reliable analytical methods are essential. With reference to pesticides, the Collaborative International Pesticides Analytical Council (CIPAC) [2] has made recommendations for preparation of standard waters used for testing pesticidal and other formulations. In addition to establishing standard recipes for hardness, pH and buffering capacity, this report provided directions for suspensibility data on pesticides. Performance also was provided of emulsifiable concentrates of DDT (dichlorodiphenyltrichloroethane), HHDN (hexachlorohexahydrodimethanonaphthalene), and HEOD (hexachloroepoxyoctahydrodimethano-naphthalene).

IV. Conclusions

In conclusion, there is a sharply increasing demand for organic SRM's for use in industrial, clinical, academic, and government laboratories. Such standards are essential in developing suitable measurement procedures in calibrating techniques. With increasing dependence on spectroscopy and other physical techniques for analysis, accurate results require specific reference standards of known composition. This need is international in scope and can best be developed through cooperative studies among scientists in several countries. Coordination through the ISO would appear to be a logical means for organizing such activities. Of course, active participation by standards organizations is essential to the success of such an enterprise. Coupled with such studies is the requirement for effective data handling systems. A national standard reference data system as described by E. L. Brady and M. B. Wallenstein, National Bureau of Standards, may well serve as a model and indeed, a center.

Table 1. Analytical Techniques for Chemical Structure

Type	Examples
Chemical	"Wet" Methods - Reaction + Titration, Gravimetry, or Spectroscopy
Electrochemical	Potentiometry, Polarography
Spectroscopy	Infrared, Visible, Ultraviolet, Mass, Nuclear Magnetic Resonance; Atomic Absorption, Electron Spectroscopy, X-Ray
Other	Radiochemical, X-Ray Diffraction, Microscopy
Separations	Gas, Liquid, Thin Layer Chromatography; Extraction, Distillation, Zone Refining

Table 2. Physical Structure (Characterization)

Measurement	Examples	Techniques
Physical Constants	d, n, b.p., m.p.	
Fluid Flow	η	Rheology
Molecular Weight	$\bar{M}_n$, $\bar{M}_w$, MWD	Osmometry, Differential Vapor Pressure; Light Scattering, Ultracentrifugation; Gel Permeation, Elution Chromatography
Particle Size		Optical, Electron, Scanning Electron Microscopy, Ultracentrifugation

Table 2 continued

Thermal	Thermodynamic Data, V.P., Thermal Conductivity, Flash Point	Differential Thermal Analysis and Related Techniques
Physical Tests		Mechanical

Table 3. Thermal Methods of Analysis

Differential Thermal Analysis (DTA)
Differential Scanning Calorimetry (DSC)
Thermogravimetric Analysis (TGA)
Thermomechanical Analysis (TMA)
Electrothermal Analysis (ETA)
Thermo-Optical Analysis (TOA)
Thermal Evolution Analysis (TEA)
Thermo-Acoustical Analysis (TAA)

Table 4. Applications of Thermal Techniques

General

Thermal Stability
Oxidation
Combustion
Solvation
Complexation
Chemical Reaction
Purity

Measurements

M.P., F.P., Sublimation Temperature
T_g, Softening Point
Thermal Expansion
Vapor Pressure
Heat Capacity, Thermal Conductivity
Crystalline Transitions
Magnetic Transitions
Electrical Behavior
Liquid Transitions

Table 5. Some Organic SRM's Available from NBS

A. Calorimetric

1.	Benzoic Acid	$C_6H_5 \cdot COOH$
2.	2,2,4-Trimethylpentane	$CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$
3.	2-Amino-2-hydroxymethyl-1,3-Propanediol (Tris(Hydroxymethyl)aminomethane)	$(CH_2OH)_3CNH_2$

B. Density, Refractive Index

No. 2 above

C. Microchemical Standards

No. 1 above

4.	Acetanilide	$C_6H_5 \cdot NHCOCH_3$
5.	Anisic Acid	$CH_3O \cdot C_6H_4 \cdot COOH$
6.	Nicotinic Acid	$C_5H_4N \cdot COOH$
7.	Cystine	$NH_2CH(COOH)CH_2SSCH_2(COOH)NH_2$
8.	Urea	NH_2CONH_2
9.	Triphenyl Phosphate	$(C_6H_5)_3PO_4$
10.	o-Bromobenzoic Acid	$Br \cdot C_6H_4 \cdot COOH$

D. Acidimetric, Basimetric Standards

No. 1 above
No. 3 above

E. Primary Chemicals

11. Sugars, e.g., dextrose, sucrose

F. Radiochemical Standards

C-14 and H-3 labeled sugars
Hexadecane -1-C-14

G. Mass Spectrometry Standards

Hydrocarbon Blends

H. Oil Soluble Standards For Trace Elements in Petroleum Products

I. Clinical Standards

Cholesterol
No. 8 above

Table 5 continued

Uric Acid
Creatinine
Glucose

J. Metallo-organic Compound

Zinc Cyclohexanebutyrate

K. Rubber Compounding Materials

Stearic Acid
Mercaptobenzothiazole
N-tert.-Butyl-2-Benzothiazolesulfenamide

L. Organic Reference Materials

1,2-o-Isopropylidene-β-L-Iodofuranose
L-Inositol
Quebrachitol

M. pH Standards

Potassium Dihydrogen Citrate
Potassium Monohydrogen Citrate
Monopotassium Oxalate

Table 6. Polymer Standards:

NBS	$\bar{M}_w$	$\bar{M}_n$	η	Melt Flow	d
Polystyrene, Narrow MWD[a]	X	X	X		
Polystyrene, Broad MWD	X	X	X		
Polyethylene, Linear	X	X	X	X	X
Polyethylene, Branched			X	X	X
Polyethylene, Narrow MWD	X	X	X		
Phillips Petroleum Company					
Polybutadiene	X	X	X		
Polybutadiene, Hydrogenated	X	X			

[a] MWD = Molecular Weight Distribution

Table 7. Polymer Standards (Continued)

Polymer	$\bar{M}_w$ (x 10^3)	$\bar{M}_n$ (x 10^3)	Source[b]
Poly(Vinyl chloride)	70-130[a]	25-55[a]	1,2,3,4
Poly(Methyl Methacrylate)	50-265	20-125	3,4,5
Poly(1,2-Butylene Glycol Phthalate)	0.7-6		2,4
Polycarbonate	40	15	3
Polysulfone	65	20	3,4
Poly(Vinyl Acetate)	330	85	3
Poly(Vinyl Butyral)	50	10	3
Poly(Vinyl Carbazole)	1,400	275	3

[a] Figures rounded off; [b] 1 = pressure chemical company, 2 = AR-RO Labs, 3 = Cellomer Associates, 4 = Polymer Bank, DPI, 5 = ROHM and HAAS

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"MEANINGFUL MEASUREMENT" IN CLINICAL CHEMISTRY

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I. Introduction

Clinical chemistry, as a distinct subdiscipline of chemistry, is a relative newcomer. The American Association of Clinical Chemists (AACC) only this year (1974) celebrated its 25th anniversary. Chemical measurements of clinical importance have been carried out for perhaps 200 (or, by stretching the definition, for over 2,000) years. It is in the last 25-50 years that the meaning of the measurements has been emphasized, both by knowledgeable intent and by the implicit practice of those engaged in clinical medicine. For an excellent outline of the analytical problems of clinical chemistry and the interprofessional and administrative relationships required, as well as a discussion of the many practical problems involved, see Bowers.[1] There has not been sufficient, nor sufficiently widespread, understanding or appreciation of the various elements that provide meaning to measurement. This is true not only in the field of clinical chemistry.[2,3]

I intend here to explore the components required to give meaning to measurement in clinical chemistry and the relationships between the components, and to propose a central program to serve as a stimulus to the further development and refinement of all of the components required for meaningful measurement in clinical chemistry.

It may be necessary at the outset to emphasize the practical importance of such an effort. There are two aspects that should be mentioned here, and these will be expanded later. First, the quantitative economic importance. There are about 12,000 clinical and health laboratories in the nation and an estimated additional 40,000 private physician laboratories. These 12,000 laboratories provide about 2.5×10^9 individual laboratory tests each year, as requested by individual physicians for their guidance in diagnosis or therapy. The direct cost of this work, to the patients or to the taxpayer, is about $\$8 \times 10^9$ per year. The second aspect is the economic and personal effect on health care of the quality of laboratory services provided. If the quality of the information provided by these laboratories is compromised so that it is misleading to the physician, the effect may be disastrous to the patient, frustrating to the physician, and, as a whole, a great economic loss to the nation, far beyond the initial basic cost of analysis.

II. Factors Involved in Laboratory Quality

The following are factors involved in the quality of laboratory results as listed in a draft document of the International Federation of Clinical Chemistry (IFCC) Expert Panel on Nomenclature and Principles of Quality Control:

> Reliability Criteria: accuracy, specificity, sensitivity, and precision
>
> Practicability Criteria: speed, cost, technical skill required, and dependability of the procedure

I will be emphasizing the importance of accuracy in this paper, not only because of its relevance to "meaningful measurements" and the National Bureau of Standards' mission, but because of its increasing importance in modern medicine and large population studies of health and disease.

To show the relationship of clinical laboratory measurements to the "National Measurement System," I will use a series of very simple figures. These figures emphasize what is well known to many of you, that measurement is a complex procedure, and that there are many implicit assumptions made in carrying out common measurements. In health laboratory measurements, there are additional implicit assumptions made when patient values are interpreted.

Figure 1 is intended to represent one laboratory result (P) on a patient. Implied (not stated) is: (1) An analytical procedure with the reliability and practicability criteria listed above; (2) A calibration system for the analytical procedure; (3) A nomenclature of measurement (quantities and units); (4) Calibration (and control) materials, with appropriately attached values for analytical purposes.

It should be noted that such a patient value (P) is of no value to anyone without additional information. For example, if this is the first value obtained by a research scientist on a cancer patient, it may or may not be relevantly connected with the patient's disease.

Figure 2 provides additional orienting information on the mean of a reference population consisting of more than 10,000 individual tests. We can say that the patient value (P) differs from that of the mean of the reference population. We cannot (or should not) yet say that the difference is meaningful or important.

Figure 3 adds additional information by showing the distribution of the values in the reference population as compared with the patient value, which we can now say is probably higher than that of most of the reference population.

As shown in figure 4, we can say this with considerably more certainty when information is added about the precision (reproducibility) of the analytical process. It is also now possible to state the statistical probability of the occurrence of the patient value (P) in a normal population when the analysis has the precision shown.

Figure 5 illustrates how a different form of the same question arises if the analytical precision is greatly decreased.

Figure 6 illustrates the importance of the careful delineation of the reference population. For example, the means of serum uric acid values are different for male and female populations. An increased differential capability for evaluating the significance of patient value (P) thus depends on a proper choice of a reference population most closely appropriate to the patient. Population parameters of choice may be sex, age, dietary history, time of day, race, etc.

Figure 7 illustrates the effect on differential capability if the reference population values are fixed (perhaps by literature references) and various analytical procedures with varying systematic bias (same precision) are applied to obtain patient values. In the extreme, the patient value will be regarded as normal and in the other as abnormal. Attempts are usually made by each laboratory (if resources are available) to minimize this effect by developing local reference population values (normal ranges) so that systematic biases are at least partially offset. See figure 8.

In figure 9, the sources of laboratory variability are arranged in a somewhat different manner and the existence of a reference population of values obtained by a "true value" method is assumed. Factor S represents the unpredictable effect of unknown components (or physical state) of individual patient specimens.

In figure 10, another attempt (adapted from Stamm)[4] is made to relate the analytical effort to its clincial operational context.

It should be clear that increased precision results in an increased capability to define both normal populations and pathological deviations from normality.

It should also be intuitively appreciated that increased specificity in clinical chemistry tests can lead to increased understanding of both group and individual deviations from normal physiological changes.

Sensitivity of analytical procedures has at least four different meanings, all basically connected with an analytical capability to detect changes in concentration. Mandel[5] has developed a definition that is similar to that of signal-to-noise ratio. It thus may vary with concentration.

The need for accuracy in clinical chemistry has been less well understood and appreciated than that of precision because of a feeling that establishment of "local normal ranges" would compensate for any systematic bias and a feeling of helpless inadequacy to even approach a definition of "true values."

In recent years, the need for emphasis on true values and accuracy has increased, partly because of unwarranted extrapolations into areas of diagnosis not justified by existing scientific data and partly because the medical profession has enormously increased its reliance on laboratory data for making diagnoses and selecting therapy. For example, the administration of digoxin for heart failure may be now guided routinely by laboratory measurements of blood levels; 20 years ago the physician relied completely on physical and clinical signs and symptoms of the patient.

III. Effects of Inaccuracy

Inaccuracy in clinical laboratory measurements has a number of effects, some of which are not widely understood.

A. Effect on "normal reference values "

The reference population of values used by the physician to interpret the results depends on the accuracy of the method used to measure those values. If the reference values are (as is usually the case even today) determined by another laboratory (time or place) without reference to a "true value" basis, the relevance of the values to the individual patient value is in doubt.

B. Effect on patient result

Today's patients are increasingly mobile. It is becoming very important especially to the patient that the results of different laboratories be referred to a common base, that is, a common measurement system. For example, if a patient whose insulin dosage has been carefully regulated to achieve a fasting blood glucose level of 90-110 mg/100 ml travels and uses a laboratory with a positive systematic bias of 30 mg/100 ml, he may inappropriately (and dangerously) increase his insulin dosage.

Inaccuracy also effects epidemiologic studies in which attempts are made to correlate disease with laboratory results, multivariate studies, time trend studies (where accuracy varies from time to time), and the capability of the physician to interpret meaningful results.

IV. Causes of Inaccuracy

The causes of inaccuracy are also varied. It may be a result of poor (insensitive, nonspecific) methods, defective technology (instruments), lack of calibration reference materials, or lack of performance specifications for materials, laboratories, and instruments, and for the definition of reference populations. One cause that is seemingly justified but far-reaching in its consequences is the clinical constrictions on the analytical procedures adopted. These constrictions include the need for speed and for small sample size. The increased use of the clinical laboratory by physicians and especially the demand for multiple analyses on individual specimens has placed enormous strains on the technological capability available.

V. Remedies for Inaccuracy

If the effects of inaccuracy are to be minimized and if causes are known, it should be possible to make a list of remedies. The choice and mode of application of these remedies is a matter of judgment and will depend on the cost-to-benefit ratio anticipated for each or for each combination considered.

A. Detection and display

Only when a defect is detected and displayed will remedial action occur. One way of enlisting the concern and the competency of individual laboratorians in an effort at laboratory improvement is to compare results obtained in many laboratories. There is a very natural effort to be "not too different" from the consensus. This is, in effect, a definition of accuracy as a central tendency of those who are being measured. It is apparent from results of interlaboratory testing in nonclinical laboratories that we in the clinical area have for one reason or another been able to achieve an enviable degree of consistency for most of the commonly applied tests. This should not lead to complacency about accuracy, however, because such apparent accuracy is sometimes relied on by laboratories (and for patients) where it is completely unjustified and with disastrous results.

Interlaboratory comparisons better known as proficiency testing can thus be used to detect "nonconsensus performance" due to method defects, instrument defects, calibration base defects, calibration material defects, etc. The remedy for these defects is generally left to the individual laboratory director. However, the individual laboratory director in most instances today cannot undertake all of the appropriate remedial steps. For one thing, no performance standards exist except for arbitrary standards suggested under the Clinical Laboratories Improvement Act (CLIA) of 1967, those of Medicare and Medicaid, and those established by professional society proficiency testing programs. Even these standards are extremely loose, vague, and unevenly applied, and generally without scientific basis.

B. The tools of accuracy

Thus, the laboratory director generally does not have the tools necessary to remedy laboratory defects. He needs performance specifications for his final results on patient specimens, for his materials (reagents and calibration references), and for his instruments. He needs ready access to well-characterized reference methods and to certified reference materials for calibration and control. Increasingly, he needs new knowledge about interferences (especially by drugs) on the routine methods available for his use.

VI. Elements Required for Meaningful Measurement

The tools needed for quality performance in clinical chemistry laboratories are actually the elements required for meaningful measurements or for assurance of quality.

A. Reliable methods

Reliable methods are methods of proven quality according to the eight criteria listed in Section II. Improvements in technology over the last 10 years have been mostly in the areas of speed, cost, technical skill required, sensitivity, and precision. Relatively little attention has been paid to increasing or even maintaining accuracy, specificity (interference effects), or dependability. However, laboratorians (including the joint NBS/CDC program of reference methodology) are not directing their attention toward the untouched areas of accuracy and specificity. The first progress in these areas was made in a program sponsored jointly by the NBS and the AACC. A serum calcium method of proven and unambiguous accuracy was developed.

When selecting an analytical procedure to use on a particular specimen, the laboratorian must consider the condition of the patient at the time of the collection of the specimen, the collection, preservation, and transportation procedures used, as well as the method of transferring data to the physician who will interpret the information and make decisions based on it.

B. Reliable materials

Reliable materials for calibration and quality control are as essential to quality performance as proven methods. Basic calibration materials (100 percent mole fraction) for many of the constituents of interest to the clinical chemistry laboratorian have been available for some years through the NBS. During the last five years, many more of these pure clinical standard materials have been developed and made available by the NBS. Many of the newer technologies at present require calibration or standardization with serum or urine surrogate materials containing specified concentrations of the pure analyte. At present, these surrogate materials are supplied by commercial sources; the manufacturer determines the label values by analytical procedures or by preparative procedures, which themselves are open to question. There is great need for a national system for relating the values assigned to such materials to "true values." This need has been recognized by the NBS and by the CDC. Under an interagency agreement, the development of serum-based surrogate materials, characterized according to the elctrolyte content (Na, K, Ca, Mg, Li, Cl), is well underway. Such serum surrogate materials, when used in conjunction with analytical methods of proven quality (accuracy, specificity, sensitivity, precision), are invaluable in evaluating other analytical procedures for the same analyte, or in performing such procedures in a given laboratory.

C. Performance standards

By this, I mean a national professional consensus about which quality performance factors are necessary for clinical laboratories and the necessary levels for each. For example, there is presently no agreement on the importance of accuracy in a given clinical laboratory, nor any agreement as to the level of precision for a given analyte required for good clinical judgment to be exercised. Such questions have been raised again and again in the past, and usually have been answered by the assertion that the physician would use his knowledge of the individual laboratory and its performance when making his decisions as to patient care, so as to compensate for local laboratory bias and lack of precision.

D. Reliable (standard) nomenclature

It is universally accepted that a common system of units and measures is necessary for communication. However, it is not universally or generally accepted that a certain specific system of units and measures be used in clinical laboratory reports. For example, the expression of electrolytes in milliequivalents per liter of serum is only about one generation old. Many of the names of enzymes and coenzymes are even younger, and the system of enzyme unit expression is still being debated. Changes do present problems to physicians; however, ambiguity also causes its own problems.

E. Systems of internal and external quality control

Quality control systems broadly conceived serve to (1) decrease the frequency of laboratory defects, (2) detect laboratory defects in accuracy and precision in order to alert the laboratorian, and (3) measure laboratory performance parameters to assure maintenance of a satisfactory level of quality. Clinical laboratory workers at all levels apply these systems internally in a manner designed to most effectively and efficiently carry out the purposes listed above. A special problem arises when the laboratory worker must know the values assigned to quality control material. There is an (apparently) unavoidable psychological effect that tends to reduce the measured variance. Various types of "blind" specimens may be introduced to avoid this particular phenomenon, but the known or "bench control" specimen is a basic requirement.

External quality control, or proficiency testing, is a similar system applied to many different laboratories. When this system is properly used, differences in laboratory accuracy can efficiently and effectively be detected and with additional associated information, attention can be drawn to probable sources of interlaboratory differences.

F. Other factors

1. Personnel. The training and experience of the laboratory personnel are so interactive with the available analytical tools that it is difficult to discuss them separately. For example, the advent of "push-button" analytical systems has led to the specialization of the electronic laboratory technician who is now responsible for trouble-shooting and maintenance. The bench analyst is now less concerned with the proper techniques of pipetting and theory titration error and more with the ambiguities of sequential analysis and "carryover" effects. Thus do the tools used remodel the "tool user."

   So also the laboratory manager is caught up in the problems of economic choices versus the quality and speed of analysis and the size of sample required. The heavy investments involved may make demands on the laboratory system that create disadvantages for the physician and his patient.

2. National system of supply, maintenance, and repair. The sophisticated technology and the technology transfer involved in making prepackaged analytical systems and supporting reagents and equipment available to local laboratories change the patterns of personnel training needed. They also place a greater premium on the continuity of such services in order that patient need (which is continuous) can be served.

3. National demand for clinical laboratory services. Various estimates place the clinical laboratory portion of hospital care at between 25-40 percent of the individual hospital bill (including x-ray) and the clinical analytical services (chemistry, hematology and serology, microbiology) at between 10-25 percent. The present national system of reimbursement for clinical laboratory services, as well as other health services, stimulates their use. Although there are 12,000 laboratories potentially controlled by CLIA-67 and by Medicare regulations, there are about 40,000 doctors' laboratories and local laboratories without any such control.

Let us consider the use made of the information developed by our national clinical laboratory system. First, much of the information is not used. A recent study showed that in a certain large metropolitan hospital, 60 percent of the doctors' laboratory orders were not carried out, and, in general, the failure to do so was not noticed. Another study indicated that results that were not normal were ignored about 40 percent of the time.

The costs of erroneous results that may mislead the physician can be staggering. It has been estimated that 25 percent of all laboratory results are misleading. Let us conservatively assume a figure of only one percent. With a total of 2.5×10^9 analyses per year, that means that 2.5×10^7 results are misleading each year. At an estimated dollar cost (excluding personal suffering) of $1,000 per bad result[6], the national cost is $\$2.5 \times 10^{10}$ per year, which is about two percent of the gross national product!

VII. What Needs to be Done

Research and development in the areas of laboratory methods and materials as well as in systems of quality assessment (internal quality control and proficiency testing) are greatly needed. Unfortunately, it is the type of research least likely to receive federal funds. Standard reference values for health populations and those with disease need to be developed and widely applied.

Many new potential indicators of disease remain to be explored, such as multiple correlation studies, new enzymes, intermediate analytes, nutrilites, and trace elements.

My own special area of concern is materials research and methods characterization. I believe successful application of the results of research in the areas suggested above will depend on methods and materials. Fortunately, there is a national opportunity presently in view that affords both an immediate task and requires clinical chemists to take an active part in decision-making.

As a simulus to development in the areas of accuracy and precision, let me propose that the vigorous attempt to characterize methods and materials with respect to "true values" will beneficially develop all facets of clinical chemistry.

A. Primary goal

The primary goal of the above program is to develop surrogate materials (biological fluids) with assigned "true values." A true value is intended to imply a result attained by unambiguous procedures.

B. Effects of program

This program will force the development of "secondary" methods for reference purposes with relationship to the unambiguous methods established by appropriate coordinated cooperative studies.

The measurement of "bias" and interferences for both secondary reference and routine methods using both surrogate materials and patient specimens will now be possible.

"True value" methods will allow truly meaningful measurement of normal or reference population values and development of real knowledge about the distribution of values in disease, facilitated by the new capability to pool results obtained by many different laboratories.

The use of well-characterized true value materials in quality control and proficiency testing will strongly influence the results of health laboratories toward true value results.

The development of a national consensus with respect to in vitro diagnostic product class standards requires the selection of reference methods, the use of reference materials, and the consensus development of limits of performance for such products. Such standards will become a standard of performance for laboratories and include accuracy and precision as well as dependability criteria.

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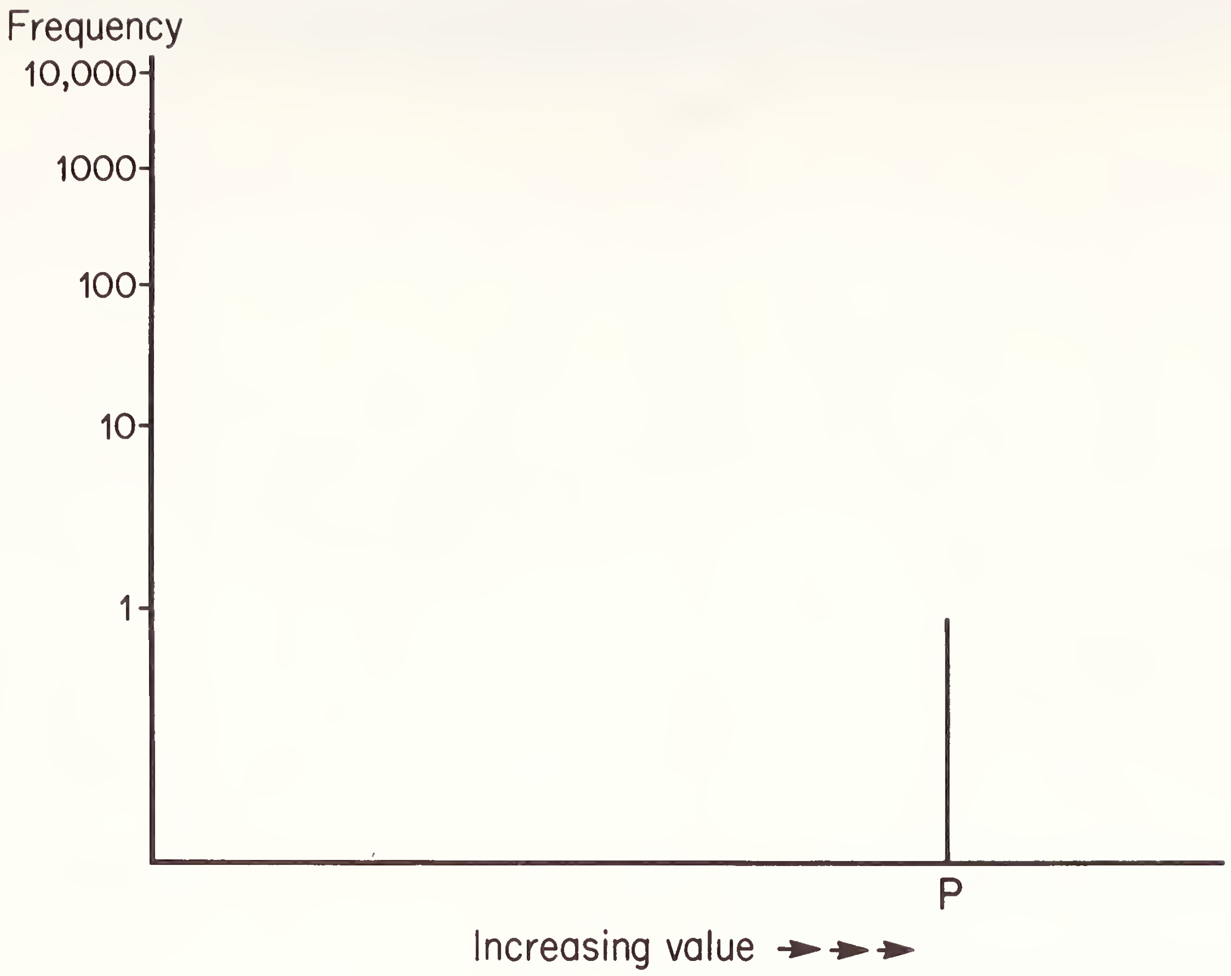

Figure 1. One laboratory result (P) on a single patient

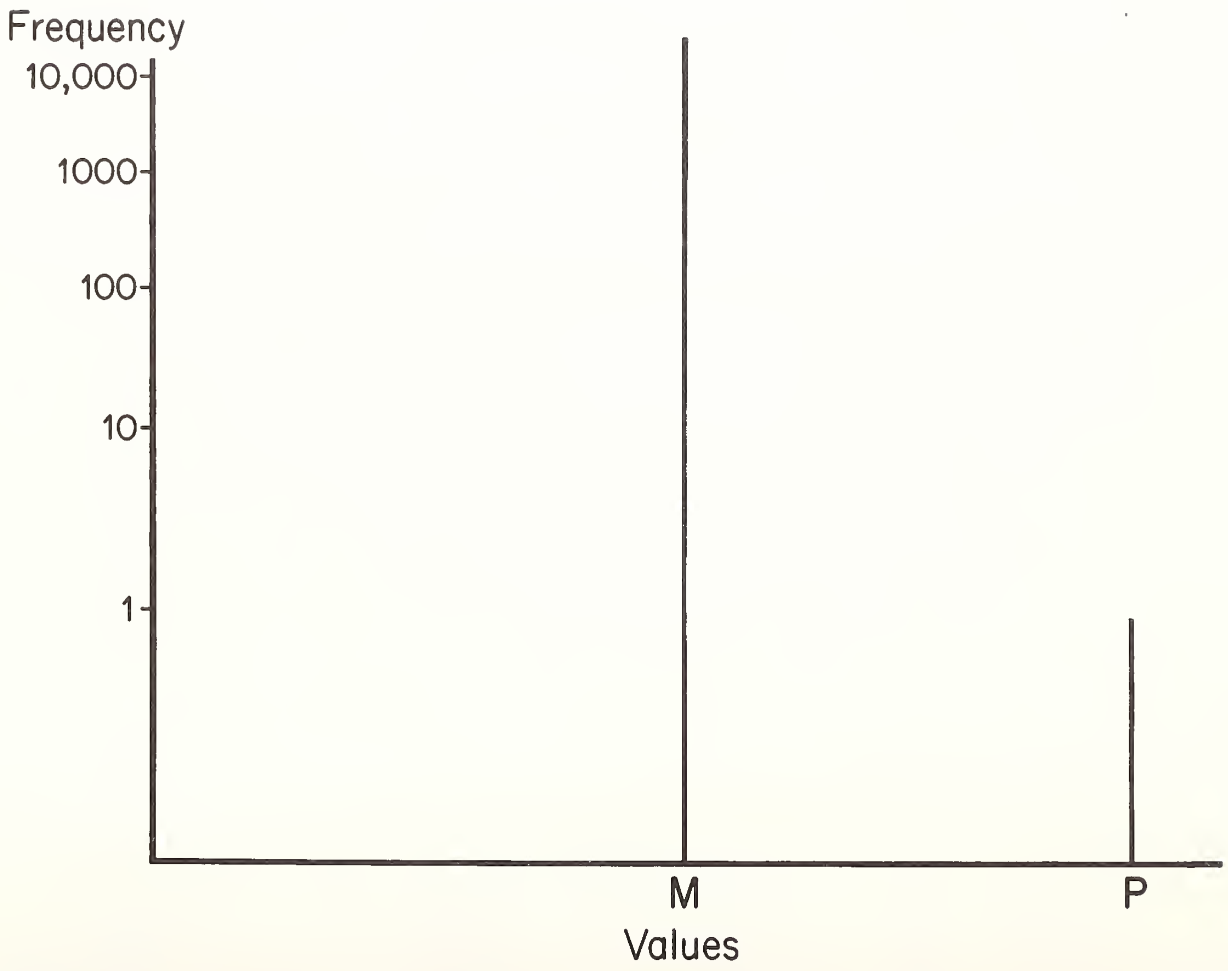

Figure 2. A single laboratory result (P) compared with the mean of the reference population

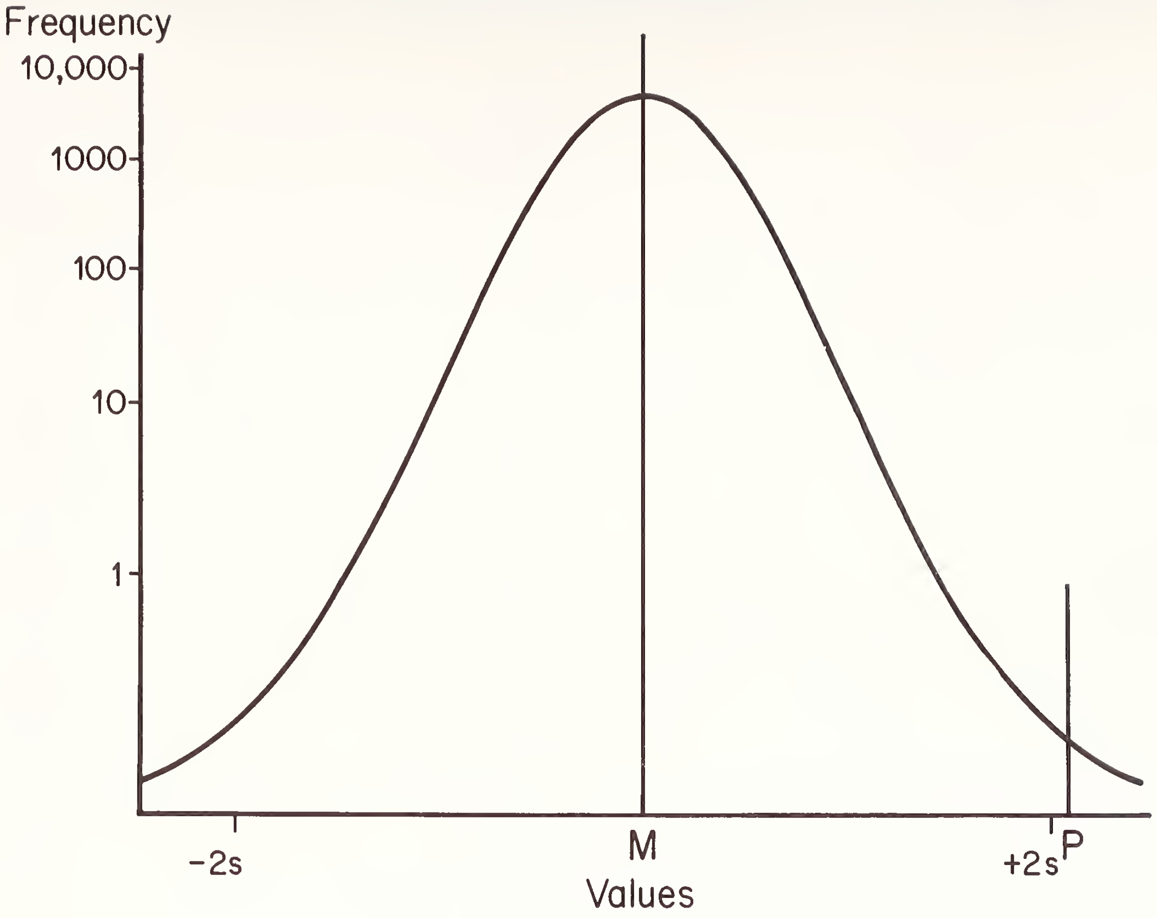

Figure 3. Patient value (P) compared with the distribution of values in the reference population

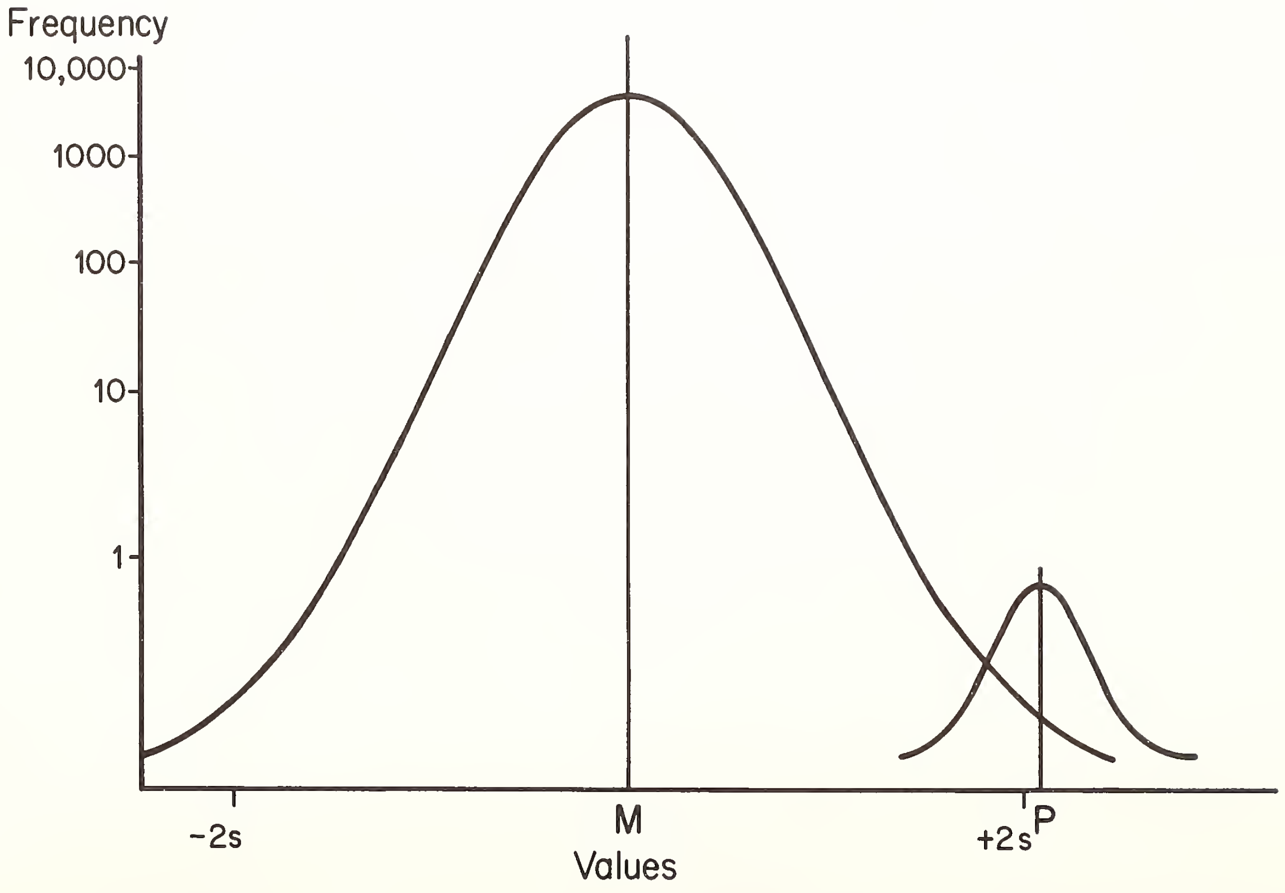

Figure 4. Analytical distribution of P's compared with reference population distribution

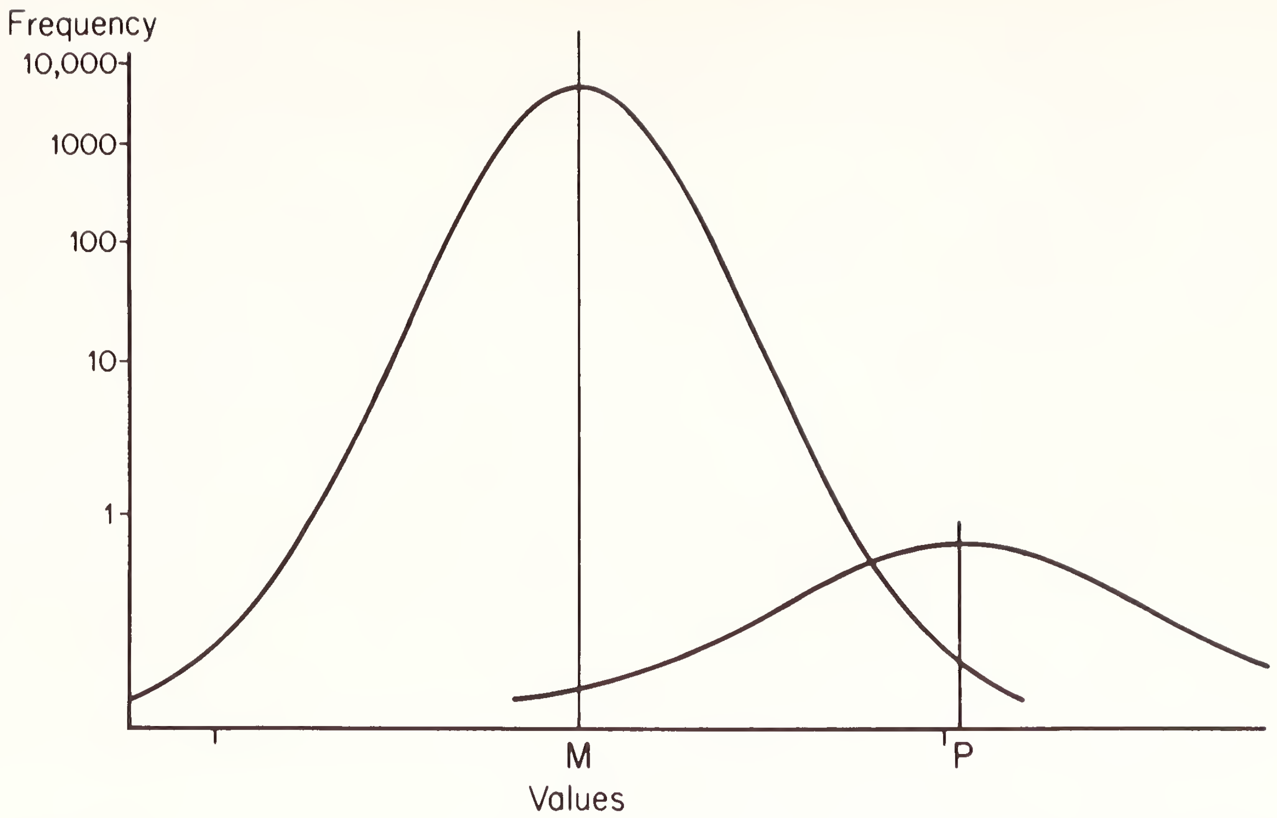

Figure 5. Effects of decreased analytical precision

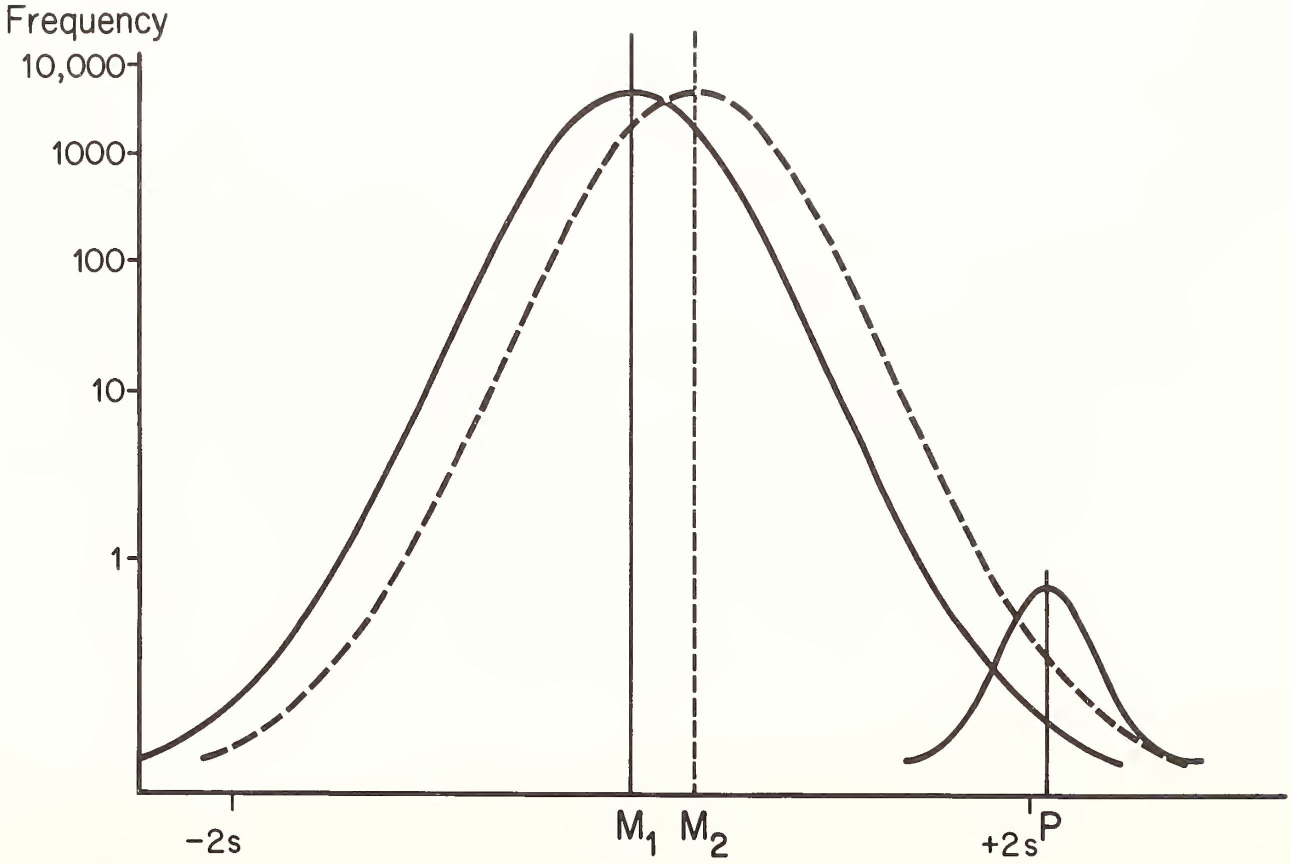

Figure 6. Effects of varying reference population results

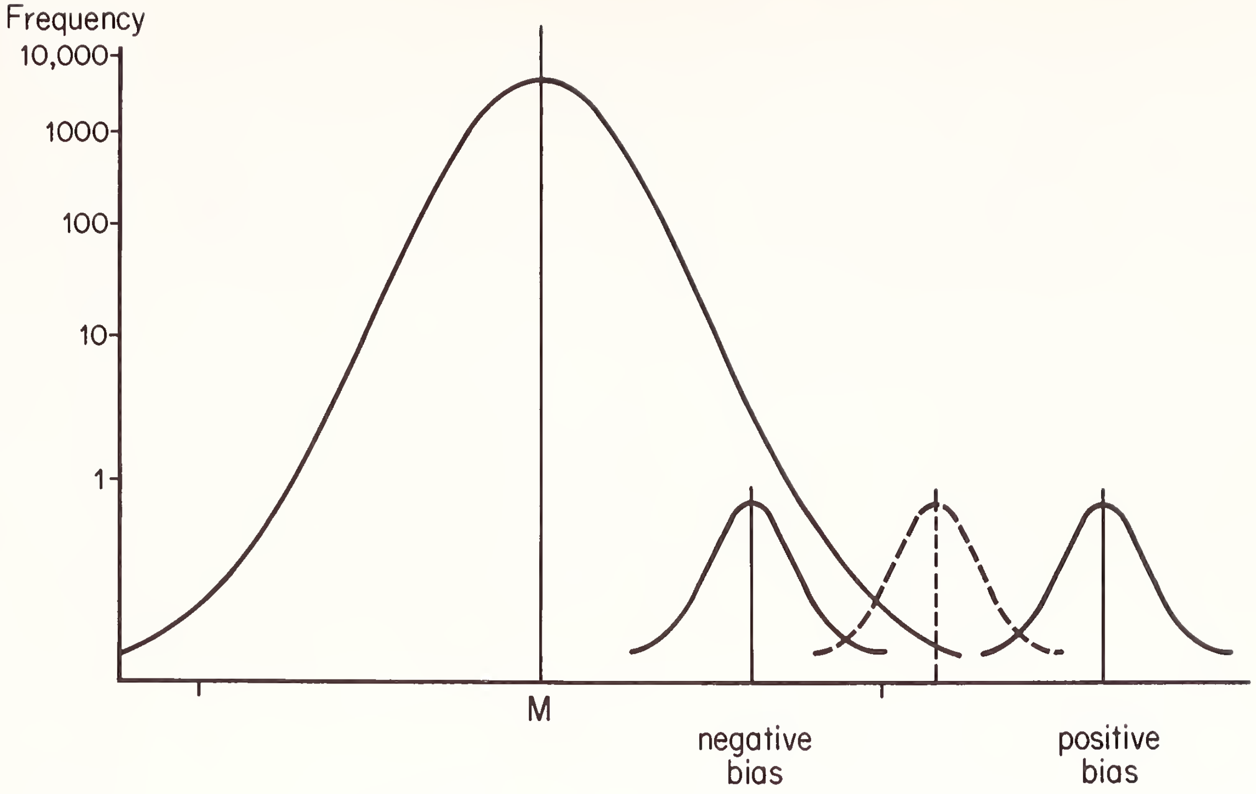

Figure 7. Effects of varying analytical bias

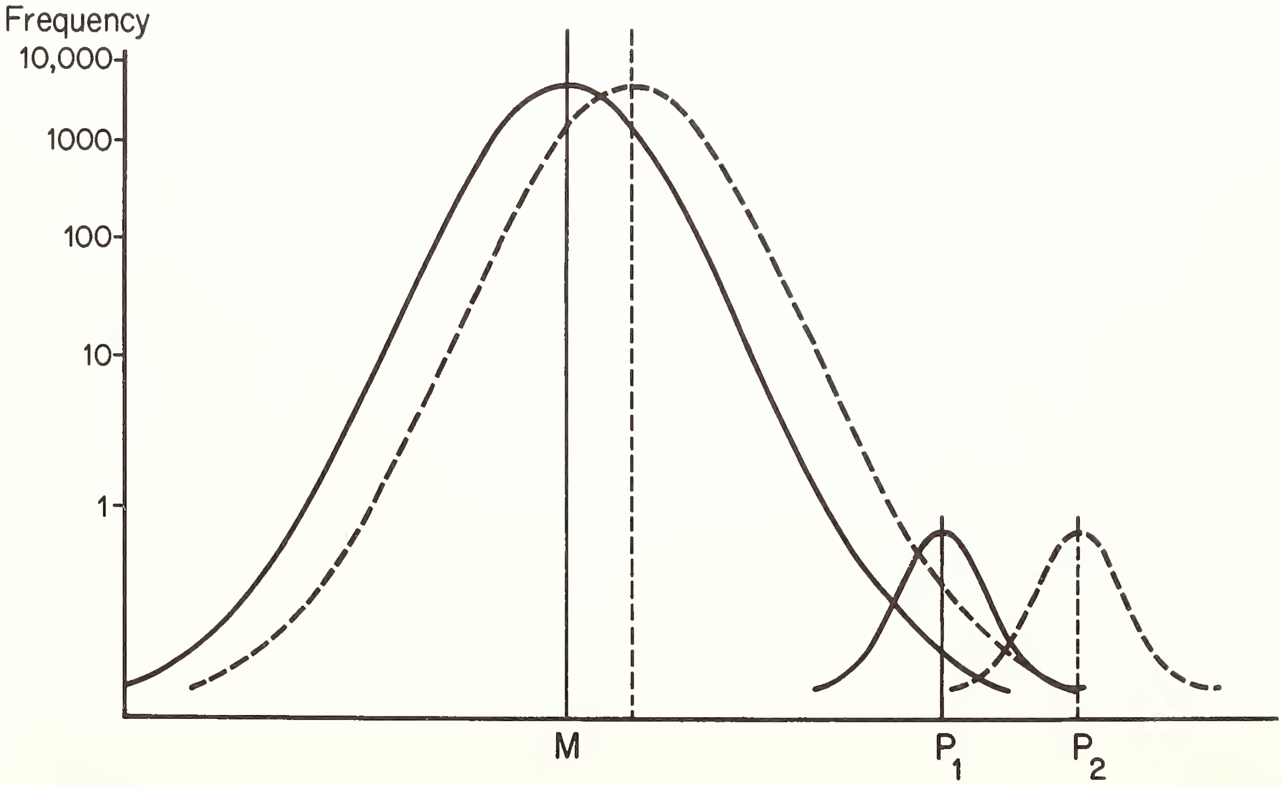

Figure 8. Compensation of local bias by local values for reference populations

$$Y = X + Z + M + L + T + R + S$$

Y	X	Z	M	L	T	R	S
Reported value of individual specimen	True value of individual under specified circumstances. The value of interest to the physician.	Deviation from the true value due to circumstances of collection, shipment, and handling prior to receipt by the laboratory	Deviation from the true value due to systematic bias of particular methodology. Related to relative accuracy of the method.	Deviation from the true value due to application of a particular method in a particular laboratory. Relative accuracy of the laboratory.	Deviations from the true value due to chance variations in application of technique in the laboratory.	Deviations due to the inherent variability of the method. Pure random error. Irreducible variation of method.	Deviation from the true value due to idiosyncratic effect of the sample itself
Reported value	True value	External deviation	Method bias	Laboratory bias	Technical deviations	Random error	
		Outside of participating laboratory control. Responsibility of testing agency and reference labs.	These components determine the relative accuracy of the participating laboratories		These components determine the precision of the participating laboratories. Major reduction in variability must come from T.		

Figure 9. Sources of laboratory variabilities

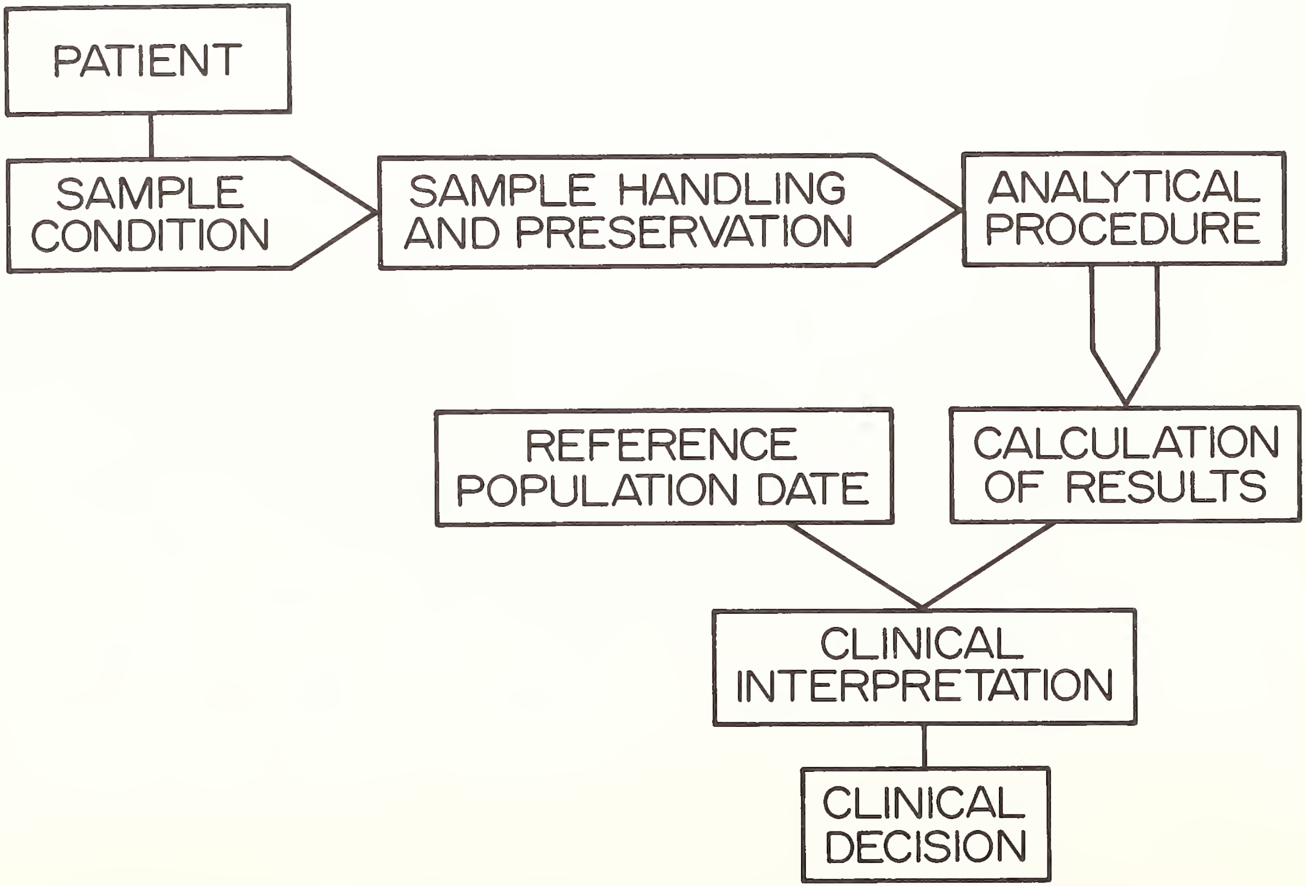

Figure 10. Steps in the patient-laboratory-clinical complex (after Stamm)

STANDARD REFERENCE MATERIALS AND ENVIRONMENTAL MONITORING

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Man has long realized that his life, health, and happiness is dependent on the quality of the environment. However, it is only recently that he has come to understand that his use of natural resources and modern technology may imperil his survival. Man is aware, at least, that he must preserve the ecosystem on a national, as well as an international basis. This awareness resulted in the National Environmental Policy Act in 1969, and ultimately, formation of the U.S. Environmental Protection Agency (EPA) in 1970. The first and foremost mission of EPA was that of a regulatory agency. With the increase in the number and variety of pollutants that are now present in the environment, and the suspicion that the interaction of these pollutants could form new and even potentially more hazardous pollutants, it is necessary to carry out a well coordinated research and monitoring program to document the distribution, sources, and effects of these pollutants. The end goal of such a program is to provide a foundation for the establishment and enforcement of environmental standards that are protective of health and welfare.

Pollution monitoring is a complex and difficult task. Pollutants must be measured, not only in air, surface and ground waters, and land, but also as they are discharged from the multitude of stacks, outfalls, and exhaust pipes. The pollutants that must be monitored number in the hundreds -- the types of sources in the thousands -- with each situation representing an almost unique problem in terms of combinations of instrumentation, monitoring locations, sampling duration, and the like. The problem is further compounded by the continuous interactions and transformations of many of these pollutants as they are discharged from the sources and as they pass through the environment.

Representative sampling of pollutant concentrations at the point of discharge or in the environment requires an understanding of the pollutant characteristics as well as specific objectives to be achieved. Only then can appropriate measurement techniques be identified and employed. Environmental monitoring may be defined as the systematic collection and evaluation of physical, chemical, biological, and related data pertaining to environmental quality and waste discharge into all media. Its main elements are:

1. Field sampling and measurement of environmental quality, emissions, and effluents.
2. Laboratory analysis of field samples.
3. Operation of technical information systems, data synthesis and data analysis.
4. Measurement sensor and technique development and testing.
5. Instrumentation and methodology standardization.
6. Quality control.

Each of the elements above is of importance - all requiring current and substantial effort. The monitoring data are used for a number of specific purposes. The most important of these are:

1. Establishment and enforcement of ambient environment quality and emission/effluent standards.
2. Evaluation of the effectiveness of control strategies.
3. Determination of trends, pollutant interactions, baseline, and patterns.
4. Assessment of pollution effects on man and his environment.

It is important here to realize that in most instances data gathered for a specific purpose may also be used for other purposes, e.g., trend data are often used in effects research. This means that it is necessary to improve and document the accuracy and validity of all environmental measurements by imposing a quality control program on all segments of monitoring activities including personnel, method selection, equipment operation in the field and laboratory, and data verification procedures. In order to meet this objective the Environmental Protection Agency Quality Assurance Program was initiated. This program was designed to assure that the monitoring data provided to EPA decision-makers are both accurate and valid.

Elements of a Quality Assurance Program

A total quality assurance program is composed of four major elements:

1. Development and issuance of procedures.
2. Intra-laboratory quality control programs.
3. Inter-laboratory quality control programs.
4. Monitoring program evaluation and certification.

All of these elements are equally essential and must be developed and carried out simultaneously.

A basic requirement of the quality assurance program is a series of manuals describing the procedures to be followed for sampling, analysis, and data handling. It is the use of such prescribed procedures that provides a uniform approach for the various monitoring programs and allows the evaluation of the validity of the resultant data. Procedures are required for all facets of a monitoring program from criteria to be used in locating stations to the formats to be used in reporting data. The required procedures may be grouped into three categories; sampling, methods selection, and laboratory procedures.

Intra-laboratory quality control is a continuing in-house activity to insure the output of valid data. To maintain a high level of competence in daily monitoring activities, quality control procedures must be implemented in the field and in the laboratory using a system of checks to evaluate the performance of monitors and analysts, and to determine the accuracy and precision of the results. The specific objectives of the intra-laboratory quality control program are to devise and implement procedures that:

1. Measure and control the precision of procedures and instruments.
2. Measure and control the accuracy of analytical results.
3. Insure data output which is computer compatible.
4. Present data in proper format.
5. Document performance of instruments and analysts.
6. Document training needs.
7. Identify weak methodology and consequent research needs.

An intra-laboratory quality control program utilizes the following tools or techniques:

1. Standard Reference Materials. These are substances that qualify as absolute quantities against which other like substances can be calibrated.
2. Standard reference samples. These are preparations of known amounts of a Standard Reference Material added to an actual environmental sample that has been previously analyzed.
3. Quality control charts. An inter-laboratory quality control program serves to select and evaluate methods, characterize their precision and accuracy, and provide data for evaluating both laboratory and analyst performance. This aspect of quality control is referred to as "cross-checks" or laboratory performance evaluations. Specific objectives of an inter-laboratory quality control program are to:

   a. Measure the precision of reproducibility of methods of analysis within various laboratory programs.

b. Identify interference in different sampling environments.
c. Measure the precision and accuracy of results between laboratories.
d. Provide a mechanism for evaluation and/or certification of laboratories and analysts.
e. Detect weak, improper, or impractical methodology.
f. Detect training needs and upgrade laboratory performance.
g. Assist laboratories or programs in obtaining new resources.

Many elements of quality control are currently being practiced to some degree in EPA and other environmental monitoring programs. The quality control programs for the different media of categorical programs are quite varied, ranging from rather comprehensive activities in some areas to essentially non-existent activities in others. Although the quality control programs are underway for air, water, radiation, and pesticides within the EPA, they are all lacking in several areas. The most critical deficients are the lack of established procedures for sampling methodology, field calibration, equivalency determination, and the lack of performance evaluation and certification. Standard Reference Materials and samples are utilized in each of these areas. The success of inter-laboratory quality assurance program thus depends upon the availability and use of high quality Standard Reference Materials and standard reference samples. Currently there is a program within the Agency, both at Headquarters and at the National Environmental Research Centers (NERC's), to provide an operational program concerning the use of Standard Reference Materials and standard reference samples, that is the type, quantity, frequency of use, etc. The state and local programs, as well as other monitoring activities, must obtain these materials from a wide variety of sources, i.e., EPA laboratories, National Bureau of Standards, and private laboratories. In some cases the reference samples are being prepared by the user laboratory itself. Increased control on the production and use of the Standard Reference Materials and standard reference samples is necessary if state and local data are to be upgraded and their validity assessed. The Environmental Protection Agency has developed its policy of making these materials available to state and local agencies. The first part of this policy is that EPA plans to purchase or develop Standard Reference Materials from appropriate sources, such as the National Bureau of Standards and private organizations, and make these available to state and local agencies. Such repositories of Standard Reference Materials and samples could be maintained by the quality control groups, at the NERC's, Regional Offices, or both. In addition, EPA will identify and support external organizations as necessary, such as the National Bureau of Standards, the Atomic Energy Commission, U.S. Department of Agriculture, and private suppliers as essential repositories for Standard Reference Materials and standard reference samples. EPA, however, would continue to support the development of these materials.

The availability of Standard Reference Materials for use in environmental monitoring is currently quite limited. Standard Reference Materials are currently available for only three of the five gaseious pollutants for which EPA has set ambient air standards, these being SO_2, CO, and CH_4. There are also no Standard Reference Materials available for calibrating size and/or assessing the accuracy of chemical analysis of particulate pollutants. In addition, Standard Reference Materials do not exist for any of the pollutants for which EPA has recently set emission standards, and which ultimately must be monitored in ambient air, i.e., Hg, Be, and asbestos.

For radiation, the situation is considerably better. Many calibrated samples are prepared from Standard Reference Materials that are obtained from organizations such as the National Bureau of Standards and the Amersham Radiochemical Center. The samples that are available are shown in tables I and II.

Future needs for Standard Reference Materials in the area of radiation center around the development of nuclear power. Nuclear power is just beginning to grow with many power plants coming on line each eyar. New types of reactors (fast breeder reactors) are being designed that will produce radionuclides different from those previously encountered in environmental monitoring. At the same time, new emission standards have been issued and are being proposed that will reduce the release of radionuclides. These developments will result in the need for Standard Reference Materials that contain new radionuclides at lower concentrations. Specifically, Standard Reference Materials will be needed for all nuclides of the uranium and plutonium fuel cycles that can be released to the environment. The actinide elements will also become more important as the fast breeder reactor is developed. Standard Reference Materials containing iodine-129 are also needed since this nuclide with its long half-life will accumulate in the environment, thus requiring more extensive monitoring. The majority of Standard Reference Materials are available in aqueous solutions. There is a need to expand the available Standard Reference Materials to all matrices that must be analyzed for a comprehensive monitoring program. These include water, air, food, soil, and tissue.

The availability of appropriate Standard Reference Materials for water is considerably greater than for either air or radiation. Table III shows the EPA reference samples currently available.

There are also reference materials available for nine of the toxic pollutants for which EPA has promulgated effluent standards, i.e., aldrin, dieldrin, benzedine, DDD, DDE, DDT, endrin, PCB's and toxaphene. There are, however, no reference materials currently available for either cyanide or asbestos.

In conclusion, it might be said that the cost of environmental monitoring is so great that no one agency can be expected to perform the task alone. The monitoring data needed for enforcement and policy decisions such as standard setting, control strategies, etc., will thus be provided by many different agencies and institutions. In order to insure that these data are accurate and valid, an adequate quality assurance program is essential. Such a program must include intensive scientific work, an organized calibration and quality control effort, and a substantial training and evaluation program. The use of appropriate Standard Reference Materials is essential in each of these areas. The cost of an adequate quality assurance program is high. Ten to fifteen percent of the entire cost of the monitoring program itself may be required by the quality control program alone. However, the cost of not having reliable data is even higher. An understanding of pollution mechanisms for policy decisions such as standard setting, control strategies, etc., requires data that are scientifically related, as well as data that are accurate and valid. Successful enforcement of environmental standards through court action also requires incontrovertible data.

Table 1. EPA Radiation Standards Currently Available

NUCLIDE	TYPE OF EMISSION	HALF-LIFE
^{90}Sr	β^-	27.7 y
^{3}H	β^-	12.26 y
^{131}I	β^-, λ	8.05 d
^{140}Ba	β^-, λ	12.8 d
^{22}Na	β^+, λ	2.62 y
^{54}Mn	λ	303 d
^{65}Zn	λ	245 d
^{137}Cs	β^-, λ	30 y
^{60}Co	β^-, λ	5.26 y

Table 2. EPA Radiation Standards Periodically Available

NUCLIDE	TYPE OF EMISSION	HALF LIFE	MONTH AVAILABLE
^{35}S	β^-	87.9 d	January 1974
^{45}Ca	β^-	165 d	January 1974
^{56}Co	β^+, λ	77.3 d	January 1974
^{88}Y	λ	108 d	January 1974
^{109}Cd	λ	453 d	January 1974
^{32}P	β^-	14.3 d	February 1974
^{55}Fe	λ	2.6 y	February 1974
^{133}Ba	λ	10 y	February 1974
^{147}Pm	β^-	2.62 y	February 1974
^{185}W	β^-	75 d	February 1974
^{204}Tl	β^-	3.81 y	February 1974
^{57}Co	λ	270 d	March 1974
^{125}I	λ	60.2 d	March 1974
^{139}Ce	λ	140 d	March 1974
^{96}Rb	β^-, λ	18.66 d	April 1974
^{182}Ta	β^-, λ	115 d	April 1974
^{195}Au	λ	183 d	May 1974

Table 3. EPA Water Reference Samples Currently Available

Nutrients	- NH_3 nitrogen, NO_3 nitrogen, Kjeldahl nitrogen, orthophosphate and total phosphorus
Minerals	- pH, alkalinity, conductance, hardness, total dissolved solids sulfate, chloride, Ca, Mg, Na, and K
NTA	- Nitrilotriacetic acid
LAS	- Linear Aklylate Sulfonate
Trace Metals	- Al, As, Cd, Cr, Cu, Fe, Mn, Pb, Se, and Zn (three levels)
Demand Analysis	- BOD, COD, TOC (two levels)
Mercury	- Organic and inorganic (three levels)

SRM NEEDS AND MEASUREMENT PROBLEMS IN SCIENCE-CHEMICAL PROPERTIES

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The topic assigned is "SRM needs and measurement problems in science - chemical properties." To reflect on this, the first question is: "What is science?"

Most universities have a school of arts and sciences, which term seems to embrace the extremes of philosophy. A total science must be completely rigorous, while a total art has no rigor at all. Mathematics represents a totally rigorous science. I have asked a number of people about a total art. Here the consensus seems to be religion, where you are allowed to worship any kind of God you please, anyway you wish. A scale showing the gradation from art to science is given in the figure 1.

Close to religion are found the classical arts, painting, poetry, and music. While a great deal of latitude is allowed the artist (or musician or poet), he does have certain basic rules (rigor if you will) to follow. Anyone who has lived with teenagers and their music has the right to dispute this. I have recently heard professional football described as an "art form," but am not going to attempt to place it on the scale.

At the other end of the scale are found the logical sciences: mathematics, thermodynamics, and electromagnetics, followed closely by astronomy. By the time we reach physics, the scientific rigor has been compromised with such terms as "ideal gas," "perfect solution," "frictionless system," etc. Chemistry is still less mathematical. Biology is largely descriptive.

Medicine lies at the mid-point. It is certainly a descriptive science with mathematical overtones. However, the ability of the physician to instill confidence in his patients (his bedside manner) is definitely an art.

I personally feel that sociology and economics are more art than science, since we have highly respected authorities in both areas with very widely differing, indeed sometimes diametrically opposite, points of view.

The point of all this rambling is that as we proceed from art to science the change is marked by our ability to assign numbers to the various phenomena observed rather than to describe their shape, color, etc. The better we are able to measure the phenomena, the more "scientific" the endeavor becomes. To quote Lord Kelvin [1]:

> "When you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind; it may be the beginning of knowledge but you have scarcely, in your thoughts, advanced to the stage of science".

Over the past 35 years, each of the philosophies below sociology in figure 1 have become more and more measurement oriented. Medicine, which was almost totally descriptive a generation or so ago, now depends heavily on measurements of body tissues and fluids. Organic chemistry, biochemistry, and biology are becoming more dependent on numerically expressed measurements. The remarkable thing is that as the philosophies tend to move toward mathematic descriptions, a void is not left in the center. New areas, perhaps only dreamed about previously slowly emerge as descriptive sciences. Possibly someday such things as telepathy, extrasensory perception, and areas of metaphysics will emerge as full-blown descriptive sciences.

To move on to chemistry. For the purpose of this Symposium, Dr. Powell and I agreed that physical chemistry would be placed on the physics side of the wall. This greatly simplifies the distinction between the two. Physics is a science of dimensioned numbers relating back to the base units of mass, length, time, and so on. The results of chemical measurements are more often undimensioned numbers (ratios), that is, parts per hundred, parts per million, etc.

Presumably two groups of chemists totally isolated from each other could analyze a given material and come up with the same numerical result. Each group could fabricate a set of internally coherent weights and relate their volumetric glassware to them. The numerical analytical results obtained by each group should be the same. The only factor that possibly could cause a problem would be the different bases for their respective systems of numbers. In the area of physics, the measurement results of the two isolated groups would have to be reconciled by a much more complex system of conversion factors interrelating the particular sets of base and derived units developed by each group.

Along with the timber wolf and the steam locomotive, one of the vanishing bits of Americana is the classical chemist, the so-called "wet" chemist. These chemists with their weights, balances, and volumetric glassware can produce very precise, and more often than not bias-free accurate data. It would seem that such chemists would not need standard reference materials. However, a large number of the NBS-SRM's are intended for just these people.

Analytical measurements are made by the producer to assure his meeting of the specifications. The consumer makes the same measurements for the same reason. If all the analytical chemists doing this work were of the calibre of John Hague, R. K. Bell, and H. S. Bright of the National Bureau of Standards perhaps SRM's would be unnecessary. Since this is not generally true, the use of standard reference materials by both parties allow the chemist and his supervisor to guard against sloppy techniques, biases, and permit the producer and consumer to arrive at generally compatible and mutually acceptable results.

One of the few tools needed by the wet chemist is the table of atomic weights. At one time it was a basic premise of chemistry that isotopic composition of the elements was the same worldwide. Nowadays this is known not to be so. In the 1971 table of atomic weights, [2] nine elements were marked by footnote d, "Elements for which known variations in isotopic abundance in terrestrial material prevent more precise atomic weight being given." These are hydrogen, lithium, carbon, oxygen, silicon, sulfur, argon, copper, and lead. Certainly, some chemicals contain certain other elements that differ from the accepted atomic weight through artificial depletion. NBS presently offers a few SRM's certified for isotopic composition. Should very accurate work be demanded for compounds of the above elements, a need for more such SRM's would appear. In work of high accuracy, a deviation of atomic weights from the accepted value would be a definite bias in the system.

Before leaving the area of wet chemistry I would call attention to a very fine piece of such work that grew out of the SRM programs. This is the "Comparison of Redox Standards" by Sappenfield, Marinenko and Hague. [3]

In 1912, the National Bureau of Standards certified its first oxidation-reduction SRM, sodium oxalate, (SRM 40). This SRM was issued at the request of analytical chemists who complained that commercial material of the time was untrustworthy. Subsequently in 1927, SRM 83, arsenic trioxide, was issued, and in 1944, SRM 136, potassium dichromate. However, these three standard reference materials have never been quite compatible. Anyone who has made maps for the Boy Scouts, or for a course in surveying, knows that there is almost invariably an error of closure. This same problem showed with these SRM's.

The resolution is shown in the figure 2.

This figure shows graphically the intercomparison of two lots of arsenic trioxide, 83b and 83c, two lots of potassium dichromate, 136b and 136c, and one lot of sodium oxalate, 40h. All of the intercomparisons were by titrimetric methods. In addition 83c, 136b, and 136c were assayed directly by coulometry and 83b and 83c also by direct titration against iodine. These direct titrations may be considered absolute. Coulometry is based on the value of the faraday, which is related back to the base units of mass, time, current, and the definition of the mole. Titrimetric iodimetry is based on the atomic weight of mononuclidic iodine, which is related back to the base units of the mass and the mole.

Ideally, the effective purity of any of these SRM's should be the same regardless of the route. This is true to within ± 0.007 percent (less than 1 part in 10000) in every case except that of 83c against 40h. Here a bias of about 0.03 was known to exist. As a result of this really fine piece of work, the three redox SRM's that have always been provisionally certified will finally appear as final certificates.

To this point I have dealt entirely with manual, or classical, or "wet" methods of analysis. Prior to World War II a number of phenomena were developed to the point that fairly good analytical measurements could be made. These included emission spectrometry, infrared absorption spectrometry, mass spectrometry, photometry, and polarography. All of these showed promise, but the real problem was accurate means of quantitating the signals. The answer came as a result of radar and other programs of World War II, which led to the stable electronics necessary. As in any new area, a great deal of information can be derived in a qualitative or semi-quantitative way without standard materials. However, eventually the place is reached where such standards are demanded.

Classical methods give results that relate pretty directly to the analyte. Instrumental methods by and large produce an electrical signal that is related to the analyte. For instrumental methods to produce accurate results or comparable results between laboratories and over periods of time a standard reference material is essential. The answer in many cases is not a simple material, but due to matrix problems, interferences and the like, the standard reference material used to calibrate the instrument must closely resemble the material to be analyzed. This immediately implies large numbers of materials, indeed more than a single institution can hope to produce. The answer is a broadly conceived plan whereby the national standards laboratories cooperate closely with each other to avoid duplication. These national laboratories would also require the close support of industrial laboratories to prepare this myriad of standard materials. Cali has already spoken on this aspect. [4]

In many cases the technology to prepare an absolute standard in a given matrix does not presently exist. Clinical chemical measurements have moved forward rapidly both in the manual area and the automatic analyzer area. At the request of the pathologist and the clinical chemist, NBS has developed a group of standard reference materials in this area. These clinical SRM's are all high-purity compounds. I have been told many times by clinical laboratory workers that they cannot use these SRM's, that what is needed is a serum sample certified for cholesterol, bilirubin, etc. However, it is an unfortunate fact of life that absolute methods of analysis for these materials in serum do not exist at this time. To achieve this end we must follow the difficult course of developing a reference method, based on a standard reference material and ideally an absolute method, that has been proven to accurately describe the amount of a given material in serum. Such a project has been completed with calcium. [5,6] Work is in progress for lead in blood, glucose in serum, and the principle electrolytes in serum. Again, these are difficult projects and demand the help of the best people available.

Analytical chemistry in recent years has been very proud of its ability to determine successively parts per million, parts per billion, and now even parts per trillion. Unfortunately, in this rush toward trace elements, the accurate determination of major elements seems to be lost. We still write magnesium pyrophosphate as $Mg_2P_2O_7$, but we don't really know what it is. Most quantitative text books use a somewhat arbitrary correction factor. The same lack of knowledge plagues the chemistry of the poly acids and the hetero acids.

A year or so ago, NBS came out with SRM 999, Primary Potassium Chloride. Even here, the measured cations, potassium with a trace of rubidium did not balance the anions, chloride with a vanishingly small trace of bromide. Somewhere there was a small bias. For this reason, SRM 999 is certified for its percentage of potassium and chlorine, rather than for total purity. I am not sure just where standard reference materials fit into the problem of accurate analysis of major components. However, it is a field that needs to be resurrected and studied hard.

Science has been plagued at various times with the appearance of new disciplines and before the house can be put in order, large amounts of data are published, each related to different units or baselines. In many cases this is the result of insufficient basic knowledge, either relating to the new discipline or to supporting areas. The x-ray wavelength scale has developed with several different units since the time of Moseley and Bragg. [7] The measurement of enzyme activity, which is a kinetic measurement, has also given rise to another host of units. Both of these have needed basic work to resolve the problem. However, in other cases a proliferation of units and base lines results simply from a void no one bothers to fill. In some cases, all that is needed is an accepted standard reference material.

In 1958 Rudolf Mössbauer reported on work relating to the recoil-free emission and resonant absorption of nuclear gamma rays in solids. [8] This, of course, became known as the Mössbauer Effect. While first used to study physics problems, it was not long before it found its place in chemical structure analysis.

As with most new methods the early parameters obtained in Mossbauer spectrometry were only qualitative or, at best, semiquantitative. It was 1965 before attempts were made to develop quantitative data. Such attempts brought about the realization of the serious shortcoming of the data appearing in the scientific literature. The Mossbauer Chemical Shift for a given series of compounds was seldom reported for the same source. The effects of the different source matrices (chromium, stainless steel, iron, palladium, copper, and platinum) on the isomer shift of sodium nitroprusside are given in figure 3. Even with the same source material and matrix, differences between laboratories were found [9].

The most practical solution to this problem was felt to be the measurement of the chemical shift of the unknown compound with respect to a reference compound. This need was anticipated by attendees at the symposium on the Mossbauer Effect held at the Gordon Research Conference on Inorganic Chemistry in 1964. This same group suggested sodium nitroprusside. The result of this suggestion was Standard Reference Material 725.

Standard Reference Material 725 is a platelet about 1 cm square cut from a single crystal of sodium nitroprusside. The larger surfaces were cut parallel to the 010 crystal plane. As shown in the slide, when the surfaces are parallel to the 010 plane the two minima are equal. The maxima half way between these two minima is defined as the zero chemical shift. To quantitate the units, the electric quadrapole splitting between the minima was measured to have a velocity of 0.17015 cm/s. [9]

The early introduction of this SRM into Mossbauer spectrometry has served to reduce the number of bases for reported data in the literature. It is unfortunate that authoritative standards groups cannot carry out such standardization activities more frequently. Such work is very expensive and more often than not the interested scientists are lost in their work and are not motivated to worry and press for the development of standard reference materials in their new areas.

Early in this paper it was mentioned that the trend for a given scientific philosophy was to emerge as a descriptive science and then move toward a mathematically described science. This trend and the use of a standard reference material has been illustrated in a very recent piece of work by Velapoldi and Wicks. [10]

Suspected narcotics taken from persons by the police are subjected to preliminary field screening by fairly simple methods. It has been said facetiously that such field tests used by local authorities in pollution control and law enforcement must cost less than $25.00 and be capable of operation by the mayor's nephew. The tests studied were spot tests in which the resulting color or change of color is more or less specific for a given drug. Descriptions of color can be most subjective and in many cases the color changes are most subtle, say from deep orange to a light brown.

For many years NBS has offered SRM 2106, the Centroid Color Charts, which contain color chips, descriptive names, and numbers for 254 of the 267 colors in the Intersociety Council on Color System. [11] In their work, Velapoldi and Wicks studied the spot tests for many drugs and identified the colors produced in terms of the ISCC-NBS color descriptions. Such a work makes it possible for the enforcement officer to accurately describe and record the color on the spot and make a preliminary evaluation of what the suspected material is. Such description also makes possible much more acceptable evidence should the case reach prosecution in court. In light of this work it is interesting to speculate on future work to relate odors and tastes to numerical parameters and eventually to standard reference materials.

A perusal of the NBS-SRM Catalog or any other list of standard materials quickly reveals that relatively few areas of organic chemistry are blessed with a variety of high-purity compounds. The American Petroleum Institute offers a wide assortment of hydrocarbons of high purity. The National Physical Laboratory offers a number of high-purity alcohols, phenols and nitrogen compounds. Both the Environmental Protection Agency and the National Physical Laboratory offer pesticide standards. Plebanski has mentioned 50 or so organic standards are available in Poland. [12] The United States Pharmacopeia and the National Formulary both offer "authentic substances" related to their specifications.

From the list of these sources it is apparent that where organic SRM's exist, there is usually a need by some specific industrial or governmental group that is willing to support the work. General sources of high-purity organic compounds are not available. There are several reasons for this:

1. Probably the principle reason is the incredibly large number of not only individual organic compounds, but of classes, groups and subgroups which simply overwhelm a potential supplier.
2. Because of the diversity of work, the average organic chemist that needs a specific material of a certain purity will proceed to synthesize and purify it himself. When the work is done, the sample is dropped in a drawer and forgotten. It is indeed unfortunate that there is not some mechanism for collecting and cataloging these materials when they are no longer needed by the maker.
3. Instrumental techniques used in organic chemistry for analysis or structural determinations are quite new and perhaps have not reached the point where SRM's are needed. For example, in most cases in gas chromatography we are interested in the elution time, which can be determined about as well with a commercial material as with a high-purity compound.
4. High-purity organic compounds, especially liquids, are difficult to keep pure. Sealing in glass ampoules under their own vapor pressure works quite well for the API hydrocarbons, but with many compounds containing functional groups, the glass not only is a source of desorbable impurities but becomes an actual reagent. Plastic materials, including the fluorinated ones, tend to breath and over greater or lesser periods of time offer problems as containers for organic liquids. Certainly some research on containing high-purity materials for long periods would be useful. Barnard has mentioned earlier that of the three basic requirements for high purity; preparation, analysis, and containment, containment is presently the most critical. [13]

A few years ago, an effort was made by the Manufacturing Chemists Association and Texas A&M University to launch a program to collect and characterize "good" samples of the 100 most important organic compounds, that is, the 100 produced and sold in the greatest tonnage. The aim of this program was to make available samples from homogeneous lots of high-purity materials to competent investigators in all areas of science. The data determined would be either published or returned to a central point, Texas A&M, for collation. Unfortunately, changing priorities have reduced the activity in this area, but the germ of it is still alive and well. Certainly there is a need for banks of well-characterized organic compounds, whether they are called standard reference materials or not.

A more conventional type of organic SRM has been proposed by ASTM Committee E-2 on Emission Spectroscopy. This proposal is for several polymer materials certified for trace elements. Such elements find their way into these polymers as initiators, antioxidants, or even as tagging elements in the production process. The need for such materials is two-fold: first, industry must monitor and control these trace elements to allow more efficient production, and secondly, the Food and Drug Administration is becoming more and more particular about the quantities and kinds of metals that may be in plastics used in food processing.

Moving on to biochemistry and biology we come to areas that are even less developed in the mathematical sense than organic chemistry. In this area NBS now offers two standard reference materials, orchard leaves (SRM 1571) and bovine liver (SRM 1577). Each of these are certified for the major and minor elements and for a number of trace elements. Additional elements are given for information, which means that they are determined by only one method.

In both of these SRM's, we certify only that the elements are there in a given amount. No attempt is made to say which elements are essential and which are simply tramp elements picked up from the environment. Actually, the concept of essential elements in trace amounts is relatively new. In the plant area, prior to 1920, it was felt that only 10 elements were essential. These were carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, sulfur, calcium, magnesium, and iron. Since 1920, seven more elements at trace levels have been accepted by the plant physiologist as essential. These are manganese, boron, zinc, copper, molybdenum, chlorine and sodium. [14] A considerable commentary could be offered on each of these, but simple enumeration will suffice for this paper.

The knowledge that certain crops ruin soil has been known since the dawn of agriculture. Crop rotation, the plowing under of certain legume plants, and allowing fields to lie fallow are age-old practices. Even as chemical fertilization came into the picture the tendency was to fertilize only for nitrogen, potassium, phosphorus and an occasional sack of lime. Knowledge of essential trace elements has changed this picture. Zinc will improve the yield of fruit trees, boron the yield of grain and forage crops. Addition of zinc, copper, and manganese to the soil has made it possible to use previously unproductive areas in the Australian Outback for agriculture. [14] As the world's population continues to increase, it may be possible to bring other areas under cultivation by the addition of trace elements and thus postpone the Malthusian famine.

However, fertilization with chemicals must be done with restraint. Many of these essential elements can become toxic if applied in excess. A few years back we heard cries that the utrification of Lake Erie was partially aided and abetted by phosphates from fertilizer run-off. To keep things in balance, horticulturists and agronomists developed techniques for analyzing leaves and grasses for various essential elements and controlling the addition of chemicals accordingly. It was to calibrate and standardize these techniques that SRM 1571, Orchard Leaves, was developed. Already this SRM is proving its value in agricultural and biochemical research, and also in the somewhat unrelated area of air pollution.

It is suspected that many more trace elements are essential, but to date this has been impossible to prove. Trace element means just that! The amounts are so small that even under highly controlled conditions of growth the needed trace elements are found in the water and chemicals supplying the major nutrients. A real help to the plant physiologists would be chemicals for sources of the major nutrient elements needed by plants that are absolutely free of trace elements or at least free of the trace element under study. Earlier Dr. Barnard also mentioned this point. [13]

Trace elements in animals are equally recent. A list of trace elements accepted as essential to the human body are given in figure 4. [15] As with the plants each element has its own story. Zinc is felt essential to healing of wounds and mending of bones. Most fascinating to me is the possibility of chromium therapy as a treatment for diabetes.

Methods of analysis for trace elements in tissue are complex and difficult. In many cases the analyses made by biologists and biochemists are not up to the quality demanded by a good analytical chemist. It was to help in this area that SRM 1577, Bovine Liver was developed.

Within the next year NBS hopes to issue a sample of bovine serum albumin certified to meet the specifications of the National Committee for Clinical Laboratory Standards [16]. This SRM will represent the crossing of the bar between organic and biochemistry in the NBS-SRM area.

We are frequently asked about enzyme standards. At present our knowledge of enzymes does not allow for the certification of definitive SRM's. Until problems of measurement are solved, until we can learn to predict the activity of a reconstituted sample of lyophilized enzyme, such standard can only be considered as control material.

This is the final plenary paper of this symposium. I do not plan to offer a benediction, but it seems appropriate to close with some words from the 19th Chapter of Leviticus, verses 35 and 36.

> "Ye shall do no unrightousness in judgement, in meteyard,
> in weight, or in measure.
> Just balances, just weights, a just ephah*, a just hin*,
> shall ye have: I am the Lord your God which brought you
> out of the land of Eygpt."

Perhaps it is not too blasphenous to paraphase these scriptures to read:

> You shall strive for accurate measures in all areas.
> Accurate weights, balances, and volumetric glassware
> you shall have, and with well-designed methods and standard
> reference materials you shall be led into the promised
> land of meaningful measurements.

*Ephah - A unit of dry measure.
*Hin - A unit of liquid measure.

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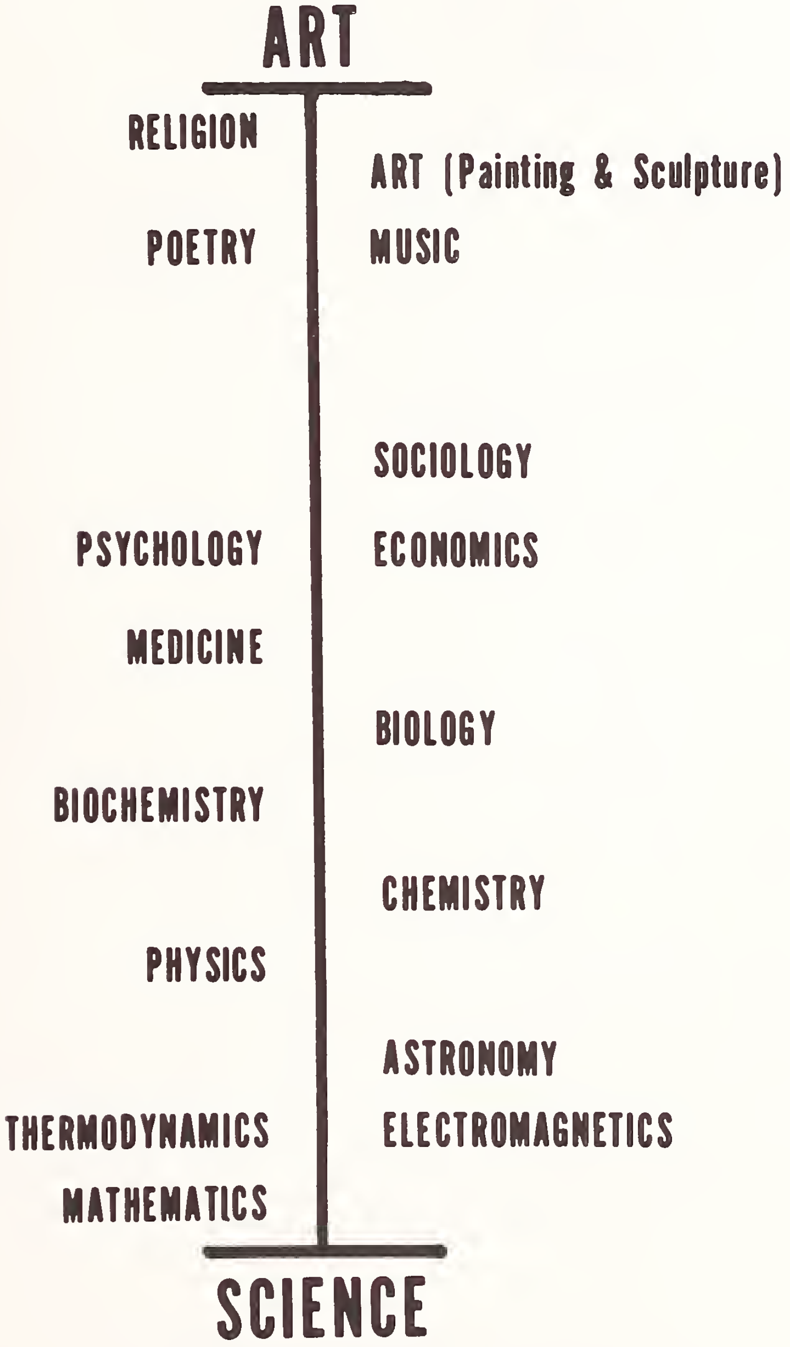

Figure 1. Distribution of various philosophies between art and science

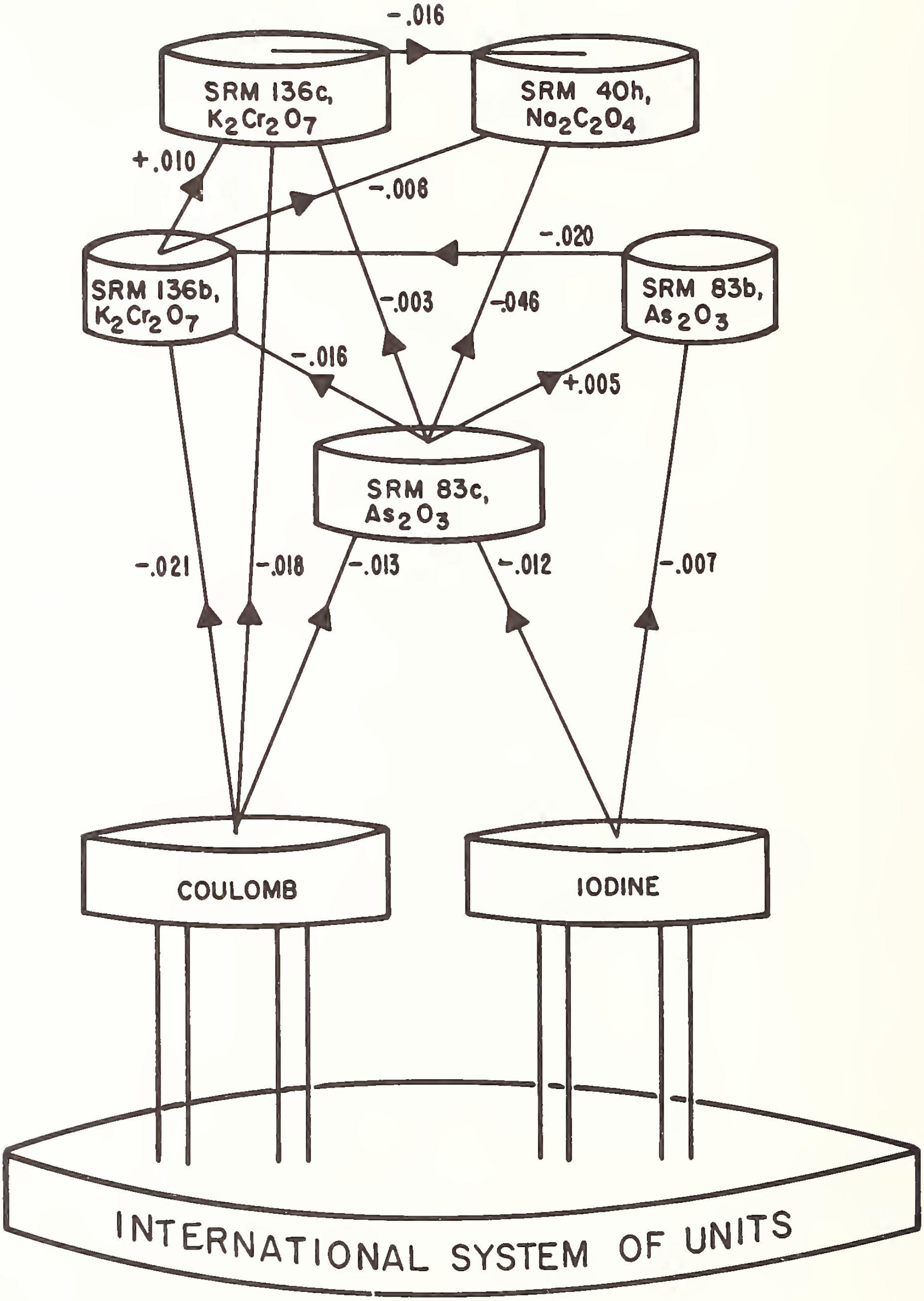

Figure 2. Intercomparison of NBS Redox SRM's and their relation back to the International System of Units. [3]

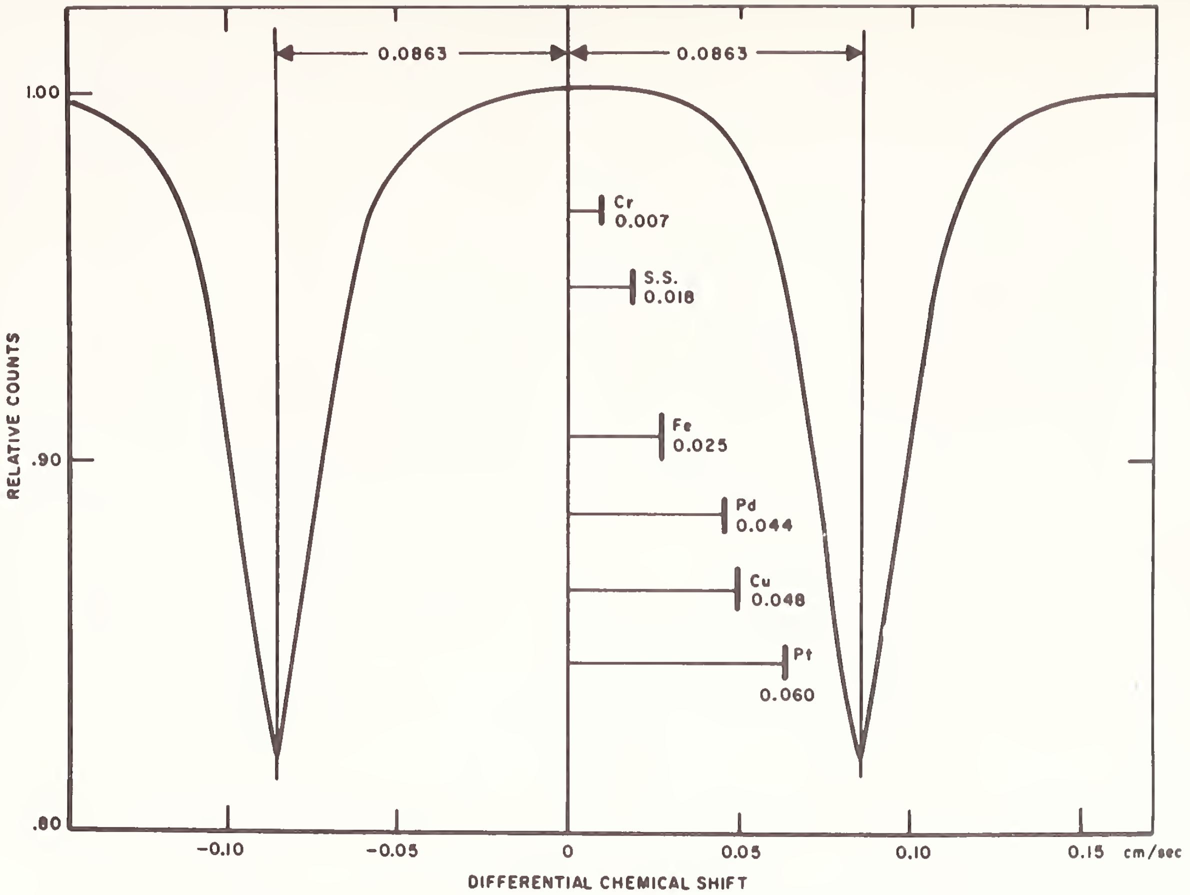

Figure 3. Chemical shift of sodium nitroprusside for different source matrices. [9]

ELEMENT	mg/70kg	MAJOR LOCATION
IRON	4200	HEMOGLOBIN
FLUORINE	2600	BONE
ZINC	2300	MUSCLE
STRONTIUM	320	BONE
COPPER	72	MUSCLE
SELENIUM	13	MUSCLE
MANGANESE	12	BONE
IODINE	11	THYROID
MOLYBDENUM	9.3	LIVER
CHROMIUM	1.7	SKIN
COBALT	1.5	BONE MARROW
(NICKEL)	10	SKIN
(VANADIUM)	<18	FAT

Schroeder & Nason, Clin. Chem. 17, 461 (1971)

Figure 4. Essential trace element content of the human body. [15]

AIR AND WATER POLLUTION

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I. Standard Reference Materials In Pollution Analysis

Robert E. Lee, Jr.

The need for Standard Reference Materials (SRM's) in the analysis of environmental samples has been recognized during the past several years and is one of the most rapidly expanding SRM development areas. Federal, state, and local air and water quality standards for protecting occupationally-exposed workers in a variety of industrial and agricultural activities require accurate chemical analysis for enforcement. SRM's can provide the analytical accuracy for enforcing environmental standards by aiding calibration procedures for monitoring instruments, evaluating new analytical methodology, providing a basis for interlaboratory comparisons, and by enabling the environmental analyst to verify measurements from monitoring networks. In addition, SRM's can help provide the compilation of an accurate data base that can be used to determine the need for new regulatory standards, to assess trends in environmental pollutants, and for research purposes.

Priority development of SRM's for environmental analysis has correctly been given to those pollutants for which standards have been promulgated. For example, considerable effort has gone into the development of permeation tubes for

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*Unable to attend

SO_2 and NO_2, two of the six Federal ambient air quality standards (SO_2, NO_2, CO, O_3, non-methane hydrocarbons, and total suspended particulate matter). New SRM's are also being developed for pollutants that are of considerable interest to the environmental chemist. Examples of these include an SRM for fly ash certified for about 13 trace elements and an SRM for ambient particulate matter certified for a number of trace and macro constituents.

It is hoped that the information brought out during these panel discussions will help focus on the need for new environmental SRM's that will have wide interest. Although SRM's for which a long term need exists would be most desirable, frequently an immediate need for an SRM arises that will have only a limited period of usefulness. For example, a gasoline SRM with certified concentrations of Pb at levels presently found in today's fuels will likely have only a short-term usefulness as these additives are phased out under proposed Federal regulations. With these general conditions, let us turn to the more specific uses and need areas for SRM's in air and water pollution analysis.

A. SRM's for Ambient Air Pollution Analysis

1. Gases

Preparation of SRM's for the ambient criteria gaseous pollutants (SO_2, NO_2, O_3, CO, and total hydrocarbons) has received considerable attention. Permeation tubes were first developed by O'Keeffe and Ortman[1] and represent a major break-through in the convenient preparation of known gas concentrations for instrument calibrations and chemical analysis. SRM permeation tubes for SO_2 are available from NBS in three concentration ranges.[2] An SRM permeation tube for NO_2 is under development jointly by NBS and EPA; however, problems have been encountered with leakage about the end seals.[3] SRM's for CO are available in the form of CO-nitrogen mixtures in cylinders in the 10 to 1000 ppm range.[3]

With the advances in development of sophisticated continuous gaseous air monitoring instruments, a need for an ultra-pure zero air standard for calibration has been recognized.[4] The sensitivity of newly developed air monitors is such that trace impurities in presently available zero air standards are readily detected. For example, a typical zero gas contains between 0.1 and 0.2 ppm of CO, CH_4, and hydrocarbons and, when used as a calibration diluent for gas chromatographic systems, can introduce a significant error.

Another SRM need is a permeation device for Hg. The Environmental Protection Agency has designated Hg as a hazardous emission pollutant.[5] This underlines the importance of making accurate ambient air measurements of this pollutant. It is certain that other SRM needs for gaseous pollutants will be brought out by the panel.

2. Particulates
It is my view that the development of SRM's for particulate pollutants is a highly important need area. NBS is presently undertaking a project to collect a sufficient quantity of suspended particulate matter from several urban areas for preparation of a SRM certified for a number of constituents. Dr. John Taylor will discuss this project in more detail. At this time, there are no standards for assessing the accuracy of chemical analysis of particulate pollutants. Hopefully, the SRM under development by NBS will go a long way toward meeting this need. The components most commonly analyzed by air pollution control agencies include SO_4, NO_3, NH_4, benzene-soluble material, benzoapyrene, and trace metals, which usually include Pb, Cu, Ce, Fe, Be, Mn, Ni, Sn, Cr, V, and Zn; these components should be certified in the particulate SRM.

In addition to a bulk SRM for particulate matter, several other SRM-need areas can be identified. Several particulate SRM's should be developed that represent various particle size fractions certified for trace constituents, especially for metals, in view of the important size relationships being developed.[6]

Consideration may also be given to the development of particulate SRM's of certified size for use in calibrating size-measuring instruments. At present, laboratory aerosols for calibration purposes, such as polystyrene latex spheres, are poor simulants of aerosols found in ambient air.

Future SRM projects for consideration would involve particulate matter deposited on selected filter material, such as glass fiber and membrane filters. These SRM's would aid the analyst in overcoming matrix effects from the filter as well as the particulate material. Of special significance would be a SRM consisting of a certified asbestos concentration in an air particulate matrix deposited on a membrane filter.

B. SRM's for Stationary Emission Source Analysis

1. Gases

Samples collected from stationary emission sources generally are higher in pollutant concentration and in potential chemical interferences than those collected from ambient air.

NBS in conjunction with EPA is developing a SRM for SO_2 emissions based on a cylinder gas mixture, and an NOx system. Other likely SRM's are associated with emission standards for new stationary sources (which generally are the same as the ambient air criteria pollutants) and include CO and hydrocarbons.

2. Particulates

Development of SRM's for specific particulate constituents will probably fall in importance behind ambient air particulate SRM's. EPA has promulgated hazardous emission standards for asbestos, Hg, and Be, [5] which represent logical candidates for SRM's. Perhaps a SRM for Hg in an iodine monochloride solution is likely to be developed as the reference analytical method is based on a flameless atomic absorption determination of Hg collected in an iodine monochloride absorbing reagent.

Although no hazardous emission standards nor new source performance standards for stationary sources have been promulgated for trace metals, the importance of trace metal emissions to the environment is recognized.[6,7] Development of particulate SRM's certified in trace elements for use in stationary emission sample analysis has been initiated with a joint NBS-EPA project to prepare bulk SRM's for coal and fly ash. The need for these SRM's was clearly brought out in a recent 68 laboratory round-robin experiment sponsored by EPA and NBS where results often differed by several orders-of-magnitude.[8] Future SRM's for emission analysis will likely be associated with those industries that emit the largest amounts of fine particulates: ferro-alloy and steel-making furnaces, lime kilns, Kraft pulp mill recovery furnaces, municipal incinerators, crushed stone plants, hot-mix asphalt plants, and cement kilns.[9] It is unclear, however, what the useful lifetime for these SRM's will be because control regulations may ultimately reduce the need for chemical analysis of specific emission pollutants.

C. SRM's for Mobile Source Analysis

SRM's in the form of cylinder gas mixtures for automotive emission analysis have recently become available and include propane in air and carbon dioxide in nitrogen;[10] also under development are carbon monoxide in nitrogen, and nitric oxide in nitrogen. Each SRM is available from NBS in a number of concentration ranges encompassing the levels ordinarily found in mobile emission analysis.

SRM's may need to be developed for particulate emissions from mobile sources if Federal standards are promulgated for specific constituents. Although fuel additive regulations may eventually control the emission of harmful particulates into the atmosphere, serious concern has been expressed by some researchers on the potential hazard associated with metal emissions from the degradation of oxidative catalytic control systems now under development.[11] A future need may be the development of an SRM consisting of automobile particulates deposited on a filter and certified for Pt, Pd, Ru, and other elements derived from catalytic systems.

D. SRM's for Water Pollution Analysis

Development of SRM's for water pollution analysis has generally been associated with Federal and State regulatory standards for effluents and water quality as in the case of SRM's for air pollution analysis. EPA's National Environmental Research Center in Cincinnati has taken the leadership in this area.

Development of future SRM's will likely be associated with newly discovered pollution problems such as the recent finding that asbestos fibers may be introduced into Lake Superior from mine tailings. Perhaps an SRM consisting of a certified asbestos content in water will have use.

E. SRM's for Special Pollution Analysis

Many reference materials are related to air and water pollution analysis although not specifically designated as such. For example, use of pesticides in agriculture can present an air and water pollution threat as well as an occupational health danger. Purified pesticide standards presently distributed by EPA's Pesticide and Toxic Substances Effects Laboratory at Research Triangle Park, N.C., are invaluable in pesticide analysis for assessing their environmental hazard.

Another category of material related to environmental pollution analysis is human tissue and other biological material. Several Federal agencies have expressed an interest in developing and maintaining human tissue banks for several purposes, one of which is to monitor trends in pollutant levels. SRM's consisting of selected tissue preparations certified for trace and macro constituents are likely to be needed in the future.

Fuel SRM's certified for specific constituents that can be emitted into the air are also useful in pollution analysis. NBS has several available such as a coal SRM certified for mercury and a fuel oil SRM certified for sulfur content.[12] Others should be available soon including SRM's for gasoline.

II. Air Pollution SRM'S

John K. Taylor

Many environmental analyses are made to determine whether some constituent exceeds a concentration limit. If the measured value is plotted with respect to the uncertainty of the measurement, one can categorize a decision to be made on the measurement as clearly no, clearly yes, or questionable (is the value true or is it a "high" low value, or a "low" high value). The greater the analytical error limit, the more often questionable values will be obtained. Our program at NBS is dedicated to reducing analytical errors, primarily by SRM's.

SRM's can serve several functions. They can be used to evaluate analytical methods, to test out the reliability of new methods under investigation, function as primary calibrants, and provide quality control of chemical measurements. A SRM can be a bona fide sample such as a typical steel or an actual atmosphere, a synthetic sample with the same properties as that being analyzed, a simulated material which will provide similar analytical problems, or an entirely foreign material which can transfer technology from one area to another. For the ordinary analyst, an SRM consisting of the actual sample material is most useful since he may not have the expertise to generate a test sample, or use substitute or analogue material. The NBS usually strives to provide actual materials for use as SRM's whenever this is possible. In the air pollution area, this approach is not always possible, so generatron devices such as permeation tubes may be required.

A technique which appears to be promising is one in which a gas with stable properties may be passed through a converter or exchanger to generate a new substance with limited stability. Other techniques that may be useful include preparative procedures based on vapor pressure, controlled thermal decomposition and mechanical systems such as the injection of a component by a piston. Dynamic dilution, based on blended two streams of gas, are attractive because they can provide a wide range of concentrations from a limited number of gas blends. Such devices are probably not feasible for laboratory use, however.

Whenever possible, the procedure used at NBS for SRM certification is to prepare primary gas standards by the gravimetric technique and also by volumetric or manometric measurement, or by dynamic blending. These primary standards can be used in turn to calibrate laboratory standards with which SRM's can be compared. We are concerned that our SRM's are stoichiometrically compatible with each other and are carrying out research in this area. The development of absolute measurement techniques is another activity.

A variety of SRM's are now available for air pollution analysis. These include: CO_2 in air--at ambient levels; O_2 in N_2--trace to atmospheric levels; CH_4 in air--1 to 1000 ppm; S in fuel oil; SO_2 permeation tubes; propane--air; CO in N_2--9 to 950 ppm; CO_2 in N_2--1 to 14 percent; Hg in coal; S and ash in coal; orchard leaves (simulated filter sample); trace elements in bovine liver.

SRM's under development include: NO in N_2 (2 to 1000 ppm); NO_2 permeation tubes; trace elements in coal, fly ash, fuel oil, and gasoline; calibrated ozone generators; urban air particulate matter.

In regard to the urban particulate SRM, a project is underway to collect two 50lb. lots of material in a baghouse-type collection device. It should require 6 months to collect each lot, one at St. Louis and the other at Los Angeles. A feasibility study has just been completed on a 100-g sample to develop techniques of analysis and to identify the problems of homogenization and packaging, for example. While awaiting this material, I would point out that the orchard leaf SRM is a good simulant for air particulate matter.

In addition to development of SRM's, the NBS Analytical Chemistry Division has been engaged in several activities related to the improvement of air pollution analysis. Reference samples have been developed and furnished to ASTM's Project Threshold for evaluation of analytical methods. In addition to permeation tubes, calibration materials have been furnished for the dustfall method, for sulfation plate measurements, for the analysis of both particulate and organic lead in the atmosphere and for the PDS method for

NO_2 in stacks. Any of these could be developed into SRM's if there was sufficient demand for them.

Assistance has also been given to EPA's program of method evaluation. Of special note was the development of simulated filters and wash solutions containing beryllium oxide and soluble beryllium compounds. Quality control materials consisting of small amounts of sodium sulfite dispersed in a solid diluent-mannitol have also been developed and have proved to be useful to evaluate the performance of regulatory laboratories.

The NIOSH measurement program has also been assisted by development of blood and urine samples containing toxic metals, charcoal absorbtion tubes on which known amounts of organic solvents were deposited, and filters containing deposits of toxic metals. Some of the above items will be produced as SRM's. In addition, gas dilution systems have been developed and described in a series of reports, and these devices can be used as adjuncts to SRM's for instrument calibration purposes.

The need for relatively concentrated gas mixtures at 500 to 2000 ppm level for calibration of source measurement apparatus has been recognized. Research is presently in progress to produce mixtures of this type for NO_x and SO_2 with the one-percent, long-term stability requirement of SRM's.

III. Remarks On Problems in Pollution Analysis

Lloyd Monkman

By way of background, I am the head of the Chemistry Division which has been in existence in one form or another for 27 years; at present we are under the Air Pollution Control Directorate, which is part of Canada's Environmental Protection Service. The Chemistry Division consists of a special projects center, which carries out analysis on polycyclic aromatic and pure polychlorinated biphenyl compounds, and vapor pressure studies of common pollutants to aid in improving collection efficiency; a laboratory services group; a methods development group; an international studies group, which is involved in international reference sample analysis; and an instrument evaluation group.

The number of SRM's that we use is small although we have all of NBS' 24 metal organic compounds. Despite the impression that few SRM's for pollution analysis are available, the NBS catalog lists 3 methane gas mixtures, 4 propane, 6 CO_2, 3 SO_2 permeation tubes, 4 sulfur in fuel oil and more. Although I have heard that an SRM can cost $160,000 I do not imagine that all are that expensive. To me, a SRM is not an end in itself but a means to an end. The value of a SRM depends on the use made by the analyst.

Development of an NOx permeation tube SRM by NBS has run into problems because absolutely anhydrous conditions are essential. However, we would like to see NBS prepare a gas mixture of 100 ppm of NO in nitrogen in pressurized cylinders. These are presently purchased from commercial manufacturers but require independent verification of the concentration levels, usually with internally prepared "primary" standards. We can accurately and reproducibly prepare these internal primary standards, which have shown that commercial mixtures are not very reliable. These 100 ppm standards should be made available by NBS.

Another desirable SRM would be a permeation tube for mercury. We have prepared one in our laboratory by sealing pure mercury in plastic tubing; the concentration of mercury from the permeation tube agrees well with syringe injections of saturated mercury vapor in air. Concentration changes are achieved by varying the gas flow over the tube.

In another area there is a need to control the electronics in monitoring instruments, i.e., the "black box." In electronic instrumentation, an electronic signal is produced and recorded continuously; some means should be found to validate the accuracy of that electronic signal.

Certifying SRM's by using two independent analytical methods cannot be overstressed. In chemistry, this has always been a well accepted method for assuring the accuracy of results. The fact that the NBS uses at least two independent analytical techniques in certifying SRM's is gratifying.

An instrument has a certain response that must be regularized and understood so we know that so many divisions on a scale means a certain concentration. It is only a hope that we can calibrate an instrument with a SRM. An SRM by itself will not necessarily provide an accurate calibration of an instrument. For example, if we try to calibrate side-by-side two sulfur dioxide instruments, one based on coulometry and the other on electrical conductivity, using a permeation tube SRM, we quickly see that comparability is a myth. Although the instruments may track each other well, the relationship between the two is not linear. Very often the instrument is calibrated with an SRM differently from the way an air sample is taken. In the case of one sulfur dioxide coulometric monitor, a glass fiber filter is used between the detector and the outside air; the filter actually removes a portion of the sulfur dioxide. Therefore, the way an instrument is calibrated by an accurately prepared SRM can seriously affect the kind of data obtained.

Laboratory instruments can be classified into two categories: those that are well designed for use in a chemical laboratory having a degree of precision and accuracy, and those that are simply "thrown together" from existing parts. In reliable laboratory instruments, the question of the chicken and the egg arises, e.g., do we have the spectra for the unknown material we have isolated from the air or do we not? This is a constant problem since it is easy to find unknown spectra of atmospheric material. We have found the mass spectrometer helpful in identifying these unknown spectra, and have prepared our own collection of polycyclic aromatic samples for reference.

In sampling particulates with a high volume sampler using glass fiber filters, it is assumed that different aliquots or portions of the filter will produce the same results in a laboratory analysis. In the past, our statisticians assured us that of the many hundreds of samples taken, particulates were equally distributed over aliquots of the filter sample. We have repeated the experiment many times since and confirmed that lead, at least, is uniformally distributed. The same exercise should be repeated for other metals such as cadmium and zinc. This system is also used to validate the analyst, insuring the quality of his analysis. We also use at least two analytical methods for metals analysis: atomic absorption and anodic stripping voltammetry (ASV). ASV is somewhat time consuming and it possesses almost too much sensitivity, which can produce some problems. Routine comparisons of ASV with atomic absorption are made for validation purposes.

The measurement of lead, cadmium, zinc, and vanadium pose some special problems. The relatively high concentrations of lead, however, minimize the blank problem. A highly clean room, free of cadmium contamination, is absolutely essential for assuring accurate cadmium data. In fact, I believe a great deal of the cadmium data reported in the literature for ambient levels are wrong. We had the experience of discovering a cadmiumcoated tray in one of our ovens used for drying glassware was a major source of contamination. Much of the analytical data we have obtained for cadmium on filters is zero or at the detectable limit of the method. Beryllium can react with the glass matrix of the filter complicating extraction; a membrane or cellulose filter with a low beryllium blank is recommended.

Filter blanks present a serious problem, e.g., there can be over 100,000 μg of zinc per glass fiber filter thereby affecting analytical accuracy. The glass fiber filter matrix for vanadium analysis by atomic absorption contributes an aluminum interference; a graphite furnace can eliminate the problem.

Several myths should be addressed. The myth of uniformity, sometimes better described as accuracy, is seldom attainable. The myth of comparability has been described in discussing the two different monitoring instruments above. Then we have the myth of the round-robin. A round-robin procedure, if not properly planned, will bring more difficulties than it will solve. Often the results of massive round-robin tests are never published because they are either not good or represent more data than can be easily handled. The arithmetic mean simply is a poor number that brings into question the meaning of pollution standards based on averages. The concept of data validity is a good one, but what do we do with the poor or incomplete data that is already in the literature?

Finally, physical methods are not completely divorced from matrix errors. For example, the x-ray physicist will find no matrix error with membrane or cellulose filters but he will on glass fiber filters.

IV. Remarks on Ambient Air and Emission Source SRM's

William Henry

I began as an analyst in both classical and instrumental chemistry; at present, I head a large diversified laboratory at Battelle. In the past year I have been associated with programs involving stack emission sampling, auto exhaust analysis, and similar types of activities. When one stays in a laboratory analyzing samples that derive from field-type work, one wonders how these samples can so often be poorly taken and labeled. But as one goes out and collects a stack sample, perhaps 60 feet up on the stack with the wind blowing, it is easy to see that you do not have ideal circumstances.

As you look at SRM's in pollution analysis, you could almost get a feeling of hopelessness. In the overall system to be measured, the sampling problem is hard to divorce from the analysis or to eliminate from the overall picture. As part of the sampling, there is the problem of a filter. Often the analyst has to deal with only a 100 mg of sample on a filter that represents a terrible substrate. In some cases, a chemically cleaner filter can be used such as a membrane filter. But in the case of stack sampling where you have a temperature problem, you are stuck with glass fiber filters. Some work is being done to develop a cleaner glass filter by going to quartz; this is certainly needed.

I differ somewhat with Lloyd Monkman pertaining to subdividing the filter, taking segments, and having absolute uniformity. I think it is degree of uniformity that is important. Sometimes we need to do a materials balance that calls for extensive segmenting of the filter. We have noticed visible variations at times on collected filters.

Although I do not want to dwell on the negative aspects of the problem, I want to point out that in many cases where we have not had standards available, we have been forced away from the instrumental analytical methods such as x-ray fluorescence. We have had to take the sample into solution and heavily rely on solution spark emission and atomic absorption methods where we can more readily prepare and use synthetic standards and minimize effects of matrices, particle sizes, and segregation.

In regard to the cost of SRM's, if an urban sample cost $160,000 I think it would be well worth it. We all recognize that there is a tremendous cost associated with developing standards. The needs for new SRM's as I see them would include pure forms of asbestos (crysotile, amosite, and others), a mercury permeation tube (which Dr. Lee mentioned), pure polynuclear aromatic compounds, a large urban sample certified in a number of components especially hazardous metals, individual industrial stack emission samples such as from the metallurgical and chemical industries, and finally, automotive pollution standards. Certainly the urban particulate SRM is of prime need, and the projected cost need not be a major factor. We need to determine what SRM's will have most use, especially in view of Dr. Lee's comment that some SRM's are fugitive and not long lasting.

Finally, I do concur with Lloyd Monkman that round-robins are of limited usefulness. A great deal of wasted effort often goes into them.

V. Remarks on Industrial Hygiene Standards

James Cavender

I would like to discuss some of the highlights of our program at NIOSH's Chemical Reference Laboratory located in Morgantown, West Virginia. The primary function of this laboratory is to provide a proficiency testing program for industrial hygiene laboratories operated by both state and federal governments. This is not an enforcement type program but one that is service oriented.

We provide monthly filter samples for lead, silica, and asbestos at four concentration levels. After the laboratories analyze these samples, results are returned to the Chemical Reference Laboratory, which determines their proficiency based on the consensus values from all laboratories. The proficiency for each individual laboratory is determined and reported back monthly in sufficient time for the laboratory to take corrective action before the next month's sample is sent.

The overall purpose of the program, which originated because of variable analytical results, is to help laboratories improve their operations. Early next year, we expect to expand this program to include cadmium and zinc on filters and an organic solvent (probably xylene) on a charcoal tube. The concentration of material on the filter sample simulates the amount that the analyst would collect on an 8-hour sample. NIOSH has a contract with the American Industrial Hygiene Association to develop a laboratory accredidation process; at that time, we expect to go to bimonthly rather than monthly samples.

The analytical samples, which are not standard reference materials, are prepared in our laboratory and distributed. SRM's developed by NBS could be expected to supplement this program. NIOSH is working with NBS to develop new SRM's in two phases: development of an analytical reference standard, which includes the analytical research, and the final development of a shelf-item SRM. Analytical standards under development include metals on filters such as cadmium, quartz, beryllium, tin, lead, zinc and manganese. In follow-up work, some will be developed into SRM's. NBS is also working on standards for mercury on charcoal tubes, inorganic lead on a membrane filter, and seven organic solvents on charcoal tubes.

VI. Water Pollution SRM's

John K. Taylor

From some of the earlier comments, one might get the impression that water pollution SRM's are in fairly good shape. However, it is my view that this is not the case. Past work has been concerned largely with the validation of the method of traditional water analysis, such as hardness, for example. We have not really addressed the problem of organic contaminants, nor other exotic substances that can get into water.

The present trend in water quality standards is to lower the permissible levels of many commonly occurring substances. In addition, effluent standards will require monitoring of many substances. Accordingly, water analysis may be considered as a growing field with many problems.

The Water Resources Laboratory of the Geological Survey has been distributing water samples for a number of years for round-robin analysis. The results of such exercises show that wide divergence in analytical results can be expected. The Analytical Reference Service of the former Analytical Reference Service, Bureau of Water Hygiene, Public Health Service has also conducted round-robins designed to evaluate methods. On the criteria those methods with total error of less than ± 25% are excellent, and those with errors of ± 50% are acceptable, not many methods have passed the test. On the basis of the kind of exercises just cited, the need for better quality control is emphasized.

The EPA Quality Control Laboratory has developed a number of water samples for method evaluations. They have used the Youden 2-sample plot to determine the acceptability of a method by the degree of scatter of the data points. An interesting fact is that laboratories often get better results for low concentration levels than at higher levels of concentration. Even on a sample pH measurement, large variability in results have been noted. Because good buffers are readily available, one would suppose that the problem may be one of method rather than of standardization but this is not clear.

The overall conclusion to be drawn from the above examples is that SRM's would greatly reduce the biases presently found in water analysis. While NBS does not have SRM's for this purpose at the present time, a program is now underway to fill this need. This will involve the development of stable samples at low concentration levels for direct use, and concentrates from which a number of levels can be prepared by dilution. Pure water will be required for this purpose, but NBS research has shown that water having impurities of less than 0.5 ppb can be made by non-boiling evaporation.

Sample presentation is a definite problem. The EPA Quality Control Laboratory has been able to stabilize concentrates by acid additions, for example. Very dilute reference standards may require other means to stabilize them. It should be possible to develop dynamic dilution systems to prepare solutions at low levels, as needed, from concentrates but little research has been devoted to such investigations.

In a related activity, NBS is working with EPA to develop sediment SRM's in which trace elements and other constituents and water analysis parameters will be certified. The sediments will be freeze-dried, homogenized, and analyzed by a multicompetence approach.

VII. General Discussion

Robert E. Lee, Jr., EPA - Dr. Philip LaFleur from NBS and Mr. Darryl von Lehmden from EPA directed a 50-laboratory round-robin study of coal, gasoline, fly ash, and fuel oil samples under development as SRM's to be certified for about 13 trace constituents. I would like to ask Dr. LaFleur to comment on the results, which often differed by an order of magnitude.

Philip LaFleur, NBS - The results of the intercomparison study were not especially startling since I have seen similar variability in results of other studies. For example, chromium at about 150 ppm in fly ash ranged from 22 ppm to 289 ppm (lab mean values) using atomic absorption techniques, although chromium should not have been very difficult to analyze. The grand mean of these values came close to the certified value. On the other hand, cadmium ranged from about 0.05 ppm to about 10 ppm with a consensus value of 3.9 ppm; the certified or true value was 1.5 ppm. One has to be very careful about consensus values since often these are not very good, especially if the results are based on only one analytical technique. In SRM development, we use at least two fundamentally different techniques that should include the total analysis, especially the dissolution step.

My group is now involved in a water analysis program using neutron activation. Dr. Taylor made the statement that sediment is not water but we view sediment as being exactly water. A water quality program should include the water, what is on the water, in the water, and what the water is on. We view the biota in the water and in the sediment, the sediment itself, and even the air above it. All of these things should be looked at as a system.

Francis J. Flanagan, U.S. Geological Survey - One of our scientists has made a study of the lead content in soils throughout the United States. The data is not too good but it does point out some of the analytical problems brought up here. There is a soil bank committee of the Soil Science Society of America that knows of a pre-1940 sediment sample which might be of interest to EPA.

In oceanic investigations, we have faced the same problems brought out this morning concerning the wide variation of data. I have recently taken an ocean sediment sample from about 50 miles off Boston Harbor which may be of interest in the future. Jim Owens, one of our geologists, has made a study of recent and prerecent sediment in New York Harbor, Chesapeake Bay, and the Philadelphia Bay that will show the differing trace element content over the past several thousand years.

Robert E. Lee., Jr., EPA - Dr. Timbrell (V. Timbrell and R.E.G. Rendall, "Preparation of the UICC Standard Reference Samples of Asbestos" *Powder Technol*. 5, 279, 1971/72) has done considerable work with asbestos standards that may be of interest. The standards were prepared from half-ton quantities of the commercially important types of asbestos for use in medical research. Several methods of chemical analysis were used to characterize the standards.

Oscar Menis, NBS - We have done some research on new methods for determining asbestos. I purchased Dr. Timbrell's sample, for $99, which consists of a selection of uniform particle sizes of asbestos. This problem of an asbestos reference sample is of interest to FDA, EPA, NIOSH, and others. These governmental bodies ought to get together to determine how we can give priorities and effectively participate.

Lloyd Monkman, APCD - We also have about five of these international reference samples that are color coded in plastic bags and have been prepared from large bulk material. Our laboratory extracted these samples with cyclohexane in order to determine the amount of organic extractable material present and to determine the quantity of polycycloaromatics. There is a small amount of extractable organic material and a considerable amount of aliphatics present as indicated by a complex gas chromatogram. Unfortunately, we have not been able to identify individual peaks in contrast to results reported in the literature.

James R. McNesby, NBS - During the next several years, it is likely that the NBS will be developing a number of SRM's in the area of water pollution, particularly for trace metals but also organics. Since we have heard of literally hundreds of potentially dangerous pollutants in water, we cannot randomly spend $160,000, or whatever the cost may be, on each SRM. Therefore, we need some means of establishing our priorities. I would like to know if EPA has a strategy for establishing priorities in the area of water pollutants.

Robert E. Lee, EPA - I do not know if I can address your question as satisfactorily as Mr. Ballinger could if he were here today. However, pollutant standards are the basis for SRM development. For example, the greatest need area for SRM's are for those constituents for which water quality standards and effluent standards are promulgated.

Seymour Hochheiser, EPA - I agree with Dr. Lee that pollutant standards are the primary selection criteria. Use of an SRM, however, does not assure the accuracy of data or the comparability of data from various laboratories and field monitoring stations. I personally think that an SRM that does not assure the comparability of data generated does not serve a very important purpose. Once a method has been established through use of SRM's, I can understand then going to pure samples to control the performance and accuracy of the system.

William Henry, Battelle - The urban particulate SRM that Dr. Taylor described will be a very complex one. I would anticipate that it would run well over the $160,000 figure we have heard mentioned. And if we go to source emission SRM's for selected industries, this would also be comparable in cost to the urban particulate SRM, although not much additional research would be needed. If, for example, the NBS prepared a fly ash SRM or an SRM from a metallurgical industry, the cost should decrease somewhat because of the similarity of the materials.

J. Paul Cali, NBS - I would like to comment on Seymour Hochheiser's philosophy in the use of SRM's. Throughout the past week, NBS has emphasized that an SRM is not the answer to all our problems. If you look at the measurement system *in toto*, it is clear that the SRM must stand in relationship to the reference method, i.e., the method of demonstrated accuracy. The SRM together with the reference method, to include the sampling procedure, provide the basis upon which various field methods can be tested for comparability, or, as we prefer, compatibility, throughout the whole measurement system. I again reemphasize that an SRM is almost a meaningless concept unless it is taken in conjunction with a method of demonstrated accuracy.

I would also like to clear up this $160,000 misunderstanding. I do not quite know where that figure came from, but SRM's as they become fixed within a given industry or technology go down in price. The original few that are made incur tremendous developmental costs in finding what the problems are; these are likely to be very expensive. But, for example, our sulfur in oil SRM cost nowhere near that much, perhaps only $5,000 production money for each one of the four we now have. A cost is determined by the research that leads to an SRM and is expensive in a new field; but after the research is completed, the cost of putting that SRM on the shelf is very much less and is of a reasonable cost. Dr. Taylor has pointed out that research monies, i.e., internal NBS funds or other governmental support, are not included in the price of the final SRM.

With regard to particulates, once you have a particulate SRM it serves even though you may want to look at one that has perhaps a different matrix. The procedures developed for the initial particulate SRM provide a baseline that can give some guidance in developing another particulate SRM of interest. Therefore, the costs go down remarkably.

Lloyd Monkman, APCD - I would like to get back to the question of the SO_2 permeation tube SRM and whether we need to do a complete or a partial analysis. What I think is wrong is that the instrument maker has built his instrument incorrectly. If the SO_2 standard is installed in one part of the instrument but the sample is collected at another part, then the analyst is in trouble. This is not the fault of the analyst but the fault of the instrument maker.

A. H. Gillieson, Dept.of Energy, Mines, and Resources, Canada - In contrast to my Canadian colleague on the panel, we are concerned with helping the industry comply with regulations. There are, however, certain toxic hazards associated with industrial safety where presently available sampling methods are not adequate. Continuous and immediate monitoring, in the sense of a warning, is a major need for the industrialist. Such monitors need not be precise but must provide immediate data, e.g., tetraethyl lead, cadmium, and beryllium. The calibration of such instruments may require a different type of SRM than can be used for air monitoring.

Robert E. Lee, EPA - Dr. Robinson of Louisiana State University has developed a continuous monitor for lead based on flameless atomic absorption. We should see more monitors of this type developed since there is a definite need as Dr. Gillieson has brought out.

Lloyd Monkman, APCD - Perhaps I should remark that there is communication between various departments of our government. The suggestion that we in air quality monitoring may be working in a vacuum is not correct. We are working, for example, on the practical problem of whether or not one can collect certain particulates. Much of the data in the literature is not accurate because the particulate matter was not quantitatively collected, e.g., mercury, arsenic, selenium, tellurium, polycyclic aromatic hydrocarbons, and perhaps cadmium. In one of our programs, we are examining the vapor pressure of some of these materials quantitatively. As a direct benefit of these studies, engineers can properly design control systems to minimize emissions of these materials to the air.

Earle Kebbekas, Precision Gas Products - Earlier this year we completed a contract for EPA, a carbon monoxide in air standard used in a round-robin study, and a contract for NBS involving a carbon monoxide in nitrogen standard. The NBS cylinders used were specially prepared in contrast to the EPA cylinders. Were there communications between EPA and NBS on these projects, and could someone comment on the EPA round-robin results?

It is our feeling that one can prepare stable standard NONOx mixtures in cylinders. We have had these standards in-house for about four years and have found them to be stable.

Seymour Hochheiser, EPA - We in the Quality Control Branch, EPA, in Research Triangle Park, North Carolina, conducted the round-robin test which Mr. Kebbekas mentioned. The final report is not out but the study indicated that a large number of laboratories showed biases, i.e., the data was linear but biased suggesting that the calibration gases used were incorrectly analyzed or had decayed.

In reference to the NBS and the EPA samples, I would simply comment that the NBS carbon monoxide standards were not ready at the time we needed them to do our study. I would like to see an SRM for carbon monoxide have an air matrix rather than nitrogen. Although the matrix has no effect on the NDIR reference method, it could make a difference to those who use flame ionization techniques for measuring carbon monoxide whether the matrix is air or nitrogen.

In addition, we asked for a 100 percent analysis on the samples your company prepared, confirmed by independent analysis in our laboratory. This becomes unduly costly in order to provide materials of this type for performance auditing purposes, which should be done frequently. Ways ought to be found to reduce this cost.

John Taylor, NBS - Our carbon monoxide SRM work was sponsored by NBS, EPA's Automotive Emissions Measurement Group, and EPA's Office of Measurement Standardization; reports have been widely circulated. It should be remembered that we at NBS prepare SRM's with a view toward long-term stability. We have developed a wax coating for the CO cylinders to enhance stability; this would have no effect on Mr. Hochheiser's short-term studies where stability is not necessarily a problem.

We used nitrogen as a matrix because it is geared to EPA's reference method (NDIR). Our studies show no difference in either the gas chromatographic or the NDIR analysis, in contrast to Mr. Hochheiser's comment. I would, however, fully agree with Mr. Hochheiser's remark on the need for standards. EPA's NDIR method evaluation study for ambient air levels of CO, in my opinion, evaluated the standards rather than the methods. If the laboratories had all used a common calibrating gas standard, rather than to supply their own standards, results would have been much better.

Alfred Eckert, Globe-Union, Inc. - In reference to sampling with the high volume sampler, what is meant by a cubic meter of air? Is this the air that occupies a cube one meter on the edge or the mass of air that occupies that cube under certain temperature and pressure conditions? What is the size of the filter that is used? What volumes are collected and at what rates are these volumes collected?

Lloyd Monkman, APCD - I have avoided mentioning volumes because in a batch sampling procedure, various accuracies relate to various portions of the procedures. The analysis of a given air sample produces a number, perhaps with six significant figures, which is then divided by the volume of air to obtain a concentration. The volume is determined usually by making a beginning and ending measurement of the 24-hour sampling period. (Since the sampling period begins and ends at midnight the measurement in fact is not usually taken at this time.) A linear relationship is assumed, a mean flow rate calculated, and a volume calculated by multiplying by the time, which is determined, at best, to the nearest minute. The volume, therefore, has a lower degree of measurement accuracy than the chemical analytical figure determined from the filter. The effect of temperature and pressure is usually ignored in actual practice although ways are known for making these corrections. We are presently carrying out experiments to improve volume measurements.

The filter size is 8- by 10-inches but the actual exposed area is somewhat smaller and depends on the accuracy with which the gasket is cut. The flow rates that we have obtained are somewhat lower than reported by others and depends on the type of filter used, i.e., high for glass fiber and lower for cellulose filters.

Robert E. Lee, EPA - The high volume air sampler is not as bad as some would lead us to believe. By way of example, EPA conducted a study in Britain where pairs of high volume samplers at four sites were operated by untrained operators over a six-month period. Out of a total of 430 sample pairs, 95% were within 10% of each other indicating the high level of precision associated with this method. The operating method was identical to that described by Lloyd Monkman, i.e., assuming a linear flow drop from an initial and a final measurement.

John Taylor, NBS - I concur with Dr. Lee's statement. We have had similar experiences with the reproducibility of the high volume sampler. Some of the criticisms I have heard relate to the question of how one correlates high volume sampler data with effects. Uncertainties in particle sizes collected and other technical questions make it difficult to interpret high volume data. Further, the fluctuations in line voltage can have a minor effect on flow.

Robert E. Lee, EPA - You have to keep in mind that the high volume sampler is one of the most inexpensive instruments one can use to make a large number of measurements. Only the dustfall jar and the sulfation candle that, in my view, generate data that has little meaning, are less expensive. For a cost as low as $100 a sampler, and with a minimum supporting chemical laboratory, the concentration of total suspended matter (defined empirically as "that which is collected by the high volume sampler") and the concentration of other constituents such as metals, sulfates, nitrates, organics, etc. can be determined. The question of particle size brought up by Dr. Taylor is a good one; we think that particles 20 μm in diameter and smaller are collected by the high volume sampler. Data from the instrument, however, is only as good as the care taken to operate it.

Lloyd Monkman, APCD - We have also gotten the same good precision Dr. Lee has gotten, but only in the hands of skilled technicians. In a study with seven high volume samplers, we obtained agreement within one $\mu g/m^3$ but only with frequent calibrations. The situation is quite different in our national network, however, where serious differences can occur.

Richard E. Brobst, Olin Brass - I have one comment on the comparison of results with EPA's standard water samples. Being a metal producer where not many standards are available, we are often called upon to provide standard samples to our customers to calibrate their laboratory instruments/procedures so that they may check our materials when they come in. In effect, they are using our numbers to check our numbers. As Mr. Monkman has pointed out, good laboratories usually produce good results. The problem is somewhat different with standard materials produced by a regulatory governmental laboratory and used for enforcement purposes. For example, in a waste treatment plant, if the standards are too low the company spends a great deal of money unnecessarily treating his waste water. If the standards are too high, he may have to unnecessarily redesign his entire waste treatment plant. I question the usefulness of these standards unless they are certified by NBS.

I have several questions for Dr. Lee. I do not understand what is meant by a zero air standard. What do you mean when you say in some cases SRM's will not be needed?

Robert E. Lee, EPA - I had some reluctance in using the term zero air myself. The problem is that some of the air monitoring instruments now under development are approaching such sensitivities that we can readily detect in a clean air diluent some of the things we wish to measure. A zero air SRM may be an unattainable goal but I have identified it as a need area.

Your second question pertains to an example I gave (lead in gasoline) to illustrate that some SRM's needed now may not have much usefulness in the future. EPA is in the process of promulgating standards for the lead and phosphorus content of gasoline. If that standard is 0.05 gm Pb/gal, a gasoline SRM that contains 2.5 or 3 gm Pb/gal common in today's premium grades, would be obsolete by 1976.

John Taylor, NBS - Mr. Brobst's comment addresses the accuracy of SRM's, particularly with regard to changes with time. The NBS is especially concerned with the accuracy of its SRM's and that no changes take place with time. This is a very important point that perhaps only a national standards laboratory can adequately treat.

Harold Rook, NBS - Most of the reference methods in use appear to require a highly-skilled analyst. However, most field technicians ordinarily do not have these skills thereby presenting problems of data comparability. In an effort to improve data quality, how does the panel view shifting the emphasis from chemical methods to remote sensing instruments that can be serviced at intervals by trained analysts.

Robert E. Lee, EPA - Unfortunately, I have never seen a trouble-free instrument. I have no strong views on whether we should use remote instruments or manual methods, however, I do think we will always need some type of sample collection somewhere, in our monitoring network. The reason for this is that we often need to reanalyze samples for those constituents we were not smart enough to look for earlier.

Lloyd Monkman, APCD - Dr. Rook has raised some important questions that we can answer only superficially here. One way of looking at this is to determine if you want the right answer. If the method is complex and demands a skilled and experienced operator, this must be accepted. I view reference methods as those done in a laboratory under optimum conditions; therefore, one should not be making reference analyses all the time.

In regard to wet methods versus dry methods, I have always been astonished that the environmental chemist from the outset has been determined to do things backwards. With wet methods, he has often used poor collection materials, ignored sample collection efficiencies, and made his analysis in the laboratory. With some hindsight, however, we now know that some pollutants such as ozone and oxides of nitrogen can best be measured by chemiluminescence, i.e., an accurate dry method. This, however, still brings us back to the calibration problem, which in the case of ozone is neutral KI, a wet method. We need to learn how to do calibrations in the dry phase and eliminate wet procedures.

Charles Plotz, EPA - Remote sensing methodologies, which are non-reference methods, will soon be published by EPA in the Federal Register. A procedure for determining the equivalency of non-reference methods will also be included.

Lee Ziegler, EPA - After we develop a method, it is then field tested by unskilled technicians to determine if it is foolproof. This is an important part of our program and includes documentation as to whether the method is satisfactory.

Oscar Menis, NBS - The selection of a reference method has to be carefully thought out. For instance, in the calcium in serum problem, the reference method was isotope dilution; but in the field, atomic absorption was used. Reference methods have to be related to field utility. In addition, all aspects of the analysis should be considered in a reference method such as the sampling, pipetting, etc.

J. Paul Cali, NBS - A reference material and a method of demonstrated and proven accuracy are essential to attain accurate measurements. A reference method in principle does not have to be a method that can be used by everyone in the field. It may be a complex method that can be used by only a relatively few competent scientists, but the transfer of the accuracy to the field methods can be accomplished by testing against the reference method.

James McNesby, NBS - In defense of physical methods of analysis, the method for ozone does not necessarily need to depend on a chemical analysis. The number of ozone molecules in a given pathlength can be measured, through freezing and revaporization, and an absorption coefficient determined. In addition, the accuracy of sulfur dioxide methods is determined by permeation tubes that are calibrated by the amount of weight lost. Absolute numbers for nitrogen dioxide will also be determined this way requiring no chemical analysis.

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I. INTRODUCTION

Portland Cement concrete is the leading structural material throughout much of the world. While most concrete is still used in parts of construction that are hidden from view such as foundations and structural frames, there is an increasing use of the material as an architectural medium and in this application, appearance becomes an important than it was previously. Uniformity has other merits, because with good quality control, a lower safety factor is possible resulting not only in lower costs but also in savings of materials and energy resources. One of the important variables in concrete quality is concerned with uniformity in the cement used to produce the concrete. Adequate test procedures are necessary for properly characterizing cements. With these tools it is possible to classify the various products, prepare purchase specifications, and, exercise quality control.

Every test for portland cement has an element of empiricism. Uniformity in test results between operators and laboratories is obtained by the development of detailed test procedures including requirements for standard test materials and apparatus. In some cases, however, the equipment cannot be adequately specified and therefore must be calibrated using a standard reference material (SRM). In others, the ability of the equipment to furnish reliable data for cements made with different combinations of materials must be determined by use of SRM's.

The two areas where SRM's have been developed and used are the measurement of fineness and of chemical composition.

The National Bureau of Standards was involved in testing portland cement for other Federal agencies for over sixty years; and during much of that time maintained testing laboratories not only in Washington, D.C., but also in other locations across the country. This activity, together with a large scale research program on cement during most of this period, led to a great deal of work on the development of test procedures, both of a chemical and physical nature. NBS, as this nation's standards laboratory, was therefore interested in and had the qualifications to issue SRM's deemed necessary in cement testing. Although the NBS no longer conducts the cement testing program and is not as actively engaged in development of testing procedures as it formerly was, the samples for the cement standards still form an important part of the NBS Standard Reference Material program. Additionally, it should be mentioned that the Cement and Concrete Reference Laboratory, a joint project of the American Society for Testing and Materials and the NBS, operates a cement reference sample program that augments the cement SRM's.

A. Fineness

1. No. 200 Sieve Residue (Dry Sieving)

The first property for which need for an SRM was recognized was fineness as measured by the No. 200 sieve. In Bureau of Standards' Technological Paper 29, Variations in Results of Sieving with Standard Cement Sieves, by R. J. Wig and J. C. Pearson (1913), results are reported on tests with different sieves and different operators. Technological Paper 42, Standardization of No. 200 Cement Sieves, by the same authors (1914), reported on cooperative tests between some 80 laboratories, and announced the issuance by NBS of standards samples for use in calibration of the number 200 sieve. The sample sold for 25¢! Prior to the selection of portland cement as the standard sample material, tests were run on a wide variety of other powdered materials and it was concluded that portland cement was as good or better for use as a standard sample than any of the other materials tested.

It was pointed out that the effectiveness of the sieve correction factor as detemined by use of the standard sample, depends upon similarity of the standard sample and the test material from a particle-size distribution standpoint. It was also pointed out that a better correction factor may be obtained by using two standard samples. Over the years a pair of standards were issued; one with residue of about 22 percent which was the specification limit for ordinary portland cement; and the other with a residue of about 6 percent. The residue on the No. 200 sieve formed the basis for the fineness requirement in cement specifications until the 1930's at which time it was gradually replaced by a surface area requirement, the value being determined by the Wagner turbidimeter.

2. Suface Area (Specific Surface)

The surface area of a powder such as portland cement is defined as the total surface area of all the particles in one gram of the material, and usually is expressed in units of cm^2/g. Routine tests for surface area of cement have usually been limited to rate-of-sedimentation, or to air-permeability methods.

a. Rate of Sedimentation Methods.

The rate at which a spherical particle sinks in a liquid depends upon, among other things, its diameter. If the rate of settlement can be measured, the diameter can be calculated using Stoke's Law. In making the test, a dilute suspension of cement in an inert liquid such as kerosene or alcohol, is prepared. A small amount of a dispersing agent, such as obeic acid with kerosene, or calcium chloride with alcohol, is required to separate any powder agglomerates. The suspension, in a suitable container, is made uniform by agitation and then allowed to settle.

During settlement, the particles of each particle-size range will settle uniformly. The concentration of that size range of particles at any fixed depth in the suspension will remain uniform until all the particles of that size initially at the top of the suspension, have settled beyond this depth.

The time at which all the particles larger than a given size, say 30 μm, have settled below a given level, say 7.5 cm, can be calculated from Stoke's Law if the particles are assumed to be spheres and their specific gravity is known, and if the specific gravity and viscosity of the liquid are known. The quantity of material that remains in suspension at a given depth and time can be measured by any of several procedures.

(1) Andreasen Pipet.

In the Andreasen Pipet method a sample

of suspension is pipeted from the settling tank at various depths and times. The quantity of solid material per unit volume of suspension is obtained by evaporating the liquid, in this case alcohol, and weighing the residue.

(2) Hydrometer Method

In the hydrometer method, which is similar to that used for measuring the particle size distribution of soils, a special hydrometer is carefully lowered into the suspension at selected intervals. The quantity of suspended material can be calculated from the specific gravities found, if the specific gravity of the liquid and of the cement are known.

B. Wagner Turbidimeter

In the Wagner turbidimeter, a narrow beam of light is passed through the settling chambers, which in this case has parallel, flat sides. The transmitted light intensity is measured by a photocell and microameter. The change in transmitted light intensity is related to the quantity of solid material in the light path by Beer's Law.

In all three methods, a series of measurements will yield, through suitable assumptions and calculations, the particle size distribution, and from this the surface areas of the powder.

The larger sized particles settle out too rapidly to permit ready measurement by a settling rate technique. The error caused thereby is corrected by measuring the fraction of larger particles by wet sieving a duplicate sample through a No. 325 sieve (44 µm). The material retained on the No. 325 sieve contributes very little to the total surface area and is ignored in the calculation.

The values obtained by any of the methods are dependent on the assumption inherent in the calculation method and on limitations in the measurement system.

Of these methods, only the Wagner turbidimeter has had wide application in specifications. The following discussion is primarily concerned with this method.

In addition to the assumption that the particles are spheres and are opaque, the Wagner determination only measures particles larger than 7.5 µm. In calculation of the surface area, it is assumed that the average particle less than 7.5 µm is 3.75 µm in diameter. Since a large portion of the surface area is associated with these very fine particles, the Wagner method is not sensitive to changes in surface area, in very fine materials. In fact, no matter how fine the material is, the Wagner method will never yield a figure greater than 5070 cm^2/g. This method could be improved by extending the particlesize measurement range to smaller sizes but this requires considerable extra time in making the test. It could also be improved by use of newer, more sensitive light detecting sources and narrowing the width of the measuring light beam. One modification that has been developed utilizes x-rays rather than light.

Due to easier grindability, much of the gypsum in the cement is concentrated in the finer particle sizes. This changes the opacity in the optical method, and the absorption coefficient in the xray method. While the Wagner turbidimeter makes certain assumptions, which are questionable, it should be possible with two similar instruments to measure the same cement, make the same assumptions in application of Stokes' Law, and obtain results in reasonable agreement. In practice, however, this is not the case, making necessary a standard reference cement for use in calibration of the instruments.

Adjustment of the instrument to get the correct value of the standard sample is done by varying the light intensity. Strictly speaking, this is not legitimate because the number 2 in the numerator of the Wagner formula is the logarithm of 100, where the latter is supposed to be the microampere reading with clear kerosene and no cement. It is not uncommon to find instruments that have to be set at initial light intensity corresponding to 120 microamperes to give the assigned surface area for the standard sample. It is evident that the Wagner surface areas involve questionable assumptions and therefore a certain degree of empiricism. This does not necessarily limit the usefulness of the test, but it requires an arbitrary assignment of a surface area figure to the standard sample. The first issue of SRM 114 carried a surface area figure that was based on tests made on a number of Wagner turbidimeters. In assigning numbers to subsequent issues of SRM 114 every attempt was made through comparative testing to keep the numbers of succeeding SRM's consistent with each other. The extent to which this succeeded is unknown.

1. No. 325 Wet Sieving (Change in Basis)

As noted above, the Wagner procedure also requires determination of percent of material passing the No. 325 sieve. Being finer than the No. 200 sieve, the No.

325 sieve presents even greater need for calibration because of weaving difficulties and consequently the SRM developed to calibrate the Wagner also carried a value for the No. 325 sieve residue. The original value was based on results obtained using a group of selected bronze sieves. These sieves had a number of oversized openings due to lack of uniformity in weaving the wire cloth. The Wagner method assumes that the largest-sized particle passing this sieve is about 60 μm, although the nominal opening of the No. 325 sieve is 44 μm. Eventually, stainless steel sieve cloth became available and this cloth had fewer oversized openings. Consequently, the sieve correction for the newer sieve became larger and larger as the sieves became better and better. The NBS was asked to revise its No. 325 sieve value on the SRM so as to base it on current stainless steel sieves as opposed to the previous bronze cloth sieves. It was decided, however, that it would be preferable to base the standard figure on electro-formed cloth sieves. These sieves have quite uniform hole size, but are not sturdy enough for routine use. Accordingly, a set micro-electro-formed cloth sieves was obtained, the opening sizes were measured by a microscopic technique, and a new residue figure was obtained. SRM 114 has been reissued many times with succeeding issues labeled 114a, 114b, etc. SRM 114-L carried two figures for the No. 325 residue, one consistent with that previously obtained with the original bronze wire cloth sieves and one based on electro-formed sieve cloth. Beginning with SRM 114m, only the electro-formed sieve cloth figure will be given.

Since the Wagner method calculations assume that the maximum sized particles passing through the bronze sieve cloth were about 60 μm, the change in the No. 325 sieve standard made necessary a change in the Wagner method. Accordingly, the Wagner method was modified so as to take the first particle-sized reading at 50 μm rather than 60 μm.

At about this same time, the ASTM sieve committee adopted ISO sieve sizes and the nominal size for the No. 325 sieve was changed from 44 μm to 45 μm. The sieve residue for SRM 114 was adjusted accordingly. The change in the Wagner method, the shift from the bronze cloth to the electro-formed sheet No. 325 sieve standard, and the change in nominal opening size for the No. 325 sieve, taken together, reduced the assigned figure for the Wagner turbidimeter on SRM 114-L from 1820 cm^2/g to 1800 cm^2/g.

The shift in Wagner value was nominal but confusion in the industry, as gauged by results obtained on comparative tests, was substantial and still continues even though the certificate for SRM 114-L gave specific instructions for its proper use.

The number No. 325 sieve is used for materials other than portland cement and the change in base required changes in specification limits for such materials as fly ash and natural cement.

Detailed information on the Wager turbidimeter together with an extensive bibiliography is given in a paper by Hime*, while additional information on the Andreasen-Pipet can be found in a paper by Grindrod.*

2. Air Permeability Methods

An air permability method for measuring the surface area of portland cement was developed in England by Lea and Nurse. In this method a stream of air under constant pressure passes through a bed of cement and also through an accurately measured capillary. Manometers measure the drop in pressure across the bed of cement and across the capillary tube. The later measure permits calculation of the rate of flow. The pressure drop across the bed of cement is related to the surface area of the cement by suitable equations for fluid flow through granular materials. Blaine developed a modification of this apparatus which is much simpler to operate, but which utilizes a variable rate of air flow and measures the time for a given volume of air to pass through the bed. Calculation of surface area by this method is more difficult than that for the Lea and Nurse apparatus and consequently the figure assigned for Blaine fineness in SRM 114 is based on measurements with a Lea-Nurse apparatus. As discussed by Hime*, the equations used to calculate the surface area by air permeability methods require certain assumptions and the arbitrary assignment of a figure to one of the constants in the equation. Consequently the air permeability method, like the Wagner turbidimeter method, is somewhat empirical in nature, and the surface areas found are therefore arbitrary ones. Also with the Blaine method, at least, it is desirable to calibrate the equipment with an SRM.

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*ASTM STP 473.

3. Blaine versus Wagner

The Blaine and Wagner methods give surface area results that are far apart in magnitude. On the average, the Blaine surface area is about 1.8 times that of the Wagner. But this ratio depends upon the particle size distribution, which in turn depends on properties of the cement clinker material, and the grinding procedures used. As mentioned earlier, the Wagner method fails to properly account for very fine material in the cement, while the Blaine results are sensitive to this fine fraction. In comparing the fineness as determined by the two methods, the role of gypsum must be considered. Gypsum grinds more easily than cement. Consequently, much of its contribution to the surface area may not be measured by the Wagner method. On the other hand, gypsum has a lower specific gravity than cement and in a sedimentation method such as the Wagner one, gypsum particles of a given size would settle slower than those of cement. Of interest are measurments made by Grindrod* by which he calculated the surface area of cements from measurements with an Andreason Pipet down to particle sizes of 1.25 μm. The surface areas obtained differ from that measured by the Blaine apparatus by less than 1/2 of 1 percent.

The Blaine apparatus is simple and easy to operate. Some feel that the particle range in portland cement that serves a useful purpose lies between 3 μm and 30 μm. Particles smaller than 3 μm hydrate too rapidly to contribute to the cement strength after placement, and those larger than 30 μm never hydrate. It is perhaps for this reason that many manufacturers find the Wagner method is better as a control instrument to maintain uniform strength. The Wagner method also, of course, permits calculation of the particle size distribution, which is useful in checking on the performance of the grinding equipment. The present system, where the Blaine method is prescribed for use in the cement specifications and the Wagner method is additionally available to those who wish to use it, appears to be satisfactory, even though both methods could be improved with resultant increased usefulness.

4. Selection of a Fineness SRM

One question faced by those selecting the cement for an SRM, concerns the properties of the materials

*STP 473

selected. It seems apparent that the particle-size gradation should be similar to the cements that will be measured by the methods used. The current SRM, 114m, has been criticized as being of too high surface area. Such criticism could be valid from at least two standpoints. From the testing standpoint the most critical surface area is in the range that might result in rejection of the cement. To get the best values, the SRM's should therefore have a fineness approximating that of the specification limit. Actually at present, most cements are ground to a fineness that far exceed the specification limit and hence this problem is not critical. However, the methods are also used for coarser cements such as those used in oil well cementing, and this might make desirable the selection of an SRM with fineness somewhere in the middle of the total range of fineness encountered.

a. Packaging

SRM 114m samples are hermetically sealed in glass. An appropriately sized lot of the selected cement is screened through a No. 50 sieve to remove any over-sized material and to break up agglomerates. The lot is then tumbled for about four hours in a double cone or twin-shell blender. It is then stored in 5-gallon, sealed, lard cans until put in the individual vials. The vial filling operation preferably takes place in the winter when the indoor humidity is low.

For many years the vials were filled manually, the cement consolidated by tapping on a table, and the vials sealed by a hand operation. It required a large staff, and there were many burned fingers. The acquisition of an automatic sealing machine, together with improved vial-filling techniques reduced the work, produced better seals, and reduced exposure of the cement to the atmosphere during packaging.

The empty vials are placed in racks similar to those described later for the chemical SRM's. Cement is added to the vials in approximately the correct amount. It is then consolidated by vibration, as described for the chemical samples, and fed into the sealing machine. For convenience, the vials used are the same size as the outer vials of the chemical samples.

b. Checking Uniformity

Uniformity of a sample lot is checked by making fineness tests on samples withdrawn during the sealing operation. None of the lots prepared in the past have given indication of lack of homogenity.

It is possible that SO_3 measurements could also be used to check the uniformity, since the gypsum fraction of portlan cement is finer and of lower specific gravity than the cement clinker fraction. The sensitivity of such a procedure would need to be checked, however.

c. Calibration

The SRM certificate values for the No. 325 sieve were obtained for many years by use of a set of bronze cloth sieves set aside for the purpose. When this set of sieves was inadvertently lost through unauthorized use, the next sample issue was calibrated by comparison with a number of previous SRM issues. Currently the figures are based on measurements with calibrated electro-formed cloth sieves.

The Wagner value was originally established by measurement on a number of Wagner instruments with the I_o set at 100 microamperes. Tests were also made using a half-concentration method. Subsequent SRM issues have carried figures based on comparison with previous issues. These comparisons involved as many as 8 NBS cement testing laboratories together with the research fineness laboratory in the Concreting Materials Section. With the demise of the NBS cement testing activity, cooperation of the cement industry was sought, and 10 or 12 cement company laboratories each make 10 tests with the current SRM issue and 10 with the one in preparation. Outlying values are discarded as had been the case when NBS laboratories did the calibration.

The certificate value for the first SRM carrying an air permeability fineness value was obtained using a Lea-Nurse apparatus. Subsequent sample issues have been compared with previous ones as for the Wagner determination. Comparisons on the Lea-Nurse apparatus were also made on occasion. It is recommended that a number of Lea-Nurse apparatuses be obtained for future use in checking the air permeability figures for the SRM.

d. No. 200 Sieve Residue (Wet Sieving)

The No. 200 sieve has not been used in cement specifications for many years and the SRM's used for calibration of the No. 200 sieve have long been unavailable. However, the No. 200 sieve as well as the No. 100 and No. 50 are important tools in the control of portland cement manufacture. The fineness subcommittee of ASTM of C-1 on cement has recently developed specifications for wet sieving using the No. 200, the No. 100, and No. 50 sieves. The specified procedure for the No. 200 sieve, is based on dry sieving with NBS glass bead SRM's. Better results could be obtained by issuing new cement SRM's whose figures are based on measured electroformed sieve cloth in the same manner as for the No. 325 sieve. From the NBS standpoint such a procedure would be straightforward, but the expense could not be justified unless demand and sale of such an SRM were sufficient to fully reimburse the activity. It was concluded at the meeting that the need for standardization on a national basis was not necessary and thht each company could establish its own internal standards for their various manufacturing units.

C. Chemical Analysis

1. Historical Information

The specifications for portland cement have included limitations on chemical constitutents almost from the start. As the role of various constitutents became better understood, special purpose cements having controlled heat of hydration, or sulfate resistance, or lower alkali content were developed. In some cases, it was found expeditious to classify the cements by chemical composition. This meant that more and more constitutents in the cement had to be measured to determine if the product met specification requirements, and better control of composition of raw materials had to be obtained. Chemical composition was determined by traditional inorganic quantitative tests.

Determination of the sodium oxide and potassium oxide content of cements, which became very important after the alkali silica reaction was identified as the source of a considerable amount of concrete deterioration, proved to be particularly difficult and time consuming. Incentives for faster methods led to application of the flame photometer for determining these alkalis. The instrumental analysis was so satisfactory, and so universally used, that many chemists lost, through disuse, their ability to satisfactorily measure the alkali content by conventional methods. About this time manufacture of the particular flame photometer that had been used by most laboratories was discontinued. The first approach to a performance-type test method resulted and the procedure was written so that any flame photometer could be used, provided it could be demonstrated that it gave the correct value for prescribed standard cements.

A word is necessary here concerning the existence of standard cements at that time. Over the years, NBS received many requests for a standard cement sample from people who were working on test procedures of one type or another. The analytical chemistry experts at NBS refused to issue such a sample because they felt that it could not be satisfactorily protected against contamination by atmospheric carbon dioxide and moisture. When an automatic sealing machine was obtained, however, for the fineness sample, experiments with an inner vial and plastic stopper demonstrated the feasibility of producing a sample with long term stability. As a result, the Concreting Materials Section packaged a sample and the NBS Chemistry Division made tests and assigned values. This was SRM 177. The Concreting Materials Section participated in the tests on this SRM and their results were in very close agreement with those obtained by the Chemistry Division. Shortly thereafter the Portland Cement Association prepared samples for use with the flame photometer. The inner vials were filled in Skokie, Ill. and were then brought to Washington to be hermetically sealed with the automatic sealing machine.

Later the Concreting Materials Section acquired a multi-channel x-ray fluoresence unit with the hope that such an instrument might replace much of the wet chemical testing in the acceptance testing program for other government agencies. To calibrate this apparatus and others, five cements were selected for preparing SRM's. An attempt was made to have a high and low value for each major and minor constitutent included in one or another of the five samples. The cements were analyzed by a number of cooperating laboratories, but in general, the spread in results was large. The NBS and PCA laboratories, however, were in close agreement and the values assigned were based largely on these results. These SRM's were 1011, 1013, 1014, 1015, and 1016, of which the supply is now exhausted. In anticipation of this situation, the NBS several years ago began producing seven new SRM's (633 through 639). Each cement plant in the United States was asked to furnish a typical chemical analysis for each of its cements. The cooperation was very good, but unfortunatley most of the plants had little, or in some cases unreliable, information on minor constitutents in their products.

2. Wet Chemistry versus Instrumental Analysis

In the conventional wet chemical analysis of portland cement, procedures are specified for determining the content of various elements in the cement and a good analysis will total about 100%. Cement, however, is made from raw materials that contain numerous constitutents not included in the specification requirements. The analytical procedures determine these minor constitutents as a closely related compound. For example, the wet chemical method for $Al_2 0_3$ measures not only the $AL_2 0_3$ but also the TiO_2, while the method for CaO also measures SrO. By contrast the instrumental methods usually measure the content of each individual element, because they involve atomic processes.

a. Flame Photometer

The first instrument used was the flame photometer. In this method the cement is dissolved in hydrochloric acid, and the solution is atomized into the flame of the photometer. The magnitudes of the energy given off at the characteristic wave length for sodium and for potassium are compared with the energies given off at these wave lengths when various stock solutions made up with various concentrations of reagent calcium, sodium, and potassium compounds, are used. To qualify as a suitable apparatus, an instrument calibrated with the reagent solutions is required to produce accurate results with specific SRM's.

b. X-ray Fluorescence

In the x-ray fluorescence method, a flat pellet of cement is produced by compacting under pressure the cement or a mixture of cement and organic binding agents, or a fused button may be produced. The button or pellet is irradiated by an x-ray beam. The beam is selectively absorbed by the various atoms in its path. The x-rays are absorbed by ejection of an electron from one of the energy levels in the atom. When the resulting vacancy is replaced by a free electron from outside the atom, an x-ray is produced that has a wavelength characteristic of the particular element. Some apparatuses are of the scanning type that measure, in order, the intensity of the energy of a preselected wavelength from each of the elements in the cement. Other equipment have a separate spectrometer for each element to be measured so that all measurements can be made simultaneously. The apparatus must be calibrated through measurement of cements of known composition.

c. Atomic Absorption

In the atomic absorption method, the cement under test is dissolved in an acid solution and atomized into a flame, as in the flame photometer. The radiation developed in the flame, however, is not utilized. Rather radiation from a lamp source is passed through the flame and absorption by the un-ionized atoms (which amount to over 99% of the total) is measured. A different lamp is used for each element measured, as the lamp must radiate energy at the characteristic wavelength for the element being measured. The apparatus can be calibrated with cements of known chemical content. In one study at least, it was found that satisfactory calibration could be obtained by using a mixture of reagent chemicals having a total composition comparable with portland cement. An instrument thus calibrated can be qualified by the use of standard reference materials.

d. Spectrophotometric Method

In another recently developed procedure, a spectrophotometer is used to measure the color intensity obtained when a solution containing the cement is reacted with specific color producing agents. For most elements, the instrument can be calibrated by the use of mixtures of reagent chemicals. But for the silica determination, cement SRM's must be used.

3. Performance specifications for Instrumental Analysis

During the period that cements were being selected as potential SRM's the chemical subcommittee of ASTM committee C-1 on cement was discussing the desirability of writing performance standards for instrumental methods of analysis. This need arose from the recent proliferation of instruments and the virtual impossibility of writing detailed instructions for each instrument. Such a specification requirement for an instrument can be written so as to require that the instrument give the correct chemical values for a series of cement. Thus, this development requires that SRM's be made available for not only calibration of the instruments, but also for qualification of them.

a. Selection of Chemical SRM's

If one had a large number of cement SRM's that would furnish, say 20 values for each element being analyzed, and if these 20 values were spread out more or less uniformly between the lowest and the highest value to be expected in use, and if all 20 points fell on a smooth calibration curve, one would be justified in using the same sample data for both calibration and qualification. Another procedure that might be feasible and one upon which the new SRM's are actually produced consists of using two high, two low, and two intermediate values for each constitutent from among the set of SRM's. One high, one intermediate, and one low value could therefore be used to calibrate the instrument, and the other group of high, medium, and low values could be used to qualify it. Once the machine was qualified, perhaps all of the samples could then be used to make a more reliable calibration curve. It was found feasible to meet the requirement of two high, two medium, and two low values each of almost all elements with only seven cement SRM's. A better selection could have been made if more information had been available on minor constitutents. A departure from the previous SRM's consists of the inclusion of a shrinkage compensating cement, which was added to give a wider range of SO_3, silica, and lime.

b. Preparation and Packaging of Cement SRM's

Upon receipt, each cement was passed through a #50 sieve to remove any inadvertent gross material and to break up agglomerates. It was then mixed for four hours in a double cone blender. Afterwhich it was placed in plastic-lined 5-gallon lard cans. The plastic liners were tied with rubber bands, and the lid of the lard can was sealed with electricians' plastic tape. The operation was carried out in the winter time in a building with temperature but not relative humidity control Consequently, the relative humidity was low. The small glass inner vials were nested in a wooden frame which had a bottom of 1/4 in hardware cloth. The top of the frame was level with the top of the vials. A second frame of the same dimensions was fitted with heavy guage 3/8 in wire screen whose purpose was to hold the glass vials in place during the vibration used to compact the samples.

The second frame was put on top of the first, but with a thin aluminum sheet between them. Cement was scooped into the frame and leveled off to a thickness found by experiment to fill the vials. The aluminum divider was removed, a lid was applied to the top frame and the assembly, which was sitting on a vibrating table, was held down tightly while being vibrated for 10 seconds. The frames and the lid were fitted with gasket material to contain the dust. The lid and upper frame were then removed, excess cement was screeded from the top of the vials. A thin metal grid about 3/4 in deep and with 3/4 in sq. grid holes was then inserted between the lower frame and the vibrator. During a short additional period of vibration, cement in the interstices fell down into the grid and the cement in the vials was further consolidated so that the plastic caps could be inserted easily without a layer of cement between the plastic and the glass. While the vials were still in the frame, the plastic caps were inserted. The vials were then removed from the frame, placed in plastic bags, and were again stored in sealed lard cans.

The small inner vials were then sealed inside larger glass vials. First, the inner vials were placed in the large ones with the plastic cap down. The cap serves as a cushion and minimizes damage during shipment. Next, several layers of heavy fiber glass paper, cut to the inside diameter of the large vials, were put in the vial to serve as a cushion at its end of the vial. The vial assemblies were then fed into the automatic sealing machine. In operation, this machine rotates the vial and subjects it to 4 gas-air oxygen jets on either side and at a point well above the inner vial. The flame is cut down at the point where the vials enter the system, and after the initial heating period, increases sufficiently to soften the glass. Two clamps come down and hold the top part of the vial while the rotating bottom part is twisted off and a seal formed. After cooling, the vials are put back in the original storage boxes. For positive identification, different colored caps were used for the different cements.

c. Homogenity Testing

After the cement SRM's are vialed, a random sample of the vials was tested for homogeneity of the cement. Because the cement clinker and gypsum from which portland cement is made have different specific gravities and because the gypsum is apt to be finer as it is more easily ground than is the clinker, these ingredients may tend to segregate. Any segregation in the cement as received or any introduced during the screening or blending process would be expected to cause variations in the SO_3 content of the cement. Consequently, the samples selected for testing were analyzed for SO_3 content. This was done using x-ray fluorescence, which has potentially high precision. In addition to the SO_3, the CaO content was also measured by x-ray fluorescence. Sixteen samples of each of the seven cements were taken and each were measured eight times. The maximum difference (in weight percent) observed between the sixteen samples for each SRM's are given below:

SRM	CaO	SO_3
	(mean of 8 Measurements)	
633	0.14	0.04
634	.14	.03
635	.34	.06
636	.34	.06
637	.21	.02
638	.22	.04
639	.26	.03

d. Certification

Having determined that the uniformity of the samples was satisfactory, the samples were sent out to a number of cooperating laboratories for analysis. They were accompanied by vials of the 5 existing standards. Some laboratories used wet chemical methods, one used spectrophotometric and EDTA methods, several used x-ray fluorescence, and several used atomic absorption methods. One of the major problems is that, as laboratories switched to instrumental methods of analysis, their analysts lost the ability to perform the traditional wet-chemical analysis with sufficient accuracy to establish certified values for succeeding issues of SRM's. The x-ray fluorescence method has the potential for high precision, and is therefore useful for measuring uniformity of materials. But, because the apparatus must be calibrated it is not suitable for establishing certified values for succeeding samples except as it is able to compare the new samples with the old. Such a limitation is not necessarily true of the atomic absorption procedure because in at least one study satisfactory results were obtained using reagent chemical standards. The spectrophotometric and EDTA methods are also relatively free from dependence on the use of previous standard samples, except for silica.

The results of the cooperative tests by different laboratories and different methods were brought together for comparison. Agreements and differences between methods and laboratories were assessed; a final judgment was made on giving relative weights to the various pieces of information and an initial certification was issued for the seven samples. Additional work using wet chemical methods will be performed on these samples to increase the certified precision.

D. Conclusion

SRM 114, cement fineness, has been available for about 40 years. Over 300,000 units have been distributed. It has made possible the use of sub-sieve size specifications for portland cement and other fine powders through standardization of instrument calibration.

The chemical SRM's are more recent, but their impact has been no less and bodes to be even greater. They do not now, but, will make possible the use of performance type specifications for cement analyzing instruments.

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I. Introduction

James C. White

Industrial chemicals present a rather difficult problem to those charged with controlling and maintaining quality. The number of industrial chemicals is quite large, their uses are varied, and their degree of purity for these uses equally varied. Thus, it is obviously not logical to establish a single policy that applies to all industrial chemicals. Economic considerations are overriding in that equal attention cannot be given to all chemicals or classes of chemicals. Concentration of effort in producing SRM's for chemicals sold in pound lots while neglecting those consumed in tonnage amounts clearly cannot be tolerated. So, four steps need to be considered.

A. Identification of the Problem Area

This identification should be made in concert among industry, government, and standards bodies. In most instances, establishment of priorities will be required because far too many chemicals exist to allow development of SRM's for all of them. Only after the problem is identified can we proceed to the second step.

B. Resolution of the Problem

This step customarily falls to an organization like NBS. Here NBS works closely with industry and cooperates in establishing the acceptability of the SRM. I think the resolution of the problem is by most measures the simplest step in the process, despite the technical difficulties that may be encountered. This is a technical problem and lends itself to resolution by technical means, a process we are familiar with and find amenable to solution by our established techniques. The other steps in the process of producing SRM's for industrical chemicals are largely subjective in nature and thus more difficult to resolve. This is particularly true of the third step in the process.

C. Funding and Support

This becomes more complex as time passes. It is not reasonable to expect full cost recovery of the development of an SRM from the customers who buy the SRM. The development cost that can easily total $100,000 cannot be borne by the customer. Likewise, it is unreasonable to expect NBS, for example, to bear most of the cost, despite the fact that this body was created to serve the public. The matter of funding is terribly complex, so subjective reasoning in establishing priorities must be resorted to and accepted after due consideration. This step will always be a problem because there simply are far more needs for SRM's than there are resouces in manpower, money, and time to provide. The final step in the process is the most crucial.

D. Dissemination of the Information

This step also closes the loop in that we can better identify future needs through proper dissemination of information. Meetings such as this are vital instruments in resolving mutual problems. NBS is to be congratulated for the manner in which they distribute information, although I am confident they would agree that communications are never perfect and that feedback is never sufficient, no matter how much effort is expended.

These four steps--identification, resolution, funding, and dissemination of information--give us the proper procedure. The following sections cover some other factors that bear upon this topic: (1) methods development and evaluation, (2) standardization of methodology, (3) accuracy, and (4) coordination of efforts to produce SRM's.

II. Status of Analytical Chemistry in the Chemical Industry

A.J. Barnard

Today, the analytical laboratory has better facilities, a better motivated staff, and reports at a high level in management. Analytical professionals are in the mainstream of management development. They aid in the interpretation of analytical results and design of experimental studies, and participate in the activities of management teams facing current problems and future prospects.

These changes stem from various causes. Emphasis is placed on high-performance, high-quality, analytically defined products. For example, the manufacture of metal oxide semiconductors requires etchants and solvents with 30 or more specifications met. The regulatory climate has also influenced the status of analytical chemistry including the force of the Good Manufacturing Practices Section of FDA regulations, environmental safeguard efforts, and the support required for the Occupational Safety and Health Acts and Department of Transportation programs. The term "preventative analysis" can be used to delineate one of the key changes in the functions of analysis. The question is often not how much is present, but how little. In other words, is there so little present that no problem is presented. Preventative analysis also implies "early warning" analysis and thereby measurement of parameters that may signal changes in products, intermediates, and raw materials.

All of these factors contribute to a greater drive for meaningful measurements in the chemical industry. The GMP regulations require improved quality control procedures and practices, more frequent and reliable calibration of instruments, and closer attention to the reliability of standards.

In addition, to better characterize reagent grade products, meaningful measurements are benefitting by the introduction of special purity products such as spectrophotometric solvents, liquid scintillation solvents and scintillators, and polymer characterization solvents, and also from the increasing availability of reagents of extreme purity.

The degree of advance secured in some sectors of the chemical industry may be over estimated, but "it is better to travel hopefully, than to arrive."

III. One View of SRM Usage

James B. Johnson

In the Chemicals and Plastics Division of the Research and Development Department of Union Carbide, we have responsibility for establishing specifications and setting up criteria for quality control of all our processes. That really throws the "monkey on our back," because we are in the position of having to develop analytical know-how and establishing the specifications for the products and then implementing them in the plant quality control laboratories. I should explain to you that I don't regard myself as an expert on SRM's. I came with a limited amount of knowledge with regard to SRM's and with the recognition that I had a lot to learn, which is justification for my being here.

I recognize that there is a tremendous need for SRM's in the industry I serve. Interestingly enough, in the production of petro chemicals or organic chemicals--heavy organic chemical production--very few standards are used in the quality control aspects of buying and selling organic chemicals. In the specifications for this area, you will find very, very few references to SRM's. One of the first ones I became aware of was benzoic acid, potassium, and phthalate. Since that time, I've seen very few used with regard to controlling quality of the products. Why is this? If you look at the specifications, not only at Union Carbide, but in the petrochemical business, they control such things as water and acidity, the carbonyl content, sulfuric acid, color tests, color of the product itself, and so on. Standards, of course, are required for measuring color, and in the quality control laboratory you don't refer to an SRM. You use some SRM to be sure your spectrophotometer is calibrated properly and so on. A point that Dr. Dunlop and others have made, interestingly enough, is that when I first went to Carbide, and we talked about the purity of organic chemicals, we asked, "is it 98.0, is it 98.5, or perhaps 99 percent?" It kept going up all the time from my day of entry until today. Now, we don't even talk about purity. We talk about the total impurities in organic chemicals. We have one product for which we determine six components we know to be present. There may be others present that we don't know about. Each one of them has a limit in terms of ppm, but the total of those components cannot exceed 80 ppm. That's the specification. So you can see that we've come a long way from a 98 percent chemical in the early forties to a product that could conceivably be well about 99.9 percent now. In the distribution of chemicals, we must have SRM's to determine ppm levels of metals in our products. We use SRM's in pollution and in industrial hygiene samples. Interestingly enough, I made a survey of other users and learned that our fire research safety group buys from NBS a smoke tunnel test calibrating material at about $35 or $40 a set. We use SRM's in physical property measurements and in ash and coal analyses. To put a little more dimension on these things, I called one of the plant laboratories and asked how many NBS-SRM's they used in their control. This is a large chemical plant and makes roughly 100 products. They use three SRM's. I mention this only to emphasize the fact that there is plenty of room for improvement in this area. Then I surveyed some of the other R&D groups. Carbon Products, for example, has 81 SRM's presently on their shelf for use in their work. This is in a research and development orientation--not quality control. Many of the future needs have been mentioned here: pore size distribution calibration, surface area, viscosity standards, etc. Standards for spectrophotometric calibration are already on the list, but more are needed. In particular, the instrument manufacturers should be deeply involved because of the importance of assuring spectral integrity.

For a big volume chemical like isoproponol in which lead must be determined, can one have a standard? To me, that is a virtual impossibility. Lead has a tendency to absorb on the sides of the vessel, and we have conclusive results to prove this. You have to be very careful when talking about analyzing a substance like isoproponol or many, many other organic chemicals for trace amounts of lead, mercury, and so forth. We don't see any plausible solution to that kind of problem. On the other hand, one that I didn't expect--and I pull this from our catalog of investigations--ethylene oxide in an organic matrix (particularly in a hydrophillic matrix) you might expect to disappear quite rapidly. Just recently, we learned of a sample that had been stored for five years--I think through accident rather than intent--it still had 20 ppm ethylene oxide.

IV. Written Specifications vs. Material Standards

Thomas W. Mears

Lawyers can very quickly and easily write a contract that essentially cannot be broken. The next day they can with equal ease break it. As these various legal problems come into the areas of chemistry, this point is going to become of more and more concern. A few years back, a description of a poisonous material was defined as so many mg per kg body weight that would result in death. This was duly written up and became legally binding. Before very long they had to write a special exception so that sodium chloride would not be labeled as poison. I tend to think of industrial chemicals in terms of boxcar load or truck load or even a freighter load, but there are a great many truly industrial chemicals that do not come in this category. Among those are chemical reagents and a lot of them are sold each year. Food chemicals are becoming increasingly important; so are clinical chemicals and various medicinals. And in each of these areas, specifications are written: the ACS reagent chemicals, Food Chemical Codex, United States Pharmacopia, the National Formulary, and others. Possibly our friends at USP and American Pharmaceutical Association are a little bit ahead of the rest of us. They have come to realize the inadequacy of a series of specification monographs that describe quite carefully what a material should be. So each of them has developed a series of standard materials: USP and National Formulary reference substances to which specifications are tied. Should occasion come to go into court on something of this sort, they are not tied down by the words, which is the lawyer's province, but they have reference materials to which they can refer. I would think the Food Chemical Codex would have to go this way. Certainly as the ACS reagent chemicals specified procedures depart more and more from the traditional wet methods, adsorption spectrometry, gas chromatography, etc., and more and more organic chemicals turn up on the list, thought will have to be given to a set of authentic compounds to reinforce ACS reagent chemicals specifications.

The other point I wanted to stress is the question of authentic substances for research. I suppose it has been said facetiously that physical chemists determine very accurate properties and so on of impure materials and that chemists determine inaccurate properties of highly purified materials. A few years back, the Manufacturing Chemists Association(MCA) along with Texas A&M University started a program where hopefully they would gather large quantities of high purity organic materials representing 100 organic chemicals bought and sold in large volume. The first seven compounds selected by Texas A&M were butyl alcohol, chlorobenzene, ethylene glycol, propylene glycol, resorcinol, sorbitol, and urea. Then, all of a sudden, priorities changed, and MCA found it necessary to withdraw their support. Nevertheless, the work is continuing at Texas A&M. Every issue of every chemical journal reveals experiments and agents for properties, be they physical properties, spectroscopic properties, thermodynamic properties, or a number of chemicals. Yet, frequently data related to the same compound cannot be matched up, simply because of the difference, small as they may be, in the purities of the material. Should a program of this Manufacturing Chemists Association-Texas A&M type get going again, it would certainly supply industry with means of getting accurate data to evaluate their compounds and supply the background for evaluating their materials--both in scientific and legal senses. I would close by making a pitch for this program. It got going so well, and other more important things, say labeling problems and the like, made it necessary for MCA to divert their attention from it.

V. What Direction SRM's

Edward C. Dunlop

I have a little different slant than people that are involved with production of materials, and would like to provide a little "food for thought."

A. Growth

Bob Michaelis said that they had 900 SRM's now and that back in 1905 they had one. I have no idea of the ratio of this to the products that the industry had. Our company is introducing many new products each year, with something like 30 ventures in operation last year. Obviously these would all be new products coming out. I raise the question: How do we stand today? Are we losing ground? Are we maintaining our position?

B. Laboratory Agreement

Those of you who heard Dr. Mandel's talk on statistics and SRM's yesterday recall the various curves that he presented. If you were at one end of the curve, the laboratories all checked out with each other, but if you extrapolated these you got wider versions. If you used an SRM and calibraiated your procedure and method, the instrument, the various procedural operations, you could bring these laboratories into general agreement. I think from a standpoint of reference and standard calibration of materials that this is a procedure that we ought to consider very seriously.

C. Needed Standards

Dr. White mentioned that we have problems in identifying what standards--what reference materials--we need. Obviously, we are going to have to set priorities for these, but if we could have a general reference material that we could refer to as an indirect standard and then work this back, I think this would help us greatly in setting the priorities. I think that this is one of the ways that we as managers or supervisors or analytical personnel or people that advise on the process--the people that hopefully are making new products--can go into our companies' operations and help in this process. This is the way we ought to be thinking, and it is partly our responsibility to come up with materials that may not necessarily be the ultimate reference standard, but would be similar enough so that we would then have a reference material that we could refer to an SRM.

D. Stability of SRM's

Difficulties exist with SRM's in regard to their stability, particle size, and segregation. I want to illustrate this by an incident that happened a number of years ago in the laboratory with which I am associated. We were analyzing some samples for our pigments department, which manufactures quite a lot of titanium dioxide. We had several procedures set up to run niobium, aluminum, tungsten, and a few other things in the titanium pigment. One of the particular things that I want to enphasize is we had made up some control standards and developed the calibration curves by emission spectroscopy for samples of titanium dioxide containing tungsten. These were made up with tungsten oxide. We carried these experiments on for about three years and then the program was completed. We stored the reference standards on the shelf. After about four or five years, the pigments department came back to us and wanted us to analyze some additional titanium dioxide samples. We did this, using the previous reference standards, but received complaints that our results were low. Now the spectroscopist had taken the standard off the shelf and had used the same standards, so he felt that nothing was wrong; the calibration curve was straight. But on further checking, we found that our calibration curve seemed to be on the low side. To make a long story short, we spent considerable time and found that what had really happened was that the tungsten oxide had settled to the bottom of this bottle, even though we tried to mix the material. The difference in density of the two materials caused this separation. We were able to get out of the bind, but it cost us considerable time. I illustrate this as an example of the significance of stability, particle size, and density of materials. This is just an example of the difficulties that you can encounter; some of these can be very subtle.

E. Analytical Control

Dr. Stenger referred to the cost of the analytical control of products. His example is very good, and 1 per cent seems to be a good figure to use for control costs of a production line. In our analytical laboratory, I have a problem of quality control of the analyses of research samples. I have a staff of B.S., M.S., and Ph.D. chemists, and they each have technicians who have varying educational backgrounds. You need some kind of quality control to see how well you are doing in an analytical research laboratory. You can't have standards in all cases, because you may never exceed six or seven samples of any one product before the project is dropped. You don't have a very good control sample to compare with. You hope the reference material you calibrated your procedures with will correspond without intereference problems. The standard addition technique is helpful in this area, and it is nice to have an SRM to use as a standard addition material. Also, you need a product to use as a control, and in this area, one of the best ways is to get a stable, large-scale product chemical that you make to use as a reference material. This need not be a really high purity material. Once you decide the method is good, then you can analyze the material and get precision, and precision is really all you need to control your laboratory. I mentioned that Dr. Stenger said 1 per cent. I have been trying to figure out how to control this; because, if you submit samples for control, that takes time away from running the regular samples. I've estimated that it will cost about 3 per cent to run a control analysis program that will give a satisfactory control of the performance of the personnel and the methods used in the laboratory. I've discussed this with several other laboratories, and I know that another industrial plant uses this system as a control. They said 3 or 4 per cent of their total analytical bill is spent in the control performance analyses required to see that the results from their analytical research laboratory turn out a satisfactory performance.

F. Univeral Calibration Curves

John Mitchell questioned the desirability of having polymer controls, and my laboratory is greatly interested in this. Dr. Bly and his group on gel permeation chromatography have spent about 3 man-years developing a universal calibration curve for GPC. I know that many other companies are doing similar things. I don't know how much has been spent in developing a universal calibration curve, but to answer John's question, I don't believe that we are ever going to have enough quality control samples to run the research-type samples we have. We must run these universal calibration procedures. Hopefully, they will be good enough to cover the production type materials. I think this is one way that we can eliminate the need for some of the wide variety of controls that would be needed for process-produced chemicals in the polymer field.

VI. Discussion

The point was made that many companies resort to making their own standards, commonly referred to as "in-house SRM's." These materials are usually well characterized and made up to represent as closely as possible a sample matrix peculiar to the requirements of the laboratory. Upon occasion, such in-house standards are used outside their origin. The primary disadvantage of such standards is that they do not have the validity of an SRM because they are not exhaustively characterized as are SRM's. There was general agreement that the use of in-house standards is quite prevalent and generally productive rather than counterproductive. The point was also made that we need better procedures to establish these materials as "quasi-SRM's" of established reliability and validity. Round-robin analyses are commonly made, but many laboratories do not agree well on the established values so that this is not necessarily a reliable practice. To ensure general knowledge of the existence of these in-house standards, they should be brought to the attention of NBS, particularly if they receive extensive usage.

The question of which SRM's should be established and how this selection process is conducted, is laregly determined in an orderly manner despite some shortcomings. Industrial input is obtained usually through committees established for this purpose, potential sales considerations are factored into the equation, and a priority list is established by the NBS Office of Standard Reference Materials. Cautionary remarks were made to the effect that so-called consumer demand for specific SRM's can often be misleading. The principle of the "squeaky wheel getting the grease" is not universally beneficial. An SRM is expected to break even; that is, "no profit, no loss." This consideration makes the selection process much more difficult. In addition, NBS cannot maintain complete analytical capabilities to produce any SRM desired; this, too, was pointed out as a limiting factor. K.F. Laurer, Bureau Central de Mesieres Nucleaires, Belgium, and J.D. Cox, National Physical Laboratory, England, told of how they are coping with this problem of selection of future SRM's in their respective organizations.

Considerable discussion was held on the matter of where SRM's can be found. The NBS survey is admittedly out of date. Representatives of ASTM told of their project, which is largely concerned with emission spectroscopy SRM's such as copper, iron, nickel, and aluminum base alloys, to provide an up-to-date catalog of existing SRM's. Their latest edition will include information on a world-wide basis. A much more ambitious project conducted by the European Economic Community was mentioned by Dr. Lauer, who made a plea for contributions from all sectors. The end product will be a catalog of existing SRM's that will be available to all interested parties.

VII. Conclusion

A.J. Barnard

I tried to hit the philosophical side of this meeting; I'll be damned or praised for it--I'm not sure which--but I've been disturbed a little bit this week by some people who don't like the word "standard." It has many meanings--that's the argument. But so does "reference" and so does "material." I want to take you back to the word "standard" and its cognate. It's had a long history from the Latin until today. It was originally a banner or device around which a military group could rally and fight, that could stand in front of the troops, in front of the reviewing stand, or when the legion was out in the foreign fields the banner or device could be displayed as a substitute for the troop. In my view, even in this day, almost every concept of a standard, in our chemical measurements at least, if not physical, partakes of that original definition. It is also something that beleagured industry and science and commerce can rally around. I'll use this illustration: Consider a 2-phase system. Call one phase the "real" and the other phase the "ideal." Standards have peculiar properties; they like to look on the interface of that 2-phase system. Anything that maintains itself at an interface rather than in the phases has special properties and special requirements and requires special study. There is a science and a study of standards that is a particularly meaningful measurement.

CLINICAL ANALYTICAL CHEMISTRY

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I. Introduction

Russell J. Eilers

In 1949, the Standards Committee of the College of American Pathologists launched a Survey Program with the objectives to define the "state-of-the-art" for laboratory testing on the national level to stimulate interest in new and better standards for the clinical laboratory field and to diminish interlaboratory variability by defining overall areas of deficiencies so that through education, these could be corrected. During the 50's and the 60's, the CAP Survey Programs were expanded to look at most basic as well as many exotic constituent measurements utilized in all segments of the clinical laboratory field.

With the passing of the Medicare Law in 1966 and the Clinical Laboratory Improvement Act in 1967, the survey concept was converted to that of Proficiency Testing of individual laboratories. Thus during the 60's, the CAP Survey Program as well as State and Federal operated proficiency testing programs, focused on the evaluation of the performance of the individual laboratory. Programs were designed to allow each individual laboratory director to compare the performance of his laboratory with that of other laboratories utilizing similar measuring systems or to performance of reference laboratories. This led to many frustrating problems in evaluation and scoring for the private and public agencies involved as well as laboratory directors. The approach did encourage the concept that performance within the individual laboratory is the responsibility of that laboratory's director. If it is unacceptable or poor performance, it is for the director to investigate and resolve by appropriate action (by education of staff, changes in methodology, reagent chemicals, or equipment, or improvement of the laboratory's measuring system if it has a bias compared to that of peer or reference laboratories). The need for reference materials and methods, and management systems for laboratory improvement became obvious. Dr. Boutwell yesterday outlined and discussed eleven elements for a national system.

In 1970, the CAP Standards Committee published a six phase management system for Total Quality Control in the Medical Laboratory, [1] based upon quality control engineering principal (See Appendix A) Surveys were defined as a part of Phase III, Control of Process within the Laboratories, and therefore, could only be considered a mechanism to monitor the performance of laboratories. The CAP Standards Committee also stressed that Survey Programs would provide a growing data base of information for analysis. In 1973, with close to 8,000 laboratories enrolled in the various CAP Survey Programs, the data base is a representative sample of laboratory practice in the United States and offers new horizons for providing useful information not only on the performance of individual clinical laboratories, but also through analysis of variance on the assessment of the accuracy, precision, and specificity of available measuring systems and how the current levels of performance are meeting requirements for good medical care.

In 1972, Paul Cali from the National Bureau of Standards proposed a systematic approach to accuracy in clinical chemistry. [2] (See Appendix B) This proposal ties in Surveys (proficiency testing) to National Reference Materials (SRM's) and methods of known accuracy (Referee Methods). Thus, the NBS proposal for a meaningful measurement system is complementary to the CAP's scheme for Six Phases of Total Quality Control for the Medical Laboratory, and provides a management system approach for the individual laboratory director to utilize to improve the quality of his laboratory's output to assure quality health care and meet requirements defined by State and Federal Laws.

The purpose of this Panel is to explore the inter-relationships of components in this management system and the future need for SRM's to accomplish meaningful measurements in analytical clinical chemistry. The panel members will present short papers on projects in the United States that relate to components of this evolving national management system to be followed by discussion.

Appendix A

Total Quality Control for the Medical Laboratory

Phase I. Design Control: Selection of the proper constituent(s) and measurement system for each particular patient care problem. Proper design of facilities and staffing (function and task analysis and job descriptions) for efficient operation.

Phase II. Incoming Material Control: Selection of reference and control materials, chemicals, reagent systems (kits) and instruments to use. Collection system to assure quality of patient's sample. Selection of new personnel by review of education, registries obtained, and lab experience (Proficiency Examination Tests and College Level Evaluation Program).

Phase III. Process Control: Internal program of reference and control materials to calibrate and monitor the measurement process, and a personnel proficiency recognition system.

External program by participation in a proficiency testing program (CAP Surveys) and/or Regional study program (CAP Quality Assurance Service)

Personnel Recertification Programs (continuing education)

Phase IV. Output Control: Reporting results in a scientific and medically meaningful format. Use of S.I. nomenclature for a metric system of quantities and units. Use of the CAP Systemized Nomenclature of Medicine in the problem oriented medical chart recording method.

Phase V. Reliability Control: Assuring medically significant results by utilization of laboratory bulletins or "ROUNDS" as communication mechanisms with the medical staff. Consultation provided at the bedside by the laboratory physician.

Phase VI. Verification Studies: Overview provided by a Laboratory Accreditation Program. Use of the CAP Workload Recording Method for Clinical Laboratories to measure productivity. Use of an Internal Management system for quality control data review.

Appendix B

NBS Proposal for a Meaningful Measurement System

1. Agreed-on, rational, units of measurement (S.I. System)
2. Well characterized materials (SRM's)
3. Methods of known accuracy (Referee Methods)
4. Field methods assessed for accuracy (via 2 and 3)
5. Process to assure long term integrity of the measurement system (Proficiency Testing)

II. SRM's for Clinical Analytical Chemistry

Robert Schaffer

The first SRM for clinical chemistry (cholesterol) was issued just six years ago. Now there are eighteen (Table I) and several more are at various stages of development (a protein SRM being prepared from bovine albumin, an SRM for the ultra-violet range of spectrophotometers, and an SRM for NADH). The interagency cooperation of the National Institute of General Medical Science accelerated the NBS activity in this area--an area not previously regarded as requiring NBS work.

NIGMS helped to support the developmental stage of the Bureau's work for chemical SRM's--the study of each individual chemical to be certified to devise chemical and physical methods most appropriate for its certification--and for physical measurement SRM's; e.g., absorbance standards for spectrophotometry or curvette pathlength standards. The developmental stage also included the construction of instrumentation needed to obtain the appropriate accuracy.

NBS work for clinical analysis first emphasized the certification of needed SRM's, the priority of need for which was established for NBS by a panel of clinical chemists and pathologists. Now, a second objective has grown to major importance. This is the establishment of the accuracy of clinical reference methods. A model for this work is the so-called referee method for total serum calcium that Paul Cali organized and carried to completion. The concept was based upon using an isotope-dilution mass-spectrometry method for the absolute determination of calcium in biological samples to establish reference point. Then selecting a field method for the determination of calcium, atomic absorption technique, to be standardized to obtain the best accuracy and precision in relation to this reference point. The details of the development of this referee method was published by NBS. [3]

Table I

911a	Cholesterol
912	Urea
913	Uric Acid
914	Creatinine
915	Calcium Carbonate
916	Bilirubin
917	D-Glucose
918	Potassium Chloride
919	Sodium Chloride
920	D-Mannitol
921	Cortisol
922	Tris(hydroxymethyl)aminomethane
923	Tris(hydroxymethyl)aminomethane HCl
924	Lithium Carbonate
925	VMA (4-hydroxy-3-methoxymandelic acid)
*926	Bovine-Serum Albumin powder
*927	Bovine-Serum Albumin (7% solution)
*928	Lead Nitrate
930a	Glass Filters for Spectrophotometry
931a	Liquid Filters for Spectrophotometry
932	Quartz Curvette for Spectrophotometry

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* In preparation

III. Performance of Precision Spectrophotometers: Results of a National Survey

Myrton F. Beeler

A. Surveys

In 1973, the College of American Pathologists conducted the third annual survey of precision spectrophotometers (instruments with a half-band width narrower than 10 nm).

Sets of eight solutions sealed in glass vials were mailed to participants in May and September 1973, with directions for use and a questionnaire. A total of 132 laboratories participated plus four selected reference laboratories chosen for their known technical excellence. Participants were requested to return the questionnaires within five days after receiving the solutions to the CAP Computer Service Center in Traverse City, Michigan. In August 1973, participants received a short monograph describing recommended methods for checking wavelengths, absorbance reading accuracy, and for cleaning cuvettes.

Results were tabulated by solution, wave length, instrument group, and reporting institution. Raw means and standard deviations were calculated for each group of instruments. Outliers (results lying outside the raw mean plus or minus three standard deviations) were rejected. This process was repeated a second time, providing the doubly "corrected" means, standard deviations, and coefficients of variation for participant results given in Tables II and IV.

In Table II also are listed the reference laboratory raw mean results together with expressions of reference laboratory variability (calculated as a percentage representing the algebraic difference between the high and low references results divided by the mean reference laboratory results multiplied by 100) for each solution at each wavelength. This expression of variability for reference laboratories is not comparable to the coefficient of variation, but may roughly correspond to the mean plus and minus three coefficients of variation.

As seen in Table II, there is good agreement between corrected mean participant results and mean referee results. Agreement is best in the visible range of the spectrum where the greatest divergence between the two sets of mean values is 1.5% (expressed as a percentage of reference results); and where interlaboratory variability is least. In the ultraviolet region of the spectrum with some readings on narrow peaks and on sharply ascending and descending limbs of absorb-

Table II

Participant and Reference Laboratory Results--Means, Variation

Constituent	Wave Length (nm)	Mean Participant Absorbance	Participant Coefficient of Variation	Mean Reference Absorbance	$\frac{\text{High-Low Reference Result}}{\text{Mean Reference Absorbance}} \times 100$
Acid dichromate 20 mg/l	240	.261	10.5	.255	3.9
	257	.289	9.0	.286	2.8
	300	.136	15.0	.131	2.3
	350	.214	8.7	.260	22.0
	400	.047	30.6	.045	4.4
Acid dichromate 60 mg/l	240	.755	5.4	.754	1.6
	257	.856	5.2	.856	2.5
	300	.402	7.0	.385	4.4
	350	.632	4.4	.632	2.8
	400	.147	11.8	.141	2.1
Acid dichromate 100 mg/l	240	1.241	5.8	1.252	3.0
	257	1.420	6.0	1.436	2.0
	300	.664	4.9	.652	4.3
	350	1.039	4.8	1.057	1.8
	400	.251	8.0	.243	4.1
Alkaline chromate 40 mg/l	240	.317	14.0	.312	3.2
	300	.160	22.8	.139	14.4
	340	.312	15.3	.322	4.3
	366	.932	6.9	.957	1.7
	375	.974	6.1	.997	2.6
Thomson's 1/5 strength	450	.149	8.0	.148	3.4
	550	.134	9.6	.132	1.5
	650	.134	9.7	.132	2.3
Thomson's 3/5 strength	450	.449	4.0	.449	2.9
	550	.409	4.2	.405	1.5
	650	.407	4.6	.405	1.7
Thomson's full strength	450	.750	3.2	.751	2.1
	550	.682	3.2	.676	1.6
	650	.678	3.7	.677	1.5
Average		.512		.512	

(Absorbance Peaks are Underlined)

ance peaks the greatest variability is seen. The largest disagreement among reference laboratories is for absorbance of acid dichromate at 350 nm (22%) because one reference laboratory reported a value of .260 absorbance units, an unexplained error. The next greatest reference laboratory disagreement (14.4%) is for alkaline chromate at 300 nm because of a low result from the same laboratory. In this case, it is difficult to decide whether the mean participant laboratory result (.160) is more reliable than mean reference laboratory result (.139). In no other set of absorbance values does disagreement between the corrected participant and raw reference mean values exceed 4.4%. Interlaboratory variability among participants (expressed as one coefficient of variation) is large for chromate solutions read in the ultraviolet. In one case, it exceeds 30%. This represents a twice-refined figure! Interlaboratory variability is least for measurements of Thomson's solution in the visible spectral range; where, the absorbances between .400 and .750, one coefficient of variation is less than 5% in all cases.

Table III contains individual reference laboratory results. The average for the sum of all absorbance readings for each laboratory has been included. The average for reference laboratory D confirms one's impression that this reference laboratory yields consistently lower results (2%) compared with results of the other reference laboratories. Reference laboratory C's mean absorbance is about 1% lower than those of laboratories A and B, whose results are almost interchangeable.

Table IV represents mean results for each type instrument utilized by five or more participants. (126 of the 132 participants are included). The corrected mean absorbances values for the Beckman DU, the Gilford 240, and the miscellaneous group are the same as the "all instrument" corrected mean and the reference laboratory mean. Means from the Beckman DB, the Beckman DBG, and the Gilford 2000 or 222 are lower than this, and that for the Zeiss PMQ is substantially lower. Those from the Coleman-Hitachi 124 and the Hitachi-Perkin Elmer are higher than all the others, including the reference means.

Except for the Coleman-Hitachi 124 and the miscellaneous group, the numbers of instruments included are probably too small for calculated within-group standard deviations and coefficients of variation to be of great significance. For what it is worth, those for the two groups mentioned (corrected) do not differ much from those from all instruments (corrected).

Table III

Reference Laboratory Results

Constituent	Wavelength (nm)	Laboratory A (Cary)	Laboratory B (Beckman Acta CV)	Laboratory C (Beckman DU)	Laboratory D (Beckman Acta D)	Mean
Acid dichromate 20 mg/1	240	.257	.260	.250	.254	.255
	257	.289	.289	.281	.283	.286
	300	.130	.133	.130	.130	.131
	350	.213	.215	.210	.260	.224
	400	.044	.046	.045	.044	.045
Acid dichromate 60 mg/1	240	.761	.761	.749	.746	.754
	257	.863	.863	.855	.842	.856
	300	.386	.393	.385	.374	.385
	350	.634	.636	.637	.619	.632
	400	.140	.142	.142	.139	.141
Acid dichromate 100 mg/1	240	1.267	1.264	1.230	1.248	1.252
	257	1.444	1.438	1.440	1.419	1.436
	300	0.664	.656	0.653	.636	.652
	350	1.064	1.060	1.060	1.044	1.057
	400	.238	.246	.248	.239	.243
Alkaline chromate 40 mg/1	240	.315	.316	.310	.306	.312
	300	.147	.142	.140	.127	.139
	340	.320	.330	.316	.323	.322
	366	.962	.966	.950	Missing	.959
	375	1.008	.998	.982	.999	.997
Thomson's 1/5 strength	450	.147	.150	.148	.145	.148
	550	.133	.132	.133	.131	.132
	650	.133	.132	.132	.131	.132
Thomson's 3/5 strength	450	.447	.455	.450	.442	.449
	550	.407	.407	.401	.403	.405
	650	.404	.408	.405	.401	.405
Thomson's full strength	450	.750	.759	.752	.743	.751
	550	.680	.681	.671	.670	.676
	650	.673	.683	.676	.677	.677
Average		.515	.516	.510	.492	.508

(Absorbance Peaks are Underlined)

Table IV

Mean Participant Results by Instrument Group and for all Instruments

Constituent	Wave-length (nm)	1 (11)*	2 (14)	3 (5)	4 (7)	5 (31)	6 (5)	7 (5)	8 (6)	9 (5)	10 (37)	Average all Instru-ments
Acid dichromate 20 mg/l	240	.236	.253	.273	.254	.270	.250	.257	.258	.248	.266	.261
	257	.270	.282	.300	.287	.300	.277	.281	.292	.191	.294	.289
	300	.123	.130	.142	.135	.145	.127	.138	.137	.111	.139	.136
	350	.205	.201	.219	.215	.226	.211	.211	.215	.204	.213	.214
	400	.041	.041	.046	.047	.053	.042	.045	.051	.039	.047	.047
Acid dichromate 60 mg/l	240	.707	.720	.784	.759	.777	.752	.734	.760	.748	.755	.755
	257	.823	.827	.885	.858	.878	.849	.828	.871	.584	.862	.856
	300	.380	.393	.419	.398	.419	.390	.381	.405	.422	.401	.402
	350	.612	.596	.641	.636	.654	.630	.616	.639	.632	.625	.632
	400	.138	.138	.147	.146	.155	.143	.143	.152	.136	.150	.147
Acid dichromate 100 mg/l	240	1.40	1.187	1.296	1.241	1.254	1.242	1.217	1.385	1.336	1.256	1.241
	257	1.368	1.403	1.455	1.425	1.416	1.410	1.382	1.515	.970	1.420	1.420
	300	.641	.651	.660	.658	.677	.647	.644	.675	.633	.670	.664
	350	.995	1.006	1.069	1.044	1.063	1.041	1.016	1.077	1.062	1.031	1.039
	400	.251	.240	.252	.249	.259	.248	.263	.259	.240	.258	.251
Alkaline chromate 40 mg/l	240	.336	.300	.333	.312	.318	.400	.297	.316	.290	.322	.317
	300	.152	.164	.151	.144	.164	.162	.236	.236	.165	.162	.160
	340	.324	.281	.341	.317	.336	.320	.283	.298	.291	.299	.312
	366	.923	.857	.958	.946	.960	.955	.845	.905	.894	.926	.932
	375	.960	.857	.999	.984	.993	.911	.831	.907	.866	.978	.974
Thomson's 1/5 strength	450	.149	.147	.155	.148	.153	.154	.150	.151	.133	.145	.149
	550	.136	.132	.160	.134	.139	.140	.134	.135	.120	.131	.134
	650	.135	.132	.160	.132	.139	.138	.134	.134	.123	.129	.134
Thomson's 3/5 strength	450	.439	.445	.455	.450	.460	.450	.437	.459	.437	.450	.449
	550	.405	.403	.470	.409	.418	.411	.398	.415	.396	.408	.409
	650	.406	.403	.464	.405	.416	.411	.400	.413	.400	.403	.407
Thomson's full strength	450	.735	.749	.758	.747	.741	.760	.742	.741	.768	.750	.750
	550	.678	.678	.772	.681	.672	.691	.678	.671	.682	.678	.682
	650	.681	.674	.767	.670	.670	.687	.676	.673	.681	.670	.678
Total labs average		.496	.492	.536	.511	.522	.512	.496	.522	.476	.512	.512

KEY: 1-Beckman DB; 2-Beckman DBG; 3-Beckman DK-2 or DK2A; 4-Beckman DU; 5-Coleman-Hitachi 124; 6-Gilford 240; 7-Gilford 2000 or 222; 8-Hitachi-Perkin Elmer; 9-Zeiss PMQ; 10-"Other"

* Number in parenthesis is number of instruments in group. Absorbance peaks are underlined.

B. Discussion

What are the correct answers? What is the state-of-the-art?

The corrected mean participant (peer) results have been found in CAP Chemistry Surveys to be the most reliable guides to hypothetically correct answers; considerably more reliable than the average of a small group of pre-selected reference laboratories. This survey differs from most of the others in several ways: a modest number of laboratories participated; the materials are aqueous solutions of pure chemicals; a reference laboratory has participated whose excellence is recognized throughout the world (NBS). Balanced against this is the possibility of vial to vial variability resulting from the process of mixing, distribution, sealing, and mailing. One committee member has demonstrated lack of stability of acid dichromate solutions resulting from subjection to freezing or to heat, a situation which could be encountered by vials in transit in the mails or storage. Another member has found vial to vial variability including instrument contribution (repeatability) not to exceed 1.6%. Since the greatest inter-reference laboratory variability is less than 5% on all but two of the sets of readings; and the mean of reference readings does not differ from the corrected mean of participants readings by more than 5% (except in one case) for this survey, the corrected mean participants' laboratory results, or the mean reference results can be used as a useful yardstick. It is not clear why the corrected participant absorbance mean is 15% higher than reference absorbance mean for alkaline chromate at 300 nm. Reference Laboratory A's result is approximately mid-way between the two in this instance.

The "state-of-the-art" appears to indicate an average interlaboratory variability (expressed as one coefficient of variation) of about 10% for absorbance readings of the chromate solutions in the ultraviolet.

Relative analytical error has been reported as low (less than 4%) for readings between .160 A and .900 A. For this range in this survey, one coefficient of variation averages 6.6%; outside this range, variability may be almost double that. All of the additional variability appears to be contributed by readings of low absorbance values in the ultraviolet region on slopes and narrow peaks. Interlaboratory agreement appears, percentage wise, to be as good in the absorbance range from .900 to 1.200 as it is between .160 and .900. From the point of view of interlaboratory variability and its implications regarding accuracy of absorbance readings from large numbers of instruments, the "state-of-the-art" is judged not to be satisfactory. If the readings are this much lower than the true readings because of decreased sensitivity, the possible error in reporting a kinetic enzyme assay becomes significant clinically. This magntiude of error in analyzing amniotic fluid could result in incorrect action by the gynecologist in pregnancy complicated by Rh incompatibility.

C. What Should Present Performance Targets Be?

Considering reference and participating laboratory results and the clinical applications, one might tentatively establish as a target for satisfactory performance values lying within 6% of corrected mean results, provided that these lie in the absorbance range from .160 to .900. Greater tolerance than this would have to be permitted outside of this range.

D. Which Instruments Appear the Most Accurate?

The survey does not provide a definitive answer. Of instrument groups with five or more participants, the Beckman DU, the Gilford 240, and the miscellaneous group yielded mean absorbance values almost identical with those of the corrected all-participant mean, the reference mean, and Reference Laboratory A mean (Cary).

The Zeiss results were strikingly lower than this; as, to a lesser extent, were those of Beckman DB and DBG and the Gilford 2000 or 222. Also interesting are the higher mean absorbances of groups using the Beckman DK2 or DK2A, the Coleman-Hitachi 124, and the Hitachi-Perkin Elmer. Because so many spectrophotometric problems result in lowering absorbance values, one might be tempted to regard the higher absorbances as more likely to be correct. Graphic representations of this survey data yield apparently Gaussian curves, with as many high as low outliers, suggesting that this intuitive feeling is probably not correct.

E. What Causes the Errors and How Can They Be Lessened?

It appears probable that instrument design is partly responsible for interlaboratory variability, and this possibility stands in serious need of investigation. Greater responsibility probably rests on the users.

The majority of the instruments (91 of 123 as reported on the questionnaire) are not provided with temperature control. Studies in the author's laboratory suggests that contribution of temperature variations from 25 to 37 °C to measurement variability are greatest with Thomson's solution at 650 nm. Here they might account for a difference of approximately .060 absorbance units at a level of approximately .700 absorbance units - a difference of 8.5%. Higher absorbances are obtained with higher temperatures.

Inadequate cuvette cleaning and matching probably contribute significantly to the variability. Only 87% of participants indicated an alternate cleaning method in case the routine method failed; and, of those that did, four specified aqua regia. Only 86 of 132 participants indicated that they scanned or checked cuvettes at multiple wave lengths. Cuvette problems could affect absorbance readings in either direction. Dirt and finger prints on the cuvettes generally have a much more adverse affect in the ultraviolet range than in the visable. Use of glass cuvettes was indicated by 19 participants. If some of these were used for absorbance readings in the ultraviolet, spuriously elevated levels would, of course, be recorded. We have specifically cautioned against this in the directions mailed to participants.

Wavelength calibration may also present a problem. Only 57% of participants indicated that they checked calibration in the ultraviolet range, and just 68% did so in the visible region.

Also, stray light likely presents a problem in some cases, and more attention will be paid to this possibility in 1974. Non-linearity of phototubes could cause apparent loss of sensitivity (flatter Beer's Law plots), as can broad half-band widths.

Obviously, continuing and intensified educational efforts are indicated. The availability of calibrating filters and solutions from NBS needs to be more widely publicized, and their use strongly encouraged. Survey results suggest the need for continual and expanded monitoring of the performance of spectrophotometers.

IV. The Relationship of Clinical Standard Solutions to NBS-SRM's

Daniel J. Hanson

The Clinical Standards Solution Program of CAP began in 1951. The stimulus for the program arose from the fact that there were very few sources for standard solutions that provided consistently reliable and accurate levels of constituents as found in blood and other body fluids by chemical assays in the clinical laboratory. [4] Since the inception of the program, the Hartman-Leddon Company (Harleco) has aided in the development of and produced the standard solutions for CAP.

The program was designed to provide working standard solutions rather than crystalline materials in order to provide convenience for the laboratory and to avoid the potential weighing and dilution errors by personnel. This approach kept the cost of the standards at a low figure.

Technical problems were immediately encountered that required resolution. First was the question concerning the type of containers and the form of packaging to be used. The containers for the standard solutions should not be stoppered or screw topped, which might introduce a number of potential sources of error and contamination. It was determined that the solutions would be prepared in hermetically sealed ampoules, which could not be re-sealed and which have to be discarded after use. The outer packaging of the sealed ampoules had to withstand the rigors of shipment throughout the United States. The packaging format decided upon was a box of standards containing six ampoules embedded in a hard plastic foam material, covered with a rubber foam protective shield, and contained within a sturdy cardboard box with very rigid corners. Included within each box are instructions for use and an order form for future orders of the standard solutions.

The package insert on one side provides general instructions for use of all clinical standard solutions. The reverse side provides specific instructions for use of the particular solution ordered by the user and the actual chemical formulation of the particular Clinical Standard Solution. The reverse side also specifies the diluent to be used for each standard to avoid improper pH levels or other undesirable conditions. Each ampoule has a 5.5 ml fill to insure the availability of at least 5.0 ml of the standard solution for use by the laboratory.

Generally, the solutions are prepared in concentrations of constituents comparable to those found in human blood. Exceptions are made for uric acid and creatinine solutions, which are prepared in higher concentrations to insure longer stability.

Originally, the three main stated purposes for which the standard solutions were developed, included:

A. To check on working standard solutions, prepared and used in the laboratory.

B. To use as unknowns to check for accuracy of a technician's work.

C. To use as a control for each day's test runs.

Obviously other products have become available that provide better materials for items 2 and 3. At present, the Clinical

Standard Solutions are most commonly used for a check on working standard solutions prepared in the laboratory, for calibration and, in the case of certain procedures, for direct calculation of unknowns. These solutions generally conform to the specifications delineated in recent publications as primary clinical volumetric standards. [5,6]

NBS became particularly interested in the problems of measurements in clinical chemistry in 1966 following a conference on cholesterol determinations called by the Standards Committee of the CAP in Boston. At this conference problems of precision and accuracy of cholesterol measurements in the United States, recognized through means of CAP surveys, were presented to a large number of interested parties from various groups concerned with such measurements. [7] Following this conference the NBS embarked upon a program of development of SRM's for use in clinical laboratories beginning with the development of a highly-purified, crystalline cholesterol SRM. At about the same time the CAP embarked upon a program to develop a Cholesterol Clinical Standard Solution and later provided traceability of the cholesterol solution to the NBS-SRM when it became available.

As new SRM's for clinical laboratories have become available from NBS the CAP has provided traceability to such materials. Even prior to the time that NBS concentrated on the development of SRM's specifically for clinical chemistry the CAP standard solutions were traceable to certain SRM's. Table V shows a list of currently available Clinical Standard Solutions. Those delineated by an asterisk are traceable to NBS SRM's. The pH control materials were recently made available to serve as controls rather than as standards in pH measurements. It was deemed desirable to have solutions available to monitor the reliability of pH measurements at a point between the usual calibration points of 6.84 and 7.38 units at 37 °C.

Table V

Available CAP Clinical Standard Solutions

Alcohol (ethyl) (150 mg/dl.)*
Calcium (10 mg/dl.)*
Chloride (100 meq/L.)*
Creatinine (100 mg/dl.)*
Flame Photometry - Normal (140 meq Na+,* 4 meq k+/L.)*
Low Flame (130 meq Na+, 2 meq k+/L.)*
High Flame (150 meq Na+, 6 meq k+/L.)*
Glucose (200 mg/dl.)*
Nitrogen (20 mg/dl.N)
Phosphate (8.0 mg/dl.P)
Uric Acid (100 mg/dl.)*

Table V (continued)

Protein (single ampoules 6 gm/dl.)
Cholesterol (400 mg/dl.)*
Urea (50 mg/dl.)*
pH Control sets (7.00 units at 37 °C)

The specific protocol format developed for establishment of traceability of the Clinical Standard Solutions to the NBS SRM's has been described by Doctors Kambli and Barnett. [8] In brief, the protocol is as follows:

The specific data concerning the constituent, lot number, date of analysis, method, and the reference material used is designated on page 1 of an assay form. Page 2 of the form lists the raw data necessary for the calculations involved in the comparative studies and provides a variety of statistical information, including the determination of bias and "t" test results. This data is derived from duplicate analyses of twelve randomly selected ampoules of the College Standard and duplicate analysis of twelve samples of the reference materials. The order of analysis of both the CAP standards and SRM standards are alternately distributed throughout the run. Vial to vial variation is also assessed by this technique. The third page of the form provides information regarding the standard error of the mean of the SRM and the CAP standard, and whether or not the CAP standard is acceptable for release. The conclusion is based upon whether or not the concentration of the constituent is within ± 1% of the stated value of the constituent.

The methods used for analyses of the standard solutions are commonly utilized clinical laboratory methods in order to assure that the standard solutions do react appropriately with such methods. The method of choice is usually that listed as the "well accepted" method in the previous year's CAP Survey Program. Since accuracy (rather than within day, or day-to-day evaluation of reproducibility) is the goal of the analysis, all assays on both materials are carried out in a single run on the same day. Automated techniques are preferred since their precision is better than most manual methods.

Each lot of a particular Clinical Standard Solution is assayed by three laboratories. Each laboratory must find the material to be acceptable within ± 1% of the stated value before a particular lot of a College Standard is released for distribution. An exception is made in the case of the protein standard, which is assigned a labeled value after assay by three reference laboratories. The CAP is currently working on a triglyceride standard of triolein in highly purified isopropyl alcohol, ethyl alcohol standards at the 50, 100, and

200 mg/dl levels, salicylate standards, and barbiturate standards.

The CAP Clinical Standard Solutions Program serves a very useful function for clinical laboratories. The materials are of high quality and are traceable to NBS SRM's. They are provided in a convenient form for use in the laboratory at concentration levels of constituents commonly encountered in clinical situations, and are inexpensive. The solutions have been found to be stable for years, even when stored at room temperature. All are stable for one year.

Their contribution to the improvement of quality of clinical laboratory measurements over the past 23 years is difficult to assess exactly. However, it would be difficult other than to draw the conclusion that they have been a significant factor in the improvement of the reliability of clinical laboratory analyses over this period of time.

V. The FDA Program to Regulate in Vitro Diagnostic Produces

Eloise Eavenson

On March 15, 1973, the Commissioner of Food and Drugs published the final procedures for the regulation of *in vitro* diagnostic products. [9]

The definition of the products which FDA will regulate is as follows: "'*In vitro*' diagnostic products" are those reagents, instruments, and systems intended for use in the diagnosis of disease or in the determination of the state of health in order to cure, mitigate, treat, or prevent disease or its sequellae. Such products are intended for use in the collection, preparation, and examination of specimens taken from the human body. These products are drugs or devices as defined in the Federal Food, Drug, and Cosmetic Act or are a combination of drugs and devices, and may also be a biological product subject to section 351 of the Public Health Service Act.

The first provision of the new regulation, is that all *in vitro* diagnostic products must bear specific items of labeling, as described, which include such information as an adequate description of the product, instructions for its use, known limitations, and indications of the quality of performance obtainable with the proper use of the product. Special provisions are made for the labeling of products intended for research or investigational use and for general purpose reagents, instruments, and equipment.

This provision for labeling means that as of March 1974 all in vitro diagnostic products must bear labeling that meets the requirements outlined or the products will be in violation and subject to compliance action. There is no provision for approval of labeling prior to marketing. This means that the manufacturer is totally responsible for determining that his labeling meets the stated requirements and that he has adequate data to support his claims for his product. The user is entitled to expect all in vitro diagnostic products marketed after March 15, 1974, to bear labeling according to the general labeling requirements in the form described as appropriate for each product.

The FDA must find those products that are not in compliance before it can take any action. Several procedures are being developed to accomplish this task. First, the regulations implementing the Drug Listing Act of 1972 include provisions for the listing of in vitro diagnostic products. Therefore, all manufacturers of in vitro diagnostic products should have registered their establishments and listed their products in the drug inventory. In this way we can identify the products marketed and examine their labeling. Second, a provision is made in the regulations that the principles of good manufacturing practices must apply to the manufacture of all in vitro diagnostic products, and to that end, an inspection program is currently being developed within the FDA. Third, product problem reporting systems are being developed such that users at many levels notify us of any problems found in any products that they use. A pilot study with the ASTM has helped immensely in developing such a system. And, fourth, we are developing a monitoring system for systematically reviewing the products, their labeling, and their performance.

Since the products that we plan to regulate are so diverse, we felt it necessary to begin our program with a minimum disruption of the practice of laboratory medicine. Additionally, we did not want to inhibit continuing research and development. As a practical consideration, we determined that it would be necessary to establish performance criteria for specific classes of products rather than attempt to deal individually with the large number of existing, currently marketed products. While the requirements for labeling already described should have the effect of identifying those products that are capable of doing a particular job, it remains difficult in a general labeling format to specify exactly how well a particular product should perform. There are two possible approaches to handling this job. 1. Examine each product and evaluate it against its own claims (which is essentially what we can do right now), or 2. determine how well a particular type of test should perform for a specific purpose and evaluate all products marketed for that purpose against those criteria. Since, for many tests, there may be many similar products, we decided to take the latter approach. Standards for the performance of classes of products will be developed that describe the performance requirements necessary to assure accuracy and reliability of results, specific labeling requirements necessary for the proper use of a particular class, and procedures for testing the product to assure its satisfactory performance. When these standards have been established, the products within these classes must meet the requirements of these standards or they will be in violation of the Act.

Two questions arise. Who sets the standards? How are product classes determined?

The regulations provide that "three procedures are available for developing product class standards and may be proposed on the initiative of the Commissioner or by petition of interested persons:

A. an existing standard may be utilized,

B. interested persons outside of the Food and Drug Administration may develop a proposed standard, or

C. FDA may develop the standard."

The Center for Disease Control is a partner with the Food and Drug Administration in the development of this program and will play a key role in the preparation of product class standards. They are using their own specifications of performance, consulting with qualified experts, and considering existing voluntary standards developed by groups such as the NCCLS, the ASTM, the AOAC, etc.

We have an Advisory Committee of qualified experts that advises us, among other things, on the priorities for establishing product class standards, the medical significance and scientific basis for in vitro diagnostic products, the selection of reference methodologies and reference materials and the adequacy and reasonableness of proposed standards. Subgroups of this Advisory Committee act as the nucleus for studying proposals for product classes and product class standards in their areas of specialization. Currently four such Subcommittees have been formed: one in hematology, one in clinical chemistry, one in microbiology, and one in statistics. Furthermore, before a standard for a product class is proposed, we may request that any pertinent information about the products or their use be submitted to the FDA. The FDA, with CDC and its Advisory Committee, will review this information during the development of the product class standard.

The product classes are simply a convenient grouping of products for the development of standards. Several product classes have been named tentatively for the purpose of developing priorities, but the universe of product classes has not yet been described. The first product class standard will be for those products used in the determination of glucose or total sugars. A request for information was published in June and comments have been received for 50 products. A request for information for a second class of products, called calibrators, will be published in the Federal Register within the next week. For the purposes of this request, calibrators are defined as *in vitro* diagnostic products, or components of these products, used in qualitative and quantitative clinical chemistry analytical procedures, which serve as a basis of reference in order that the amount, concentration, or presence of an analyte may be determined in specimens taken from the human body. Products to be reviewed for the development of this product class standard include:

A. Chemical products (analytes) of a defined purity (e.g., bilirubin 98% purity) intended for use as calibrators.

B. Calibrators with the analytes in a completely defined matrix (e.g., bilirubin in distilled water with a specified amount of a specified preservative present).

C. Calibrators with analytes with assigned values in an incompletely defined matrix. An incompletely defined matrix includes biological matrices (serum or urine) as well as a solvent to which incompletely defined substances (e.g., 95% NADH, human albumin, etc.) has been added. Concentrations of analytes contained in the product may be specified by assay or addition.

Work is currently underway for the development of product class standards for General Culture Media for Neisseria gonorrhoeae, Hemoglobin, Hemoglobinopathies, Rubella, Calcium, Coagulation, Syphilis (Non-treponenemal tests), and Rabies. Additional product class priorities have been reviewed by our Advisory Committee and work has begun to develop the information needed for these product class standards as well.

The procedure that we are following for establishing the performance requirements for our product class standards involves a three step approach.

A. Determine all the known current uses for results. For each use, determine the "critical" factors for evaluating a particular patient result. For example, for a qualitative test, what is the consequence of a false negative result? For a quantitative test, is the absolute value of importance or is it a difference or changeover for some specified time that is used? Absolute results may need more specific methodology whereas day-to-day reproducibility may be more important if one is looking for changes from day-to-day in a particular patient. Both specificity and precision may be necessary for epidemiologic studies, while highly sensitive methodology may be unwarranted in mass screening programs in which the risk of a false positive result is more hazardous to the patient than a false negative result.

B. After the performance requirements for the various uses of the results have been determined, the available methodologies that are potentially capable of giving such required performance must be determined. This may include selection or designation of a reference method to serve as a yardstick for comparison of products, selection of materials to serve as calibrators and specimens for assessing performance, and development of appropriate testing procedures to detect products that fail to meet the proposed performance requirements.

C. The available products must be surveyed to determine whether or not they have the potential to meet the performance requirements. Such surveys would include studying manufacturers' claims and data submitted in support of these claims, and laboratory spot checking of specific products.

FDA, CDC, and the Advisory Committee would review all of the information gathered--the reference method with its documentation and field testing results, the proposed performance requirements for each appropriate use category, and the "state of the art" data from manufacturers and users. From these would come the proposed product class performance standard and any specific labeling requirements considered necessary. The product class standard would then be published as a proposal for comment.

Application of the procedures just outlined varies considerably from one class of products to another. For example, there is an accepted reference method for hemoglobin quantitation and an accepted calibrator or standard, cyanmethemoglobin. For glucose, on the other hand, there is an SRM but no accepted reference method. Candidates for the reference method proposed are o-toluidine, glucose oxidase, and hexokinase procedures. Work is currently being done at CDC in a cooperative venture through an AACC committee to develop a hexokinase reference method. Identifying the critical values for hemoglobin quantitation is a relatively straightforward matter. For glucose determinations, there are needs for specific quantitative results and for semi-quantitative results. The requirements for measuring glucose in urine are different from the requirements for measuring glucose in plasma or spinal fluid. We have taken these different requirements into account in developing the specifications of performance for products intended to be used in the glucose determination.

Our intent is not to inhibit the availability of useful materials from the marketplace. Our intent is to provide the laboratory user with materials that he may confidently expect to give the quality results he needs. We do not expect to eliminate all of the problems with any class of products with the publication of a performance standard. As our information base grows and better products become available we expect to revise our performance specifications to reflect these changes.

This is a new program and it requires a lot of help from a lot of people. There are many opportunities for input into the program. Anyone may recommend a standard at any time. When the need for a standard for a particular class of products has been determined, a call for information is published in the Federal Register. Any interested person may submit comments and views on the need for a standard, the degree of risk or injury associated with the use of any product within the class, information related to the sciences upon which the various products are based, the medical need for the product, as well as data on specific product performance. All standards will then be published as proposals and again anyone having pertinent information may (and should) comment. In addition, we try to maintain a close liaison with other government agencies, scientific societies, and voluntary standard setting groups as well as industry representatives.

We believe the program, which the Agency has developed, is one that will result in an immediate and useful improvement of the development and research work that preceeds the marketing of products, and improvement in the labeling of products, which will allow for their more effective use, and a re-evaluation of most of the products currently being marketed. We have attempted to design this program in a way that will not interfere with valid investigational and research activities or new products or existing products. We believe that the benefits that will accrue to the laboratory user, and the person who is ultimately affected by these products, the patient, justify the expenditure of the resources that we are devoting to this program.

VI. The Size and Source of Analytical Error in Clinical Chemistry

Roger K. Gilbert

The chemical samples in the CAP Survey Programs are currently mailed out to between 6-7000 laboratories. The participants include laboratories of all types throughout the USA. The data from a program of this size provides a unique opportunity for evaluating the levels of performance throughout the country and determining whether these levels are meeting the needs of medical care.

The simplest measure of agreement that can be obtained from a Survey Program is a measure of the agreement among the assay results submitted by all the participants for analysis on a single common sample. However, this type of measure does not relate in direct terms to the needs of medical care, and in addition, this type of measure cannot pinpoint the sources of any shortcomings so that an effective strategy can be drawn up for improvement.

The challenge to the CAP Survey Program Committee is to be able to measure the size of analytical error in terms that can be related directly to the needs of medical care and to identify the sources of analytical error in a manner that allows specific identification of problem areas. Beginning in 1971 a plan for the chemical samples for the Survey Programs was designed in an attempt to meet these requirements. The plan recognizes three potential levels of agreement among assay results obtainable by statistical analysis of variance. The levels range from minimal to ideal from the viewpoint of medical care.

The first level is any laboratory, anywhere, anytime. This level is plainly the ideal. It implies that a patient can go to any of the 10,000 laboratories in the Unites States and obtain an assay result that could then be compared to a second result obtained in any other laboratory at any other time. The problems of achieving this level of agreement are very complex. If the requirements of medical care are not stringent, if, say a 5% level of agreement is satisfactory, then this level of control may be achievable. If, however, the requirements of medical care call for a close level of agreement, say 1%, then it could be a very expensive undertaking to achieve 1% agreement 24 hours a day, 7 days a week in 10,000 laboratories.

The second level is within one laboratory, over six months. This implies that a patient can visit a single laboratory at any time during a six month period and that the analytic result will then agree within the required limits with a second result produced in the same laboratory. This level of agreement does not allow the results to be directly related from one laboratory to another, but if both are in control a correction factor may be applied that will allow interconversion. This level of agreement is far simpler to achieve than the first level and it is a level of agreement that meets many of the needs of medical care.

The third level is within one laboratory on a single day. This is the least satisfactory medically as it only assures that the assay results agree when the specimens are run on the same day in a single laboratory.

This Survey Plan can measure how well agreement is being achieved at each of these three levels. It is also possible to determine the relationship between the levels and whether the factors that contribute to error at one level is far larger than the factors that contribute at the others.

I would now like to talk in further detail about how this is done and the implications of the findings.

The measure of agreement for level three is reported as precision in the Survey Program. It is determined by statistical comparison of the pair of the assay results reported by each laboratory for the two specimens that are sent out in each mailing. The factors that contribute to the variance (error) at this level are dependent on the methods being used by the laboratories and the skill with which the methods are carried out. The level of agreement could be improved if the analysis were repeated and the results averaged. Agreement at this level has few direct applications to medical care. However, the values calculated at this level are a very useful measure for comparing methods and the amount of "error" at this level is a controlling factor in determining the size of error at the other levels.

An example is shown in Table VI for the types of values for the precision of calcium analyses in 1971 and 1972. There is a wide difference between the levels of precision shown by the individual methods, approximately a threefold difference. There is close agreement between the precision values found for the individual methods in 1971 and the values found in 1972.

Table VI

Precision of Calcium Analyses 1971/1972
Coefficients of Variation (%) (r = .91)
College of American Pathologists-Survey

System	No. Labs.	1971	1972
S.M.A. 12/30	121	1.5	1.7
S.M.A. 12/60	785	2.2	1.8
Atomic Absorption	162	2.4	2.8
Autoanalyzer	263	2.5	2.3
Calcein Fluorometric	407	3.8	4.1
Flame Photometer	611	3.8	3.2
Chloranilate Ppt.	415	4.7	4.2
Oxalate Ppt.	89	4.9	4.6

Table VII shows the precision values for glucose analysis. The range is twofold between the lowest values and the highest values and again there is close agreement between the size of the measures in 1971 and the size in 1972. The findings for each of the other Survey constituents are similar. The average difference throughout the Survey between the best levels of precision and the worst levels of precision is over twofold. The worst level is 2.4 times larger than the best level.

Table VII

Precision of Glucose Analyses 1971/1972
Coefficients of Variation (%) (r = .98)
College of American Pathologists-Survey

Reagent-System	Analytical System	No. Labs.	1971	1972
Neocuproine	S.M.A. 12/60	554	2.6	2.0
Ferricyanide	Auto Analyzer	840	2.6	2.3
Neocuproine	Auto Analyzer	102	2.6	2.5
O. Toluidene	Manual	2431	3.9	3.3
P.M.S.	Manual	98	4.3	3.8
Somogyi Nelson	Manual	133	4.9	4.3
Folin Wu	Manual	106	5.3	4.6

Figure 1 compares the levels of precision found for all the various methods for all of the constituent analyses included in the Survey Program. The precision levels are listed from 0-10%. There are no methods with a precision of less than 1%. The lowest value is 1.2% and was provided by sodium analysis. There are very few methods that have precision levels below 1.5%. The majority are in the 2-5% range. The highest levels are shown by triglyceride analysis, some values exceed 10%.

One aspect of the measure of precision is the contribution of the errors due to lyophilization and reconstitution of the serum samples. Studies from the Survey Program carried out in 1973 for sodium and potassium analyses suggest that the contribution from these sources is negligible. This study is being completed and will be published.

Table VIII shows a comparison between the levels of precision found for all methods in 1971 and the levels found in 1972. It is apparent that all the 1972 levels (except for potassium) are lower than the 1971 levels. A similar relationship is apparent when the best levels are compared and also when the worst levels are compared. This relationship provides strong evidence that there was a real improvement in the level of precision during the two year period, because on a chance basis it would be expected that approximately equal numbers of these values would be higher or lower.

Table VIII

Precision for all methods

College of American Pathologists-Survey

Constituent	Precision %	
	1971	1972
Calcium	3.8	3.6
Chloride	2.0	1.9
Cholesterol	4.9	4.0
Glucose	3.6	3.2
Potassium	2.3	2.8
Sodium	1.8	1.7
Total Protein	2.7	2.0
Urea Nitrogen	6.9	6.4
Uric Acid	4.8	4.5

Examples of the second level of agreement are summarized in Table IX. This is measured in the Survey Program by calculating the levels of agreement between the assay results obtained on duplicate specimens that are sent out to the participants 3-6 months apart. This measure is referred to as "month-to-month" or long-term precision in the Survey Program.

Table IX

Ratio of Short-Term and Long-Term
Within Laboratory Components
College of American Pathologists-Survey

Constituent	Precision		
	Short Term	Long Term	Ratio
Calcium	3.6	3.7	1.0
Chloride	1.9	1.5	0.8
Cholesterol	4.0	4.0	1.0
Glucose	3.2	4.5	1.4
Potassium	2.8	2.6	0.9
Sodium	1.7	1.0	0.6
Total Protein	2.1	1.9	0.9
Urea	6.4	10.7	1.7
Uric Acid	4.5	7.3	1.6
		Average	1.1

This measure includes the factors that contribute to short-term, within day precision, which were described in level three, and also includes a series of additional factors that contribute to long-term change within each laboratory. Examples are changes in standards, instruments that change over a period of time or reagents that deteriorate. All of these factors can be summarized under the general heading "internal quality control."

The values for short-term and long-term precision expressed as coefficients of variations are similar in size for each of the constituents and the average ratio between the two is 1.1. This relationship implies that quality control adds an approximately equal amount of error to the error arising from precision within-day sources. This relationship also implies that if the precision is reduced by any maneuver and is for example halved, then it can reasonably be expected that the contribution from internal quality control will also be reduced and will probably also be halved.

Estimates of variability at level two should be comparable to the variability that the laboratories find in their own internal quality control programs. The two are compared in Table X. The variability found by the laboratories are based on results of the CAP Quality Assurance Service for approximately 400 laboratories. The variability in the Survey Program are larger in each instance. Since the "all method" figures could be high due to method biases, the SMA 12/60 figures are also shown for comparison to the large well-defined method group. The Survey values are again larger. These findings suggest that laboratories underestimate their long-term variability when they base their findings on the values from their internal quality control programs. This is probably to be expected. The internal pools are being used for daily quality control and usually allow ± 2 s.d. changes in the daily assay found on the control specimens.

Table X

Estimates of Variability-C.A.P. Survey vs Laboratory's[a]

	All Methods (C.V.)		SMA 12/60 (C.V.)	
	Laboratory	Survey	Laboratory	Survey
Calcium	2.9	5.2	2.6	3.1
Cholesterol	4.6	5.7	4.4	4.8
Glucose	4.1	5.5	3.7	3.8
Potassium	2.5	3.8	2.1	2.5
Sodium	1.5	2.0	1.4	1.5
Bun	5.8	12.3	4.6	7.0
Uric Acid	4.7	8.7	3.2	5.4

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[a] Laboratory's own Quality Control Data obtained from Q.A.S.

The measures of agreement at this second level most closely relate to the needs of medical care. Agreement over a six-month period is required if a doctor is to use a laboratory effectively and if a patient is to be followed for a period of time in a hospital or in an outpatient laboratory setting.

This is a complex comparison and detailed comparative figures are being published. [10] At present, the evidence suggests that the methods with the best levels of agreement are producing results that meet the needs of medical care for most analyses, while at the opposite extreme the methods with the poorest levels of agreement are probably not.

The first level of agreement is the ideal. It implies that a patient can go to any laboratory at any time and compare the result with a second value obtained in another laboratory at another time. If this level of agreement can be achieved, it would imply that normal ranges could be universally applied and that physicians could forget the problems of method bias and laboratory differences. However, it is important to stress that failure to meet this ideal does not imply that laboratory results are valueless for medical care. Agreement at the second level is widely useful and agreement at the first level does have some practical application.

The errors that enter into level one include the factors described at levels three and two. In addition, the factors that make this estimate larger are related to the differences between the standards being used and to any bias of the methods being used. These can be summarized as "between-laboratory" factors.

It is possible to determine the overall contribution provided by the "between-laboratory" factors, and this is summarized in Table XI. The figures compare the percentage of the total analytical error that stems from factors within laboratories and the total that stems from factors between the laboratories. It is apparent that the "between-laboratory" factors provide the minority of the analytical error and that the overall average percentage contribution is on the order of one-third.

Table XI

Contribution of Sources of Analytical Error-1972

College of American Pathologists-Survey

Constituent	Within Laboratory	Between Laboratory
Calcium	70%	30%
Chloride	78%	22%
Cholesterol	62%	38%
Glucose	62%	38%
Potassium	77%	23%
Sodium	71%	29%
Total Protein	66%	34%
Urea Nitrogen	74%	26%
Uric Acid	77%	23%
Average	71%	29%

Method bias is measured in the CAP Survey Program by comparing the mean values obtained for each method with the mean values provided by a second selected method. The values for the selected method are then regarded as the reference point. Some of the findings from 1972 are shown in Table XII, which lists the size of the median average bias shown by an individual method for each of the eight specimens that are mailed out during the year. The order of magnitude of the method bias for each constituent is small with the exceptions of glucose and cholesterol.

Table XII

Median Average Bias for a Method in 1972
College of American Pathologists-Survey

Constituent	Bias (%)
Calcium	+ 1.7
Chloride	+ 0.2
Cholesterol	+ 6.9
Glucose	+ 4.7
Potassium	+ 0.6
Sodium	+ 0.3
Total Protein	- 1.1
Urea Nitrogen	+ 1.5
Uric Acid	+ 3.8

A more detailed study of method bias was carried out last year in cooperation with NBS. CAP submitted the full series of 1971 chemical samples to NBS where the calcium content was measured using isotope dilution mass spectrometry. The values obtained by this method can clearly be taken as a far more accurate estimate than any value obtainable by a routine clinical method in current use. This exercise allowed a comparison between the mean values obtained in the Survey Program and the "true" value of calcium for the specimen determined by the NBS method. The findings are summarized in Table XIII. Again the average deviations for the individual method assays are small. In addition, the maximum deviation for a method assay throughout the series is also small. This is an extremely valuable study and the College is indebted to NBS for this work. It is hoped to continue this study with vials from 1972 and 1973.

Table XIII

Calcium Method	Number of Labs	% Deviation of Mean Values Average	Maximum
Oxalate Precipitate	108	0.6	3.4
Chloranilate Precipitate	550	-1.8	-4.1
Flame Photometer	666	2.8	5.1
Calcein Non-Fluorometric	286	-0.9	-1.7
Calcein Fluorometric	502	-2.3	-3.2
Cresol Complexone Auto Analyzer	257	1.4	1.6
Cresol Complexone SMS 12/30	139	0.0	-1.0
Cresol Complexone SMS 12/60	704	-1.4	-2.1
Atomic Absorption (Participants)	104	-0.4	-1.3
Atomic Absorption (Referees)	10	-1.5	-2.3
Atomic Absorption (NBS)	1	0.7	1.4

These statistical studies on CAP Survey data offer practical implications for at least two large areas. First, the Survey Program provides objective data on the performance of methods. The most striking finding from the comparative method data is the wide range of precision for the different methods. The figures from the Survey data are average figures and it is theoretically possible that any laboratory may operate with a substantially better level of precision than the average. However, it would appear unlikely that a laboratory can overcome the two- to threefold differences that are demonstrated by the Survey data.

The studies suggest that laboratories should stop using many of the methods that show poor precision unless they can demonstrate with certainty that in their hands the method is providing satisfactory results. This implies a need for a protocol for measuring and monitoring method precision. It is important that the protocol is designed to provide objective data because the Survey evidence suggests that laboratories underestimate the levels of analytical variability in their routine quality control data.

These findings are particularly important for areas such as calcium analysis where the medical requirements are stringent and many of the methods fall short of the desired goals. They are less important for areas such as total protein analysis and phosphorus analysis where most methods meet the needs of medical care.

The ability to measure method performance also has major implications for the field of product evaluation. Many methods are in fact commercial products whether they be instrument systems or kits. It is apparent that the Survey can provide valuable performance data. Guidelines are currently being drafted for disseminating this information to all interested parties.

The comparative data also allow measures of method bias and it is interesting to find that these values are small. This suggests that the contribution that method bias makes to total analytcal error has been overestimated.

A second area also has many potential implications. The Survey data provide a basis to develop a theoretical model of analytical variability. The data suggest that the total analytical error can be regarded as the sum of three separate sources: A short-term within-laboratory component, a long-term within-laboratory component and a between-laboratory component. They also suggest that these three component sources provide approximately equal contributions to the total error. The findings are similar for each of the constituents included in the Survey Program. This implies that if a national goal is set that requires a coefficient of variation between all laboratories of say 4%, then this can be achieved if the individual laboratories can operate with a precision level of

$$4 \times \frac{1}{\sqrt{3}} \text{ or } 2.3\%.$$

While the values are not exact they provide an indication of the magnitude of the problem and allow some appraisal of whether the goal is technologically possible.

The model also can be used to define the theoretical limits of the present technology in the clinical laboroatory. It appears that no routine methods exist that operate with a precision lower than 1.2% at present. This implies a potential level of agreement between the results provided by all laboratories of $1.2 \times \sqrt{3}$ or 2.1%.

If the needs of medical care call for closer levels of agreement, it will be necessary to develop new technology or change the number of times that each analysis is carried out.

Developing a new technology may be a difficult undertaking because attempts to reduce precision below 1% become increasingly more complex and potentially expensive. It may well be that the simplest strategy is to assay critical samples more than once. If an analysis is run four times then the precision error will be halved and this may be sufficient improvement for some analyses.

Realistic goals become crucially important in this area. Cotlove's study of human variability suggested the need for a C.V. for sodium analysis within a single laboratory over six months of 0.36%. [11] The Survey data suggest that this would be achieved if laboratories could operate with a within-day precision of 0.25%. Sodium analysis is the most precise in the clinical laboratory at present, but the proposed level is one-fifth of the present level. A fivefold improvement would be a major undertaking with enormous cost implications, and should be undertaken only after balancing the potential advantages with the potential costs.

I hope that in addition to providing an overview of some aspects of clinical chemistry today I have provided some perspective on the potential role of the Survey Program.

A large Survey Program is an entirely new tool for the clinical laboratory. It has become a reality through a marriage of advanced manufacturing techniques with advanced data processing techniques. The techniques in these areas have reached the required level of sophistication only during the past few years. The Survey Program is now at the stage of developing the methods of statistical analysis required for digesting the data. This is an exciting stage and, as with any new technology, the full implications and potential applications are only beginning to be tapped.

Laboratory improvement presents a scientific and a technological challenge. It will be achieved only when it is firmly based on factual data. The CAP Survey Program is beginning to provide the type of data that is needed. The challenge that faces us now is to define the goals more clearly and to develop the strategy to achieve them.

VII. Process Control and Medical Significance

Roy M. Barnett

In the realm of meaningful measurement, it is always necessary to ask, "Meaningful for what purposes?" In the present discussion, the purpose is to provide proper measurements for medical care of sick and healthy persons in a clinical, as opposed to a research environment. Those who wish to do research in biological measurements may have different needs, but these should not be imposed on the general medical community, particularly if added expense is involved. In approaching this subject we must consider accuracy (closeness to the truth) and precision (ability to reproduce measurements) separately.

I would like to discuss briefly some of the situations in medicine for which accuracy is needed. These include:

A. Conformance with published values when accepted levels exist for separating normal from diseased individuals. Examples are the assay of glucose in evaluating diabetes and the assay of uric acid in gout.

B. When a physiological reciprocal relationship exists between two or more analytes in the same sample, as in electrolyte studies.

C. When dosage of medication is predicated on the assay level of some blood constituent, for instance the hemoglobin level in blood transfusion.

D. When metabolic exchange studies serve as a guide to diagnosis or treatment. An example is calcium excretion in control of metastatic breast cancer.

Precision is much easier to evaluate and in most medical applications is more important than is accuracy. Generally speaking, increasing precision carries an increasing price tag, so we must balance plausible medical benefits against cost.

There have been three general approaches to setting desirable precision limits in the medical field. These are, in order of publication:

A. Tonks, [12] based on the normal population range.

B. Barnett, [13] based on how physicians commonly use laboratory data.

C. Cotlove, [14] based on variability of analyte levels in individual people over a period of time.

Each of these approaches has advantages and disadvantages.

Dr. Tonks' approach is easy to calculate because it assumes that the method standard deviation should not exceed 1/4 of the normal population range, and this appropriately relates normal values to measurement. The disadvantages can be enumerated as follows:

A. Normal ranges differ by methods and by sources of publication, as well as by age, sex, and other demographic characteristics. Which range is to be the reference point?

B. Published normal ranges include variability introduced by the analyses as well as those inherent in the individuals tested. Because imprecision varies for different analytes and different methods, the contribution of this factor may be large or small.

C. The whole system is obviously not equally appropriate for all analytes because Tonks himself makes exceptions in the case of six of the nine analytes he studies.

D. There is no logical reason that population ranges should be the basis for demands based on day-to-day care of individual persons.

Dr. Cotlove's "Tolerable analytic variation" is defined as one-half the estimated biological variability. It has a sound basis because the figures were derived from actual data rather than from published normal ranges. Additionally, they were based on the best methods available and in use at that time. The calculations were straightforward and can easily be carried out for analytes not already studied.

The disadvantages follow:

A. The limits are so narrow for some analytes, many methods commonly employed cannot meet these requirements. This implies that we must develop better methods, possibly at considerable expense.

B. Should we accept ability to detect minimal changes within single healthy individuals as a meaningful goal? Consider what happens when unexpected biochemical abnormalities are detected; the physician quite often is unable to arrive at a useful diagnostic or therapeutic decision. For example, in a study of 1000 Metropolitan Life Insurance personnel [15] the following results were obtained using 12 channel chemical screening and population normal range.

Positive Abnormals	# Cases	%
New positives	24	2.4
Recognized disease entity	11	1.1
Pathophysiological biochemical syndrome	13	1.3
Confirmatory positives	38	3.8
Unclassified positives	190	19.0
Negatives	748	74.8
Total	1000	100.0

My own values were based on how physicians actually used laboratory data at the time of the inquiry. The advantage of this approach is that the true ultimate consumer, the attending physician, determined what deviations from the normal are meaningful and what changes within a single patient's values are significant. It is also appropriate for each analyte.

The disadvantages of my approach are numerous:

A. It is not easy to calculate. Most physicians do their statistical thinking on a subconscious level, very difficult to quantitate.

B. Securing an adequate sample of physicians is almost impossible.

C. There is the same type of circular reasoning as with the Tonks approach, namely that the observed method imprecision plays a considerable and variable role in the limits chosen. The clinician's interpretation might be quite different if the method in use were much more precise.

There are two further aspects to this choice of precision limits which I would like to discuss.

First is the question of medically misleading results, that is ones which are so far wrong that inappropriate diagnosis or treatment is rendered; the glucose of 50 mg instead of 300 in a diabetic, or the BUN of 200 instead of 25 in the comatose patient. This sort of error is considered an "outlier" in most studies and is omitted from further calculations. Such a false result may cause serious injury or death and is therfore medically far more important than a discrepancy between 50 and 80 mg of glucose, or between 20 and 30 mg of BUN. Interestingly, in the smaller laboratories enrolled in the CAP Basic Survey in 1971, there were almost twice as many such ouliers than in the larger laboratories enrolled in the Comprehensive Survey (1.5% vs 0.8% for glucose, cholesterol, calcium and chlorides). We do not know whether such medically misleading results are the result of poorer methods or poorer personnel in smaller laboratories. Certainly we must use every precaution to avoid such results and methods likely to give them.

A second problem is that of changes that may occur in a single individual under stressful conditions. Examples are the fall of 0.5 to 1 Gm/dl of hemoglobin after changing from a standing to a recumbent position, and rise of 40 to 50 mg/dl of glucose due to emotion. Physicians familiar with these changes ignore alterations of test results of the size indicated, and those who are not familiar with them are easily misled anyway; therefore, there is little need for methods capable of detecting such fluctuations.

Having indicated so far that there is a valid concept of medically useful limits, and that they can be approached in many ways, how does the existing state of the art meet the needs? The best index we have is from large proficiency surveys such as those conducted by the College of American Pathologists and the Center for Disease Control. Dr. Gilbert has performed valuable pioneer work in determining the factors that lead to imprecision in surveys, and he has presented this work today. [16] For most common chemical analytes, the existing good practical technology meets the medical needs, whereas existing poorer methods are unsatisfactory.

This brings me to two further aspects of laboratory medicine practice.

First is the matter of diagnostic products and devices. Modern technology is absolutely dependent on reagents and instruments prepared by commercial suppliers. The number of these is so great that individual laboratories find it almost impossible to decide which to use. Some of the reagents and instruments are unsatisfactory because they are poorly made or because their performance is inadequately described. CAP in 1960 set up a Product Evaluation Program to encourage proper description of the use and performance of products and to validate manufacturers claims for performance. This voluntary program has evaluated claims for a number of reagent kits and test instruments, and permits the manufacturers to use these claims in advertising with the College's consent. This is not a seal of approval, but a record of confirmed claims. The charge to manufacturers is substantial and the economic benefits hard to measure, so industry participation in the past has not been great.

Because many poorer products have been marketed, as we demonstrated in extensive studies of cholesterol and glucose kits, [17,18] and because these poor products are felt to be a real risk to consumers, the Food and Drug Administration is now taking a major role in the field through their In Vitro

Diagnostics Division. The question of needs for medical usefulness is obviously of utmost importance in deciding whether any products perform acceptably. Both FDA and the CAP Standards Committee are therefore anxious to investigate these limits further and to develop generally acceptable goals.

Another aspect of laboratory practice related to needs for medical care is the quality control of existing performance, both internally in each facility and externally through proficiency surveys. These are powerful tools for maintaining surveillance of performance. I mention with sorrow that one NBS Division, the Technical Analysis Division, has recently cast doubt on the value of such proficiency surveys in two recent publications. [19,20] After inventing a square wheel in the form of a poorly conceived and executed proficiency survey of their own they concluded that round wheels would not turn! I trust the data Dr. Gilbert has presented today has given some insights into the real value of such surveys.

[Editor's Note: Dr. Barnett's position on this work has since been presented in several publications, e.g., Clinical Chemistry, Vol. 22, No. 2. pp. 314-315 (February 1974). Replies to Dr. Burnett by the NBS authors have also been presented, e.g., Clinical Chemistry, Vol. 22, No. 4, pp. 521-524 (April 1974).]

One implication in all of the studies and conclusions of the panel is the need for improved process control. I include in this the following:

A. Reagent preparation and storage;

B. Pipetting and specimen handling;

C. Instrument cleaning, adjusting, and calibration; and,

D. Reading and recording of results.

I am confident that in the next few years we will see the general level of clinical laboratory testing rise to meet medical needs in every field.

VIII. Discussion

Dr. Milazzo:

First of all concerning the paper that Dr. Schaffer gave. I have a proposal. We speak of reference materials for standardization. In my opinion, standardization is a combination of reference materials and methods. Particularly for clinical chemistry, I feel that standardization of methods would be a great help for laboratories concerned with the clinical analyses that should be used by the physicians to decide diagnosis or therapy. Therefore, my proposal is that there be for methods, some kind of reference materials that have been assayed by qualified laboratories and would be distributed as controls to laboratories concerned with clinical analysis. This would be in the form of reference laboratory assay reports so that some kind of standardization in clinical chemistry could be achieved. This is a simple proposal that can perhaps be taken into consideration. I can give an example. I had developed myself a good analysis for creatinine. I gave a sample to two highly qualified laboratories in Rome. They gave me the values of 0.7 and 1.2 and they were both wrong. The second was nearly at pathological levels. They used two different methods. One was enzymatic and one was colormetric. This means the physician who sees the reports of analysis of 0.7 or 1.2 must draw different conclusions. Therefore, standardization of the methods concerning the clinical analysis is in my opinion of the same importance as the distribution of reference materials for controlling the methods.

The second point I would make is concerning the paper given by Dr. Beeler. I could rapidly go through the tables you have shown and I could state that the individual values obtained by all the individual laboratories and even of the so called reference laboratories are in general lower than the values I obtained myself, and gave in my talk yesterday, and lower than those obtained here at the National Bureau of Standards. This means probably that there were instrumental errors by the participants in this very large cooperative study. Particularly, the fact the numerical values for the two maxima of acid potassium dichromate at the same level of concentration I and NBS used were not obtained. Probably the most important error is that all the users were not sure whether or not stray light error was present in their instruments. It is known that the presence of stray light usually lowers the final value obtained. To calculate a mean most probable value from such a large number of laboratories who are not all of the same quality is, in my opinion, wrong; because the most badly working laboratories impair the final value that should be used for controlling and checking all the laboratories, equipment, or procedures of the operators.

In particular, the slides showing the largest deviation from the mean values for the Zeiss instrument, showing a large deviation for the values of potassium dichromate at the short wavelengths is in my opinion a demonstration of this point. The stray light error is larger at shorter wavelengths. This is an indication that many of the instruments in the study were not stray-light free. In an investigation I presented yesterday, concerning the assessment of the numerical value for potassium dichromate, I completely dismantled the spectrophotometer I had at my disposal. I also dismantled the measuring equipment; so that by recomposing I could investigate each source of errors mentioned, stray light, band pass width, linearity of the photomultiplier, and linearity of electronics. All these errors were either eliminated or taken into account by considerable mathematical procedures. The final values I obtained and showed yesterday in slides are all within one hundred units of absorbance higher than those in the table distributed. Practically, none of the values in the tables are at the same level of those obtained by myself or obtained by NBS. I think, therefore, that the best values to be considered for distribution for checking all other instruments and laboratories should be only those obtained by very qualified laboratories which have investigated and eliminated instrument errors.

Dr. Schaffer:

I would agree entirely that it would be delightful to not only issue a reference material, but also a reference method as you suggest; if in fact, it were feasible to carry out all the accurate methods with the speed and accuracy and the low cost that medical people require. We live in a real world. At NBS, we are not really so down-to-earth in the amounts of money we will spend to get the most accurate numbers. What our emphasis has been is to find out how accurate these chemical procedures can be and then help to evaluate the field methods. Certainly, we do not want to stifle the ingenuity of the chemist on the outside and what they want to do, but we want to give them as much flexibility as possible. If it were entirely possible to come up with a cheap highly accurate method, I would agree with you entirely, but due to the fact that we do not have many of these, except with calcium run on the SMA 12/60, I think we will have to go along with issuing SRM's and finding out how accurate certain reference methods are and proceed from there.

Dr. Beeler:

I think the question about the fact that in the tables that we handed out the absorbance values were lower than those obtained by the questioner is based on a misunderstanding of what was done. As I stated, the batch tolerance permitted to the manufacturer was 2.5% so that the indication of concentration on those graphs are simply approximate and may be 2.5% lower than stated. I think that would probably bring them within the values that the questioner had in mind. His second point regarding that they were lower than the values established by NBS is again the same answer. The values established by NBS were on pure material prepared at NBS. The Survey sample is commercial material perpared for a large survey and the concentration is not known that well. I could give you a much better answer if I were able to identify Laboratory A. Stray Light: I agree that this is probably a major component of the error in the ultra-violet and for that reason, we are including an iodine solution next year that we will ask the participants to read in an area of the spectrum where they should have approximately an infinite optical density. We will assume readings less than that will give us some hint about the magnitude of stray light. As for the correct values for the Survey, I must disagree with the questioner. We had a second mailing in September and invariably for each solution of acid dichromate, the readings are consistently lower. This is after storage in the dark in a cool environment for a period of several months over the summer so that these are not stable. I think that the correct values have to be determined on vials that arrive at the same time as they arrive in the participant laboratories and not in a research laboratory at the time they are prepared. As far as analyzing more specifically the causes of these variabilities or the variability of the measurements and sorting them out, we are very fortunate that Dr. Wernimount is here in the audience and I am sure many of your are familiar with his matrix algebra approach analysis for the problem that he published when he was at Eastman Kodak. He has very kindly offered to serve as the consultant to the committee and we hope to have a pilot project that will submit some of the data to an IBM 360 in the future to see whether he can do this for us. In the meantime, our analysis has to be rather crude and obvious, and we realize that there is a lot of improvement that can be made in our statistical approach to the data. This is my first year as Chairman of the committee, and the survey is only in the third year. I guess I can only plead that we all need time to learn how to do these things.

Dr. Wernimont:

I talked to Dr. Beeler about this and I had not planned on saying anything about it, but I think it might be appropriate to explain very briefly why the method that I use is superior. It is very easy to explain to you what was done in my method that has never been done in any other technique. All of the studies of spectrophotometry up to the time we did this work at Kodak were using the technique that is essentially being used here to get the means and standard deviation of the absorbances at different wavelengths and treats them independently of each other. Now as you can readily see there is a very high correlation between these readings because we have a continuous curve. The method that I use takes advantage of this. It computes what is called a co-variance matrix, and there is an awful lot of information in the co-variance matrix that is being completely ignored by just treating the values at each wavelength individually. Now what happens when you do this? Well it turns out that you can characterize a pattern of behavior of a spectrophotometer when they are in proper order. You can immediately make a first check on a spectrophotometer to see if it is behaving as the pattern says it should. Now it turns out in our study, roughly one-third of all the instruments that we have looked at, which were in normal use and were not being checked too carefully, were not in this condition. What was even more striking to me was the work done by Vandenbelt, which was referred to yesterday. We analyzed all of this by this approach and fully 60-70% of those spectrophotometers were not in good working order. Now why are they not in good working order? Well it turns out that in almost all cases we have the things mentioned: stray light; slit width mechanisms not working right; dark currents not working right. There can be hundreds of reasons why an instrument does not work. It is very important to find out whether the instrument is in the class that needs to be fixed, or whether it is normal and you need not do anything about it. In other words, the method I proposed is diagnostic and also helps you decide what to do with the instrument.

Dr. Boutwell:

One question. The spectrophotometric study gave some warnings concerning not using a glass cuvette in the U-V region. We have found some of the commercial cuvettes fall outside their tolerance limits, i.e., for their absorbance path. I wonder if any caution or way of measuring this was proposed for the next series of studies.

Dr. Beeler:

We had suggested in the little monograph that we sent out two weeks prior to the second mailing this year, ways of checking the cuvettes, one against the other, over the entire range of the spectrum in which they will be used. If this checks out, in other words, if you get reasonable reproducibility over the entire wavelength to be used--switching them, the blank in one and the working solution in the other, and then reversing them--I think this would probably take care of any problem of wavelength mismatching. There is another problem we encountered a number of years ago. Most of the manufacturers specify the maximum absorbance at some wavelength in the UV down around 240 or 260 either with distilled water or with air (if the cuvettes are properly cleaned). A number of years ago, Bradley Copeland and I took a large number of Beckman cuvettes and found that we could not get them to match the manufacturers specifications in spite of numerous attempts to clean them and using many different brand new cuvettes. Finally, we found out that they had recently gone to a new batch of silica and were not able to get them to match their own specifications.

Dr. Boutwell:

I was thinking more of path length.

I admired Roger Gilert's new method for in depth interpretation of proficiency testing data and I admire his capabilities in interpreting of proficiency testing data, I think that it illustrates the necessity as well as the advantages of relying on the private sector to do these studies rather than depending on federal resources. Your third level of precision, where you indicated measurements were made within one day on two different samples, and their relationship, you indicated you knew of no medical usefulness of this particular type of measurement. Well there is one, not in chemistry, that I know of; that is a comparison of antibody levels on sera submitted for titers indicating an antibody response and usually these are analyzed on one day because of the large between-day variability. Secondly, I would like to issue a caution, with respect to average biases. In CDC Surveys as well as the CAP Surveys, the average bias in the country is very close to zero taking all methods and all samples. If one then looks for a change, or an improvement over time of the average bias, one is doomed to disappointment. One cannot look for much change from zero when close to zero. I agree that this is a very valid way of looking at the effects of individual methodologies, the bias of individual methods, but to lump all of those and to look for changes in time, or changes between groups is probably a very insensitive method of interpreting that type of result. Secondly, with respect to bias, it is not entirely clear, and I presume it will be in your paper, how this bias was calcuated--calculated for the individual laboratory and then averaged, or the results averaged, then the bias determined--that makes some difference.

Dr. Gilbert:

I thank you for your kind comments with regard to the within day precision. There are a number of uses as you say. Glucose tolerance test is a prime example. I think the key to this is maybe that of controlling the level of variability, which will control the size of the variability at other levels. With regard to the bias it is a very hard thing to come up with in any practical fashion and that is why this year it was with some hesitance that we took to quantitating it and trying to use exact figures. We decided to do this in the end, just to provide some overview of how large it was. I think the thing that butresses the argument about the size of bias is that one can determine the overall contribution from both method differences and bias between laboratories, which come out to be a third. Thus, this is the total amount that you are dealing with, even if you may not be exactly measuring the amount that comes from an individual method. In terms of the ways these are calculated, they are calculated by taking a mean value for all the participants who use one method and then subtracting that mean value from the mean value of all the participants who used what we were referring to as the comparative method. This is done at the end of the year, then averaged for the overall year, and the median and the rest are calculated. These data are going to be published next week. I would also want to echo one point you made, and I think that gets back to what Dr. Barnett said. We tend to use words like proficiency testing and the rest for Surveys. To me this is such a small fraction of what these programs can do, that it has been a real danger that these programs can get overwhelmed by these legislative requirements that are being heaped on to them. It is a role that Survey can fulfill and should fulfill, but we have to keep a sense of balance so that we can do the rest of these things. I think in Mr. Cali's description, I don't personally believe that we can achieve the standard we wish to achieve without this type of program. I think this is the program that is going to show us the way there.

Unknown:

I wonder if, in this calibration of spectrophotometers, it wouldn't be useful to send out glass absorption standards along with the liquid standards, maybe even screens or carbon particles in glass to calibrate the instruments.

Dr. Beeler:

For a number of years, the CAP Standards Laboratory has had some NBS glass filters. I think they have had the carbon yellow and several others and have offered to pathologists belonging to the College, if they write in, to send the filters out and give them the readings obtained over a period of time at the College. I think this was set up originally for the cyanmethemoglobin certification system when they had the CAP Standards Laboratory certifying commercial cyanmethemoglobin standards, and they needed to have some way of checking the spectrophotometers at industry plants and CAP against those at NBS. The trouble is the expense involved. It costs the participants $88 to participate in this for one year, and I suppose it would be another $100 to include a filter. It is a possibility that we considered, and we are purchasing some filters for the Committee members themselves who act as Referee Laboratories. There are other problems with filters that I suppose we shouldn't get into so deeply, but it is my understanding that the English experience with neutral gray filters with their hemoglobin studies found that filters do not act like solutions in cuvettes. We have encountered the problem in the Committee that on some of these filters, the instrument of one of the committee members gave acceptable readings, but on the solutions did not. So it appears at times the filters may give you accurate absorbance readings and the solution in the cuvette may not, even though the cuvette itself has been properly checked.

Dr. Eilers:

I would like to come back and ask a question of Dr. Hanson in regards to the Clinical Laboratory Standard Solution Program. Is it not also another valuable asset to the program in-as-much as you are providing a working standard solution for the laboratory to use?

Dr. Hanson:

Is that a statement or a question?

Dr. Eilers:

I would like to come back and ask a question of Dr. Hanson in regards to the Clinical Laboratory Standard Solution Program. Is it not also another valuable asset to the program inasmuch as you are providing a working standard solution for the laboratory to use?

Dr. Hanson:

That's right, that point should be emphasized that these solutions are used in laboratories of all degrees of sophistication and all degrees of size and all locations, etc. The principle behind making them up in solutions as they are, is to make it easy for a small laboratory or a large laboratory to use conveniently and inexpensively without the errors attendant that you might run into. Who knows what shape some analytical balances are in, what kind of weights are being used for the balances, etc. It is all right there and is all ready to use. That is one of the very practical advantages of the program for the user from small to large out in the field. Let me add, too, that the availability of SRM's is kind of a complementary sort of program and is just fantastic, I think this is great.

Dr. Eilers:

I think this also begins to tie in when Dr. Boutwell said yesterday 40-60% of the reagents in the USA are currently being bought by the laboratories. We are getting out of this workload factor in the lab. I think this ties in beautifully to what the FDA is trying to do in proper labeling as well as assuring the quality of that type of reagent. I wonder, Dr. Eavenson, if you have any comments to make about the need for SRM's and reference methods from the FDA viewpoint.

Dr. Eavenson:

Yes, I believe the most important (or the key element), and particularly in developing product class standards in clinical chemistry, is having adequate reference methods and reference materials. We have right now only one reference method, I guess, in calcium. We have a number of reference materials. The work at NBS is very important to the good development of the product class standard program of FDA.

Dr. Hanson:

Some of you may have noted, in the labeling of package inserts for the clinical standard solutions, that you probably wondered whether or not they were going to meet FDA standards and we are seeing to it that they do. The labels have already been taken care of and the package inserts are being worked on at the present time. They are all being done completely.

Dr. Wernimont:

I would like to ask what the CAP does with respect to outliers or people who do not conform. In our study, we learned more by chasing down all the people that weren't using the standards and finding out whey they were wrong. You begin to see what was the problem. Does the CAP use that approach at all?

Dr. Gilbert:

The evaluation the participant gets back shows quite clearly how far he differed from the mean of the rest of these things, but the program is primarily for self improvement. It is up to him to take it from there. We don't monitor it in the terms of pursuing that individual. We do, through the CAP Inspection and Accreditation Program refer these back to a further party in the CAP that monitors these laboratories in detail. Any pattern that appeared to a Regional Commissioner that a laboratory showed continued poor performance, he would require the director to report what corrective action was taken if he wished to remain in our Accreditation Program. I think the further problem we have here is that many of these are clerical errors, computer errors, but I don't think that we can necessarily assume that a laboratory would have produced that value on a routine clinical specimen. A number of things happen--a misplaced decimal point, and the rest.

Unknown:

Do the CAP standards represent materials made from SRM's or materials that have been calibrated back to the SRM's?

Dr. Hanson:

They are calibrated back to SRM's.

Dr. Boutwell:

I do want to make two more points. First to Dr. Gilbert's point about the clerical errors in Surveys that we may assume that these same errors might not be applied to patient's specimens. I don't think you could assume they could not happen anyway.

Dr. Gilbert:

No, I agree with that.

Dr. Boutwell:

Secondly, I would like to add a little emphasis to the importance of the standard material in aqueous solutions. This, I think, is an area that has not previously been mentioned this week. These solutions cover a hole which exists in the National system for providing meaningful measurements. We have SRM's and solvents. We have the National mechanism developing for attaching numbers to surrogate type specimens such as serums, urines. Regulations are coming up that will be enforced and commercial products will have meaningful numbers attached to them. But, we need something intermediate here too. These are calibrators to be used as calibrators or checks. They provide a very meaningful filling of a hole that exists by virtue of the fact that we don't have a sufficient number of well trained analytical chemists or analytical bench artisans to do this kind of work. They have not been trained and supplied to the country. The analytical balances, calibrated or uncalibrated, well used or abused, are just not in clinical laboratories today. They have vanished or are down under somebody's desk collecting dust.

Dr. Barnett:

One comment to what Dr. Boutwell just said, we are doing a survey on balance weights. So we hope to get some kind of handle on how they are acting. The other is the suggestions that Dr. Milazzo made about reference methods. This worries all of us a great deal. It is one thing to say--here is a reference method and here is exactly how it should be done. This is what we are trying to do right now in the glucose field. It is another to say that all the laboratories in the country might follow this, because you freeze progress at exactly that moment in history. As I have mentioned to some of you before, the great example was the standards in water and milk analysis which held up progress for many years. Because, this was now a government standard and you had to abide by it or you couldn't analyze water. It would really terrify me that we would have frozen calcium measurements, where for example, we used to do all of this washing business. Those were terrible methods. They were slow, they were crude, and they were inaccurate. Yet, they would have been frozen for all history. I think therefore, I would suggest that he take a hard look at not making his recommended methods for everyone but just saying, here is a good method and a good way of doing it, against which you can compare any method.

Dr. Eilers:

Yes, Dr. Schaffer.

Dr. Schaffer:

Thank you for commenting on that point Dr. Barnett. I am sure that I did not make myself clear enough. If we can establish that a routine method, which is convenient and inexpensive, has all the attributes that we would all require for a reference method in the clinical laboratory, and if it is as accurate as you would want, as Dr. Beeler would want, and as others in the field would want, then we could very well have a single method that would serve as the routine and reference method, and say, "Let's all use it."

Dr. Barnett:

Now a guy comes in with a new accurate method 10 years later and it all changes again.

Dr. Schaffer:

No, not if we had correctly established the accuracy of that method. The point to remember is that, because of its demonstrated accuracy, a reference method establishes a solid, non-floating baseline against which other methods can be assessed. I would favor a new reference method only if it could be demonstrated to be more accurate than the old one, <u>and</u> that improved accuracy was required! If the old method's accuracy is within 0.2 percent and everyone is content with that accuracy, what is the advantage of a method having 0.1 percent accuracy? What will it do for you?

Dr. Barnett:

I meant cheaper and simpler or of that nature.

Dr. Schaffer:

I would not rule out change; each situation needs to be evaluated.

Dr. Gilbert:

I really think the point that Dr. Barnett made about calcium is a prime example. Obviously, there were years that the oxalate percipitate presumably would have been taken as being a standard method. Now are the years of the atomic absorption, which is still widely used, but according to all the survey data simply does not work out in individual laboratories. What does work in individual laboratories; are SMA systems widely despised by chemists as being inaccurate, yet the evidence is they are not inaccurate. These are practical methods that are producing worthwhile results. I think in this instance, we could have frozen at any one of these stages. It could be that there is still something else coming that is going to cut out some of the biases of the SMA systems. Maybe more specific, but I hope, what the Survey Program can do, which I think is such a powerful role here, is to continually appraise what is happening in the field and to be used as a data resource by the laboratory director when he evaluates what they are up to, so that they continue to improve their methods. This sort of data has not been available in the past and there has been far too much hearsay about whether a method is accurate, whether it is inaccurate, whether it is precise or whether it is imprecise.

Dr. Pickup:

Yes, there has been a lot of discussion in the last couple of minutes about standardizing or freezing on one particular method. Isn't it perhaps just as important and maybe more useful to discard proven bad methods than to settle on proven good methods. There is already a lot of very strong evidence that emission flame photometry as practiced in routine laboratories is no good. Perhaps, then we should start by saying we should not use this method and give the evidence for it.

Dr. Hanson:

The Standards Committee of the College has done this in the past and I presume we will continue to do so in the future. We haven't said you can't use something. We have recommended what you do not use because of these specific facts.

Dr. Milazzo:

The reason why I proposed standardization of the methods is based on experience on the way the physician conducting laboratories for analytical chemistry are choosing and using their methods. They look in some textbook. They find something that could be simple enough, perhaps suitable for their glucose analysis without any adequate description of the method and they use them. The results are what I mentioned. This is the reason why the standardized methods suggested by qualified bodies should be published. Then it is by the decision of the physicians conducting laboratories for clinical chemistry for diagnostic or therapy use to follow good or bad methods. This seems to me from the general point of view of health a very important problem. As reference materials can be replaced by better ones, in the same way, new methods can replace the older methods. That is a system of eliminating all the old reprints and replacing them with new ones, but always let the physicians directing laboratories in clinical chemistry have a reliable basis for methods. That is not always the case.

Dr. Boutwell:

I would like to make one short point in response to Dr. Gilbert's comment that the SMA system for calcium is an accurate method. I would perhaps want to translate that in order to get us in agreement by saying the <u>results</u> are accurate. They are accurate not because the SMA has an accuracy base in and of itself, but because they are utilized for the calibration base, a material that has now been traced to a different accuracy base completely. It does not exist in and of itself as an accurate method.

Dr. Eilers:

I thank everyone who has participated, the Panel for their papers and keeping on time and the participants in your discussion and for sitting through the papers. Thank you.

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METALS (CHEMICAL PROPERTIES)

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I. Introduction

The panel co-chairmen were asked to arrange for presentations representing the viewpoints of ASTM E-2 (Emission Spectroscopy) and E-3 (Chemical Analysis of Metals) with respect to metal SRM's, their use in evaluating methods, calibration of instruments, methods of certification, and evaluation of homogeneity. Each presentation given is reproduced in its entirety to document the important interplay and dependence on one another of ASTM and NBS. The discussion following the presentations is paraphrased.

At the beginning of the session, the panel made an award presentation to the Office of Standard Reference Materials for past services to E-2 and E-3 with a pledge of their continued and indeed increased support of NBS in the future. The efforts of the panel reinforce the contention, and document it, that industry must have NBS Metal Standard Reference Materials for the foreseeable future. Also documented is the fact that industry must be prepared to do more as its share in the future if these SRM's are to be forthcoming. The panel also points out the fact that more international cooperation is needed to prevent duplication of effort in both SRM's and methods.

The co-chairmen are pleased that NBS included the viewpoints of ASTM Committees E-2 and E-3 in this Symposium of Standard Reference Materials and Meaningful Measurements. The attendance at the panel session and its duration of some four hours supports the view of the importance of the interplay of these two standard bodies, NBS and ASTM.

II. SRM's for Spectroscopy - What's the Problem

W. R. Kennedy

It is certainly with pleasure that I co-chair this panel on Metal Standard Reference Materials with M. D. Cooper of General Motors and Chairman of Committee E-3 on Chemical Analysis of Metals. He and I are supported by capable E-3 and E-2 personnel with many years of experience in chemistry and spectroscopy of metals. Both Bob Michaelis and Joe Woodruff are past Chairmen of ASTM Committee E-2, and ASTM Award of Merit winners. Each of us will bring to you a different aspect of metal SRM's as we see them in production, in use, and on the way. You should expect a personal viewpoint as well as one from ASTM.

Within the body of presentations I will tell you: my definition of a standard method and how SRM's relate to it; one quality SRM's should have in relating to methods or vice versa; one way to evaluate your equipment and NBS-SRM's; some method and instrument limitations, the qualities of a standard method, the value of use of NBS-SRM's, and how you can help in betterment of future SRM's.

Behind every successful project you will find that people make it "go." Every NBS-SRM and its certificate is a successful project backed by the integrity of the people in the OSRM, especially, and NBS, in general. We can say that every NBS metal SRM represents the best that is currently possible with the production techniques and analytical procedures available today. Exploring what can be done to more meet the needs of the SRM customers - the most important adjunct of SRM's - is the reason we are here today. The people on this panel are representative of the kind of people who make projects "go" in NBS and ASTM. They all have in common the desire to make SRM's better and more useful to you, within the limited resources available. By better, I mean more accurate certifications, more homogeneous samples, more expanded ranges of elements covered and in greater quantities. By more useful, I mean to imply that they are available in the physical and metallurgical forms desired by the analyst who applies them to his methods.

In thinking about these qualities, I am reminded of my first visit to NBS on Van Ness Street in the District in

1947. Charles Corliss, one of those "go" people, who was then in the spectroscopy section, asked me, "Which is more important, the standard sample or the standard method?" Almost without hesitation, I replied, "Give me the standard samples, and I will write the method." I believe this answer is still what I would say today.

The only current reservation I have from a spectroscopist's standpoint is that I want to know the definition of a "standard sample." We all know what a standard method is! Let's see if I can put it in words:

> "A standard method is a written set of rules, or procedures, to follow, which, when followed explicitly by 10 labs, let's say, using a standard reference material from NBS, will produce 10 identical numbers -- *if* you don't carry the decimal too far!"

The definition points out the relationship between the SRM and the method: each has its capability and since the SRM is the proof, it should be the better of the two in all measurable respects.

Recently, I read a brochure from Hewlett-Packard, wherein directions for calibrating a very sophisticated electronic instrument stated that, field calibration should not be attempted unless the accuracy and precision of the calibration source was at least 10 times better than their instrument. Analog Devices, another electronics firm, states in one of their publications, two times better. OSHA says four times better. So we should expect our SRM's to be between 2 and 10 times better than our instruments or methods, preferably 10 times better.

The electronics people must be much better than we as analysts, because I can say that the electronics of our direct reader, which is 12 years old, is capable of resolving something two to ten times better than certificate values on SRM's. If you investigate your instrument you will probably find you can do better than I do. However, excitation of SRM's with sparks or arcs gives coefficients of variation that say that, method-wise, the SRM's are at least no worse than the best samples we can produce locally. My total method then, sample, excitation, optics, and electronics is not better than the SRM's we have today, precision-wise or accuracy-wise.

Many of our E-2 Standard Methods call for the use of NBS-SRM's for calibration, but sanction the use of "secondary" or "in-house" standards providing they meet the qualifications of homogeneity, metallurgical form, mass, and size, and provided they are analyzed by ASTM E-3 methods. The terms primary standard, secondary standard, and tertiary standard appear in the ASTM Data Series, DS2, which is still in print although it was last compiled in 1963. The qualities of secondary standards became the target of two very excellent E-2 Sub IV discussion groups in the last two years. Sub IV concerns Standards, Reagents, Electrodes, and Pure Materials and one of the task groups is concerned with how to produce secondary standards. Nicholas Christ, Chairman of Sub IV at the time, found you couldn't produce them if you didn't know their characteristics. From a questionnaire he circulated, the discussion groups assembled brought out the following ideas: how one might classify standards (if indeed anyone wants to), how one might design a suite of standards to get the most out of an instrument, a scheme to evaluate your own instrument using NBS-SRM's, schemes for evaluating homogeneity and revival of an old term with a new twist called a "benchmark" standard. The only consensus I could detect (and I've listened to the recorded sessions many times) is that a primary standard is one which is issued by a recognized standardizing agency - such as NBS. In E-2, we have found that due to the reservation scientific circles give to the term "Primary Standards" for units of length and time, we must change our nomenclature. We simply call them Standard Reference Materials. "Secondary" standards (again the consensus of the discussion groups) have all the characteristics of SRM's except they are not issued by a recognized standardizing group. They may even be better in some respects (homogeneity, accuracy, or metallurgical form). Since Bob Michaelis was one of the later participants in these discussion groups, I feel he will throw more light on these definitions appearing in DS2 as well as interject some thoughts on homogeneity as shown on a certification sheet in his presentation.

An interesting and helpful way to evaluate NBS-SRM's and your own instrumentation is to make repetitive runs on each standard - 17 to 20 runs on each SRM is adequate. Calculate the coefficient of variation for each element. Using log-log graph paper, plot for each element the percent element versus its coefficient of variation as in figure 1. If you consider that coefficient of variation has meaning only for uniform Gaussian distribution, then a plot of element percent versus its C.V. should give a locus of all uniformly homogeneous samples with a slope of minus one. From such a plot there will be some upper percent above which coefficient of variation does not improve (become smaller). This is the instrument-bound condition and you cannot get better because of optics, hardware, or samples (chemists: your balances, weights, pipettes, burettes, etc.). At low concentrations, the system is noise-bound. The concentration where C.V. is 100 percent is defined as the limit of detection. This limit is set by how well you can repeat your background (chemists: this is your blank).

From such plots, the limit of detection can be extrapolated and it is relatively easy to tell when you have an inhomogeneous sample (or SRM). For example, we know cast iron is more heterogeneous than rolled steel, and for some elements like silicon, such a plot will reveal this easily.

Another example shows NBS-SRM 1264 (figure 2), one of the five NBS-SRM graded series for steel. Using our direct reader, we cannot get the correct result for titanium in this SRM and figure 2 shows its coefficient of variation is not what one would expect. This really doesn't worry us too much because we don't normally make any iron or steel with this amount of titanium. However, this brings out one of the philosophies of SRM's, and one which NBS continually expounds: in a graded series of SRM's, such as the 1100 series steels, now replaced by the 1200 series, and the 1100 series cast irons - in such series, if any of the points fall off a curve relating instrument output versus percent, then something is wrong with the method. Generally, this philosophy is correct, and the issuance of graded series is a help to discover optical emission instrument line interferences (and there are many) and also to generate absorbance corrections for x-ray plots. That one of the standards does not agree with others, does not mean that the method is completely wrong, but it behooves the user to determine why and to make the instrument operators aware of it. An example for emission spectroscopy involves the 3414 Ni line. Two of the original 1100 series steels fall off the curve as does one of the 1200 series. If you study the wavelength tables, you discover Zr interference and that the zirconium in these three is in the neighborhood of 0.10 to 0.30 percent, and this is enough to make these samples appear to contain much higher nickel. The solution, of course, is either to correct for zirconium content, or switch to a line that is free of the interference. Certainly, if you don't make a steel with zirconium, you have no problem.

Getting back to which is more important, "the SRM or the method," I have uncovered some data that illustrates the importance of methods. In 1947 we were using chill-cast iron pins in the a.c. arc on the spectrograph. The wet lab was using a sulfide gravimetric procedure. In these days and times when you can push a button on a calculator to achieve a linear regression correlation coefficient, another button for slope and intercept, I think it's time we dispense with the slide and speak in statistical terms. Suffice it to say that the correlation coefficient between the two labs for copper in 1947 was $0.965R^2$ (Slope 1.05 and intercept - 0.044), which on a scale of zero, for no correlation, and one, for perfect correlation, was pretty bad. Neither method is used today. Chill-cast pins are about the worst way to sample cast iron and an a.c. arc is not the best excitation for copper in the range of 0.03 to 2 percent. The wet method, although still endorsed by E-3, is subject to more error because; it uses two weighings, it is less flexible, and possibility of iron contamination occurs frequently.

Today we do much better; with the direct reader and chill-cast discs in a spark in argon, and the wet lab using the ASTM Neocuproine method, the correlation coefficient is $0.997R^2$, (slope 1.003 and intercept - 0.0003). Certainly this is better than the metallurgist requires -- a requirement, by the way, which points up that the laboratory must be better than the control requirements, just as the SRM must be better than the method. We are not about to do away with our wet laboratory at ACIPCO, because, after all, it is the referee, and we depend on our wet lab cross-check program to keep the D.R. "in line." In a month's period every curve and every alloy will have a wet check against the D.R. output. Needless to say, only ASTM wet methods, or slight modifications therof, are used. We do quite well, and we know our weaknesses, and we apply most of our effort to these.

In the last year, I became involved in a study conducted by the Steel Founder's Society of America on corrosion and erosion of stainless steel. Some 14 stainless steels selected for the program were circulated to seven laboratories for both optical emission and wet chemical analytical results. If you are interested in seeing the results of all the coded data, I'm sure it can be arranged with a letter to Dr. Peter Weiser of SFSA. There is too much data to present here, but to summarize; (1) in only two instances of 14 was there a significant statistical difference in the average of each specific method and both of these were for phosphorous in the 0.01 to 0.02 percent range; (2) the coefficients of variation for chromium and nickel ranged from two to five percent for both optical emission and chemical results; coefficients of variation for Mo in the one to three percent range, Nb in the 0.5 to one percent range and copper in the three to five percent range were all considerably poorer than one would expect. Nickel and chromium by wet means using ASTM methods should show a repeatability of about 0.5 percent C.V. We can achieve C.V.'s of 0.5 to one percent on our D.R. for these elements. Mr. Cooper will tell you probably that it takes a lot of planning to get this kind of agreement between wet labs and it is most important that all use the same standards and the same method. There was attention paid to sampling in this SFSA program, but for the ultimate in agreement, not enough information was given to give a true picture of analytical capabilities today. Dr. Weiser stated that the specification committees in ASTM are considering a statement in writing specification, to the effect that in a dispute, that ASTM E-3 wet methods be used and in addition, that the repeatability of the method be taken into account. Such a statement would surely eliminate the problem between producer and consumer who differ by 0.05 percent at the 20 percent level; one being at 19.98 percent and the other at 20.03 percent. All of this is to give further evidence that others are vitally interested in SRM's and methods as well as this panel and you in the audience.

Why do we need secondary standards? First of all, NBS-SRM's are not available in all the ranges needed, nor are they available in the solid form in which most industries prepare their control samples. Even if they were, you wouldn't want to use up NBS-SRM's in daily calibration. This is just too wasteful. When we contributed aid to the manufacture of the NBS cast iron SRM's some 15 years ago, we needed some sixty secondary standards to analyze all the elements. So, for us, the eight 1100 cast irons replaced some 60 standards. In daily calibration of the D.R. we use a series of high-low standards. When you have thirty curves, it is economical in money and time to have as many highs in one standard and as many lows in another so you need run only two standards to establish all 30 curves. We have not reached that point yet. Although we do have all the highs in one standard, the lows are scattered among about 10 SRM's, most of which are NBS-SRM's. In practice, we calibrate the highs first because when you correct for background, the high will not be affected by background significantly, since the signal to background ratio is about 100 to one. Rotation of the curve is controlled by the background of the low standard where the signal to background ratio is low, approximately one to 10. This "low" is rather arbitrarily chosen as a compromise between repeatability at that level and the necessary level we must achieve. We have defined all our lows and the next project is to attempt to make a standard with this composition. You might ask, why not use NBS-SRM 1265? Most elements there are below our limit of detection and so are of no use to us. Every control laboratory needs secondary standards to match his compositions, and his physical requirements. It is incumbent on the control lab to see that his curves are traceable to NBS-SRM's for accuracy. The NBS-SRM's establish the curve shape, while local standards eliminate possible biases. It is the primary aim of the method to make such biases negligible and bring about accuracy: hopefully all will be on the same curve.

Better standards is the NBS prerogative; better methods is the aim of ASTM E-2. Methods arise either from a single user, or a task group, and are designated suggested or proposed methods. Before they can become standard methods they must pass editorial scrutiny, interlaboratory tests, subcommittee ballot, committee ballot, and Society ballot. It is a process fraught with pitfalls, negative votes, months of delays when data doesn't come in or samples become lost, or disqualification because of lack of interested volunteers. If a method becomes standard, it automatically appears in the ASTM Book of Standards and in the E-2 Compilation of Methods. A proposed method can appear in the Book of Standards for two years only. A suggested method can only appear in the E-2 compilation as it has no status in the Society. It is becoming apparent that while our E-2 standard methods make adequate precision statements, those about accuracy are slightly ambiguous and we must work on these.

There has been an attitude in E-2 that standard methods must be achievable by everyone, regardless of the instrument that may have been used by the submitter. If excitation unit "A" is used, the excitation unit "B" must also be included. This attitude is slowly dying. We realize that if a method is reduced to the lowest common denominator, only mediocrity can result. We must maintain high standards: we think we do.

One of the discussion group participants brought out that precision improved when particle size got smaller, or when volume or mass of material consumed increased. (He also loudly proclaimed what we all should know; accuracy can be no better than precision). NBS has information on its standards regarding optimum use, but this inforamtion does not always appear on a certificate. Perhaps it should, for this might lead to their better use in the field. As surely as we in ASTM E-2 get better for the bulk of determinations, NBS and E-3 can devote more time to those elements and ranges needing more concentrated effort.

Many of our E-2 and E-3 methods are tied directly to NBS-SRM's and the philosophy of a recognized standardizing agency. We depend on these SRM's being renewed when supply is depleted. I can tell you that the E-2 executive subcommittee is quite concerned that NBS might abandon SRM's. You've all heard the song, "Blowin' in the Wind," a haunting set of lyrics concerning sociological problems of today. What's "Blowin' in the Wind" today regarding SRM's, methods, and laboratories is hauntingly frightening. NBS is not, from what I gather in my travels, eternally committed to manufacture, certification, and distribution of SRM's. I have heard some say there is only <u>one</u> nationally recognized standardizing agency - NBS. They have reached this position through integrity and consenses. Others, just as staunchly have said that commercial standardizing agencies could do as well in accuracy and precision and this could come about if the consensus is granted. It behooves you in this room to know where you stand on this issue because if it occurs that commerical standards are accepted, you must consider the mechanics of how consensus will be achieved; how accuracy and precision will be certified. If we see this direction coming, we in E-2 and E-3 should begin thinking about priorities and organizing the necessary certification means now.

We see the rise of federally-sponsored regulatory agencies such as EPA and OSHA establishing standard methods, means for accreditation of laboratories, and even making and issuing their own standard reference materials. One wonders where the consensus lies in such mandates. If you suscribe to the philosophy of consensus, this is the time and place to speak out.

If you feel consensus is an important part of SRM's, and I am committed to this philosophy in ASTM, I challenge you to get involved! Can we do without NBS-SRM's? For how long? Could E-2 and E-3 write a universal method for any metal, independent of NBS-SRM's? I do think we need NBS to concentrate more on those horizon areas we well as provide "benchmarks." We also need them to be there to help solve problems such as SRM 1264 when they arise.

In the neatly wrapped package containing an NBS-SRM, there are five stages involved: planning (based on input to NBS from ASTM and others), production, evaluation, certification, and use. I have been involved in one way or another in all five stages and can tell you that there is excitement and fulfillment in other than just using them. There is no better service you can do for your company or your country than to get involved in NBS and ASTM. Help plan, help produce, help in cooperative testing and evaluation, and help test methods. You are needed.

A material's analysis is certified by a method; a standard method is certified by SRM's in a round-robin test (consensus); SRM's are certified by standard methods and consensus agreement. In ASTM the whole theme is "Voluntary Consensus." For SRM's I think I would add one more qualifying adjective and say "Voluntary Scientific Consensus." It is very important that we have consensus, because even if we are all wrong, we are all together.

Since the theme of this Symposium is meaningful measurement, a little philosophy may be in order in parting. Einstein once intimated that the measure of success was value. Using this criteria, NBS is the greatest success for industry in the United States today. Again, a recent writer said the measure of freedom is choice. Applying that criteria to SRM's, we don't have much freedom, but only because the choice is ours. We recognize our success lies in restricting our choice to one recognized body - NBS.

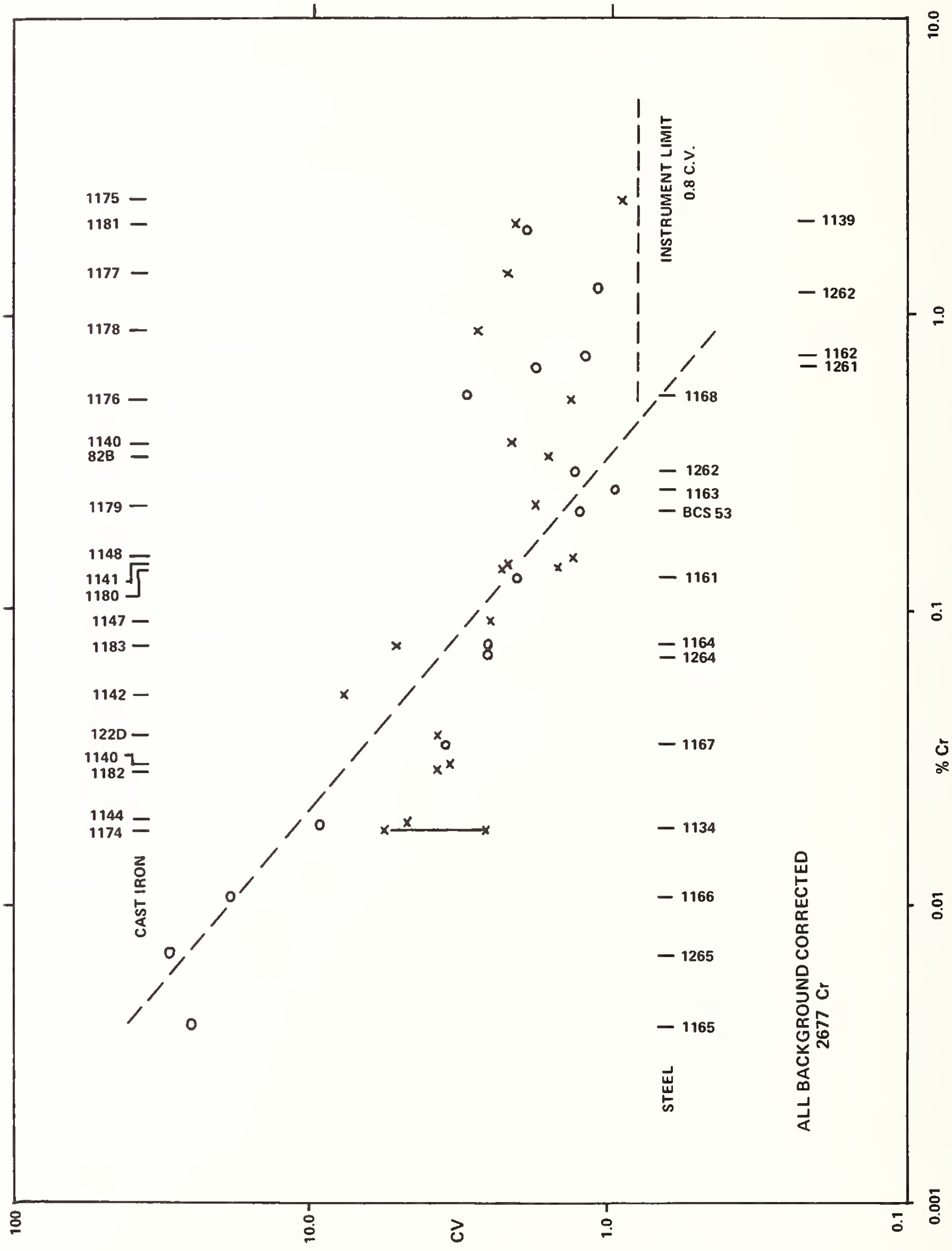

Figure 1. Coefficient of Variation versus Concentration. Steel and Cast Iron SRMs, Chromium 267.7 nanometers.

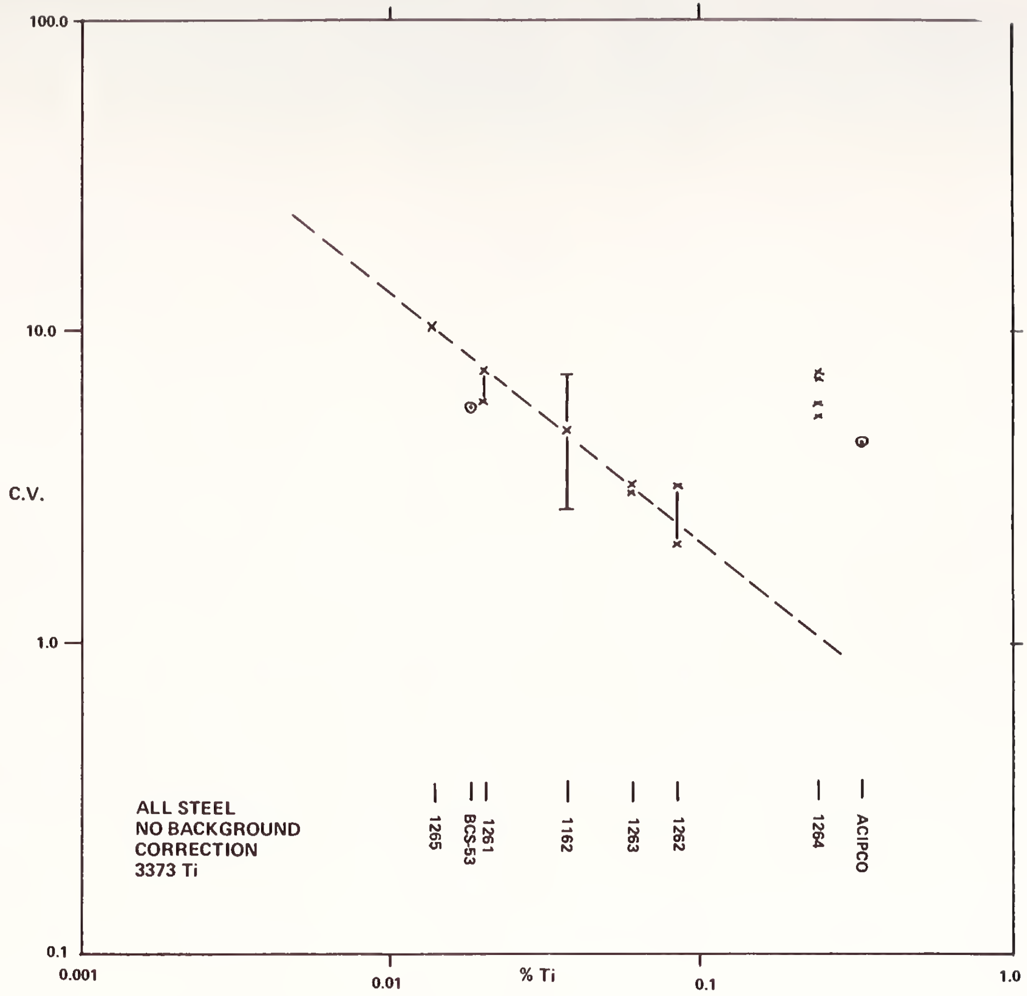

Figure 2. Coefficient of Variation versus Concentration. Steel SRMs, Titanium 337.3 nanometers.

III. Chemical Analysis Of Metals

J. F. Woodruff

We are now at the crossroads in ASTM Committee E-2 - an ASTM Committee on Emission Spectroscopy. We need to know the direction SRM's should take, and thus make realistic recommendations to the hosts of this Symposium - The National Bureau of Standards. At no time in history has the demand been greater for new and unusual SRM's. SRM's are needed in such diverse fields as air and water pollution control, aerospace, pathology, agriculture, food processing, and criminology to name a few. Secondly, SRM's having trace concentrations of elements, are needed in basic research in a wide variety of materials. Thirdly, less exotic, but vitally necessary are the SRM's covering the macro concentrations of elements in a multitude of materials that are the life blood of commerce. The latter are the bread and butter SRM's needed to maintain our present position of meaningful measurements. Hopefully, at this international conference some guidelines can be given to NBS and other non-profit standardizing agencies around the world. With the International Standards Organization diligently working toward consensus standards and practices, we need to take a good hard look at the SRM's now being used in the metals industry and what will be needed to meet the world needs in the future. These future SRM's will be the means of developing methods and practices that will be acceptable to all nations. Also, if we want to look at the commercial aspect, these SRM's will play a very important role in the buying and selling of goods between countries.

There have been many changes in our living standards, so far, in the twentieth century, and the influence of SRM's during this period has been unmatched when compared to any other period in history. Our lives have become more and more related and governed by material things - things that our parents and grandparents never even dreamed of. For example, most of us accept the mechanical appliances around our homes and associated with our daily lives as a matter of fact: radios, televisions, electric refrigerators and freezers, electric and gas stoves, vacuum sweepers, canned foods, high-speed cars, and numerous other items. All of these things and many others have become available to the average family during our lifetime. Meaningful measurements by SRM's in this country and throughout the world have helped to make all these things possible. We, in the United States, are especially proud of the role the National Bureau of Standards has played in raising our standard of living. It is our hope that our government will continue to recognize the importance of this agency and provide the monies necessary for expansion so that they can meet the critical SRM needs now and in the future. The Bureau and other international standard groups must not be allowed to regress, but must exert even greater efforts to meet the needs of industry and technology in the next few years. Actually, the needs in many areas should have been met yesterday if manpower and monies had been made available.

In line with this thinking let me present one example of how the steel industry and the Bureau have worked together to meet a common need. In March 1967, I sent Mr. Robert Michaelis, Chief of Metal Standards of NBS, a letter affirming a need in this country for particular steel standards. Portions of this letter read as follows:

"The steel industry and their customers are sorely in need of high-silicon steel standards of certified composition.

"The alloys are applied broadly in the areas of transformers and dynamos where the electrical properties, which have been imparted by the high silicon, are of paramount importance.

"With numerous and increasing specialized application of these high-silicon alloys, the tolerances for variation in behavior and properties, and thus the chemistry, have become severe; therefore necessitating reference standards. The lack of such standards is extremely wasteful to the industry and consumers since differences in customer and producer analyses cannot readily be resolved.

"The monetary significance per year of the oriented and non-oriented silicon steels covered by such standard reference materials would be over 100 million dollars for oriented and over 100 million dollars for non-oriented, or a total of over 200 million dollars based on the tonnage sold by the industry in 1965.

"Experience to date has indicated the desirability of producing these standard reference materials both in the form of chips primarily for chemical analysis, and in the form of solid sections for x-ray and optical emission analysis.

"All of the silicon steel producers have expressed a definite need for such SRM's and they are not available from any other source. More significantly the National Bureau of Standards is believed the only source qualified to produce these materials and to secure the required accurate analysis for certification.

"The silicon steel alloys presently are used in considerable quantity in the electrical steel industry and the need is rapidly expanding. The strict specifications for these alloys require more frequent use of the standards for composition control.

"The Armco Steel Corporation is willing to work with the National Bureau of Standards to develop the requirements for the material for these SRM's and is further willing to furnish the material in adequate quantities to the Bureau gratis. It is believed desirable to prepare the standards in sufficient quantity so that renewals would not be needed for the next 15 to 20 years. This will insure that NBS will have an adequate supply of the material for continued composition control for years in the future."

This was the first step of a program that lasted for six years and resulted in two SRM's in disk and chip form, namely SRM's 1134 and 1135 in disk form, and 125b in chip form. The material for the standards were taken from commercial heats, melted and rolled to slab at one of the Armco plants, and processed into rounds at a second Armco plant.

A steel ingot weighing 9500 pounds was rolled to slab and slow cooled in a furnace. The end of the slab representing the top of the ingot was removed with a torch and represented 15 percent of the length of the slab; five percent of the length of the slab was torch cut and represented the bottom of the ingot. These slab portions were discarded. Homogeneity test samples were then removed from the ends of the slab, which were 1 1/4 inches by the slab width. After identification (T and B) the material was shipped to the Bureau for homogeneity testing (see figure 1). After receiving word that the homogeneity was satisfactory, 25 percent of the material was torch cut from the center of the slab and discarded (See figure 2). The 6" x 6" x 65" billets were then cut from the outside portions of the original slab, identified and sent to the machine shop to remove hair-line cracks, which resulted from the torch cutting. Eight of these billets were then shipped to a second Armco works for processing. There, 2,600 pounds or four billets were forged to 1 5/16 inch diameter rounds and then centerless ground to 1 1/4 inch diameter rods. This material was then cut into disks by the Bureau. The other four billets, also weighing 2,600 pounds, were forged into five inch diameter rounds and shipped to the Bureau. The five inch diameter rounds were processed into chips for chemical standards. The Bureau then sent the materials for the two standards out to cooperating laboratories for final certification of C, Mn, P, S, Si, Cu, Ni, Cr, Mo, Sn and Al.

This is just one of many instances where the Bureau has given the producer and the consumer, base standards from which to work. Now imported or exported silicon steel alloys can be checked for the composition specified using basic standards for common measurements. The Bureau and all such impartial standardizing agencies in other countries can also help us come to a consensus agreement not only in ISO but also in international trade.

I continue with an industry with which I am associated - the steel industry. Since this panel was asked to discuss SRM's for metals, let's take a look at this industry. We have had steel in its various forms for the past 100 years and before that we had iron. Iron is obtained from iron ore. It is reduced by burning coke, which also furnishes sufficient heat to melt the iron and separate it from the waste material with which the ore is always associated. This iron is further refined by mixing it with scrap in a refining unit, such as an electric furnace or BOF furnace and subjecting the molten metal to chemical treatment for removal of carbon and sulfur. When it has been sufficiently refined, alloying additions are made, the steel cast into molds or continuously cast and processed by mechanical means into products such as slabs, plates, sheets, strip, wire, etc., which serve as basic raw materials. In 1951, my company produced 4,357,562 net tons of ingots - 497 net tons per hour; 11,938 net tons a day. If we continue to produce the remainder of 1973 as we have the first eight months, we will produce over nine million net tons or an average of approximately 25,000 net tons every day this year. We are producing twice as much steel in a short span of 12 years. With this increased production, extremely tight melting specifications are necessary to produce steels with the required properties needed in today's markets. The analytical chemist and spectrochemist are being required to provide more rapid analyses of higher and higher degrees of accuracy and precision. To do this requires extremely accurate and homogeneous SRM's in order to calibrate the elaborate instrumentation used in the steel industry. Also, we would not have had the advanced technology in the steel industry today without the SRM's provided by NBS. Indeed, in many cases, improvements in properties and new alloys could not have been developed until new and improved SRM's permitted more accurate analyses. Consider this in reference to measuring systems 50 years ago. A melter in the steel industry determined when a bath of open hearth or open hearth steel was ready to tap without the aid of chemists or SRM's. A melter used a pair of dark glasses to observe the working of his heat. When he was convinced that the heat was ready to tap it was tapped. His skill and his glasses determined the quality of the steel produced. Later, a melter used the break test and the slag pancake to better control his furnace. Then came the chemists with their test tubes, carbon analyzers, and SRM's. Specifications were tightened and tightened and tightened. Sure, we are producing better steel now but only with the help of improved technology and SRM's produced by NBS. They are not only produced the needed standards, but also helped industry to better understand and use the new analytical equipment. However, even now with all these advantages in instrumentation and steel technology we must think of where we are and where we are going. Basic oxygen processes, vacuum melting, vacuum degassing, continuous casting, control-pressure pouring - what SRM's do we need for these new operations? With computers being used in the melting and processing of steel, do we need less emphasis on reference materials for furance operations and processing and more on reference materials for raw materials such as ores, ferroalloys, hot metal, and refractories?

The manager of our melting department, C. R. Taylor, believes that in the near future 75 to 80 percent of the steel produced in the United States will be continuously cast. He also envisions this process to be tied in with a direct reduction process within 10 years.

Atomic energy, electricity, electrolysis of water, hydrogen, direct reduction of iron ore (H_2 plasma torch by magnetic field and current), continuous cast steel, in this latter process he feels that only continuous analysis of the molten iron for oxygen and temperature will be needed. What SRM's will be needed for either of the two processes?

Before such events take place, should we exert time and effort to provide the necessary reference materials for today's world in the steel industry? A program to fulfill all the needs would require considerable effort and monies. It may not be too far in the future that continuous analysis will be made of the bath such as (by) withdrawing a dust or aerosol sample from a molten bath of steel through a lance to a chamber of a piece of analytical equipment. E. A. DuBois of BISRA has described such a process.[1] If continuous analyses of the bath are successful, what SRM's will we need then? In other words, do we really know what SRM's we need? Do we really know what direction we should go?

In closing, I know that ASTM Committee E-2 and the steel industry will work closely with NBS to meet today's needs and the needs of tomorrow.

[1] "The Continuous Analysis of Molten Steel," E. A. DuBois MG/D/Conf. Proc/688/68, pp. 65-75.

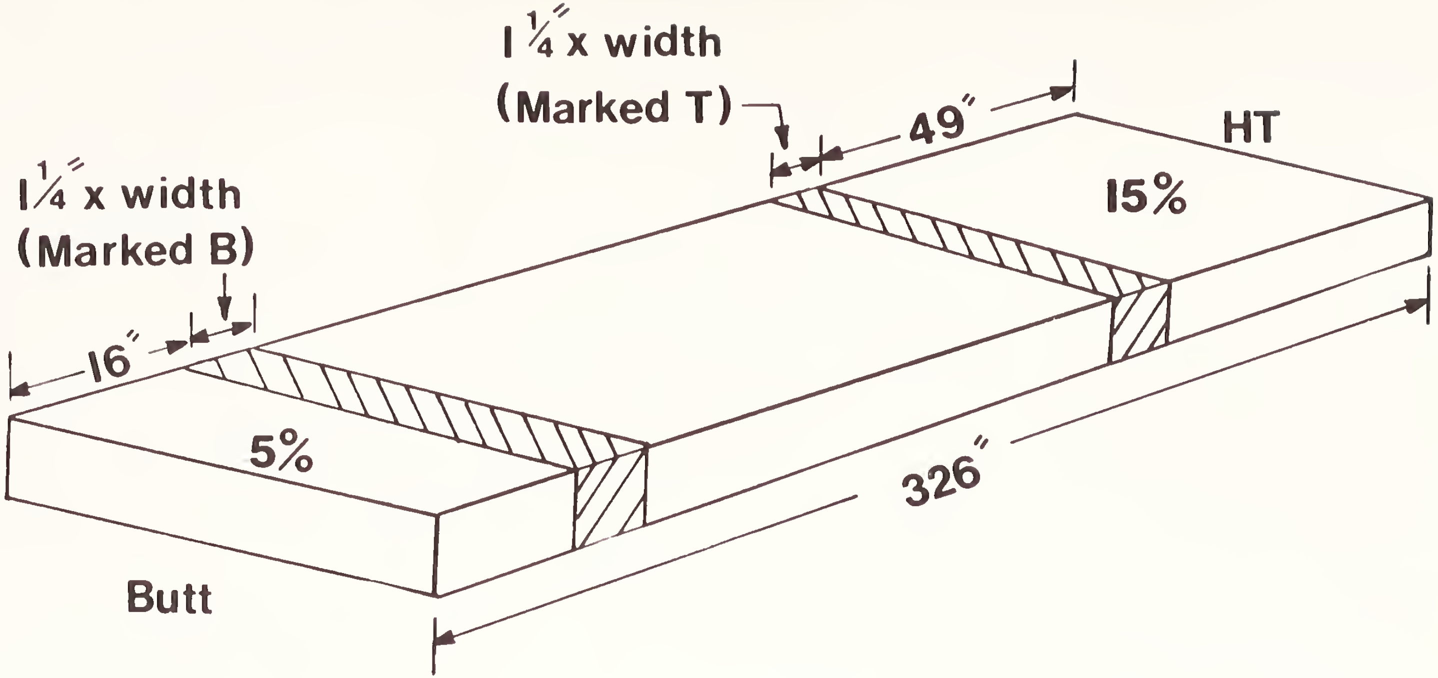

Figure 1. Preparation of Slab for Homogeneity Test Samples

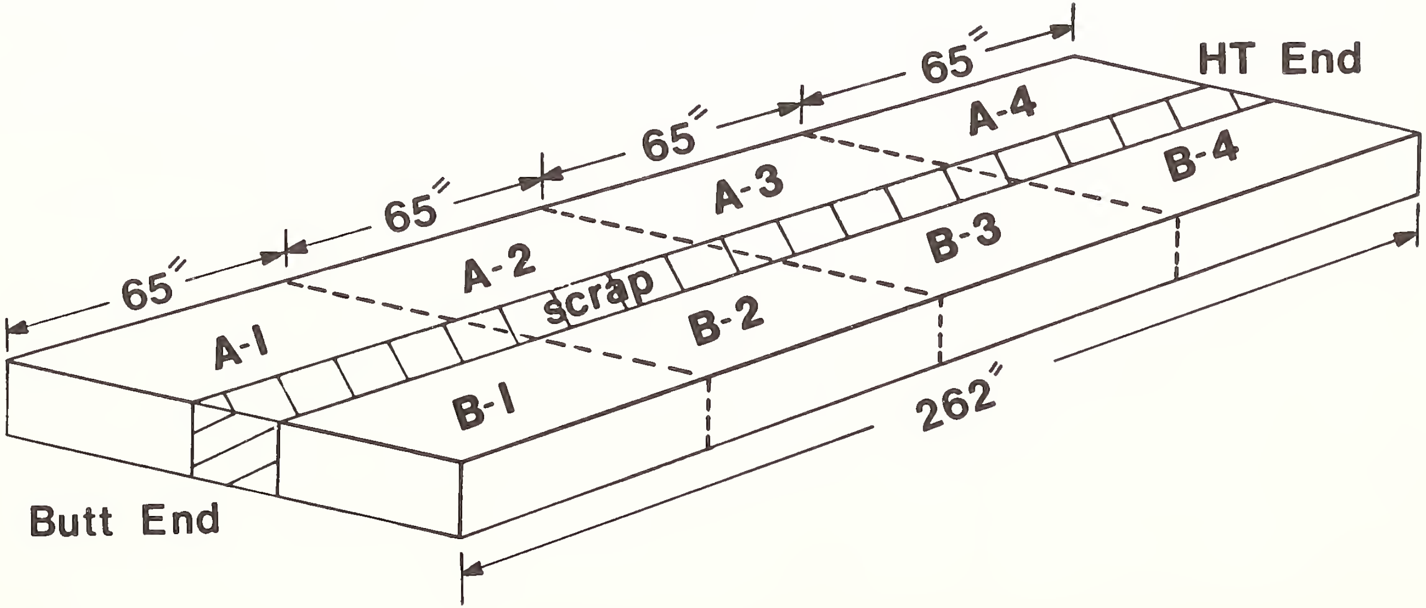

Figure 2. Removing Billets for Processing into Rounds

IV. SRM's In Industry

S. H. Degenkolb

The chemists and spectroscopists in the USA have been very fortunate to have NBS assume an interest nationally in the standardization of reference materials. Many of you, perhaps are not aware that NBS issued its first standards for sale in 1906. The American Foundrymen's Assocation turned over a set of pig iron standards to them in 1905 comprising four sets that covered a wide range of composition. Before distribution, NBS together with some commercial laboratories reanalyzed the pig iron standards and gave them a certified value. In 1905 the American Chemical Society assigned their zinc ores to NBS for distribution. Thus was launched the SRM program. It wasn't long until other industries requested the need for standard analyzed material, mainly the steel industry.

Upon reviewing some material, I came across the NBS catalog issued April 14, 1932 and in Section 11, "Function and Standard Samples," I'll quote: "The time at a chemist's disposal for investigation is limited and research must be conducted along lines of great efficiency - the results being the evolution of standard analyzed material. This may be defined as a material resembling as closely as possible in chemical and physical nature the material with which the chemists expect to deal and which has been analyzed by a sufficient number of methods and analysts to establish its average composition with considerable certainty."

After 41 years, the same definition describes a SRM. I defy any statistician to qualify an SRM any better. He might use different terms, more oriented to computerization, but they wouldn't be any more meaningful to the people using the definition. Several other factors have also changed. As technology advanced, the SRM's have been produced in various forms. Initially all SRM's were chips for wet chemical analyses - and these are very much in evidence today for most metal SRM's. However, the SRM presented to the optical emission instruments have changed from 7/32 in. pin to 1/2 in. to the 1 1/2 in. round or square, at least 1/2 in. thick. With optical emission, more analyses can be made on the surface before resurfacing and x-ray needs a larger mass presented for accurate reproducibility of analyses. Also it has been proven that a larger mass of sample is more reproducible for optical emission spectrometer analyses. Besides the change in size, more homogeneity checks are made, after production, before analytical work is done. Also, let's note that the word "standards" has been replaced by "Standard Reference Material" as authorized by E-2 in March 1972 and which had been used by NBS for some time before that. All these changes have resulted in better SRM's for the analyst.

Regressing somewhat, the word "Standards" or "Standard Reference Material" has been utmost in importance to me since joining the spectroscopy field. It has been ever present and in many cases and times just beyond one's reach. Being then a member of a larger steel company with 26 laboratories, all needing some material (standards) by which a laboratory comparison could be made, it became obvious that something must be done. We all had the available NBS-SRM's, but they were not sufficient to meet our needs as many elemental compositions had large "holes" in the calibration, or maybe a particular element was only certified in one SRM. In 1948, we formed a standards committee and began issuing our own standard reference materials. Our initial attempt at producing SRM's yielded two commercial and two induction heats. This clearly pointed out the pitfalls in SRM preparation. About a year and a half after their production, these four SRM's were certified. Needless to say, this certification represented much work; chemical, spectrochemical, and statistical, as well as much sweat and an occasional swear word. One can definitely state that a standard program shows the weaknesses in methods and analysts. Truly, it is good for any company as it "points" to the necessity for better analysis and shows the weaknesses in particular laboratories. We learned a lot in 20 years by producing over 100 SRM's. Some of these SRM's, which were used in daily routine analyses for "setting-up" instrument calibration, were made in enough volume so the company presented some of this material to NBS to be issued as SRM's, as they knew such material was useful on a national scale. This company is still making steel SRM's and some of these are being sold commercially. In fact, due to the cooperative program between U.S. Steel and NBS, both in production assistance and analytical methodology these SRM's, although secondary, are NBS-traceable. The other members' companies on this panel have also produced their own SRM's and have had similar problems. All these have been steel.

As everyone tells me, there are other metals than iron. Let's turn our attention to aluminum. Alcoa needed SRM's of the various alloys that their laboratories were required to analyze. The same story; they were forced to make their own SRM's as there were very few available commercially. Their story of the growing pains encountered with determining the best type of sample (wrought or cast) and the best size sample that would give the best homogeneity, would fill a book. However, they did decide on a chill-cast disc 2 1/2 in. diameter, approximately 1/2 in. thick. This size is still being produced today as well as the 1 1/2 in. diameter by 1 in. size. Since the consumer had no aluminum SRM's to use for his calibration, Alcoa gave to NBS four aluminum alloys, representing high-tonnage alloys, to be used for SRM's. These became the four aluminum SRM's listed in the catalog. These SRM's did show heterogeneity, but still were useful to the customer. Again, this was a cooperative program primarily for methodology. Let us not lose the fact that aluminum major alloy SRM's, in the chip form, are always available at NBS. The instrumental analyses of aluminum does present some problems but time does not permit this discussion; however, x-ray spectrometry is being used most successfully today and the large volume sample is much superior for optical emission. (In passing, the aluminum industry has made a formal request through ASTM E-2, Subcommittee .04, by Subcommittee .07 for a series of SRM's to be produced at NBS.)

As the needs for metal SRM's increased, it was beyond the realm of any one producer to make the SRM's requested or needed. Every analyst felt that he needed a series of standards for each material produced that he was required to test in order to make a reliable calibration curve.

For a moment, let's just think about such a request. It's beyond our power of imagination in some laboratories. Speaking personally again, I'm working in aerospace. Our list of metal specifications, which we work with constantly, numbers over 1400. The old conception was at least three SRM's for each type of material with an elemental range of composition. In our case, this would be a minimum of 5200 SRM's, but we should have SRM's in both wrought and chill-cast form, so our requirements now double (using this concept) to over 10,000. This now is becoming ridiculous -- the storage space, the catalog, the calibration, etc.

Let's discuss some of the ways that ASTM E-2 has aided the spectroscopist with his SRM needs. In 1963, ASTM E-2 and NBS collaborated in publishing STP 58 E, "Standard Samples, Reference Samples, and High-Purity Materials for Spectrochemical Analyses." This publication aided the analyst as it listed the available SRM sources together with tables of elemental composition. The groups had also collaborated earlier on such publications and in writing and testing methods. A new booklet will be published soon, DS2, which will list all the SRM sources in the world with a good address and the particular SRM produced by each company. Tables will be deleted from this publication.

In 1964, J. Woodruff, then E-2 chairman, decided that E-2 should have a liaison to NBS and one from NBS to E-2. As a result of this appointment, it was agreed to send out a questionnaire to E-2 members who numbered 210, requesting their immediate SRM needs. We received answers from 119 persons representing 110 different laboratories and 150 E-2 members, since several laboratories had two members in E-2. The minimum of SRM requests was 550 sets, covering 35 different kinds of materials. All wanted a range of elemental compositions in sets that would include from three to seven samples per set. The questions appeared to be answered honestly. The request for SRM's was sincere and listed only the immediate needs with no attempt to list the future SRM needs. It was pointed out repeatedly that NBS leaned toward metals, especially steel. Copies of all the returned individual questionnaires and the summary were sent to NBS for review and tabulation. This material was studied thoroughly at NBS and acted as a guide for future planning of the SRM's most urgently needed by the world. The summary was sent to all E-2 members, as well as NBS. When a person took a look at the summary, they wanted to run rather than tackle such a mountainous problem. It was evident that NBS needed help. Some foresighted companies began making SRM's that are secondary, but bridged many of the gaps that the NBS-SRM's didn't do or could never do. This survey had many advantages as it specifically pointed out that NBS would have to work primarily on specific metal problems and other industries' needs and leave most of the routine SRM's to other producers. A point here: the sales of some of these exotic SRM's such as the five nines Zn, etc., definitely shows that these were a poor choice for industry, but perhaps the users of such materials were elated with their choice.

Due to the E-2 questionnaire, correspondence, etc., NBS made available to all E-2 members a status report of the SRM's covering April 14, 1965 to October 1, 1966 concerning what was available, the deletions, and the proposals. From this report, the new suppliers were again able to fill in with the needed SRM's that the summary of the questionnaire showed were definitely needed.

In 1968, when the 1160 series of steel standards were to be replaced, all the steel company representatives in E-2 were asked to assist with the elemental composition of the new replacement series and to help determine the number of standards needed. Sixty-three replies were received and the results showed the 1200 series could be reduced from eight to five SRM's covering the full range of analyses in the eight 1100 series.

This has definitely been a two-way street, as ASTM E-2 has assisted any standard producers with any problem with which he needed assistance. Many of the SRM's that have been produced outside of NBS are traceable to NBS through E-2-NBS relationships.

In 1971 the copper industry, through E-2 Subcommittee .05, requested NBS to make a series of copper SRM's. With the entire industry supporting such a project, and also offering to supply some of the material, this project is 80 percent production completed. Some pre-analyses have been done, homogeneity tests for acceptance are completed and some back-up figures are available. But the project is a long way from completion, as the referee analytical methods must be established and the analyses from two or more laboratories must agree within the assigned tolerance.

Two other E-2 committees have written to Sub. .04 of ASTM E-2, requesting help in obtaining a series of standards for titanium and slags. The groundwork is being laid and in the near future formal requests will be made to NBS for the consideration of these two series of standards.

In June 1973, E-2 authorized another "Standard Reference Material" survey. It is in progress now. The questionnaires were sent to ASTM E-2, Emission Spectroscopy; E-3, Chemical Analysis of Metals; and E-16, Sampling and Analysis of Metal Bearing Ores and Related Materials; members of which number approximately 400 persons. These three committees represent most of the people who need and use SRM's. To date, we have received 160 replies. The first question was: "Do you have any pressing needs for new or renewal SRM's?" Ninety-two have answered in the negative, but the others have requested over 50 different types of SRM's. Many of these would require from five to 10 SRM's for a reliable series of any value. The major needs listed in order of requests are high-temperature alloys and superalloys (nickel, cobalt and iron base), environmental (air and water), slags, titanium alloys, ores (all types including ferro-alloys), high-purity metals including nuclear as well as numerous others.

This survey points to many changes since the last questionnaire:

1. The analyst no longer depends primarily on NBS for all their SRM's.
2. The analyst, due to computerization, has been able to bridge many gaps with fewer SRM's.
3. A good series of SRM's with certified values can be used to establish the validity of the existing calibration curves.
4. and the analyst has become more self-reliant due to better instrumentation.

As stated, the SRM's most needed by industry are the high temperature and superalloys. I'll agree 100 percent.

This group of user needs to face their problems and unite so that their needs can be met. The monetary value of the products to be tested with such SRM's would be a billion dollars or more. One individual does not carry the needed weight to have such a series of SRM's made at NBS. There are very few high temperature-superalloy SRM's available any place in the world and, to my knowledge, none is traceable to a primary certified producer.

During this discussion, I have avoided as much as possible the use of the words primary, secondary, tertiary, etc., mainly because there is so much disagreement in their meaning. Perhaps if these terms were used in parenthesis it would help. In E-2, we consider NBS-SRM's as primary and all other producers as secondary, even though their SRM's may be traceable to NBS. The SRM's used by each laboratory, collected from their own production, could be listed as tertiary. A new word, in regard to standardization, has reared its head -- "benchmark." You've been told this type exists, so it behooves each of you to find out for yourself just how this new group of SRM's will fit into your system. It is evident from recent work, primarily on the microprobe, that the time is fast approaching when SRM's will have to be classified as to homogeneity, etc., such as Class A, B, C. This is another hurdle that we will jump when it is evident that we must.

Any individual company can produce a SRM and give you an analysis sheet. What confidence would you have in it? Could you trace the source of the material? Would you know the process under which it was produced? What methods were used to determine the elemental values listed? Who did the analytical work? Could you determine the calibre of the analysts in respect to that particular analysis? These are just a few of the many questions that would arise if you honestly thought through the problems. Now, let's turn to the SRM's issued by NBS. The certificate lists the "planning, preparation, testing, and analysis of the material." It specifically lists the cooperative laboratories, the analysts' names, and the method used to determine the certified elemental values. Perhaps some of today's producers should consider listing the same data as NBS lists, concerning the SRM's they issue.

Let us also state here, very emphatically, that all the cooperative help was voluntary and not mandatory as in some of our neighboring countries. ASTM E-2 and NBS are all voluntary with the goal of advancing our scientific technology to the best of our combined abilities.

Let us not lose the fact that, unless our methods of analysis are good, all the SRM's in the world cannot produce good analytical values. ASTM E-2 needs more people to become interested in writing methods, testing, etc., so that our analytical results can be the best possible under our own instrumental conditions. More and more today, people don't want to become involved in assisting with a program such as E-2, but these same people are the first to yell, "wolf" if the methods, SRM's, etc., are not available at their finger tips. Anyone gets out of any project only what he specifically wants and the more involved with it, the better his work will be. Come join us; we will welcome you!

V. Metals as Standard Reference Materials: Certification and Utilization

M. D. Cooper

I am grateful to be here; to be priviledged to take part in this symposium here at the National Bureau of Standards. Where could one hope to be where he would find more charitable friends, individuals more highly regarded for their pursuit of truth, and with greater humility because of its elusive character?

Among my feelings, also, is a deep-seated pride in my association with the American Society for Testing and Materials (ASTM), with its dedication to our voluntary standardization system. The administrators at ASTM Headquarters have described their role as "an authoritative, unbiased forum, free of control by any special interest, yet responsive to the needs of each -- a forum in which voluntary standards might be developed for the use of and in the best interests of every segment of our society." ASTM standards usually are specifications or test methods, not to be confused with tangible standard reference material that are to be discussed today. In any event, we hope to stimulate a forum, insofar as that word is defined as an open discussion. We are here to explore ideas on the certification and utilization of SRM's as they pertain to the measurement of the composition of metals.

It is my purpose to review the ASTM procedures for processing chemical methods for the analysis of metals. A further plan is to show that those methods should be rated among the best that can be readily and practically applied to the analysis of the various metals and alloys with which we are concerned. Finally, I shall mention ways that the basically sound ASTM approaches can be made even more effective than they are. The interplay between the ASTM and NBS will be emphasized as follows: the ASTM methods are an important means of certifying SRM's to be issued by NBS and the SRM's are important in the ASTM precision studies and likewise in the day-to-day performance evaluation of the methods and the analyst. My opinions of the indispensability of the SRM program at NBS and a few suggested ways that it, like the ASTM work, can be made even stronger will be enumerated.

Mr. Kennedy's group emphasized the utilization of SRM's in physical analytical methods. You recognize, of course, that their methods fill a need that could be served in no other way in these modern times in the quality control of metal and alloy composition. The remaining members of the panel are here to discuss chemical methods of analysis of ferrous and non-ferrous metals and alloys.

My own thoughts, in particular my references to specific matters, are related to steels, cast irons, and high-temperature alloys, which are under the jurisdiction of Subcommittee E-3 .01. Dr. Davis who will follow me on the program is likely to concentrate on non-ferrous alloys and Subcommittee E-3 .05. The formal presentations will be completed by Mr. Shultz who has held important positions both in ASTM and NBS for many years.

The ASTM Subcommittees to be covered by Dr. Davis and me, and other subcommittees in Committee E-3, have on-going interlaboratory programs designed to permit the addition of meaningful precision statements to published methods that are to be retained. The same goal applies to any newer methods to be evaluated. Test specimens for such interlaboratory programs must possess certain critical attributes, among them is homogeneity. That property is known to be carefully checked by NBS before certification analyses begin, therefore, the list of NBS-SRM's is consulted first when choosing ASTM test specimens. British chemical standards have been used for the same reason. Non-standardized samples are used occasionally, but with caution regarding possible inhomogeneity, when specimens are not at hand from the other sources.

Perhaps I should dwell a while on the importance of homogeneity in the chip form materials used to establish the precision of chemical methods. First, it is readily apparent that the tolerance we have for <u>in</u>homogeneity depends upon the size of the chips, how well they were mixed, and the size of the portions that are to be used. The latter frequently depends upon the concentration of the element to be determined. In any event, it is our aim to be assured that the variance arising from inhomogeneity among portions of the samples distributed to the cooperators is minimal, preferably inconsequential.

The subcommittee has published two methods that are empirical, basically similar to the physical analytical methods discussed by the earlier speakers on this panel. The instruments indeed are calibrated by means of SRM's. One is the combustion sulfur method, which the task group proved to be empirical. It does not challenge the homogeneity with regard to the sample size; the smallest portion used is 500 milligrams. The gravimetric method published by the subcommittee covers the same lower concentration limit, namely, 0.005 percent sulfur, but it, of course, calls for much larger sample sizes.

The other is total carbon by the combustion - gas chromatographic method. It, like the sulfur method, covers a low concentration range. As little as 50-mg portions of the SRM must be used, however, for the calibration curve. Such small portions are required because the combustion-gravimetric method, which has been accepted as an umpire method, provides certified values no lower than 0.05 to 0.06 percent.

For other elements, samples as small as 200 milligrams are used, because the concentration is high -- this is characteristic, of course, of high-alloy materials.

Returning to generalities, another important consideration is related to elements, other than the one to be determined, that are present -- particularly those whose interferences must be taken into account. Again, NBS is highly regarded because they prepare SRM's that related to industrial alloys.

Finally, the range of concentration provided by the test specimens is of great importance. When preparing this paper, I checked the precision statements in ASTM Designations E350 through E354 where some 15 to 20 elemental methods were published in the 1973 issue of Part 32 of ASTM standards for steels, cast iron, and high-temperature alloys, and I learned the following: SRM's from NBS were used in 205 instances, the British chemical standards in 10 instances; 25 non-standardized specimens were used; but in nearly 80 cases a sample providing needed concentrations was not available from any of those sources. This was true despite our minimal need to evaluate each method at the low, median, and upper limit of the specification range. Thus it appears that only in two out of three instances do we have the SRM's needed to evaluate chemical methods. I believe, however, that improvisation has led thus far to fairly adequate precision statements in the ASTM methods I just mentioned. We must agree, of course, that appreciably more SRM's are needed for day-to-day control of chemical methods.

The ASTM committee considered at great length the inclusion of a pointed reference to the accuracy of the ASTM methods. Eventually the decision was reached, however, merely to indicate in the test specimen description the value certified for the SRM's that were used. The agreement between the certified value and the average value found by the task group, we believed, seldom could be cited in terms of the method's accuracy. We were painfully aware that in many instances we had evaluated the same method, intrinsically, that was used to certify the SRM. The combustion carbon method is an example of one that is quite free of competition at concentrations greater than, say, 0.1 percent. Personally, I get very nervous, invariably, when I hear someone speak of "true values," because I know they have an infinite number of significant figures. It has been my observation that mortals seldom can justify reporting four; perhaps three and one half significant figures can be defended.

I shall now speak of ASTM methods, how they are born; and I'll brace myself as I say I believe they have merit when accurate results are needed -- for example in the SRM certification process.

The evaluation of ASTM chemical methods proceeds as follows:

1. The need for a method is brought to the attention of a subcommittee that has jurisdiction over a particular kind of material, and a task group chairman is appointed.
2. Candidate methods are considered and, after appropriate discussion by the subcommittee, one or two are chosen for preliminary evaluation.
3. At least two laboratories initially evaluate the methods and present their data and comments.
4. The subcommittee decides which method merits further evaluation, and additional volunteers are chosen to comprise a task group, preferably with at least 10 members to statistically evaluate the method. Also, the write-up of the method is reviewed by the Editorial Subcommittee. Next the subcommittee chairman consolidates the editorial suggestions.
5. Test specimens are chosen covering the concentration range of interest, which frequently has been established by other ASTM committees on specifications.
6. Each task group member runs two analyses on two different days and the data are treated by the task group chairman by an ASTM statistical method; he then adds a statement of repeatability and reproducibility.
7. The task group ballots on the acceptability of the method.

8. The subcommittee chairman provides copies for final review by the Editorial Subcommittee; after their approval, he conducts a letter ballot at the methods subcommittee level. If there are negative votes, he attempts to resolve them. If his direct attempts fail, the reasons for the negative votes are brought to the attention of the subcommittee where a two-thirds majority is required to override them.
9. Finally, a letter ballot is conducted at Committee E-3 level where negative votes may occur but rarely do. Constructive comments are, however, carefully considered, and the method then goes to press.

How can this program fail to provide reliable certification methods?

A subcommittee made up of about 50 men experienced in the determination of the element chose the method, but then not until it has been given a preliminary evaluation.

Another subcommittee of about 17 members with both editorial and analytical capability make a valiant attempt to remove all ambiguity.

At least five experienced analysts, from five laboratories, report the minimum of eight pairs of values required for the precision statement; frequently 10 or more participate, and we have had as many as 22. If there are eight or more, only one pair of values is reported by each laboratory.

The balloting procedure - task group - subcommittee - committee, and the serious attitude toward negative votes blend to lend credence to the substance and format of the method.

Because of the extensive testing and the scrutiny to which the methods are subjected, they should be free of systematic errors and hence accurate -- at least within earthly limits.

The claim just made for ASTM methods -- freedom from systematic errors -- is not trivial as I am sure everyone will agree; neither is the clarity of the method descriptions. Any deficiencies, I believe, are quantitative in nature, not qualitative. Here is a list of such deficiencies that have come to my mind related to methods published in the modern format:

1. Not all elements of commercial interest are covered.
2. Certain elements are not covered in the full concentration range that is of commercial interest.

3. Precision statements altogether too frequently are based on marginal numbers of interlaboratory participants.
4. For certain elements, only one type of method has been published, whereas other methods might well prove acceptable if evaluated.

(It will be noticed that I have not mentioned methods that have been in print for many years for which re-evaluation is long overdue!)

The only way to overcome these deficiencies that I can see calls for more workers. At this point the procedures for processing methods and data are quite adequately defined. The need is for greater numbers of participating laboratories. I believe this, in turn, calls for analytical chemists who acknowledge that their laboratories have an obligation to themselves and to the common good; next they must prove their personal dedication by selling their managements on the need for support of the program, perhaps by more adequate staffing. The reward will be a compendium of umpire methods, updated to reflect advances in analytical chemistry with method reliability documented. Through no other agency than ASTM will such a goal ever be realized, because it can come only through cooperative effort by volunteers. That statement is made on the rather safe assumption that only those with expert capability in the handling of given classes of metals and alloys are likely to invest their time voluntarily.

Let us hope that we never lose sight of the value of cooperative effort with respect either to standard methods or standard reference materials. In recent years NBS recognized the need for a much broader SRM program than ever before, one which would embrace not only metals and alloys, but several other types of material as well. It became clear that in each category the users of the SRM's would, themselves, have to do more than ever before to bring them into existence. NBS indicated that it could not be expected to shoulder as large a share of the responsibility as before.

With regard to metals and alloys, I believe the message just mentioned was misinterpreted. Industries with a need for SRM's began to exchange their internal company standards rather than to continue to invest as extensively as before in the NBS-SRM program. Here, as in ASTM, a meaningful program requires only more volunteers, more cooperators, more workers. It is not too late to reverse the trend and to make available to everyone an adequate supply of SRM's issued by our one and only source of primary standards, the National Bureau of Standards. It's conceivable that homogeneity testing and certification analyses could be handled through ASTM Committees E-2 and E-3. Members from NBS could guide the work and participate in it to the extent that NBS would have no reluctance to issue certificates and to market the SRM's.

I would disappoint Mr. Cali and Dr. Meinke, and most of the members of their staffs if I failed to mention one particular type of SRM's, namely, high-purity metals, for which specific needs are currently being surveyed by NBS. To qualify, those metals might well be certified for both metallic and non-metallic impurity elements so that the assay could be calculated and the concentration of each impurity would be known. They would bridge a gap that I believe is taken too lightly by many analytical chemists; namely, the need for additional inherently sound primary standards. As an aside, in E50 published by ASTM Committee E-3, seven metals for the preparation of standard solutions are specified. The purity of one is required to be 99.7; three, 99.8; and the other three, 99.9 percent. I doubt that anyone can be sure he has them.

In addition to serving as primary standards, the high-purity metals would also open the way to the use of reliable synthetic solutions to test methods for elements in extremely low concentrations where impurity elements in the simulated matrix constituents are sure to be significant.

Let me close by saying that if you do not endorse the positions I have taken today, I'll not be too downcast. Perhaps you will tomorrow, at which time the problems associated with shortages of metals and increased use of scrap that are forecast will lead to "tramp" element challenges the likes of which none of us has ever seen before. We might even consider the day after tomorrow when SRM's and the associated certification methods we discuss today will be archival according to surveys based on rates of depletion of natural resources -- compositions yet to be conceived will challenge us, or our successors. My one hope is that the same cooperative spirit, between industrial laboratories and groups such as NBS and ASTM, that pervades the atmosphere today will still exist as the inevitable technological adjustments become necessary.

VI. Metals as Standard Reference Materials: Certification and Utilization

C. Manning Davis

It is a pleasure to be on a panel where the relationship between the NBS and ASTM is discussed. There are many advantages - and disadvantages - of being late in a program of this nature. The major aspects of our discussion have already been excellently covered by my colleagues on the panel. It is then, not my purpose to present any striking new concepts, but to add a few thoughts as they have occurred to me. I speak from two positions.

My first position is that of an analytical chemist. Sometimes I am called an "analyst." Let us set the record straight: the word "analyst," as far as I am concerned, is in no way related to the field of psychiatry. The second position from which I speak is that of a member of ASTM. Specifically, as Mr. Cooper has mentioned, I am presently Chairman of Subcommittee E-3.05, which is the subcommittee on chemical analysis of non-ferrous metals.

At the outset, I would like to enlarge on one word that has been mentioned here several times. The first speaker today, Bill Kennedy, mentioned this word. The last speaker also mentioned this word. In fact, it appears on the ASTM stationery. The word is "voluntary." The verb form of this word is "volunteer." Many of us here today have volunteered our time and talents in one capacity or another because both the activities of ASTM and NBS are an integral part of our profession as analytical chemists. What would the field of analytical chemistry be if it weren't for the proven ASTM methods and the SRM's established and supplied by NBS? The verb volunteer may be used as a transitive verb (one which requires an object). What I am suggesting here today is that you volunteer someone from among your subordinates. If we would deliberately do this we would find that the average age of this group would not be 39 plus, but would be closer to 29. If we could encourage these younger people to join ASTM and participate in NBS standardization programs, we could be assured of a solid bridge between the present and the future, as well as profit by the enthusiasm and fresher outlook of our younger analysts.

Turning now to another subject, the ASTM task group, Mr. Cooper has very precisely outlined the organization of Committee E-3 and how it operates. My experience in the ASTM organization up until recently has been in the task group. This group was formerly called "task force." Let us focus for a few minutes on the organization and operation of the task group. To me, the task group is the firing line of the entire ASTM society. It is here, where the action is. This is the scene where standards are born, nutured, caressed, molded, and finally tested before presenting them for the Subcommittee and Main Committee ballot. If they do not pass (with the fine polish given them by the Editorial Subcommittee) they are often sent back to "GO" for reshaping by the task group and the task group chairman. Who are these people who patiently go through the painstaking process of screening and selecting the candidates for the "best" method that will hopefully become an ASTM Standard Method? Who are these people who volunteer their time and energy testing candidate methods through round-robin evaluation and final selection? A task group is a group of professional men and women who have a mutual interest or a common interest. It is this common interest that holds them together and allows them to pursue their assignment when the going gets rough. These people are either "volunteers" or people who have been "volunteered." In the nickel task group there were 21 elements suggested, for which there was need for an up-to-date standard method. After selection of two from this list there were six different chemical methods listed from which the task group picked two. In this process of screening, the democratic process was heavily relied on. And what's more, it worked. Who said that doing things by a committee doesn't work? The ASTM task group is a committee.

Let us look at the make-up of this task group or committee. We have already stated that all are volunteers (or were volunteered). Other than this, it is extremely important to see how it is made up or who are the members. A careful examination shows that they are not just interested professional analytical chemists, but they are representatives of both producers and consumers of the material by which the task group is designated. This, of course, is as it should be. The ultimate use of an ASTM "standard" method, is to possibly arbitrate between two members of the task group or the companies they represent. Finally, what better scheme could there be, than one in which both parties of a possible arbitration participate in the screening and selection of the final standard method to be used?

In light of the above, a comment on the nature of the method itself may be in order. Since the method is selected by representatives of the producers and consumers, it is only natural that it be a method compatible with the equipment and skills of all participants in the task group. The question has often been raised: "Don't the ASTM methods represent a collection of the classical methods?" The implication here is that the ASTM standards are good methods but being "classical," they are not used routinely because of the time and skill required. Often complaints are heard: "The ASTM methods are out-of-date or they are old fashioned."

In answer to these questions or complaints, as I see it today, the ASTM standards represent what the producer, consumer, and other interested people think, and subsequently have proven, to the best of their ability, to be the best methods. This does not imply that they are classical or routine, but just the best. This is a very valuable aspect of the ASTM task group operation.

A more specific area is the current needs for standard reference materials. ASTM Committee E-2, specifically Mrs. Sarah Degenkolb, has recently begun a survey on this most important matter. She has indicated in her comments that nickel-base high-temperature alloys with certified values for trace elements are certainly among the current needs. The subject of trace element analysis was discussed in a day and a half symposium in October 1972, at Miami Beach, Florida. This was sponsored by the Metallurgical Division of the Electroplating Society. In the discussion period, which followed the presentation of the papers, there were two comments from the floor to the effect that, if the specifications for certain trace elements continue to be lowered, the only method available to determine these trace elements is the spark source solids mass spectrometer. I took exception to these comments since I firmly believe there are several other alternatives. In fact, to agree that the solids mass spectrometer is the only choice, would appear to me to be turning our back on a challenge and thereby abandoning our responsibility as analytical chemists. Let us look at this problem more closely. Table 1 is a tabulation of the General Electric specifications for acceptable limits for trace elements for cast-nickel and cobalt-base superalloys[1]. This specification was issued in February 1970. It should be noted that in this table, bismuth is listed as 1 ppm (0.0001 percent) maximum. I understand that today (1973) the maximum is now 0.3 ppm. Lead has been reduced from the 10 ppm value listed. Other elements also have been lowered. This has all happened in the past two years. There is no question that one segment of industry requires reliable methods to analyze certain trace elements down to the 1 ppm level. It is also apparent that the spark-source solids mass spectrometer is certainly one approach to the problem. But, I would like to point out that an ASTM task group specifically for trace elements in nickel, was formed in June 1970 to develop a chemical method that would not require an expensive solids mass spectrometer. I am pleased to report that the task group has reviewed various alternatives and have tested an extraction-atomic absorption method

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[1] Morykwas, S., Foundry, Vol. 100, No. 9, p. 106 (1972).

that, after the careful scrutiny of the Editorial Subcommittee, may be published as an ASTM standard in the near future. Currently, it is only capable of analyzing down to 1 ppm of lead and bismuth. Through further work it may be extended to other important trace elements. Here we see the function of the ASTM task group and the resulting value of the efforts of its members.

Mr. Cooper has commented on the use of the term: "true value." I would like to emphasize his comments by an incident that happened to me several years ago. In a discussion of some analytical results with my boss, the director of research, he asked: "What is the value which you plan to report?" My answer was: "The true value is______." He stopped for a second and queried: "Do you spell that word true with a capital t?" Of course, my immediate answer was "absolutely not." This story reminds me of an expression I have heard in our laboratory. I am sure there is no intent to be irreligious. The expression goes: "Only God knows, but He ain't telling." I would like to say to this, that God has given us a mind and two hands to use to search for the truth. With the proven standards supplied by ASTM and with the SRM's available through the NBS, we <u>can approach</u> the truth. This is not to say, find the truth; but to approach the truth. This is my idea of what every good practicing analytical chemist does.

Perhaps the foregoing comments could be characterized as a discussion of <u>accuracy</u>. Let us return to the other all important dimension of analytical chemistry: <u>precision</u>. Precision, as we all know, is how well we get the right answer or the wrong answer over and over on repeated analyses. There are more precise ways of defining precision, but this will suffice for the moment. In the development of every ASTM method, the precision has been established and a statement pertaining to precision has to appear at the end of the method. Here again, we see the interaction of ASTM and NBS. No matter how good the method is, if your test specimen is not homogeneous (consistently the same from on portion to another) the precision will not be good. On the other hand no matter how good (homogeneous) the sample is, if the method is not good, the precision of the results will be poor. In other words, it is impossible to establish the precision of a method and the homogeneity of a test specimen at the same time. The answer to this dilemma is to use a test specimen that has already been proven to be homogeneous. One of the most valuable attributes of an NBS-SRM is that these materials have undergone a test for homogeneity. A division of the company, for which I work, supplies secondary standards. A statement appears on each certificate of analysis to the effect that there has been no homogeneity test. This is of extreme importance when the point-to-plane technique is used in the emission spectrographic laboratory. In this technique, less than one milligram of sample is excited and thereby analyzed. Fortunately, the "wet" chemist usually uses one gram or more of the sample, which lessens the importance of a completely homogeneous sample. The tremendous value, which cannot be emphasized enough, of the NBS organization is their experience, their know-how, and their assurance that the SRM's are homogeneous. In summary, then, the accuracy depends on the method and the SRM, and the precision is also related to both the ASTM standard and the NBS-SRM. We can see that there is a marriage or an interdependence of these two organizations: One for the best materials and one for the best methods.

In closing, let us refer back to where we started. If we as professional chemists and spectrographers depend on these two great organizations -- and unquestionably we do -- it is absolutely necessary that we either do some "volunteering" of others or do a lot of volunteering ourselves.

Table 1. Acceptable Limits for Trace Elements

Critical Elements	Maximum, %
Bismuth	.0001
Silver	.0010
Lead	.0010

Other Elements Covered	Maximum, %
Thallium	.0003
Tellurium	.0005
Zinc	.0080
Arsenic	.0100
Selenium	.0100
Gallium	.0100
Columbium	.0500
Tantalum	.0500
Copper	.0500
Other elements, each	.0025
Other elements, Total	.0400

VII. The SRM Factory

J. I. Shultz

When I was asked to serve as a member of this panel, I was told that "our combined purpose is to show the relationship between the ASTM and the broad category of Standard Reference Materials." Since the ASTM is a broadly-based organization consisting of better than 100 committees and somewhat less than 2000 subcommittees, and since the Standard Reference Materials program covers the issuance of more than 800 different standard materials, I will confine my comments to a small, but very important sector of the SRM program covering the preparation, analysis, and certification of metals, alloys, and ores, and its relationship and interaction with a number of ASTM Committees.

On our campus-like grounds here at NBS, we have a busy "factory." It is housed on parts of two floors of the Chemistry Building and its output is measured in mere pounds. But it casts a long beam over the quality of the millions of tons of ferrous and non-ferrous alloys as well as a variety of ores and chemicals produced in the U.S. every year. As a part of the Bureau's wide and varied service to American industry, this compact little factory produces the SRM's that serve as production benchmarks for a host of basic industrial products. Each one is a specimen of a given metal or other material, the composition of which is stated by the Bureau to as exact a degree as science permits. Produced under the most exacting conditions, each tiny shipment, and I say tiny because they are sold in quantities that would fit into your pocket, is accompanied by a Certificate of Analysis.

Now, how do the Committees of ASTM, in particular, and industry, in general, relate to this tiny factory? Well, it was recognized many years ago that a cooperative program with industry was an important factor to the success of the SRM program. Only with such cooperation has the Bureau been able to issue the large number of SRM's that are now available. With metals and ores, for example, industry and organizations such as committees of ASTM not only offer suggestions in the selection of materials to be standardized, but in many cases provide the starting material and, after the Bureau has prepared a homogeneous product in suitable form, participates in the extensive analysis required before the SRM can be issued with a certificate of composition.

As you may well imagine, the preparation of SRM's involves many factors. In selecting the types and compositions of the SRM's to be issued, NBS is often guided by the number and kind of requests received and by the advice of those engaged in the industries interested. I might say that the probable demand for the SRM is expected to justify the time and expense of preparation.

A historical note or two will illustrate the point. In late 1946, after considerable negotiating, the Chairman of ASTM Committee A-7 on Malleable Iron Castings in a letter to NBS, cited reasons why the malleable iron industry of the U.S. needed authoritative reference standards. There was a well-defined idea by many malleable iron chemists that misleading results were obtained by using steels and gray iron standards, particularly by those chemists who were involved in the production of white iron by the duplex process. Sulfur and chromium were reported to be the elements that gave more than the normal amount of analytical trouble. It was agreed that if NBS would provide suitable white iron standards, industry would contribute the material, arrange for the processing through the Malleable Founders Society, and then use its influence on such Committees as E-3 and A-7 to provide analytical data. After overcoming a number of technical difficulties, the malleable iron industry was finally provided with a much needed, well-characterized chip standard for wet chemical use to be supplemented later by three solid white iron standards for use by the spectrographic community. Taking part in the original certification work were nine industrial laboratories all of whom were well represented on a number of ASTM Committees. An outgrowth of this association was the development of analytical procedures that were uniquely applicable to this specific type of alloy.

In the late 50's, a group of 11 persons in Committee E-3 formed a Task Force for the purpose of evaluating an ion-exchange procedure for the determination of Nb, Ta, and Ti in ferroniobium, a very important industrial ferroalloy. Ion-exchange techniques appeared to be the answer to solving the complex analytical chemistry of this combination of elements, particularly at the levels found in ferroniobium. An appeal to NBS for assistance resulted in the acquisition of a typical commercial grade of ferroniobium, which was prepared in our tiny busy factory, for ultimate use as a NBS-SRM. After many months of evaluating the procedure and the acquisition of many data, the outcome resulted in the acceptance and publication of the procedures in the ASTM Book of Methods and the issuance of the first NBS ferroniobium SRM. Of course, there are many instances that could be cited to show the interplay between our two organizations, but the two I have just given should suffice.

Because we receive frequent inquiries concerning the specific operations involved in the production of our metal SRM's, I would now like to speak briefly of the preparation, analysis, and certification of that sector of the SRM program that accounts for about 30 percent of our sales.

Preparation of Steel SRM's: The steel is obtained in the form of round bars about 12.7 cm in diameter and 91.4 cm in length, weighing about 200 pounds. Six to 12 bars are generally used for one SRM and must be from the same heat and sufficiently homogeneous so that the entire lot can be issued under one certificate of analysis. The outside surface is removed on heavy-duty lathes and the bars are then turned into chips with a special high-speed tool having a serrated cutting edge. Cutting is discontinued when the core section approximates 2.8 cm. As it is rarely possible to produce directly the form of chip desired, it is necessary to crush or grind the millings in a chilled iron crusher to obtain material of suitable particle size. The material is next sifted and the proper-sized portion, usually that between a 16- and a 40- mesh sieve is retained for use as the SRM. On a six-bar lot, about 1000 pounds of finished material are obtained, which represents approximately 80 percent of the original material.

The entire sample is then mixed in a large cone-shaped porcelain-lined mixer for an hour or two. Preliminary tests are made at NBS to check homogeneity, and if the material is uniform, portions of the steel are then analyzed at NBS and by a selected group of analysts representing producers and consumers. I might add that we maintain a list of approximately 170 laboratories that are well qualified and willing to cooperate in our analytical program.

Preparation of Cast Iron SRM's: Cast iron samples for SRM's must be carefully prepared. Chips are cut from hollow cylinders, 76.2 cm in length and 29.6 cm in outside diameter with walls about 5 cm thick. The machined material is first sifted to remove the fine particles of iron and of free graphite. It is then mixed in the mixer, through which a strong current of air is passed to blow out any free graphite. The mixing gives rise to a certain amount of fine material through crushing, and the mixed sample is therefore again sifted to obtain the final sample, which is the portion that passes a 16- mesh sieve and is retained on a 30- mesh sieve.

The preparation of ferroalloys sometimes presents problems, and better homogeneity is obtained if the particle size is fairly uniform; usually the portion between a 120- and 140- mesh sieve is most satisfactory.

Preparation of Non-ferrous SRM's: The preparation of non-ferrous alloys presents many obstacles, a major difficulty being that of obtaining homogeneous castings. Leaded bronzes, for example, are cast in hollow cylinders having a wall thickness of about 2.5 cm. Phosphor bronze, 63b, was cast centrifugally in hollow cylinders approximately 17.8 cm in length having a wall thickness of 4.4 cm and an outside diameter of 20.8 cm (weight about 45 pounds). For this SRM eight castings representing approximately 200 pounds, comprised the starting material.

Methods used at NBS for the analysis of SRM's are selected or designed to give the best obtainable results. Many of them can now be found in the ASTM Book of Methods. There are, of course, certain practical considerations involved in the degree of accuracy sought or required. For example, if the needs of practically all users are met by a value of 0.050 percent sulfur in a steel SRM, the additional expense and time involved in an attempt to add the third significant figure are not justified. When possible, several methods of analysis for an element are employed at NBS. Parallel controls are run on synthetic solutions of known composition or on prior SRM's. A relatively large number of determinations are made; for example, in the analysis of an NBS high-temperature alloy, 15 elements were determined involving more than 150 determinations split into replicate runs of two to five determinations per set.

No specified methods of analysis are designated when the samples are sent to the cooperating analysts, nor has any definite schedule of the number of determinations, sets, or analysts thus far been requested. The cooperators, however, have been asked in recent years to submit all results arranged to show the number of determinations in each set and the number of sets, both keyed to the analysts who made the determinations.

The appraisement of the values submitted by the cooperators for inclusion on the certificate of analysis is based on what may be called "chemical judgment." This process involves, among other factors, (1) experience as to the accuracy that might be expected with superior handling of suitable methods, (2) interpretation of the probable accuracy of the Bureau's results, (3) survey of the data from all laboratories with respect to agreement, deviations, and ranges, and then, (4) setting up the limits preferred for SRM's. Those analysts whose values are outside these limits are asked to check their analyses.

Finally, when the average value submitted by each laboratory for an element is within the desired limits, or as close thereto as practical, the average of these individual averages is indicated on the certificate as the value for the percentage of the particular element. This is the general practice but is subject to occasional exceptions.

The overall average value on the certificate of analysis obviously does not represent absolute certainty for the number of decimal places indicated - that is, if the average value of all the analysts for phosphorus in a steel is indicated as 0.055 percent, it is not implied that the "5" in the third decimal place is absolutely correct, although occasionally some individuals attempt to make such interpretations.

As the value on the certificate is an average of a number of determinations by a number of procedures, these determinations are in turn useless for a statistical treatment to set up limits for the true content, unless it can be shown that there are no additional precautions that would exert any determinate effect. However, it would seem consistent to consider that the true content is within the limits of three sigma of the individual averages reported by the cooperators.

In conclusion, I think it is safe to say that there will be an ever-increasing need for accurate compositional SRM's. With the great expansion in instrumental methods, and consequent tremendous increase in the amount of analytical data, it is essential that correct SRM's be available for calibration and checking; otherwise, much erroneous data will be turned out by analytical laboratories, and bad results, in most cases, are worse than no data. There is, therefore, a continuing need for top-grade analytical chemists capable of analyzing primary standard samples of composition.

VIII. Homogeneity of SRM's

R. E. Michaelis

At this Conference, we have witnessed considerable confusion with respect to the term "Standard Reference Materials." Many attendees believe the word "standard" should be omitted. A few felt the word "reference" was redundant. Some suggested new terms such as "materials of certified chemical composition." Fortunately, all agreed on the word "material." Clearly international acceptance of nomenclature and definitions is a challenging goal and must be achieved for full understanding by all concerned.

My part in this panel discussion is to address the subject of homogeneity - more specifically material homogeneity. This also is a very important term seemingly little understood and desperately needing further definition.

The word "homogeneity" like "purity" really has little meaning unless fully qualified. The inclusion of a modifier such as high-, super-, or ultra-, adds little or nothing. To be meaningful, homogeneity, or purity, must always be further defined by reference not only to the specific measurement system, but also to the specific amount of material viewed in that measurement system.

In general the requirements for homogeneity in chemical analysis are well understood. If the measurement system involves the analytical chemist, the amount of material usually is a few tenths of a gram. If the measurement system involves the spectroscopist, the amount of material is reduced to milligrams. If, however, the measurement system involves the microanalyst, the amount of material is further reduced to micrograms, or even to nanograms. Each of these three measurement systems has considerable latitude with respect to the amount of material used in making a determination. This will depend in part on the element sought and its concentration level. Nevertheless, homogeneity, or perhaps a more apt term material variability, is an integral part of the measurement system and is dependent on the sample size. The crucial point that must be understood is that meaningful measurement in chemical analysis must involve the concept of material variability.

In "The SRM Story at NBS,"* details were given concerning the preparation and characterization of a high-purity zinc material. One main use of this material was to serve as a defining fixed point on the International Practical Temperature Scale (1968). In the certificate for the zinc freezing point, SRM 740, table 1, it is stated: "The zinc for this standard is of exceptional purity with the total of all other elements that affect the freezing point less than one part per million." This is purity as viewed by a particular measurement system. Indeed, significant quantities of elements may be present that do not affect the freezing point.

A selected portion of this high-purity zinc also was chosen as an SRM to be certified for its chemical composition. Extensive characterization was carried out utilizing every possible physical and chemical method for the certification. The results of this study are given in the certificate of analysis for SRM 682, table 2. Based on the chemical information provided, conclusion is made that the total impurity content - not just those that affect the freezing point - is less than 1 ppm. There is, however, one important reservation -- providing sufficient sample is used in the measurement system! Your attention is directed to footnote 2 of this certificate: "Spark-source mass spectro-

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*See page 246.

graphic results on some sample sizes of 20 to 50 mg showed definite evidence of gross inhomogeneity for the elements Bi, Pb, and Tl. This was partially confirmed for Pb as determined by polarography using 1 g samples, which showed Pb heterogeneity but to a lesser degree. Residual resistivity ratio measurements made on about 10 to 15 g samples also indicated some limited variability for the electrically active elements such as Bi, Pb, and Tl; however, the minimum ratio of 33,000 (R_{273K}/R_{4K}) would be inconsistent with any one of the three elements exceeding 0.1 ppm (by weight) on a 10-15 g sample size." (The assumption is made that, for RRR measurements, Bi, Pb, and Tl are in solid solution with the zinc.) Let me then emphasize the main point of this discussion. It can be concluded that this zinc is reasonably homogeneous and contains less than a total of 1 ppm impurity content - providing the sample size is at least 10 to 15 grams. Observe that when sufficient sample is used, the specific measurement system employed is relatively unimportant.

Let me further dramatize the necessity of providing full characterization of a material. Suppose, if you will, that a minimum sample size was not given on the zinc certificate. Further suppose that a measurement system was available to make determiantions on a sample size of perhaps a nanogram. It is entirely conceivable that some minuscule portion of this zinc material would reveal nearly pure Bi, Pb, or Tl, or any combination thereof. In the absence of full characterization data, material variability (or purity) lies strictly in the eyes of the beholder - and is the amount of material viewed by the measurement system.

Let us broaden our perspective with respect to homogeneity or material variability by another example. In the late 1950's, NBS prepared a set of eight ingot iron and low-alloy steel SRM's, designed primarily for use in optical emission and x-ray fluorescence methods of analysis. These were produced by the most modern melting, casting, and fabrication procedures to provide material of the highest possible homogeneity. Several years ago investigations were carried out on some of these SRM's to ascertain definitive numbers for homogeneity. [Details of these studies are reported in the 260 series of publications, for example, NBS-SRM 461 is reported in 260-3, and NBS-SRM 463 (and SRM's C1102 and 1102) in 260-10.] For NBS-SRM 461: "It is concluded that this steel is sufficiently homogeneous that any present microanalytical technique can be carried out with little chance of inaccuracy due to inhomogeneity. It is further concluded that the homogeneity level corresponds closely to the grain size of the material."

The grain size of this steel was deduced to be two to four micrometers, and structurally homogeneous at the five micrometer level. This also, then, is the compositional level of homogeneity. You may well ask what are the ramifications of this finding.

For other microanalytical techniques, such as spark-source mass spectrometry, a 50 micrometer sphere was assumed to be a representative sample. This corresponds to about 0.52 microgram of the steel or about ten thousand times the amount investigated by means of electron probe microanalysis. A commonly found grain size in many steels corresponds to ASTM number 5.5 or 6.0. In this case, the 50 micrometer spherical volume would sample only one or two grains. However, it has been shown that the average grain size of NBS-461 steel corresponds to ASTM number 13.5. The resultant average number of grains in the 50 micrometer sphere is about three thousand -- certainly a fair sampling for analysis. (For optical emission spectrometric analysis, the number of grains could be multiplied by many millions.)

Two points should be emphasized. First, the metallurgical structures of the NBS-SRM's may differ appreciably from the real live samples with which the analyst has to deal. These differences can introduce significant biases depending on the measurement systems employed and the amount of material utilized in these systems. Second, the NBS-SRM's of proven and stated homogeneity may be especially valuable in evaluating the precision of analytical methods, since material variability is at a minimum and should not contribute to the error of the measurement system. Furthermore, these SRM's may be utilized to improve sampling procedures or to investigate the homogeneity of other materials of certified chemical composition.

I would be quite remiss if some remarks concerning SRM 1264 were not included. This is one of five SRM's that replace the original eight "1100 series," iron and low-alloy steels. SRM 1264 has been the subject of many discussions. For the uninitiated, let me briefly describe these two series of SRM's. The "1100 series" was air-induction melted and cast in lot sizes of about one ton. They contained a graded concentration range for about 25 elements. The "1200 series" was vacuum-melted and cast in lots of seven and one half tons to contain a graded series for 40 elements. Also, the "1200 series" have expanded concentration ranges. SRM 1264 can best be described as a high-carbon steel containing appreciable quantities of refractory metal carbide-forming elements. There are no chemical composition specifications covering a material such as 1264; in fact, there never should be. The first time we attempted to make 1264, the five ton ingot would not even support its own weight and broke in half in the forging operation. After lowering the aim concentrations for some of the deleterious elements to permit fabrication (but still retaining the high carbon and relatively high amounts of most refractory metal carbide formers), 1264 was remade and processing was completed successfully. Following certification, a problem arose in optical emission analysis in that some of the refractory carbide elements would not fit on analytical curves developed through use of other materials of certified composition. Table 3 is a copy of the certificate of analysis for 1264. Here I must state that SRM 1264 is entirely satisfactory for optical emission analysis for all those elements normally determined to meet chemical composition specifications. Moreover, it has been proven entirely satisfactory for calibration in x-ray fluorescence methods of analysis including determination of the refractory metal carbide elements.

I have already alluded to the many problems that exist in sampling a large lot of production material. For SRM 1264, it appears that directions on "how to" sample the SRM are also critically important.

Why is SRM 1264 different from other steel SRM's for optical emission analysis? The first clue is a significant difference in its microstructure. A critical important axiom with relative type methods of analysis is that the SRM and the sample for analysis be matched as closely as possible with respect to all variables that could influence the measurement system. SRM 1264 is totally different in microstructure from any of the other "1200 series," and most surely will be different from any steel that the analyst might be called upon to analyze. The closest match among all these SRM's would be found between 1263 and 1264. Figure 1 shows a photomicrograph etched to show the iron carbide structure of 1263 versus that of 1264. The difference in amount is understandable, since 1263 contains about 0.6 percent C and 1264 contains about 0.9 percent C. The significant difference however, is in the size of the iron carbides. Those in 1264 are at least twice as large as those in 1263. Such a change in metallurgical structure could lead to a bias with relative type method of analysis, particularly optical emission.

Hidden in the photomicrograph for 1264 is unsuspected gross inhomogeneity with respect to some of the refractory metal carbide-forming elements, such as Nb, Ti, and Zr. Figure 2 shows a scan by means of the electron microprobe along the transverse direction. Material variability with respect to the refractory metal carbides is made clear immediately. The trace for Nb reveals only two major pips. By metallographic studies it was deduced that these refractory metal carbides essentially are equiaxed; that is, they are not in long stringers. By calculation it was determined that a one millimeter cube of material must be utilized in the measurement system to achieve homogeneity for Nb.

The situation is better with respect to Ti. By similar calculation, it can be stated that for all practical purposes, each 0.1 millimeter cube is equivalent.

Figure 3 shows the same detail with respect to Cr and Ni. For Cr, the amount of material for equivalence now has been reduced to 0.01 millimeter cube. Nickel is shown to be nearly uniform, even at the micrometer level of spatial resolution.

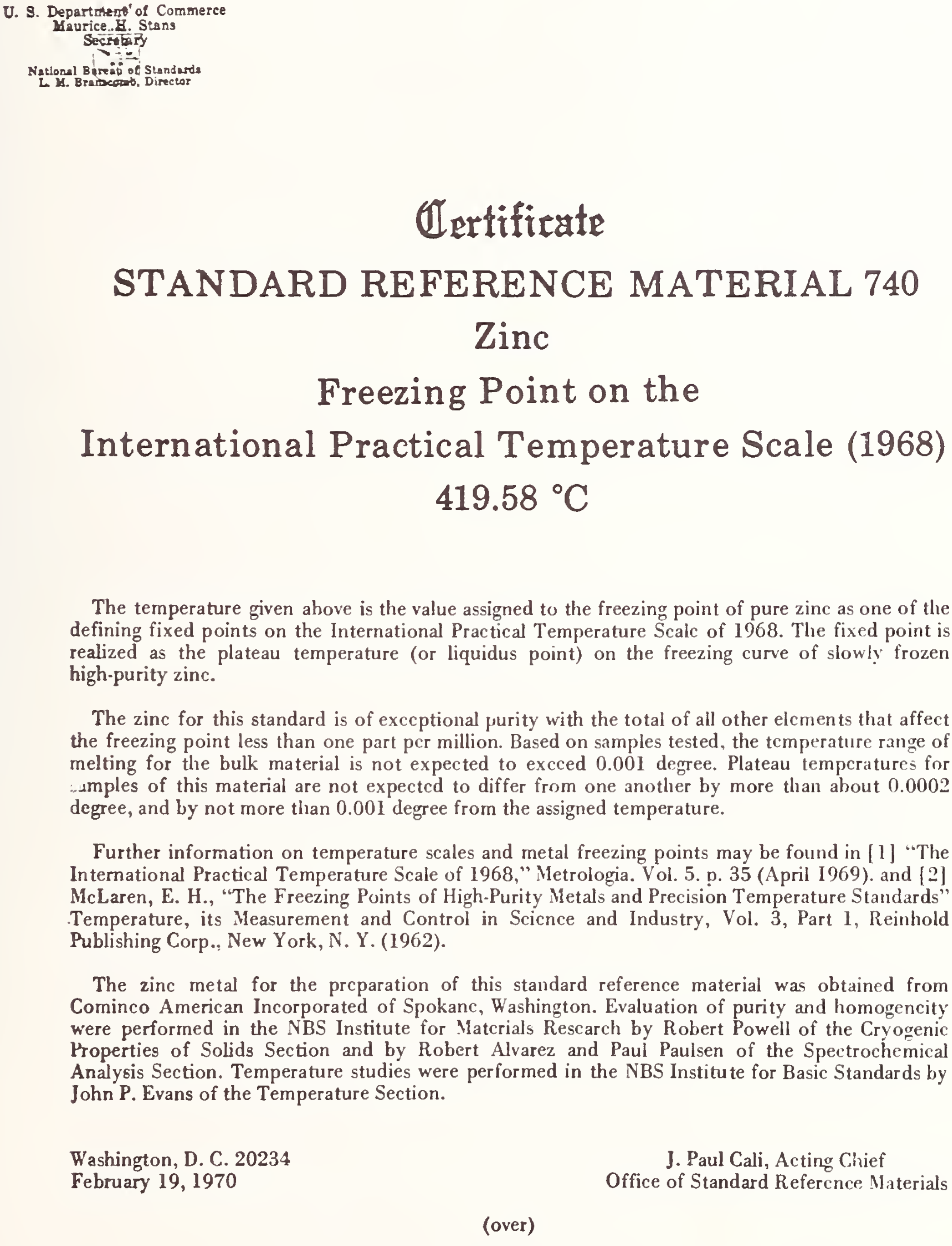
Providing the amounts of material indicated are used in the relative type methods of analysis, reproducible numbers should be achievable; that is, material variability should not play an important role toward affecting precision. However, even though the proper amounts of material are used in the relative type methods, the determinations may be highly inaccurate. It is entirely possible to reproduce a biased number due to other metallurgical differences - such as the relative amounts and sizes of iron and refractory metal carbides in 1264 versus any other SRM or sample for analysis.

Several spectrochemical techniques for optical emission analysis have been suggested to minimize (if not eliminate) inaccuracies as described above. One ASTM procedure used successfully in equating the SRM to the sample for analysis is to remelt and recast each specimen. A rapid remelt (preferably in an inert atmosphere) and recast (preferably unidirectional solidification) not only eliminates possible biases that exist between chill cast and wrought metallurgical conditions, but also makes the structure of the SRM and the sample as nearly alike as possible. (Unfortunately, remelting and recasting negates the NBS certificate of analysis.)

One final point still needs to be made. Material variability can (and almost always does) depend on how the specimen is viewed in the measurement system. A determination made on a transverse section may differ appreciably from that made on a longitudinal section (for both wrought and cast materials). This is due to directional changes in metallurgical structure with attendant differing response by the relative type methods.

I must emphasize in closing that critical relationships exist between meaningful measurement and homogeneity; and that homogeneity must be fully qualified by reference to the specific measurement system and to the specific amount of material viewed in that measurement system.

Table 1. Certificate SRM 740



U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

Certificate

STANDARD REFERENCE MATERIAL 740

Zinc

Freezing Point on the International Practical Temperature Scale (1968)

419.58 °C

The temperature given above is the value assigned to the freezing point of pure zinc as one of the defining fixed points on the International Practical Temperature Scale of 1968. The fixed point is realized as the plateau temperature (or liquidus point) on the freezing curve of slowly frozen high-purity zinc.

The zinc for this standard is of exceptional purity with the total of all other elements that affect the freezing point less than one part per million. Based on samples tested, the temperature range of melting for the bulk material is not expected to exceed 0.001 degree. Plateau temperatures for samples of this material are not expected to differ from one another by more than about 0.0002 degree, and by not more than 0.001 degree from the assigned temperature.

Further information on temperature scales and metal freezing points may be found in [1] "The International Practical Temperature Scale of 1968," Metrologia. Vol. 5. p. 35 (April 1969). and [2] McLaren, E. H., "The Freezing Points of High-Purity Metals and Precision Temperature Standards" Temperature, its Measurement and Control in Science and Industry, Vol. 3, Part 1, Reinhold Publishing Corp., New York, N. Y. (1962).

The zinc metal for the preparation of this standard reference material was obtained from Cominco American Incorporated of Spokane, Washington. Evaluation of purity and homogeneity were performed in the NBS Institute for Materials Research by Robert Powell of the Cryogenic Properties of Solids Section and by Robert Alvarez and Paul Paulsen of the Spectrochemical Analysis Section. Temperature studies were performed in the NBS Institute for Basic Standards by John P. Evans of the Temperature Section.

Washington, D. C. 20234
February 19, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

Table 1. Certificate SRM 740 (continued)

SUPPLEMENTARY INFORMATION
PREPARATION, TESTING, AND HANDLING OF HIGH-PURITY ZINC FREEZING POINT MATERIAL

PREPARATION: The zinc was prepared to obtain material of the highest possible purity and homogeneity.

1. The starting material was a carefully selected lot of electrolytic special high-grade zinc (99.99+).
2. Processes included vacuum distillation, zone refining, and homogenization.
3. Analytical control was maintained throughout the entire preparation.
4. The final bars (about two feet long) were individually sealed in argon filled polyethylene bags.

TESTING: Selected samples were taken for testing which were representative of the entire lot.

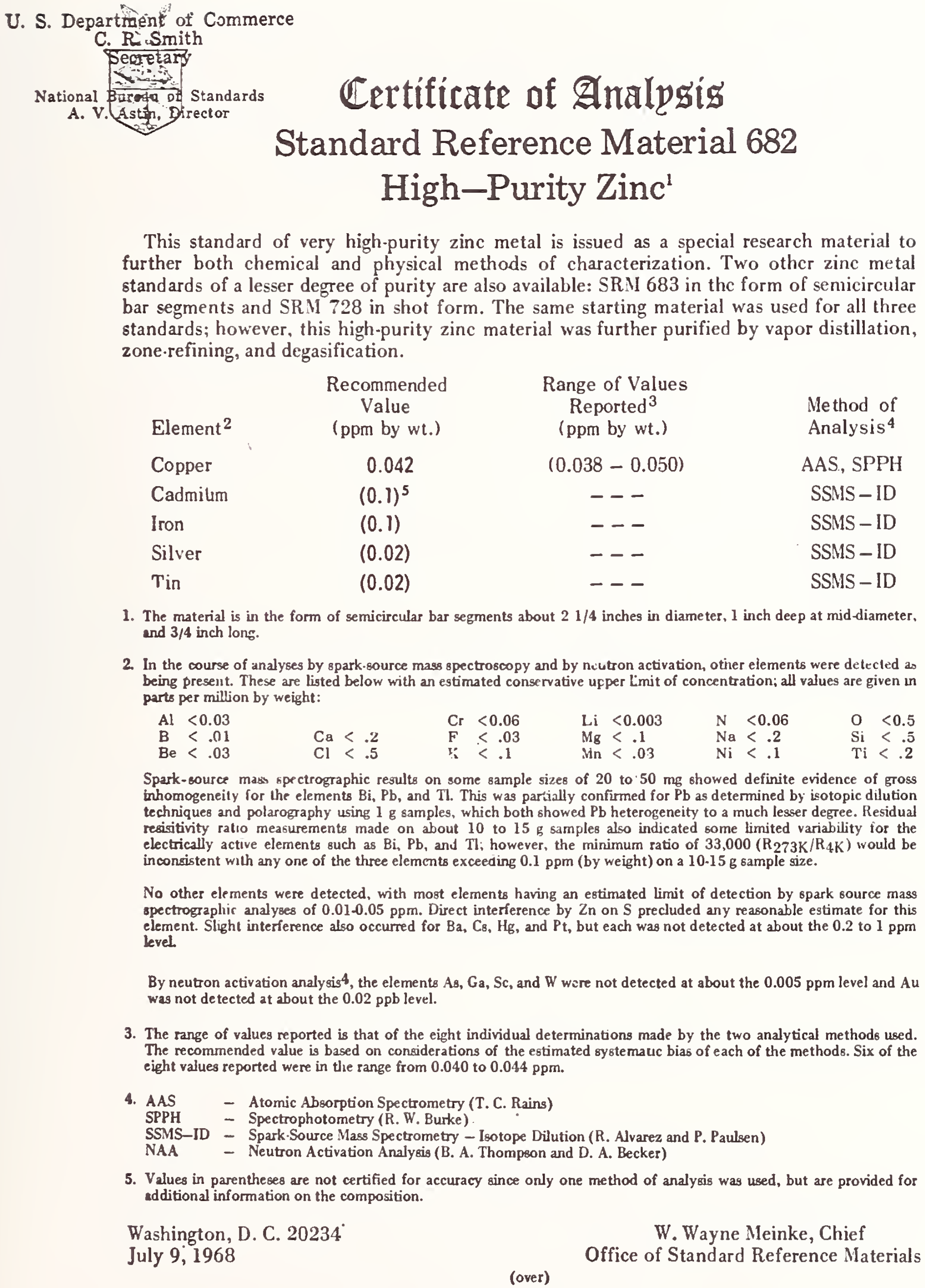
1. Testing initially was performed by optical emission and spark source mass spectroscopic procedures and by resistivity ratio measurements. As a result of this testing the material tentatively was accepted both from the homogeneity and composition standpoints.
2. Finally thermal analysis of selected samples was performed to determine the suitability of the material for the freezing point standard. Based on the samples tested, the temperature range of melting for the bulk material is not expected to exceed 0.001 degree, and by not more than 0.001 degree from the assigned temperature of 419.58 °C.

HANDLING: Any handling procedures on ultra high-purity material are apt to introduce contamination. The procedures which follow were established to minimize contamination particularly with respect to the elements that could affect the freezing point measurements.

1. The zinc bars were cut dry with a carbide tipped cutter (to form 350g bar sections) in such a way that only the carbide tip touched the zinc metal. At no time were the zinc bars touched by hand (polyethylene gloves were used), and at no time were the bars in contact with any part of the milling machine other than through the polyethylene cover.
2. Following cutting, the samples were acid cleaned in high-purity dilute nitric acid, rinsed with distilled water, and then air dried.
3. Individual samples were bagged in polyethylene and sealed.

SHOULD ANY CUTTING OF THE SAMPLES BE REQUIRED OR SHOULD ANY CONTAMINATION BE SUSPECTED, IT IS RECOMMENDED THAT THE APPROPRIATE HANDLING PROCEDURES DESCRIBED ABOVE BE EMPLOYED JUST PRIOR TO USE.

Table 2. Certificate SRM 682



U. S. Department of Commerce
C. R. Smith
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis
Standard Reference Material 682
High—Purity Zinc[1]

This standard of very high-purity zinc metal is issued as a special research material to further both chemical and physical methods of characterization. Two other zinc metal standards of a lesser degree of purity are also available: SRM 683 in the form of semicircular bar segments and SRM 728 in shot form. The same starting material was used for all three standards; however, this high-purity zinc material was further purified by vapor distillation, zone-refining, and degasification.

Element[2]	Recommended Value (ppm by wt.)	Range of Values Reported[3] (ppm by wt.)	Method of Analysis[4]
Copper	0.042	(0.038 – 0.050)	AAS, SPPH
Cadmium	(0.1)[5]	– – –	SSMS – ID
Iron	(0.1)	– – –	SSMS – ID
Silver	(0.02)	– – –	SSMS – ID
Tin	(0.02)	– – –	SSMS – ID

1. The material is in the form of semicircular bar segments about 2 1/4 inches in diameter, 1 inch deep at mid-diameter, and 3/4 inch long.

2. In the course of analyses by spark-source mass spectroscopy and by neutron activation, other elements were detected as being present. These are listed below with an estimated conservative upper limit of concentration; all values are given in parts per million by weight:

Al <0.03		Cr <0.06	Li <0.003	N <0.06	O <0.5
B < .01	Ca < .2	F < .03	Mg < .1	Na < .2	Si < .5
Be < .03	Cl < .5	K < .1	Mn < .03	Ni < .1	Ti < .2

Spark-source mass spectrographic results on some sample sizes of 20 to 50 mg showed definite evidence of gross inhomogeneity for the elements Bi, Pb, and Tl. This was partially confirmed for Pb as determined by isotopic dilution techniques and polarography using 1 g samples, which both showed Pb heterogeneity to a much lesser degree. Residual resistivity ratio measurements made on about 10 to 15 g samples also indicated some limited variability for the electrically active elements such as Bi, Pb, and Tl; however, the minimum ratio of 33,000 (R_{273K}/R_{4K}) would be inconsistent with any one of the three elements exceeding 0.1 ppm (by weight) on a 10-15 g sample size.

No other elements were detected, with most elements having an estimated limit of detection by spark source mass spectrographic analyses of 0.01-0.05 ppm. Direct interference by Zn on S precluded any reasonable estimate for this element. Slight interference also occurred for Ba, Cs, Hg, and Pt, but each was not detected at about the 0.2 to 1 ppm level.

By neutron activation analysis[4], the elements As, Ga, Sc, and W were not detected at about the 0.005 ppm level and Au was not detected at about the 0.02 ppb level.

3. The range of values reported is that of the eight individual determinations made by the two analytical methods used. The recommended value is based on considerations of the estimated systematic bias of each of the methods. Six of the eight values reported were in the range from 0.040 to 0.044 ppm.

4. AAS – Atomic Absorption Spectrometry (T. C. Rains)
SPPH – Spectrophotometry (R. W. Burke)
SSMS–ID – Spark-Source Mass Spectrometry – Isotope Dilution (R. Alvarez and P. Paulsen)
NAA – Neutron Activation Analysis (B. A. Thompson and D. A. Becker)

5. Values in parentheses are not certified for accuracy since only one method of analysis was used, but are provided for additional information on the composition.

Washington, D. C. 20234
July 9, 1968

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(over)

Table 2. Certificate SRM 682 (continued)

This standard is intended as research material which should be of interest to the chemist, physicist, and materials engineer. Its very high purity makes it ideal as a starting material for the preparation of phosphors and as a solid-state matrix, where a knowledge of the purity of the material is important. It will also meet the urgent needs of analysts working at trace level concentrations of elements in high-purity zinc. The material should serve for the development of new or improved methods and techniques in extending the sensitivity of detection in the determination of trace constituents by chemical, optical emission and spark source mass spectrochemical, activation, and resistivity methods. The material was prepared by Cominco American, Inc. from a special lot of high-grade electrolytic zinc which was further purified by vacuum distillation, zone-refining, and degasification. Each bar was etched, dried, and sealed in a polyethylene pouch to minimize contamination.

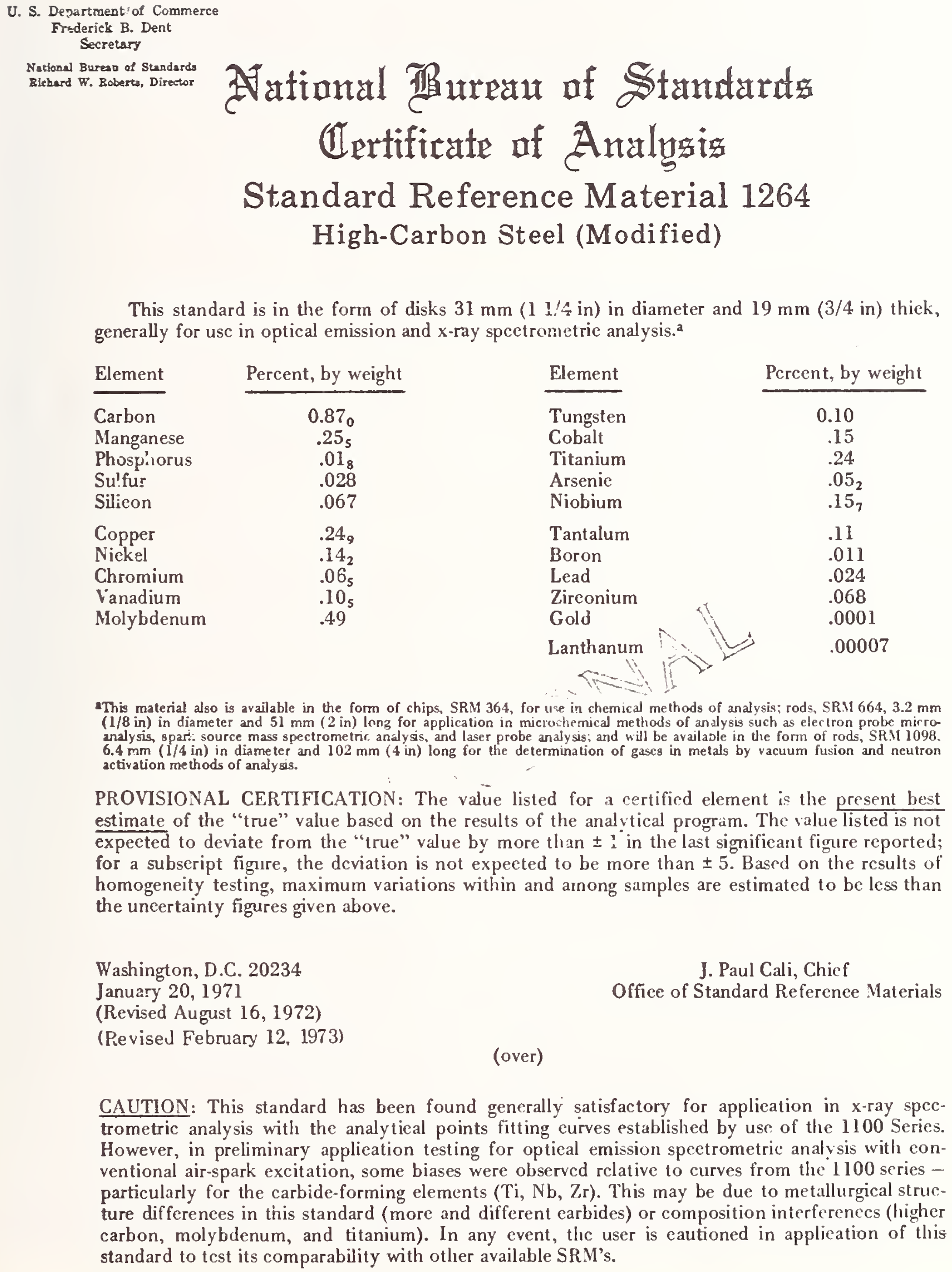
Homogeneity testing was performed by NBS Washington and NBS Boulder with samples selected for the testing carefully chosen to represent the extreme variations that might be expected as a result of the preparation procedures. Although the spark–source mass spectrographic results indicated gross inhomogeneity for lead, thallium, and bismuth, the residual resistivity measurements indicate that this segregation should be minimized provided the sample size is increased to ten grams or more and is representative of the full cross section. Activation results revealed some relatively minor inhomogeneity for sodium and antimony. Residual resistivity ratio (R_{273K}/R_{4K}) results varied from 33,000 to 38,000.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

CAUTION

Before use, it is recommended that possible surface contamination be removed by placing the sample in high-purity dilute nitric acid for about one minute, followed by rinsing in distilled water.

Table 3. Certificate SRM 1264



U. S. Department of Commerce
Frederick B. Dent
Secretary

National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards
Certificate of Analysis
Standard Reference Material 1264
High-Carbon Steel (Modified)

This standard is in the form of disks 31 mm (1 1/4 in) in diameter and 19 mm (3/4 in) thick, generally for use in optical emission and x-ray spectrometric analysis.[a]

Element	Percent, by weight	Element	Percent, by weight
Carbon	0.87$_0$	Tungsten	0.10
Manganese	.25$_5$	Cobalt	.15
Phosphorus	.01$_8$	Titanium	.24
Sulfur	.028	Arsenic	.05$_2$
Silicon	.067	Niobium	.15$_7$
Copper	.24$_9$	Tantalum	.11
Nickel	.14$_2$	Boron	.011
Chromium	.06$_5$	Lead	.024
Vanadium	.10$_5$	Zirconium	.068
Molybdenum	.49	Gold	.0001
		Lanthanum	.00007

[a] This material also is available in the form of chips, SRM 364, for use in chemical methods of analysis; rods, SRM 664, 3.2 mm (1/8 in) in diameter and 51 mm (2 in) long for application in microchemical methods of analysis such as electron probe microanalysis, spark source mass spectrometric analysis, and laser probe analysis; and will be available in the form of rods, SRM 1098, 6.4 mm (1/4 in) in diameter and 102 mm (4 in) long for the determination of gases in metals by vacuum fusion and neutron activation methods of analysis.

PROVISIONAL CERTIFICATION: The value listed for a certified element is the present best estimate of the "true" value based on the results of the analytical program. The value listed is not expected to deviate from the "true" value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than the uncertainty figures given above.

Washington, D.C. 20234
January 20, 1971
(Revised August 16, 1972)
(Revised February 12, 1973)

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

CAUTION: This standard has been found generally satisfactory for application in x-ray spectrometric analysis with the analytical points fitting curves established by use of the 1100 Series. However, in preliminary application testing for optical emission spectrometric analysis with conventional air-spark excitation, some biases were observed relative to curves from the 1100 series — particularly for the carbide-forming elements (Ti, Nb, Zr). This may be due to metallurgical structure differences in this standard (more and different carbides) or composition interferences (higher carbon, molybdenum, and titanium). In any event, the user is cautioned in application of this standard to test its comparability with other available SRM's.

Table 3. Certificate SRM 1264 (continued)

PLANNING, PREPARATION, TESTING, ANALYSIS: This standard is one of five replacements for the original eight 1100 series iron and steel SRM's. Material from the same melt is available in a variety of forms to serve in checking methods of analysis and in calibrating instrumental techniques.

The material for this standard was vacuum melted and cast at the Carpenter Technology Corporation, Reading, Pennsylvania, under a contract with the National Bureau of Standards. The contract was made possible by a grant from the American Iron and Steel Institute.

The ingots were processed by Carpenter Technology Corporation to provide material of the highest possible homogeneity. Following acceptance of the composition based on NBS analyses, selected portions of the ingot material were extensively tested for homogeneity at NBS by D. M. Bouchette, S. D. Rasberry, and J. L. Weber, Jr. Only that material meeting a critical evaluation was processed to the final sizes.

Chemical analyses for certification were made on composite samples representative of the accepted lot of material.

Cooperative analyses for certification were performed in the analytical laboratories of Ford Motor Co., Dearborn, Michigan, G. A. Nahstoll; Kawecki Berylco Industries, Inc., Boyertown, Pennsylvania, F. T. Coyle; and Lukens Steel Co., Coatesville, Pennsylvania, J. H. Morris and J. Scott.

Analyses were performed in the Analytical Chemistry Division of the National Bureau of Standards by the following: J. R. Baldwin, R. K. Bell, R. W. Burke, D. M. Bouchette, B. S. Carpenter, T. E. Gills, G. J. Lutz, L. A. Machlan, E. J. Maienthal, L. T. McClendon, J. McKay, L. J. Moore, T. J. Murphy, P. J. Paulsen, S. D. Rasberry, B. A. Thompson, J. L. Weber, Jr., and S. A. Wicks.

The overall direction and coordination of the technical measurements at NBS leading to the certification were performed under the direction of K. F. J. Heinrich, O. Menis, B. F. Scribner, J. I. Shultz, and J. L. Weber, Jr.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

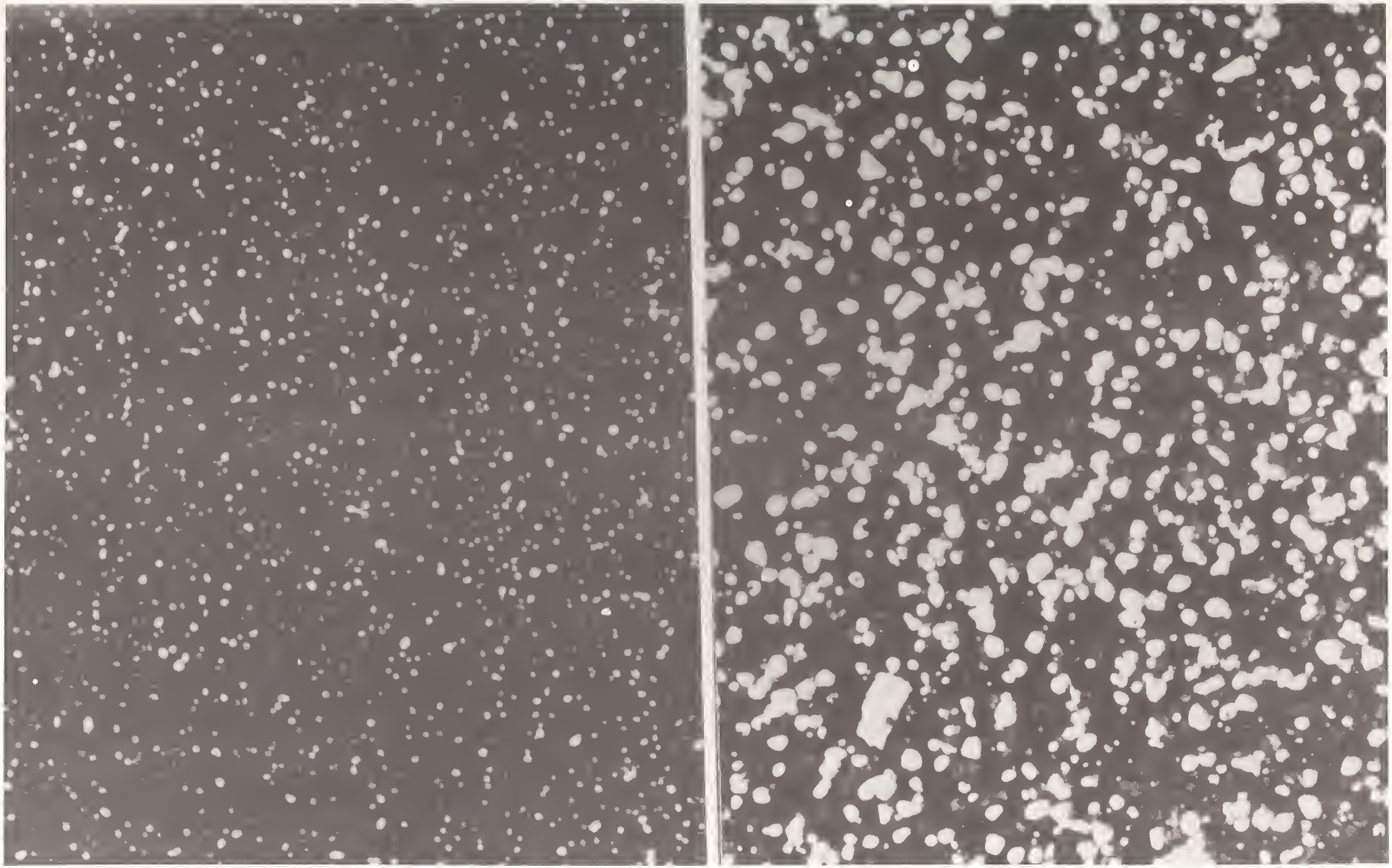
ADDITIONAL INFORMATION ON THE COMPOSITION: Provisional certification is made only for the elements indicated. The five replacements, however, contain a graded series for 40 elements and information on the elements not initially certified may be of importance in the use of the material. Although these are <u>not certified</u>, values are presented in the following table for the remaining elements. (Some may be certified at a later date.)

Value from a single method of analysis:

Element	Percent, by weight
Aluminum (total)	(0.008)
Antimony	(.035)
Bismuth	(.0009)
Silver	(.00002)
Calcium	(<.0001)
Magnesium	(.0001)
Cerium	(.00025)
Neodymium	(.00012)
Praseodymium	(.00003)
Iron (by difference)	(96.7)

Approximate value from heat analysis:

Tin	[0.005]
Selenium	[.0003]
Tellurium	[.0002]
Hafnium	[.005]
Nitrogen	[.003]
Oxygen	[.0017]
Hydrogen	[<.0005]
Germanium	[.003]
Zinc	[.001]



1263 1264

Figure 1. Transverse sections etched with Beraha's etchant to show carbide content and distribution (∿ X 1600)

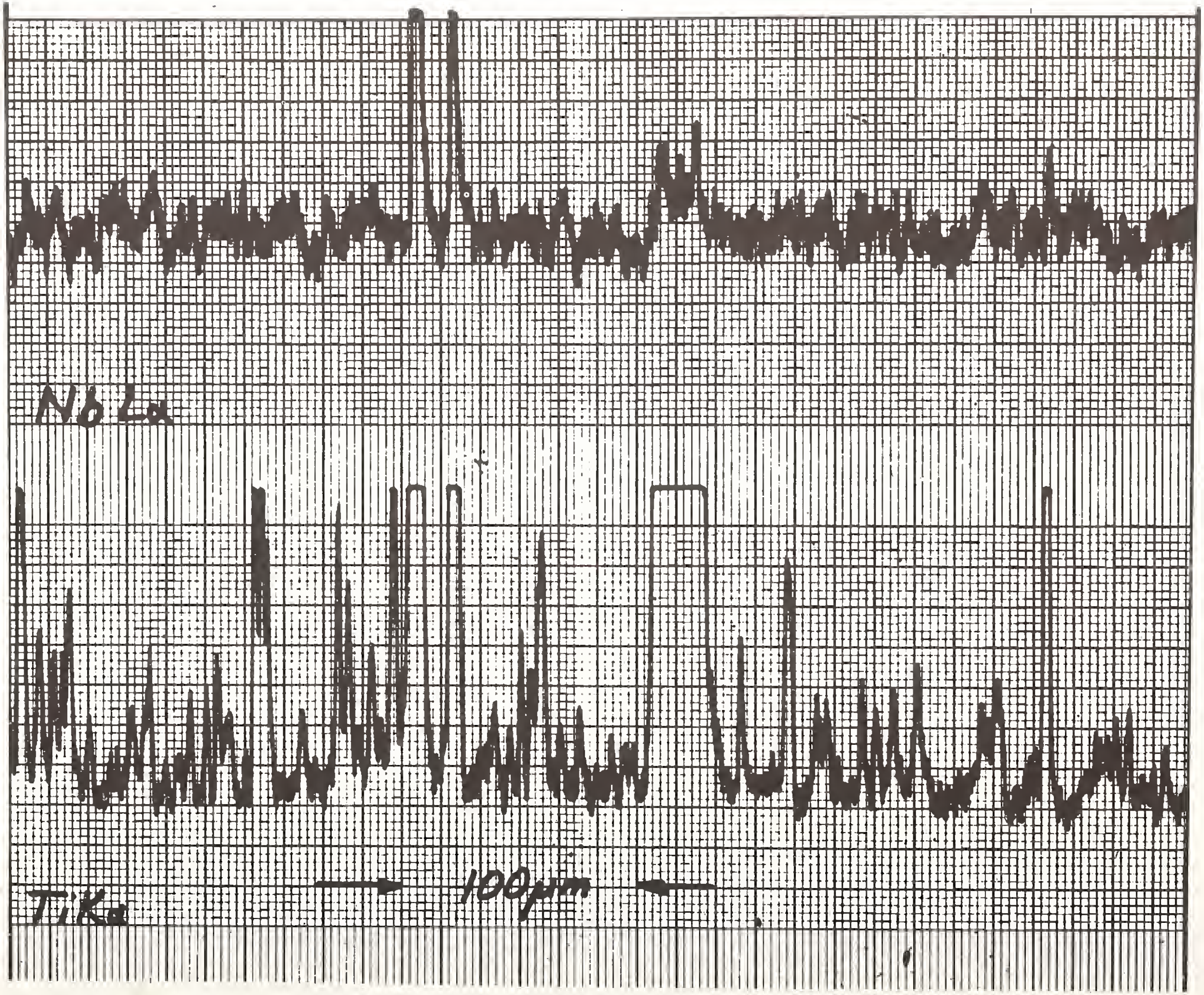


Figure 2. Transverse Microprobe Scan SRM 1264, NB & Ti

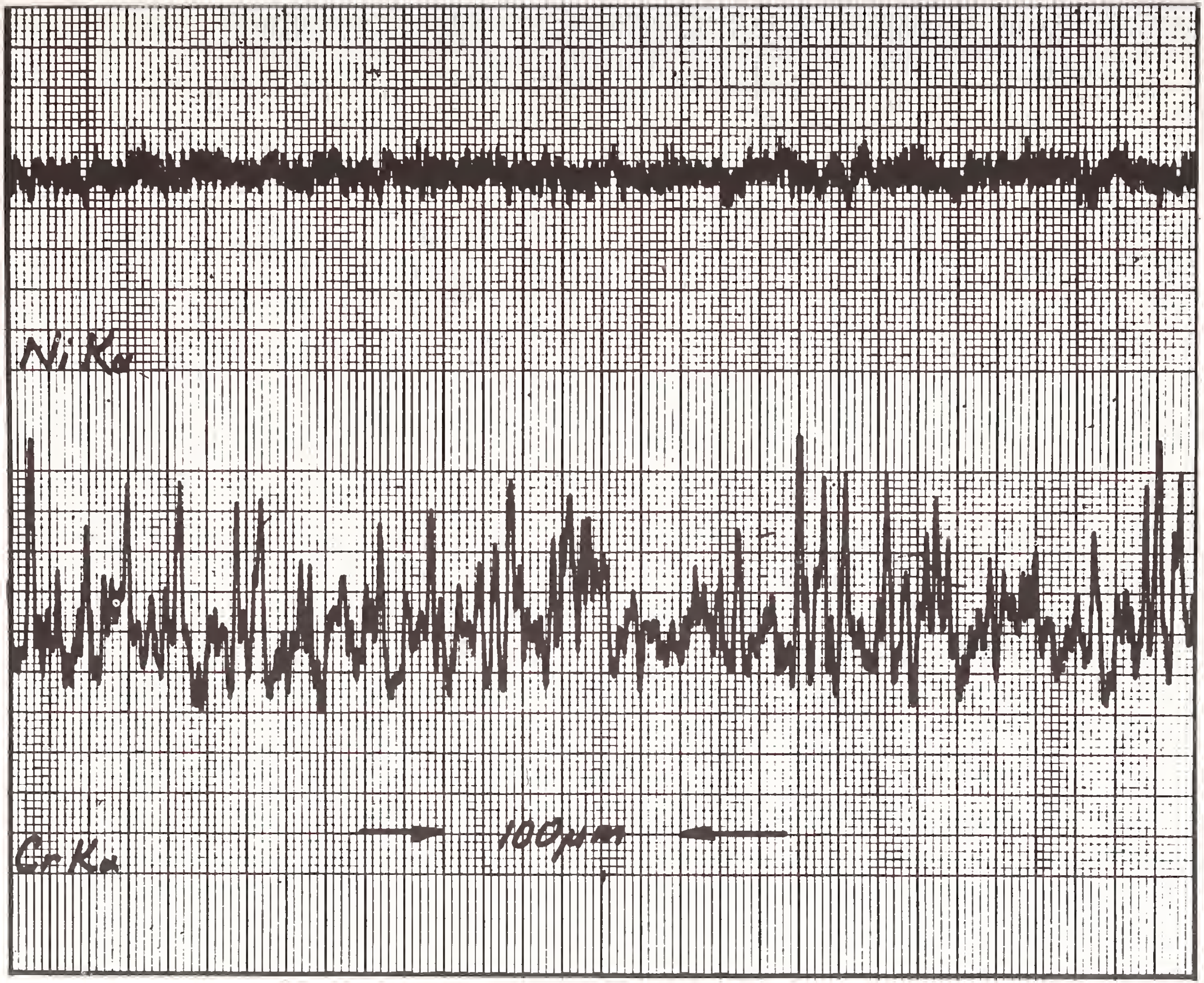


Figure 3. Transverse Microprobe Scan SRM 1264, Ni & Cr

IX. NBS-Industry Cooperation

J. P. Cali

For many years there has been a very strong, mutual interaction between NBS on the one side and ASTM and the metals industry on the other. To say that there are no problems in this relationship would be to fly in the fact of current realities. In brief, simply stated, we must face the problem that the demands - the legitimate demands - of the metals industry, speaking primarily through ASTM, cannot be fully met by NBS. What are some possibilities by which these demands for greater participation and a greater output of SRM's from NBS might be met?

First, you should all be aware of the Research Associate program at NBS. Let us assume that the ferrous industry has need for some new alloy SRM's and that NBS cannot respond quickly enough to fill these needs. It is possible for the industry to supply to NBS one or more Research Associates who would work here at Gaithersburg, say, under the sponsorship of either individual companies or trade associations such as the American Iron and Steel Institute (AISI) on a full time basis for a period of one, two, or more years. Under the terms of a formal agreement, the sponsor would assume financial support for the Research Associate, and NBS would supply supporting facilities, equipment, services, etc., including technical guidance and supervision. The Research Associate would work on a full-time basis on the characterization of the proposed new SRM's thus helping to bring into being needed new SRM's. Recently, the lead battery producers association came to NBS to ask if we could begin work on badly needed SRM's for that industry. Because of commitments in areas of health, environmental protection primarily, we had to say that our resources were spread too thin and that we could not start a new program. We mentioned the possibility of a Reserach Associate and that route is now being investigated as one possible answer to this problem. It is quite amazing what one well-qualified scientist can do given the time and support to work on one distinct problem.

The second possibility open to industry to have its work pressed forward is to support specific technical areas through the use of dollar and/or material grants to NBS. NBS may legally accept such grants and has done so in the past.

In order for industry to make an assessment of how your R&D resources are being allocated, let me give you a few figures. The current, direct input to the SRM program is about $\$2.2 \times 10^6$. Thus, the SRM program is currently running at two percent of the total NBS effort. Tomorrow, you will hear of the new SRM program being mounted within the European Economic Community (EEC). Its first year budget is the same as ours! Furthermore, it is scheduled to grow at a faster rate than that of the U.S. Unfortunately, the NBS has had funds for expansion of the program impounded for fiscal year 1973 and this has slowed our progress. We have not been successful in having our program considered for FY 1974, but we do have hopes for 1975. These certainly are matters you should be aware of, since it is your program and your tax dollars and SRM purchase dollars that support the program.

In terms of the total R&D effort of the U.S., which stands between \$15 and 18×10^9 this year, I think you may question whether the SRM effort in this country is in proper balance, given the importance of SRM's to industry.

Since this situation is not likely to change dramatically or quickly, is there something we can do right now to help ameliorate the situation to bring about a greater supply of urgently needed SRM's for industry? NBS as a whole, including the OSRM, has seen the need to divert technical resources to other areas of national concern, like health and the environment, many at the expense of industrial concern areas. What I am going to propose for your consideration must be considered highly speculative. It is a plan that must be thought out carefully with due concern for any legal implications, and also with assurance that the "third party" independence, which has always been associated with NBS, be maintained. What I am proposing for your consideration and deliberation may be called a "Joint NBS-ASTM Measurement and Certification Procedure for SRM's for Industry." This proposed plan will depend upon a concentrated and enlarged effort by industry, working within and through the ASTM structure. The plan involves no elaborate new infrastructure except the establishment of "liaison committees" for each major industrial concern area now active within the ASTM. The liaison committee composed of ASTM representatives and one or more NBS staff members would meet on a regular basis to perform the following functions:

1. Establish needs and priorities for additional SRM's not currently available.
2. Establish technical requirements for the needed SRM's (material requirements, properties to be measured, accuracy required, etc.).
3. Recruit industrial supplies of candidate materials; establish qualifications and recruit cooperation of measurement laboratories.
4. Assist NBS in development of a technical plan of work (schedules, experimental and statistical design, etc.) and its implementation.

Having done these things (assuming that a candidate material is actually forthcoming and that a sufficient number of qualified laboratories agree to work on its measurement), then after NBS has assured material acceptance and homogeneity (using cooperating labs if necessary), the actual measurement network goes into operation to produce the measurement data.

The data is gathered by NBS and evaluated. If discrepancies are found these are resolved using NBS technical resources, either alone or in collaboration with highly-qualified reference laboratories.

The final, reconciled data is then assessed by NBS and appropriate members of the Liaison Committee and a certificate jointly prepared. The SRM is then issued by NBS through the usual distribution channels. [Editor's Note: Since the Symposium, steps have been initiated that are aimed toward having an ASTM-sponsored Research Associate work at NBS to refine and help implement the plan outlined above.]

I might add parenthetically that a precedent for joint certification has already been set. Two years ago the NBS issued a set of DTA SRM's that were prepared, measured, and then certified jointly by NBS and the International Confederation on Thermal Analysis.

Another example, closer to the hearts of this panel and dating even further back (the "first" for NBS) is the blast furance and white iron SRM's (1143-44 and 1147-1149). Had this proposed policy been in formal existence at that time (1969), the current Certificate of Analysis would have the phrase, "In cooperation with the Ductile Iron Society" prominently displayed in the heading.

Further, it is of signal interest that the homogeneity testing of these SRM's was performed at the Research Laboratories of the General Motors Corporation by A. C. Ottolini under the direction of M. D. Cooper, one of our co-chairmen of this panel; and that the original analyses for certification were performed by members of the Ductile Iron Society under the direction and coordination of W. R. Kennedy, ACIPCO, our other co-chairman of this panel.

Let me add a little story to give insight as to how some individuals in industry view the SRM program. When Bill Kennedy asked Ford Bryan of the Ford Motor Company to cooperate in the analytical program for certification of these blast furnace and white iron SRM's, Ford replied, "We are more than willing (on strictly a non-redemption basis) to analyze the samples. We have been practicing for about 40 years for this opportunity!"

I have not thought out the legal implications of such a process (as outlined above) although it seems to me that since ASTM provides, indeed only operates, on the consensus principle where producer, user, and general public interests are all protected, that the legal questions may, in fact, be relatively minor.

In closing, I would reiterate once again that this proposal is highly speculative. It needs discussion both within the ASTM and NBS, but I can assure you that NBS will do all it can to see if it can happen.

X. Discussion

After the presentation of the formal viewpoints of the panel members, as well as that of Mr. J. Paul Cali, the discussion period began in a light vein with the pretense of a conference telephone call in which all the audience was asked to participate. The reason for beginning in this way was to show the participants how easy it really is to get answers to their SRM problems from NBS with a simple phone call. Examples were given of specific aid they are most happy to perform when asked to help; e.g., supplying literature <u>or even sometimes</u> producing a standard needed for evaluating a method for precision and accuracy.

The first telephone call went to R. E. Michaelis asking him to expand on the term "benchmark" as related to its use with SRM's.
<u>R. E. Michaelis</u>: We attempted to seek a term for what we will call a crucial reference point material -- one that has been fully characterized from the standpoint of homogeneity and from the standpoint of being as near to the "true" value as humanly possible. We like to refer to such a reference point material as the essential "benchmark" to which industry can relate. An anchor point is perhaps an equivalent term for it; i.e., the anchor point or "benchmark" of a measurement system. With this term we are incorporating the idea conveyed by Dr. Huntoon in his paper; that of establishing the "benchmark" material so well that other materials can be effectively and directly related to it.

We realize the dictionary will give other meanings, and its use by others such as the Geological Survey, Standard Reference Data, and lawyers does not give us exclusive use of this term. Nevertheless for this class of materials, the term "benchmark" appears most appropriate.

With the many hundreds of thousands of different kinds of materials that are needed to control industrial processes, the probability of any individual group producing all of them is essentially nil, no matter how large the group. At NBS all we can hope to provide is the essential benchmarks to which industry can relate. At present, we consider the following as benchmark SRM's: For a metal matrix, the "1200 Series," irons and steels that contain a graded series for some 40 elements; for an inorganic matrix, the four trace element glasses containing a graded series for some 60 elements; and for an organic matrix, both the orchard leaves and bovine liver SRM's. Additional benchmark SRM's are underway in each of the three matrices.

Actually, the interchangeability of the three matrix systems indeed is limited only to the chemical talents one has to interrelate them. It was implied a year ago at the Electrochemical Society meeting in Florida that with present day sophistication in chemical manipulation of a particular material, one might be able to eliminate the matrix, per se, by means of dissolutions, separations, extractions, preconcentrations, etc. The final critical requirement is that the chemical manipulations on the sample for analysis and on the SRM's render a match between the two with respect to the variables that could influence the measurement system. This is not to suggest that we are recommending the bovine liver SRM for the determination of trace elements in high temperature alloys (the super alloys, which have been brought up numerous times already) -- the roadblocks would be more than a little horrendous -- but believe me, it is not a total impossibility. There is an interdependence of these three different matrices - one may be related to another to serve the end purpose. Since all standards cannot be prepared, these benchmarks can serve to guide industry with accurate numbers that they can ascribe to their own system.

Kennedy: The word "priority" has also been used when referred to SRM's needed. Perhaps Mr. Cali can expand on this term as it relates to SRM's.

J. Paul Cali: Two things must be considered here; justification first, then priority. Justification takes in such things as: what properties should be certified, what the matrix should be, what the market is, and so forth. These questions must be answered and documented to establish the need for a SRM. Now, since the needs always exceed the resources available, there has to be a process at NBS whereby we can establish the priority of these needs. Questions to be answered here are: are the technical resources available, is there technical interest in solving the problem, what are the overall costs, what is the schedule, is a national concern area involved, will it be done for an industry that has already accepted the concept of standardization though the processes we have been discussing today? These documented lists are carefully evaluated and we end up with an order of priority-ordering that covers the entire spectrum of the SRM program; not only metals, but health, environment, etc. With this listing of projects, and a list of dollars available, the program for the ensuing year is developed.

Kennedy: There is one instrument manufacturer in the audience who can give us a different viewpoint on SRM's we may not all have considered.

Monte Dawkins (Baird Atomic): The SRM's are very important to the instrument manufacturer. One point could be entirely missed because the people here all represent either research laboratories or the better laboratories of manufacturers. Most people here have some determined resources and technology that is not available to the small manufacturer. Frequently we sell an instrument to a plant whose personnel have never seen the inside of a laboratory, and perhaps have never experienced wet chemistry. Small companies making aluminum extrusions and materials like this, may have no analytical background at all. It is very important that they have calibration materials on which to base their product and their analytical procedures. These materials cannot always be NBS-SRM's because they are not available, although they would prefer them if they were. In the case of aluminum, Alcoa standards are usually chosen. For steels, it can be NBS or the Bureau of Analysed Samples, or Brammer Standards. These small foundries (and there are thousands of them) are really suffering. They have no ability to make their own in-house standards and wouldn't know how if they could. Mostly they start collecting samples and then they send them out to independent laboratories to get some kind of analysis on them and perhaps achieve some kind of standards of their own they can use in their day-to-day operations. Instruments have come a long way in the last few years, especially the electronics with all kinds of diagnostic techniques to tell whether an instrument is working properly or not.

There are really two things that affect small companies products. One is the standardization on which to base all its analyses and the other is the ability to make samples and present them to the instrument in a repetitive manner. Many individuals tend to disregard the second one, but without the SRM's they are "dead." So, we have to rely very heavily on recommending to the small manufacturer where to acquire these standards. In many cases we buy the standards and give them to a manufacturer (the instrument having been calibrated prior to shipment with the standards we buy). In the course of a year we may buy several sets of standards from Brammer, NBS, and the Bureau of Analysed Samples. We have to rely on them to give us the calibration materials to help these small manufacturers get started down the path of correct analyses.

Kennedy: Does the availability of SRM's sometimes influence instrument design?

Dawkins: Whatever it is that is available, we have to design a holder to hold it!

Peter Ridsdale (Bureau of Analysed Samples): If I might change the subject just a little bit, I'd like to say as a representative of an organization which prepares standard reference materials, that we depend entirely on the cooperation of laboratories, government departments, research organizations, and laboratories of industry. We would support very much the pleas that were made by speakers this morning for more people, the right kind of people, to cooperate in this work. We rely on them for both the selection of materials and in some cases preliminary examination of the materials, and of course for the analysis of the prepared samples. We would point out, however, and I'm sure it's obvious to you, but perhaps not to everyone, there are many side advantages in this work. I think every laboratory learns something from participation in cooperative work. We're often told that chief analysts find that it is stimulating to their personnel to participate in this work to compare their values with those obtained in other laboratories with similar interests. For that reason, we find that many whom we might call "group advisors" welcome this work. In many cases, also, I think it leads to an elimination of laboratory bias, and occasionally it reveals errors a laboratory has that it didn't know about. So I would just like to help promote this, although I'm sure here today, one is speaking to the coverted!

I was very interested in Mr. Kennedy's method of checking the homogeneity of standard samples and I'm glad one of our samples was included in his list; we didn't come out too badly! Also, it is seen here that a number of our samples have been used by the ASTM committees in evaluating methods. It's always interesting to hear how some one else does their job, but time doesn't permit one to go into the details of the British methods nor I'm sure those of other contacts just as well known to the people at NBS.

I would also like to support the suggestion for some form of international classification of standard reference materials. I think this is a highly desirable state of affairs. It has been stated in this room that there is only one source of primary standards. However, I think we from across the Atlantic think you're probably only talking about this side of the Atlantic! I think tomorrow morning when we hear something from Dr. Lauer of the work that is going on in Europe, may of your friends across the Atlantic would think that their samples could justify thier being classified as primary standards. I think there could be some international understanding on this. Let's hope that this is something which might come out of this meeting.

I would also like to support the suggestion that has been made for some form of international harmonization on the program for the preparation of standard reference materials within the metals field. We are all agreed that there is a much greater demand than the means for meeting these demands and hence a means is necessary to prevent the duplication of effort when not necessary. As you will hear tomorrow, this has been done within the European Economic Community (EEC) and I'm sure an extension of this across the Atlantic and ultimately world-wide is possible, although I was glad to hear Paul Cali say that the actual international standardization of samples is probably a long way off.

I would finally just like to thank the Bureau for all the help and support that we have had in our efforts, for over fifty years now; and to hear that in the USA you just have to ring a certain number to get the right man is a help! It costs a little more to ring across the Atlantic, but certainly when we've contacted NBS, we've always had a lot of help and advice and we are very grateful for that and the opportunity to participate in this Symposium.

Kennedy: Thank you very much Mr. Ridsdale for your comments. We appreciate it very much. I think Bob Michaelis has some comments about "primary" standards.

Michaelis: Yes, I would like to offer this comment to Peter, if I may. NBS has not classified standards available from other sources or countries as primary, secondary, or anything of the sort. Such a classification, I believe, originated in the "Report on Standard Samples for Spectrographic Analysis" by Wallace R. Brode and Bourdon F. Scribner in 1944, originally prepared under the sponsorship of the War Metallurgical Committee, with the revised report published by the American Society for Testing and Materials. This nomenclature has been consistent and has appeared in all subsequent publications, the last one appearing in 1963. These terms of classifying standards as primary, secondary, etc., offered an understandable system seemingly widely accepted. As the number of sources for standards increased over the years and included many of those from foreign countries, a more subjective classification was made based on the author's interpretation; in the latest compilation (1963), the spectrochemical standards available from the Bureau of Analysed Samples Ltd. were shown as being "primary."

So, in the context of the original definition, "a standard is classified as primary when, 'The composition is certified by a recognized standardizing agency or group, generally as the weighted result of the work of two or more independent laboratories, and the reliability and limitations of its application for the intended analytical procedures have been determined.'" Primary standards now are probably available from a number of different foreign sources.

Within this country, NBS is often referred to as the primary source of these materials for this country.

M. D. Cooper: May I ask Mr. Cali if perhaps there is a plan to include in the proceedings of this meeting a listing of the SRM's that are available in the other countries, at least those who have participated in this Symposium?

J. Paul Cali: I think not because the proceedings will be quite long, if we are going to include all the papers that have been presented and many that will be presented in the panels. For example, the papers that were given in this panel should be published verbatim (with a little polish for publication): were they not, this would be a serious oversight on everyone's part. I'm not concerned that the proceedings will probably run 600 to 800 pages, and I really hope we publish everything. Another reason, Coop, is that within the next few months, the European Economic Community will make available the results of a world-wide survey of all the SRM sources, their addresses, availability, ordering information, etc. I'm sure that Dr. Karl Lauer will have more information on this tomorrow, including whether there will be a slight charge or not. We expect to publicize the availability of this document in the proceedings.

C. Manning Davis: Commenting on standards available from England and from NBS, I find myself constantly referring people to the availability of one standard that, primary or otherwise, is only available from Mr. Ridsdale's laboratory. It is a copper-nickel alloy that I don't seem to find in the NBS folder at all. Almost every month we tell people, "You just have to get that from the Bureau of Analysed Samples." So there is an area where they do not overlap and I think that is a good sign.

Kennedy: There are a few slag standards that are that way, too!

Davis: And, possibly, some ductile cast irons!

Kennedy: Bob Brammer is another standards manufacturer in the audience who may wish to comment.

Bob Brammer (Brammer Standards Co.): We're a small company. We do have a list of cooperating analysts throughout the steel industry. They help us with the certification of our material. We do depend on NBS and ASTM. We use NBS standards to trace to and E-3 methods for our chemical analysis, and E-2 methods to check our material homogeneity. So we are dependent on these two programs and we want to see them go on full force. One question I did have was about the comment Sarah Degenkolb had about grading or classifying standards as A, B, C, or D. Is there a subcommittee working on such classifications now?

Sarah Degenkolb: It is going to come under Subcommittee .04 and will be discussed in March 1974 in Cleveland in more detail. We will have to find out what the people want and what they feel is necessary. When we come to that final hurdle, we will just have to take it. If it is like everything else, it will be, "Let's put it off as long as we can!" Speaking about that, there were two gentlemen here from India who wanted to know if they could help in our program either chemically or spectrochemically. I told them we would welcome any foreign country that wanted to help in any of the E-2 or E-3 programs; and that goes for any of the rest in the audience. We will welcome your help.

Kennedy: These same two gentlemen from India also inquired if there were any published instructions for the preparation of standards available anywhere. I don't believe Sarah told them, but for their information and yours in the audience, there are two NBS 260 publications available; one on the preparation of the cast irons, and one on the preparation of the copper standards. These have very extensive descriptions of the preparation of these alloys. I'm not aware of any others, but there may be some in preparation. Incidentally, the NBS 260 series of publications is quite helpful to ASTM E-2 and E-3. Two additional publications in this series deal with wet chemical methods used in certification of these respective materials.

J. I. Shultz: I'd just like to make a comment. I see as far as I know, there are representatives from but two steel companies in the audience. We usually get many questions and phone calls from these people regarding trace elements in high temperature alloys. I know they are concerned with the current inability to come up with what they need. I wonder if they would like to make any comments from the floor regarding their needs in this area?

The discussion which ensued covered a considerable length of time and involved M. D. Cooper, Al Sloan, Manning Davis, Sarah Degenkolb, Larry Zickefoose, Paul Cali and others unrecognizable from the taped session. As is known, there is a squabble going on currently between manufacturers and suppliers of jet engine parts involving tramp elements in the ppm and fractional ppm ranges. To those participating in the conversations, it appears that rather arbitrary and highly controversial specifications have been set; also the specifications seem to exclude all but one "chosen" method as a means of arbitration. The specification involves all parts of the engine that move. Two specifications are being talked about, one that involves only five elements and the other some 55 elements. It appears that some standards are on the way, by the name of Tracealloy. These three common matrix (nickel-base) materials will contain ppm levels of the needed elements. Of course, the standards are still some time off, but at least they are on the way. From the heated discussions this is indeed a priority of first order that not only involves an expensive material, but also may involve expensive litigation in case of failure of such parts.

Manning Davis made a final comment regarding the other helpful programs that NBS has going that are always a help to E-2 and E-3. Those mentioned were the published manuals that NBS has for time-shared computer programs and also helpful documents on basic programming for many spectrographic and chemical equations in use today.

GLASS AND CERAMICS

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I. New Chemical Analysis SRM's for Soda-Lime Glass

W. P. Close

At the request of ASTM C-14, NBS has initiated a program to provide new soda-lime glass composition standards and to replace old standards out-of-stock. A few years ago the situation arose where the industry had no glass chemical composition standards. The old SRM's were very much out-of-date, one being made before 1930 and the other in the 1930's. They no longer related to present soda-lime glass composition. Furthermore, they were powdered material and unsuitable for use as samples for x-ray fluorescence analysis (XRF). Since 1965, XRF has become the technique of choice and practice in composition control of glass manufacture.

Prior to asking NBS for new SRM's, ASTM C-14 collected five typical soda-lime glasses including flat and bottle glass. These glasses were prepared as flat squares, about 2 x 2 in, or as discs, 1-1/2 in dia., melted from cullet. They were analyzed by a round-robin cooperative effort and established as useful for XRF standards. However, what was drastically wrong with our program was that only the participating laboratories, about ten in all, received the sample material; there was no resupply. But we did learn we had the capability to develop standards for reference.

When we went to the Bureau concerning our problem, they agreed to certify new standards if C-14 acquired the material and obtained a consensus analysis. About two years ago, we acquired a sampling of a flat glass production, selected by the people making the glass as homogeneous and free of flaws. It was cut into 2 in squares, so as to be suitable as XRF standards. The lot was divided into sublots and the Bureau checked it for homogeneity by XRF. No attempt was made to take real numbers, rather repetitive fluorescence readings were made on random samples from the sublots. It was a good statistical analysis of homogeneity of the lot. The Bureau passed it as acceptable. A round-robin analysis was conducted by C-14 to establish its composition. The analysis went rather nicely. For data that did not come up to results within the expected ranges, the analyses were repeated so that all values were eventually resolved.

The Bureau accepted this data and issued the material as Soda-Lime Glass SRM 620. Recently a bottle glass composition has been remelted from cullet and extruded into rods 36 x 1-1/2 in. The Bureau has examined this material by XRF as before and passed it as being acceptable. It is now in the process of a round-robin analysis to establish its composition.

These two SRM's certainly will not provide XRF operators with sufficient SRM's to do a lot of analysis for the simple reason that a wide variety and number of SRM's are required. However, they will serve mainly as a check on the operation of the instrument. XRF operation requires some calculation program to provide matrix absorption corrections. These programs vary from operator to operator, but when they work with rather limited compositional ranges, almost any program will work. When compositional ranges become large, more complicated equations are required to correct for matrix absorptions and to calculate the true percentages of the glass composition. So, most operators work in rather limited ranges with a specific program, and use somewhat different corrections for glasses in different ranges.

For example, magnesium has an effect on determining silica by XRF and of course the effect is not linear, it's curved. Nor does a single absorption coefficient extend over the normal range of MgO in soda-lime glasses. A given correction may be satisfactory for MgO over the range of 3-5%; below 3% another correction is necessary, and when MgO is a few tenths, the correction is negligible. So while working with XRF, one has to be very selective in the use of SRM's for comparison.

With a thoroughly developed computer program such as the one developed at Corning called CORSET, you can extend the range of composition vs SRM's and calculate XRF data to a better degree of correctness. It is believed that we will need at least two more SRM's for soda-lime glass so that we can have a good composition range in all major components--silica, soda, alumina, calcium, and magnesium oxides, and the minor constituents, iron, potassium, and sulfate; all of which are determined by XRF.

In passing from glass SRM's to ceramics, some of those available are extremely old, like some of the early glasses. They only represent the silica-alimina, or clay-type refractories. There are two SRM's suitable in considering basic refractories of MgO and Cr_2O_3 composition. These are a burned magnesite and a chrome refractory, which is essentially a low-grade chrome ore of about 35% Cr_2O_3. One can use these two materials and simulate a good number of compositions. However, there is no alumina-zironia-silica type SRM at all and there is probably as much of this refractory used by the glass industry for glass melting as other types. Other ceramic materials, also not available now, will probably fall in the category of naturally occurring oxide materials. The need and use of SRM's representing these ceramics will have to await the initiative of producers of these materials.

In time, it is believed we will have a sufficient number of soda-lime SRM's for compositional control and use as XRF standards. In concluding the discussion of glass standards, the series of trace element doped soda-lime SRM's should be mentioned. Prepared by Corning, these glasses contain some 60 trace elements and are present in concentrations of 500, 50, 1, and 0.02 ppm respectively. These SRM's are of interest to geologists and mineralogists as well as people in glass. They are small pieces and rather expensive. They are considered most useful to prove a given procedure or analytical technique once the details have been established.

II. Optical Materials Measurements

C. L. Babcock

This covers experimental work done by graduate students as partial fulfillment toward Master of Science degrees. The effects of glass composition on stress-optical coefficient and elastic moduli is covered in some detail. These studies are parts of related research on refractive index, specific volume, dispersion, and microindentation hardness of glasses.

The glass melts, ranging in size from 600 to 2000 grams, were made in platinum crucibles, homogenized by quenching, and carefully annealed. Measurements of refractive index, n_D, using the central illumination system (Becke line), showed that the compositions were reasonably close to the theoretical ones used in these studies.

A. Relative Stress-Optical Coefficient C

This work is described in a paper by T. R. Nissle and C. L. Babcock in the November 1973 issue of the J. Amer. Ceram. Soc.

The measurement method was similar to that used by R. M. Waxler and Albert Napolitano (J. Res. NBS, 59, 121-125, 1957). However, the loading apparatus was scaled down in size to accomodate a smaller sample size of 1 x 1 x 3 cm. All six sides of the samples were polished. The 1 x 1 ends were parallel to 0.02 cm. and the 1 x 3 sides to 0.002 cm.

Figure 1 shows a schematic of the optical system. A photmultiplier and oscilloscope were used in the present study to furnish objective instrumental readouts of the data. Linearly polarized light of 5461 Angstroms wavelength became elliptically polarized during its passage through the compressed glass sample. The resulting birefringence was determined by measuring the retardation between the ordinary and extraordinary rays.

The retardation can be expressed in terms of the angle through which the plane of polarization is rotated as indicated by the following sequence of equations:

$$r = Ctd \qquad (1)$$

where $\underline{r}$ is retardation (Angstroms); $\underline{C}$ is in Brewsters; $\underline{t}$ is stress (bars); $\underline{d}$ is distance of light path (mm.).

$$r = 1.752\ C\ (\Delta\omega)\ d/bd \qquad (2)$$

where $\underline{\Delta\omega}$ is weight increment (lb.); $\underline{d}$ is thickness of glass (in); $\underline{b}$ is width of glass perpendicular to light path (in).

$$r = 2\ (\Delta y)\ \lambda/360 \qquad (3)$$

where $\underline{2(\Delta y)}$ is twice the rotation of the analyzer in degrees and $\underline{\lambda}$ is the wavelength of light (Ångstroms).

Equating equations (2) and (3) and solving for C gives

$$C = 2\ b\ (\Delta y)\ \lambda/1.752\ (\Delta\omega)\ 360 \qquad (4)$$

In the present study $\underline{\lambda}$ = 5461 and $\underline{\Delta\omega}$ = 5.507 lb. Therefore

$$C = 3.1445\ (\Delta y)\ b \qquad (5)$$

The loads in order of measurement were 35.5, 30.0, 24.5, 19.0, 13.5, and 8.0 lb. The angular rotation of the plane of polarization is a linear function of the applied load. The correct Δy was taken as the least squares estimate of the Δy's corresponding to the load increments. Averaging 6 values recorded for each load to obtain a retardation of y degrees reduced possible errors in the measurements. Coefficient C was measured 5 times for each glass.

The apparatus was calibrated using NBS Glass BaF 588/534 measured by Waxler and Napolitano in 1957. The following data show good agreement with those obtained at NBS. NBS has since made available SRM 708 data on two glasses for this purpose.

NBS Value (at 5893 Å)	C = 2.35 ± 0.026
Present study (at 5461 Å)	C = 2.315 ± 0.004

Table I shows data obtained on Na_2O-Al_2O_3-SiO_2 glasses in the Nepheline primary phase field. It will be noted that the computerized least squares equation represents the measured data with good precision.

Table II shows data on Na_2O-TiO_2-SiO_2 glasses in the $Na_2O.TiO_2.SiO_2$ primary phase field. Here again the computerized equation for C gives a good representation of the measured data.

B. Elastic Moduli of Glasses

This research will be described in a forthcoming paper by R. A. Johnston and C. L. Babcock.

Rectangular shaped samples, of nominal size 12 x 2.5 x 0.3 cm., were used following the recommendation of ASTM Tentative Method C 623 - 69T. The samples were parallel to ± 0.002 cm. and were fine ground using 30 micron Al_2O_3 grit.

Figure 2 shows a schematic of the resonance method used. The driver is shown in position for flexural vibrations in the measurement of Young's modulus E. The detector was placed close to the nodes to minimize further loading of the sample. The driver for torsional vibrations, in shear modulus measurements was placed over a corner at the end of the glass sample and the detector placed near the node at the center of the sample. The average of 100 frequency readings, 10 at each of 10 different detector positions, was taken as the resonance frequency. The resonance frequencies were determined by oscilloscope patterns and readouts on a frequency counter were determined to ± 0.5 Hz. Frequency ranges used in this study were: flexural 900 - 4000 Hz; torsional 3200 - 6500 Hz.

Equations used were those recommended by S. Spinner and W. F. Tefft (Proceedings ASTM, ASTSA, 1961, pp. 1221-1238)

$$G = \rho R (2Lf)^2 \qquad (1)$$

where G = shear modulus, ρ = density, L = length, f = the fundamental torsional frequency and R = a correction factor involving the length, width, and thickness of glass sample.

$$E = 0.94642\ (\rho L^4 F^2/t^2)\ T \qquad (2)$$

where E = Young's modulus, F = the fundamental flexural frequency, t = thickness of sample and T = a correction factor involving glass sample dimensions.

The factor T in equation (2) also involves Poisson's Ratio and determination of E made use of an iterative computer program. Densities of glasses were determined by weighing samples on an analytical balance after they had been washed, cleaned with alcohol, and dried. Two to four separate samples of each glass were measured and averages of the measurements were determined.

The apparatus was calibrated using NBS Standard Reference Material 718 (A7) Polycrystalline Alumina resonance frequency standard. The certified flexural frequency of this SRM and that measured in this study were respectively 2026.47 and 2027.1 Hertz (in Air at 25 °C.) The torsional frequency of the 718 standard, 11200.4 Hz, was outside the range of our equipment.

Tables III and IV show data on E and G in two different primary phase fields. It will be noted that the respective computerized equations give good representation of the measured data on these properties.

Figure 3 is a plot of E vs G for glasses in the two primary phase fields. This plot suggests that glasses in these two phase fields have different ionic substructures. See paper on other properties of this system by C. L. Babcock (J. Amer. Ceram. Soc., 56, 527-530, 1973). Extrapolated G/E relations in metals are shown for comparison. The value for fused silica (primary phase Cristobalite) is also indicated.

Table 1. Stress-Optical Coefficient C

Na_2O-Al_2O_3-SiO_2 Glasses in Nepheline ($Na_2O.Al_2O_3.2SiO_2$) Primary Phase Field

Mole Fraction Compositions	A1	A2	A3	A6	A7
SiO_2	0.620	0.620	0.620	0.650	0.590
Al_2O_3	.100	.150	.190	.125	.125
Na_2O	.280	.230	.190	.225	.285
Measured C (in Brewsters)	2.6233 ±0.0144	2.7944 ±0.0067	2.9495 ±0.0131	2.8057 ±0.0257	2.6510 ±0.0190
Calculated C*	2.6311	2.8070	2.9476	2.7964	2.6417
Difference (M - C*)	-0.0078	-0.0126	+0.0019	+0.0093	+0.0093

$$C^* = 3.25921\ SiO_2 + 4.19831\ Al_2O_3 + 0.68054\ Na_2O$$

Table 2. Stress-Optical Coefficient C

Na_2O-TiO_2 Glasses in E ($Na_2O.TiO_2.SiO_2$) Primary Phase Field

Mole Fraction Compositions	E1	E2	E3	E4
SiO_2	0.500	0.450	0.400	0.550
TiO_2	.200	.250	.300	.200
Na_2O	.300	.300	.300	.250
Measured C (in Brewsters)	2.6848 ±0.0132	2.8993 ±0.0125	2.9898 ±0.0106	2.7376 ±0.0082
Calculated C*	2.7054	2.8580	3.0105	2.7376
Difference (M - C*)	-0.0206	+0.0413	-0.0207	0.0000

$$C^* = 2.28800\ SiO_2 + 5.33880\ TiO_2 + 1.64560\ Na_2O$$

Table 3. Elastic Moduli of Glasses

Na_2O-TiO_2-SiO_2 Glasses in D (Unknown) Primary Phase Field

Mole Fraction Compositions	D1	D2	D3	D4
SiO_2	0.650	0.600	0.600	0.670
TiO_2	.150	.150	.200	.120
Na_2O	.200	.250	.200	.210
Measured E (Dynes/Cm^2)X10^{11}	7.8821 ±0.0186	7.4237 ±0.0112	8.2018 ±0.0200	7.4270 ±0.0056
Calculated E*	7.8170	7.4144	8.2296	7.4890
Difference (M - E*)	+0.0651	+0.0093	-0.0278	-0.0620
Measured G (Dynes/Cm^2)X10^{11}	3.2066 ±0.0081	2.9834 ±0.0068	3.3114 ±0.0066	3.0105 ±0.0022
Calculated G*	3.1731	2.9786	3.3258	3.0425
Difference (M - G*)	+0.0335	+0.0048	-0.0144	-0.0320

$$E^* = 8.18973\ SiO_2 + 16.44176\ TiO_2 + 0.13725\ Na_2O$$

$$G^* = 3.49280\ SiO_2 + 6.54790\ TiO_2 - 0.39724\ Na_2O$$

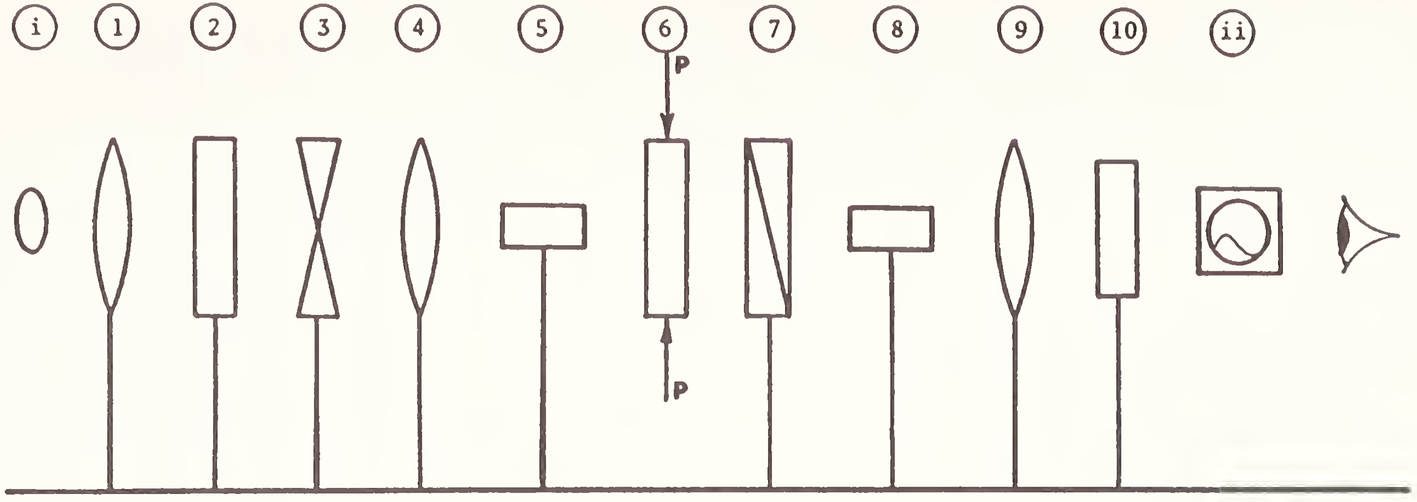
Table 4. Elastic Moduli of Glasses

Na_2O-TiO_2-SiO_2 Glasses in E ($Na_2O.TiO_2.SiO_2$) Primary Phase Field

Mole Fraction Compositions	E1	E2	E3	E4	E5
SiO_2	0.500	0.450	0.400	0.550	0.500
TiO_2	.200	.250	.300	.200	.240
Na_2O	.300	.300	.300	.250	.260
Measured E (Dynes/Cm^2)$X10^{11}$	7.3759 ±0.0017	7.8255 ±0.0449	8.1557 ±0.0000	7.8361 ±0.0414	8.1721 ±0.0337
Calculated E*	7.3778	7.8008	8.2239	7.8796	8.1177
Difference (M - E*)	-0.0019	+0.0247	-0.0682	-0.0435	+0.0544
Measured G (Dynes/Cm^2)$X10^{11}$	2.9294 ±0.0023	3.1067 ±0.0192	3.2178 ±0.0020	3.1360 ±0.0178	3.2618 ±0.0086
Calculated G*	2.9328	3.0921	3.2514	3.1550	3.2380
Difference (M - G*)	-0.0034	+0.0146	-0.0336	-0.0190	+0.0238

$$E^* = 8.69661\ SiO_2 + 17.15713\ TiO_2 - 1.33972\ Na_2O$$

$$G^* = 3.62908\ SiO_2 + 6.81475\ TiO_2 - 0.81560\ Na_2O$$



Schematic of apparatus. ⓘ = light source; ① = lens; ② = filter; ③ = pin hole; ④ = lens; ⑤ = polarizer; ⑥ = glass sample under uniaxial compression; ⑦ = Babinet compensator; ⑧ = polarizer (analyzer); ⑨ = lens; ⑩ = photomultiplier; (ii) = oscilloscope.

Figure 1. Schematic of the optical system used to measure the relative-stress optical coefficient of glasses

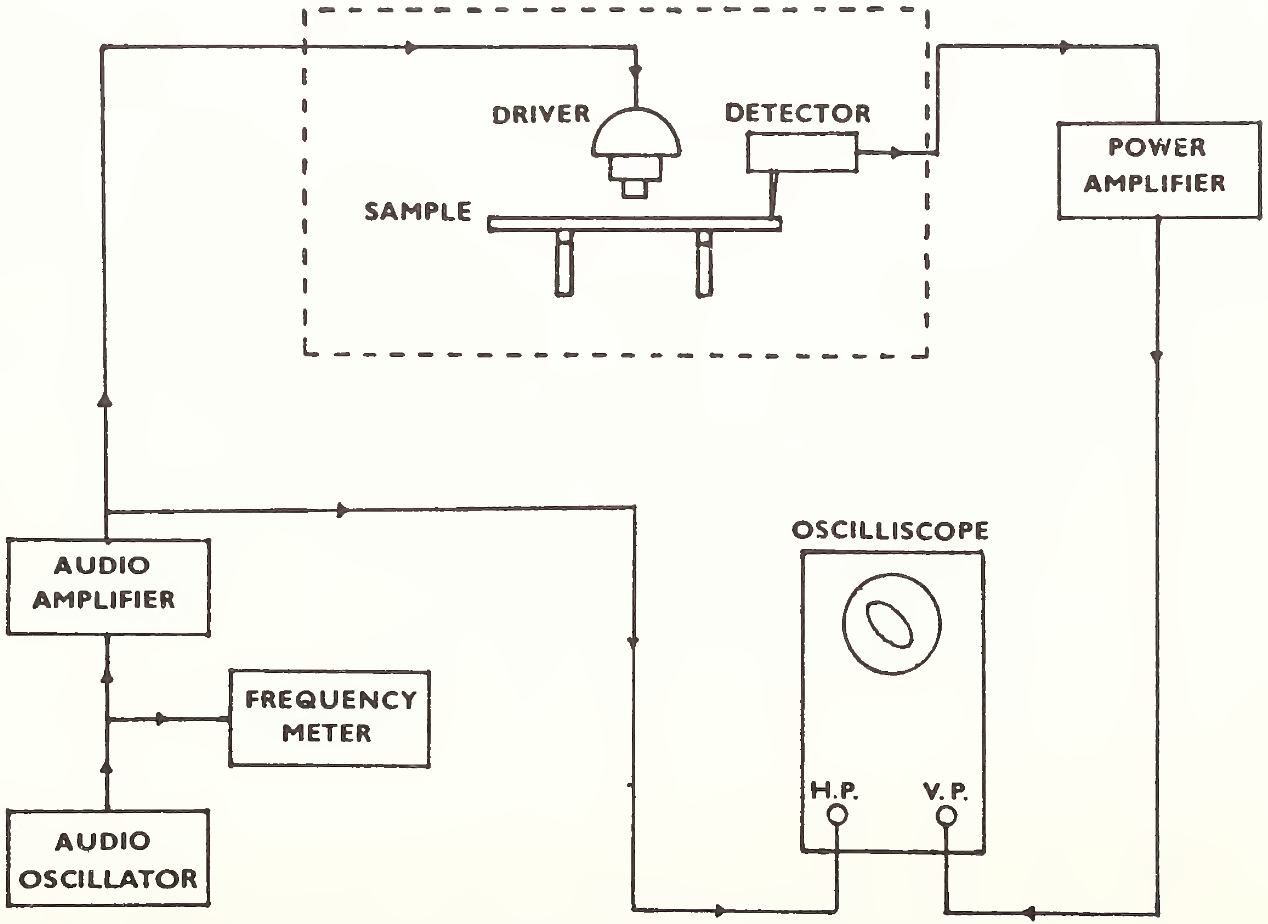


Figure 2. Schematic of the apparatus used to determine elastic modulus of glasses by the resonance method

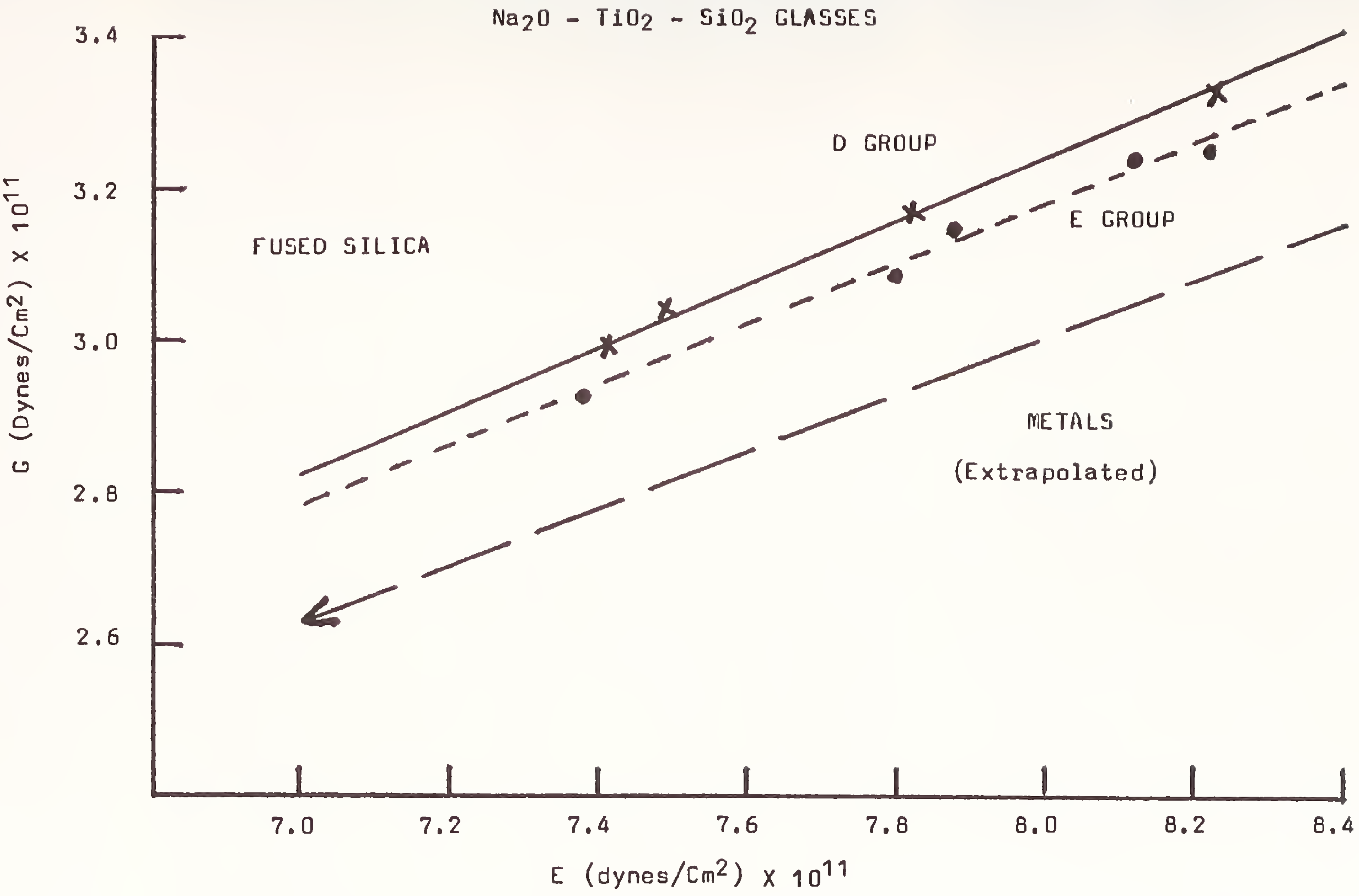


Figure 3. Young's modulus (5) is plotted against shear modulus (6) for glasses in two primary phase fields

III. Utilization of the Glass SRM's by ASTM Subcommittee C-14.04

H. E. Hagy

A. The Annealing and Strain Point Problem

In the late 1950's Subcommittee 4 was in the throes of changing the definitions of the annealing and strain points for glass. Up to this time these reference points were defined by specific viscosity levels. Experience showed that this created much disagreement among laboratories. Part of the problem could be traced to the traditional fiber elongation method used at that time. Uncertainties in thermal expansion and effective length corrections, coupled with problems in producing fibers of uniform cross section along the length, make high accuracy a difficult task in establishing true viscosity.

Recognizing that a firm viscosity value really is of no importance in practical annealing, Subcommittee 4 set forth to generate calibrating glasses with the National Bureau of Standards. The first of these was SRM 710, a soda-lime-silica composition, which was followed by an additional eight glasses, thus creating the present series, 709 through 717. At the same time, ASTM Designation C336, the annealing and strain point measurement procedure, was being rewritten. Definition by viscosity was eliminated, and a redefinition was established by reference to a specific test procedure incorporating the glass SRM's for calibration. This has been a very successful program, and NBS is worthy of much praise for helping Subcommittee 4 solve a difficult problem.

B. The Glass SRM's

Table 1 lists twelve glass SRM's certified for various physical properties. An underscored x signifies the primary certification; an x without underscoring signifies additional certification; an x in partheses indicates that the glass has been used to establish a property value by round-robin testing, but that no certified value has been issued for that property; and empty parentheses indicate tentative plans to establish values for that property.

C. Viscosity Measurements

Through round-robin testing, NBS established softening points, annealing points, and strain points for ten of the glass viscosity SRM's. In addition, complete viscosity curves from 10^2 to 10^{12} poises were determined for three of these glasses: SRM's 710, 711, and 717.

The complete curve data is very useful in certifying or calibrating viscometers, the most common of which is the rotating cylinder type. An example of the data dispersion experienced in the round-robin testing is shown figure 1. This is a graphical analysis of the data for SRM 711, lead-silicate glass. Departures from the "best fit" curve are plotted as a function of temperature for each laboratory. Ordinate units are $\log_{10}$ viscosity in poises. The data for Lab G was eliminated in the "best fit" mean curve calculation. With the exception of Lab G, all data fit within the ± 10% or ±5 °C limits shown.

As a follow-on to the annealing and strain point program, the softening point procedure, ASTM Designation C338, was recently rewritten to call for direct calibration using these same viscosity SRM's. This should bring about better agreement among laboratories making this measurement.

Beam bending was established as a tentative alternate method of test for the determination of annealing and strain points in 1967. This procedure, ASTM Designation C598, was recently rewritten to call for the use of SRM's for calibration. Before advancing this procedure to standard, subcommittee 4 subjected it to a round-robin test. Participating laboratories were sent three glasses. One was identified as SRM 710 and intended for calibration. The other two, unidentified, were to be used for annealing and strain point measurements following calibration. The two unidentified glasses were, in fact, SRM's 711 and 717.

Results of the beam bending round-robin are shown in Table 2. Results were judged satisfactory, since values and scatter compare favorably with the fiber elongation data used for the certificates. This proved C598 worthy of becoming a standard method of test, which it has since become.

D. Knoop Hardness

Subcommittee 4 recently drafted ASTM Designation C730-72T, "Tentative Method of Test for Knoop Indentation Hardness of Glass". At the final stages of preparation of this procedure, a round-robin testing program was carried out using four glass SRM's: 710, 711, 715, and 739. SRM 739 is a fused quartz thermal expansion standard.

The round-robin results have been included in the appendix of C730 for reference. Table 3 is a reproduction of the tabular data as they appear in that document. Although these glasses are not certified for this property, they have proven to be valuable references for people working in this field.

E. Stress-Optical Coefficient

A stress-optical coefficient procedure was recently approved as a tentative. Here, again, it was felt advisable to have some glasses certified as SRM's for this property. Subcommittee 4 convinced NBS to do the measurements and certification, and, accordingly, three glasses were selected--lead-silica, borosilicate, and extra-dense lead--with stress-optical coefficients of 2.857, 3.652, and -1.359 Brewsters, respectively. The first two glasses have the same composition and properties as SRM's 711 and 717 and have been issued as SRM 708. The extra dense lead is SRM 709, which with its high lead oxide content and negative coefficient is certainly an interesting addition to the SRM family.

The new procedure and SRM's will definitely go far in improving accuracy and precision in the measurement of this property.

F. D-C Volume Resistivity

Subcommittee 4 is presently conducting a round-robin testing program for d-c volume resistivity using the procedures as described in ASTM Designation C657-72. This testing program is incomplete. Three laboratories have reported data to date as summarized in Table 4. The agreement of the values reported is very good which reflects very favorably upon the procedure written by Subcommittee 4, and the care taken by the participants in making the measurements. Other laboratories, including NBS plan to submit data in this program. If the agreement in the values remains good, these glasses will appear in the future as SRM's for this property.

G. Density

Subcommittee 4 and NBS have discussed possible needs for glass density standards. Since by basic requirements, the glass SRM's are of high homogeneity, they would also serve well as density standards. A wide range of densities is available. For instance SRM's 710, 711, and 709 offer densities of approximately 2.5, 3.6, and 6.3 gm/cm^3, respectively.

H. Liquidus Temperature

Subcommittee 4 has started to work on standard procedures for the measurement of liquidus temperature for glass. It is too early to report on this, but we intend to do some laboratory work with the present glass SRM's to see if they are suitable. "First looks" will probably be done with 710, the soda-lime-silicate, and 717, a borosilicate.

J. Conclusion

In review, this is where we stand at the present and what we plan to do in the utilization of the glass SRM's. Special mention should be made of the two thermal expansion SRM's--731, Borosilicate glass, and 739, Fused silicon. These are most welcome additions. On the theme of utility, it came to mind that SRM 739 should be considered for an annealing and strain point standard. With these points considerably above 1000 °C, the calibrating range of the viscosity SRM's would be extended significantly. It is urgent that Subcommittee 4 and NBS embark on a round-robin testing program leading towards certification.

In conclusion there are two points that I wish to emphasize.

1. Existing NBS, SRM's can be and should be, if possible, used for other property certification. The more ways these materials are physically and chemically defined, the more useful they become. The only limit to going this route is the supply itself-and this can be a problem.

2. The role of the National Bureau of Standards is a vital one. Credibility of data is firmly established when ASTM procedures are used and backed up by calibration with NBS SRM's. We in Subcommittee 4 and my associates at Corning are grateful for their hard work and cooperative spirit.

Table 1. Present and Future Physical Property Roles Served by the Glass SRM's

	708	709	710	711	712	713	714	715	716	717	731	739
Viscosity & Viscosity Fix-Points	x	x	x	x	x	x	x	x	x	x		
Hardness			(x)	(x)				(x)				(x)
Stress-Optical	x	x										
Resistivity				(x)						(x)		
Expansion											x	x
Density		( )	( )	( )								
Liquidus			( )							( )		

Table 2. Beam Bending Annealing and Strain Point Round-Robin Data

	SRM 711		SRM 717	
	A.P.	St. P	A.P.	St.P
Lab A	432°C	393°C	517°C	476°C
B	431	391	516	470
C	434	397	518	466
D	435	391	514	468
E	433	395	516	472
F	434	395	520	470
Avg.	433	394	517	470
Range	4	6	6	10
Certificate	432	392	516	471
Certificate Range	6	7	2	9

Table 3. Knoop Hardness Data from the Round Robin Testing Program

Laboratory	NBS 710	NBS 711	NBS 715	GE Fused Quartz	NBS 710	NBS 711	NBS 715	GE Fused Quartz
	25-gf Load				50-gf Load			
A	486	411	589	614	497	394	575	559
C	594	450			537	415		
D	479	426	505	541	478	380	538	501
E	521	415	608	620	497	392	574	586
F	498	414	568	643	484	403	567	577
G								
Avg	516	423	567.5	609.5	499	397	563.5	556
Departure, max, percent	15	6	11	11	8	5	5	10
Range, max, percent	22	9	18	17	12	9	7	15
	100-gf Load				200-gf Load			
A	475	387	558	554	468	380	550	523
C	478	387	554	593	468	371	544	530
D	452	368	521	473	433	360	529	474
E	490	396	544	530	488	372	546	510
F	467	381	538	524	457	367	524	502
G	481	388	550	558				
Avg	474	384.5	544	539	463	370	539	508
Departure, max, percent	5	4	4	12	6	3	3	7
Range, max, percent	8	7	7	22	12	5	5	11

• NBS 710—NBS standard soda-lime-silica glass. NBS 711—NBS standard lead-silica glass. NBS 715—NBS standard alkali-free aluminosilicate glass.

• These data were obtained from ASTM round-robin testing.

Table 4. Preliminary Data for the Volume Resistivity Round Robin Testing Program

	$\log_{10}$ dc Resistivity, ohm-cm					
	SRM 711			SRM 717		
	250°C	300°C	350°C	250°C	300°C	350°C
Lab A	10.9	9.7	8.7	10.2	9.2	8.3
B	10.8	9.75	8.9	10.2	9.1	8.2
C	11.05	9.95	9.0	10.2	9.15	8.3

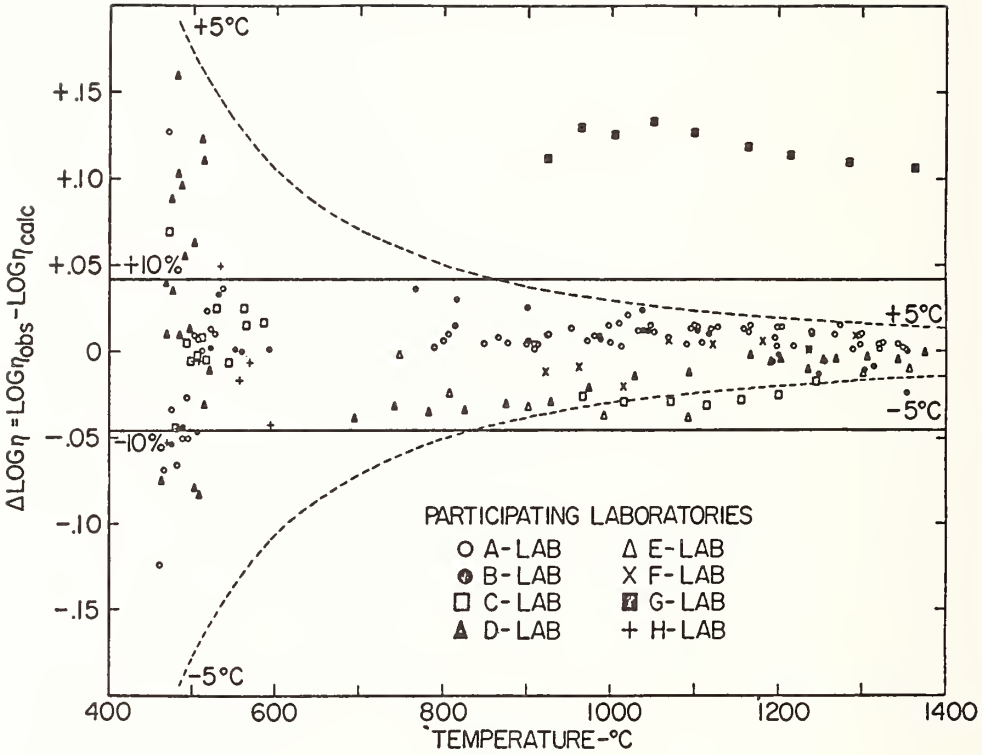


Figure 1. Differences in observed and calculated $\log_{10}$ viscosities of participating laboratories for SRM 711

IV. Ceramics for Electronic Uses

D. B. Briggs

Applications of ceramics for electronic uses can be broken down to three broad categories: 1. Components required to withstand electrical energy; 2. components to pass electrical energy; and 3. components to support electrical energy. The first use is historically traditional; the last two have been largely developed over the past twenty years.

Components to withstand electrical energy are generally classed as insulators. As ceramics they are usually porcelains, steatite, and mullite compositions. Magnesia is used for some high temperature applications. These materials are all high-temperature processed ceramics as opposed to hot-pressed, single crystal or similar type processed materials. Newer versions of ceramics for low-loss high-frequency application include alumina and beryllia ceramics, and possibly spinels, which appear to have excellent low-loss properties.

Properties of interest for insulators include dielectric or break down strength--important for high voltage application--arc resistance, and volume and surface resistivity. Good flash-over voltage resistance is important for high voltage applications, as is the loss index for high-frequency application. Good mechanical strength is essential for power line use, and chemical inertness for uses under corrosive environments. Nuclear inertness is required for nuclear power applications.

Ceramic components required to pass electrical energy may be classed as windows. Of sophisticated application, they are required to pass infra-red energy, light in the visible region, and electrical magnetic energy--in some cases, all three. Materials passing IR energy are generally processed by hot pressing techniques and are quite restricted as to size. Spinel is applicable when all three types of energy must be passed by the window device. Alumina and beryllia are used as microwave windows. Recrystallized glasses (glass ceramics) have been used for nose cones because they possess excellent thermal-shock resistance.

Properties of importance are dielectric constant, and in the IR or visible-light regions, refractive index. Design of the device is important to maintain constancy in transmitting energy. The loss index is important at low frequencies, as are the absorption and scattering coefficients in the visible and IR regions. Isotropy and homogeneity are likewise important properties for transmission of energy. Abrasion resistance is essential for high speed applications such as use in missles. Mechanical strength is important where thermal stresses may develop in use. Thermal shock resistance becomes important in devices subject to high temperature changes--beryllia is excellent here because of its high thermal conductivity, about ten times that of alumina. Metalizability, coating the ceramic with metal, becomes an important consideration in fastening the device to metallic parts; tensile stresses must be avoided. Frequently, these joints or seals must be vacuum tight.

Ceramic components required to support electrical energy are generally classed as "substrates". Substrates are used to support a variety of circuitry, as transistor bases for heat dissipation, in microwave applications, and as wave guides where the ceramic material is coated with a reflecting metal surface. Occasionally, the substrate material may be porcelain or mullite, even carbon resistor cores find application. Generally, though, alumina, beryllia, and spinel are used as a low-loss material in high frequency application. Single crystals also are important substrate materials.

Quality of ceramic materials is measured, as far as possible, by using ASTM Methods for Testing. However, in testing for mechanical properties, it must be kept in mind that ceramic materials are brittle and are characterized by poor tensile strength as compared to ductile materials.

Tensile strength is measured by the Alumina Manufacturer's Association (AMA) Test No. 4. This test loads a test cylindrical specimen in its center perpendicular to its diameter. Load at failure is a measure of tensile strength.

Flexural strength is measured by AMA Test No. 2 which is a 3-point flexural bending test. A biaxially strength test has been developed at NBS, specifically for substrates, which eliminates edge effects from preparation of the specimen for test. The test piece is supported on three balls in a circular configuration, and the load is applied centrally.

Abrasion resistance is tested by a sand blast technique simulating field use conditions. Velocity and hardness of the abrasive are applied to compare to a use environment.

Hardness is measured by a Rockwell Tester, using a diamond point under a 45 kilogram load. This is a rather harsh test, crushing large areas of the test specimen. A "microhardness" test where the load applied is but 500-1000 grams supplies more useful information. By bridging crystals in the structure, the specimen can be examined for grain boundaries, porosity, and secondary phases. Metallic standards are used for calibration.

ASTM Method C408, Thermal Conductivity of Whiteware Ceramics, is used to evaluate this property. Armco iron and oxygen free copper are used as calibrating standards.

Thermal expansion is determined using a quartz dialotometer or an interferometer. Metals and single crystal sapphire are used as standards.

Neither standard methods nor standard materials are available for determining thermal shock resistance. Simulated use conditions are therefore resorted to for evaluation.

The optical surface and light-scattering parameters of materials are evaluated using integrating sphere spectrophotometers. Surface characteristics involves measuring the surface finish with a profile tracing instrument, and examination with the scanning electron microscope for grain size. Specimens are compared to standards. Reflectance is measured by laser beam techniques. Measured surface qualities are related back to the performance of the device in use. Since no standard reference maerial for surface finish and properties of ceramics are available, standards in use are set up on a vendor-user basis.

Dimensional tolerances of many ceramic devices are very critical. Quality standards are therefore used in checking the accuracy of measuring instruments. Helium leak tests and bubble tests are also applied to final ceramic devices. Standards are available for leak testing. Bubble tests are empirical; the material is crushed under a liquid and observed for escaping bubbles.

Metalizability of ceramics is an important property and is tested by ASTM Method F19, "Tension and Vacuum Testing of Metalized Ceramic Seals". The test involves coating a ceramic with metal, making a joint, and testing the joint for vacuum tightness and tensile strength.

Electrical properties of ceramics are determined by ASTM standard test methods or under simulated field use conditions.

Volume and surface resistivity is measured using ASTM methods D1829, Test for Electrical Resistance of Ceramic Materials at Elevated Temperatures, and D257, D-C Resistance or Conductance of Insulating Materials. Tests at elevated temperatures are made at 1400-1600°F.

Arc resistance is measured by ASTM method D2132, Dust-and-Fog Tracking and Erosion Resistance of Electrical Insulating Materials, a method pertinent to ceramic insulators. ASTM method D495, High Voltage, Low-Current, Dry Arc Resistance of Solid Electrical Insulation, is pertinent to materials or devices which may decompose under arc. Corona resistance is determined by ASTM method D2275, Voltage Endurance Under Corona Attack of Solid Electrical Insulating Materials, and involves measurement of corona resistance in the presence of high electrical fields.

Flash-over resistance is measured by testing under simulated environmental conditions, and is influenced more by design features of the device than by its material component.

Dielectric constant and loss index are measured by ASTM methods D150, A-C Loss Characteristics and Dielectric Constant (Permittivity) of Solid Electrical Insulating Materials, and D2520, Complex Permittivity (Dielectric Constant) of Solid Electrical Insulating Materials at Microwave Frequencies and Temperature to 1650 °C. Impedence of new materials or devices are compared under simulated use tests to standard materials. Some of the SRM's available from NBS for this purpose include silica, glass, and a 99.5% Al_2O_3 ceramic.

V. Applying For, and Obtaining New SRM's

G. W. Cleek

One function of NBS is to develop, produce, and distribute SRM's. More than 800 NBS-SRM's are available for various materials and represent a wide variety of interests. The standards include, among others, SRM's of interest as clinical laboratory standards, chemical composition standards of all types and application, color standards, physical properties, and coating and thickness standards. Detailed listing and properties of these SRM's are found in the NBS SRM Catalog, SP260, 1973 ed. This publication gives information for ordering, purchasing, and method of shipment of SRMs. Also found in the catalog is a policy statement and guide for submission of requests for the development of new, or the renewal of old SRM's.

Requests for new SRM's far exceed the capacity to produce and certify them. SRM's provide the basis for scientific measurements on materials, and aid the control of quality and production of industrial processes. Thus, NBS must evaluate the requirements of science, industry, and government for carefully characterized materials to be certified as SRM's. Emphasis is given - first, to provide SRM's for which attainment of the needed accuracy of analysis of measurement is not economically or technically feasible elsewhere; second, the need for a neutral supplier, not otherwise available, of an industry-wide standard for commerce; third, the continued availability of highly-characterized material from common sources.

The determination of which requests are to receive top priority is based upon the information received from industry or science, either through its own representatives or through interested committees such as ASTM, ANSI, etc. In the field of glass, NBS has relied heavily on ASTM C-14, and on the cooperation in round-robin tests for chemical analysis, viscosity standards, and other properties.

Requests for new NBS SRM's should include the following information: A short title describing the SRM. The purpose for which it is needed, and any special characteristics and/or requirements. An estimate of present and future demands for the SRM should be given. A statement should be included as to whether the material can be produced or obtained from a source other than NBS; and if so, reasons to justify its preparation by NBS. Other, miscellaneous comments may include an estimate of the range of application, and the scientific and technological significance of the proposed SRM and supporting letters from industry, trade organizations, and interested committees.

This briefly is the procedure and information needed to consider a new SRM. In some cases, for example many of our glass SRM's, those of us at NBS have obtained the pertinent information by talking to the interested people, and have put it together, and then submitted it to the Office of Standard Reference Materials for their approval.

A brief review of existing SRM's that are of interest to the glass industry may be pertinent. These include 38 materials certified as chemical composition standards: such as batch materials (limestone, feldspar, fluorspar, sands, borax, and soda-ash) and glasses. Glass SRM's for physical properties include 3 for high-temperature measurements, 9 for use as softening, annealing and strain point standards. There are also SRM's available (either as glass or other suitable material) for use in making measurements of stress optical coefficient, elasticity, heat capacity, thermal expansion, melting point, DTA, specular reflectance, photometric scale of photometers (developed primarily for clinical standards) and glass beads to calibrate testing sieves for particle size.

METALS (PHYSICAL PROPERTIES)

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I. Introduction

H.G.F. Wilsdorf

Although metals are being used for decorative purposes, metals and alloys are being employed overwhelmingly because of their physical properties. In particular, the combination of strength with ductility as well as the electrical properties make metals and alloys unique materials in today's technology. Clearly, the application of these materials depends on the knowledge of their properties, which have to be determined reliably and to a high degree of accuracy. The ever-increasing demands of industry require the continuous improvement of measuring techniques in order to characterize the physical properties of metals and alloys with higher precision and lower cost, if possible.

It is logical to look to a reliable standard reference materials and measurements program in order to accommodate these urgent needs. On the following pages we will present approaches to the solution of some complex measurement and test problems that are being encountered in metal producing industries, in the manufacturing industry, and in research laboratories concerned with the characterization of microstructures. It is thought that these articles are representative for the development of SRM's in the next decade.

II. Metal Property Standards

G.E. Spangler

The desire to achieve increased reliability in metal structures has brought about the development of new tests for new properties, as well as increased signifance on some older tests. Three areas will be covered: (1) fracture toughness and fatigue crack growth rate, (2) stress corrosion cracking, and (3) formability.

In each case, the type of test currently being used to evaluate the respective properties will be discussed, as well as their problems and needs for improvement.

Fracture toughness and fatigue crack growth rate measurements are discussed together because these two properties go hand-in-hand in determining the life of a structure. Fracture toughness is the measure of the strength of a metal in the presence of a flaw, and fatigue crack growth rate is the rate that a fatigue crack (flaw) grows per stress cycle. Hence, the structure life is determined by: (a) the time required to grow to the critical crack length for rapid failure and (b) the fracture toughness which represents the critical crack length at which catastrophic failure will occur at a given applied stress.

Fracture toughness is measured in terms of stress intensity factor, K_{1_c} or K_c, which have the dimensions of ksi-$\sqrt{in}$, representing a product of stress and the square root of crack length. Thus, these permit calculation of the relationship between stress and the critical crack length for rapid failure.

K_{1_c} is the term used for the stress intensity factor measured for bulky body samples such as plate, and K_c is used for that measured for sheet samples. K_{1_c} is determined primarily by the compact tension specimen shown in figure 1. K_c is determined by use of the center notched panel test shown in figure 2.

Fatigue crack growth is generally measured using the constant compliance sample shown in figure 3. The sample is designed to keep the stress intensity constant as the crack grows.

The problems with the previous test are as follows. The K_{1_c} test, which is now actually being used as a lot acceptance test, is quite costly, both to machine and to test. Prior to fracturing the sample in a tensile machine, the sample must be stressed in a tension fatigue machine to grow a fatigue crack to a specified length. The fatigue precracking is used to assure attaining a suitably sharp notch in the specimen prior to pulling it to fracture. The test is fairly well standarized now, but does exhibit some effect of specimen size. The size also must be adjusted according to the toughness of the metal being tested.

The K_c test is not yet used as a lot acceptance test. It has not been sufficiently standarized because of a significantly greater size effect problem than encountered in the K_{1c} test.

The fatigue crack growth rate test is quite time-consuming and is also susceptible to environmental effects.

Thus, all three tests are primarily laboratory tests rather than quality control tests. Because the K_{1c} test is beginning to be specified as a lot acceptance test, work is being carried out to find a simpler substitute test that could be performed in plant test facilities. Data are now being collected on the notch tensile sample shown in figure 4 for correlation to K_{1c} compact tension values. This will not provide K_{1c} values directly, but may be used as an indication of K_{1c} values.

Beyond the testing problems there are also problems in establishing minimum and typical property values. While K_{1c} and K_c values are somewhat related to the standard tensile properties, they can vary significantly at a given strength for different alloy purity levels and processing techniques. Thus, the standard temper designations do not sufficiently guarantee achieving desired K_{1c} and K_c values. Work is going on, however, to accumulate statistical data, taking into account purity and processing, to attempt to resolve this problem.

Stress corrosion cracking results from the combination of stress and a corrosive environment. It is of importance because it can, for example, result in cracking in the short transverse direction at stresses on the order of one-tenth the yield strength. Susceptibility to stress corrosion cracking of aluminum alloys can be determined by testing in alternate immersion in a 3.5 per cent sodium chloride solution using the samples and fixtures shown in figure 5. In each case, a tensile strain is applied to the sample during the duration of the test. Although the alternate immersion test is considered an accelerated test, it is generally carried out over a period of 30-90 days.

Since it is now being used as a lot acceptance test for certain aluminum alloy tempers, the delay it causes between completion of an order and release for shipping is very undesirable. The test is also quite variable, often with one sample cracking in a triplicate test with the other two samples going the duration of the test without cracking. Hence, interpretation becomes difficult.

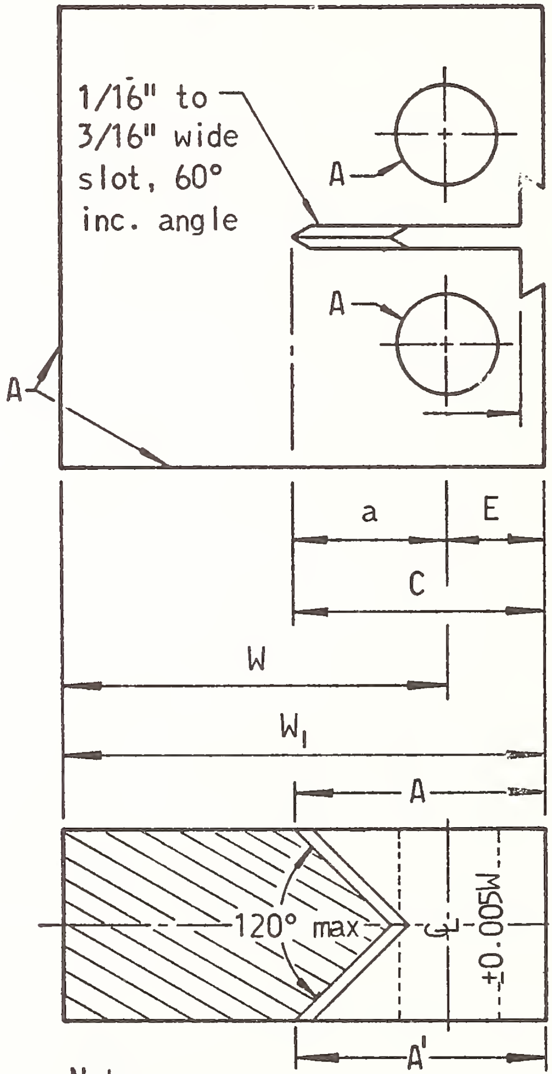
Also, there is always the question of the relationship between the accelerated test and the performance of the metal in service. The correlation is not always as good as would be desired. Hence, there is need for better and shorter tests for stress corrosion cracking.

Formability testing is a problem that has been around for many years, but still no single test has been developed to predict performance in production drawing or forming operations. Formability has, however, assumed new importance because of the new safety and exhaust emission requirements in the automobile industry. The increase in weight resulting from these new requirements have made the auto manufacturers very weight-conscious. Hence, they are now looking very hard at high-strength low-alloy steels and aluminum alloys for use in auto bodies and bumpers. Although they have a vast amount of experience in forming steels, they now are faced with the question of how these new metals will form.

Two old tests, which have been and still are being used, are the Swift and Olsen cup tests shown in figure 6. A new type of test has been developed recently to determine what is known as a forming limit curve as shown in figure 7. Actually, it is a series of forming tests with varied biaxial strains in which the major and minor strains are measured at the point of maximum deformation by menas of circular grids printed on the surface of the metal. The forming limit curve thus represents the formability of the metal under the widely varied conditions one might find in practice.

It is, however, a laboratory-type test for rating materials. For material quality control testing, a simpler test such as the Olsen or Swift cups or one of the tests used to develop the forming limit curve must be used. The men in the plants and die shops, also, are still convinced that there is a big gap from testing to actually trying to make a part, and it is a cut and try process, dependent very largely on personal experience. Thus, although the various formability tests show that both the high-strength low-alloy steels and proposed aluminum auto body alloys are not quite as formable as deep drawing steel, the designers still do not know what limitations these new metals will place on auto body configurations.

Briefly in summary, in each of the areas discussed the material property specifications are becoming more critical and the testing more costly and sophisticated. Thus, there is still need for better and cheaper test, as well as better understanding of the relationship between test performance and actual service performance.



Notes:

1. A = A' to within 0.010 W
2. Cutter tip angle 90° max.
3. Notch tip radius 0.010 or less.

Figure 1. Compact Tension Specimen

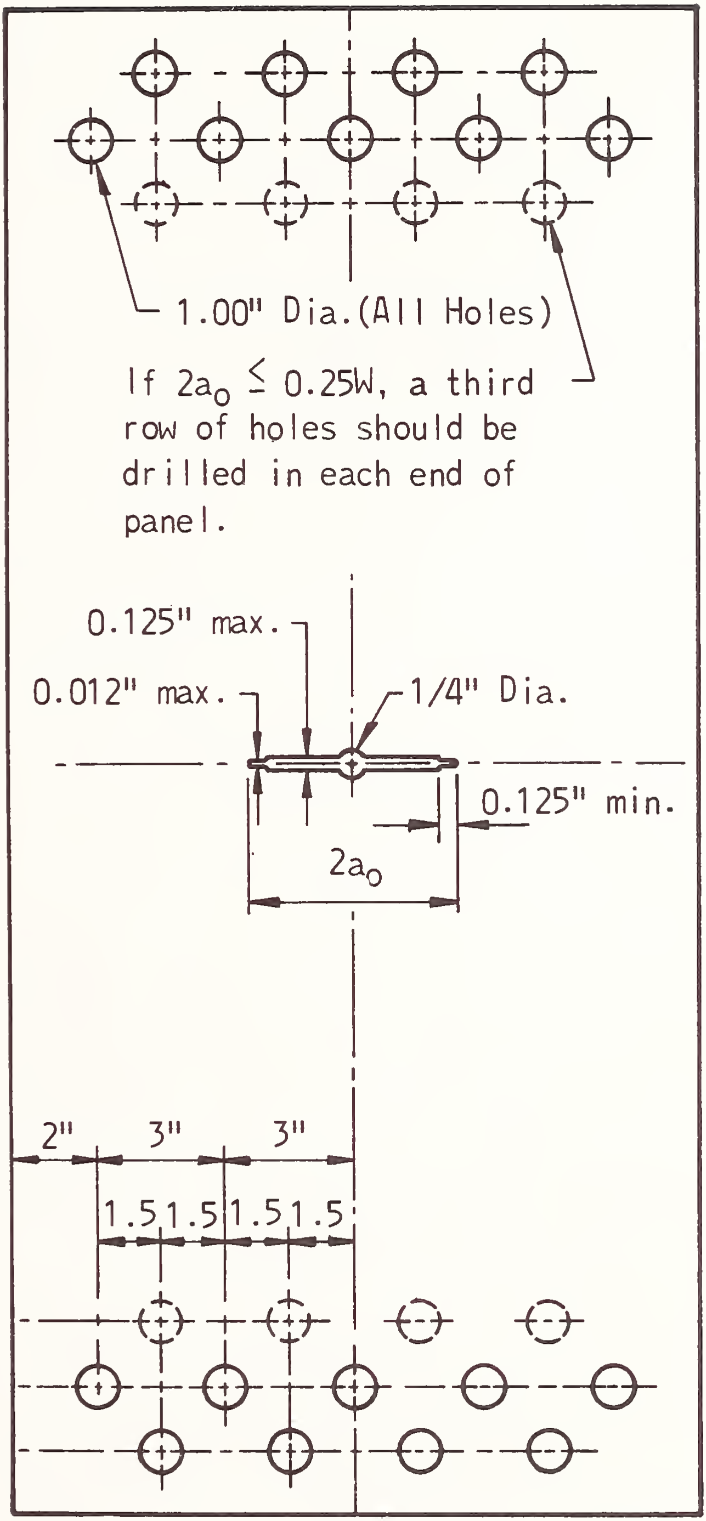


Figure 2. Center Notched Panel Tensile Specimen

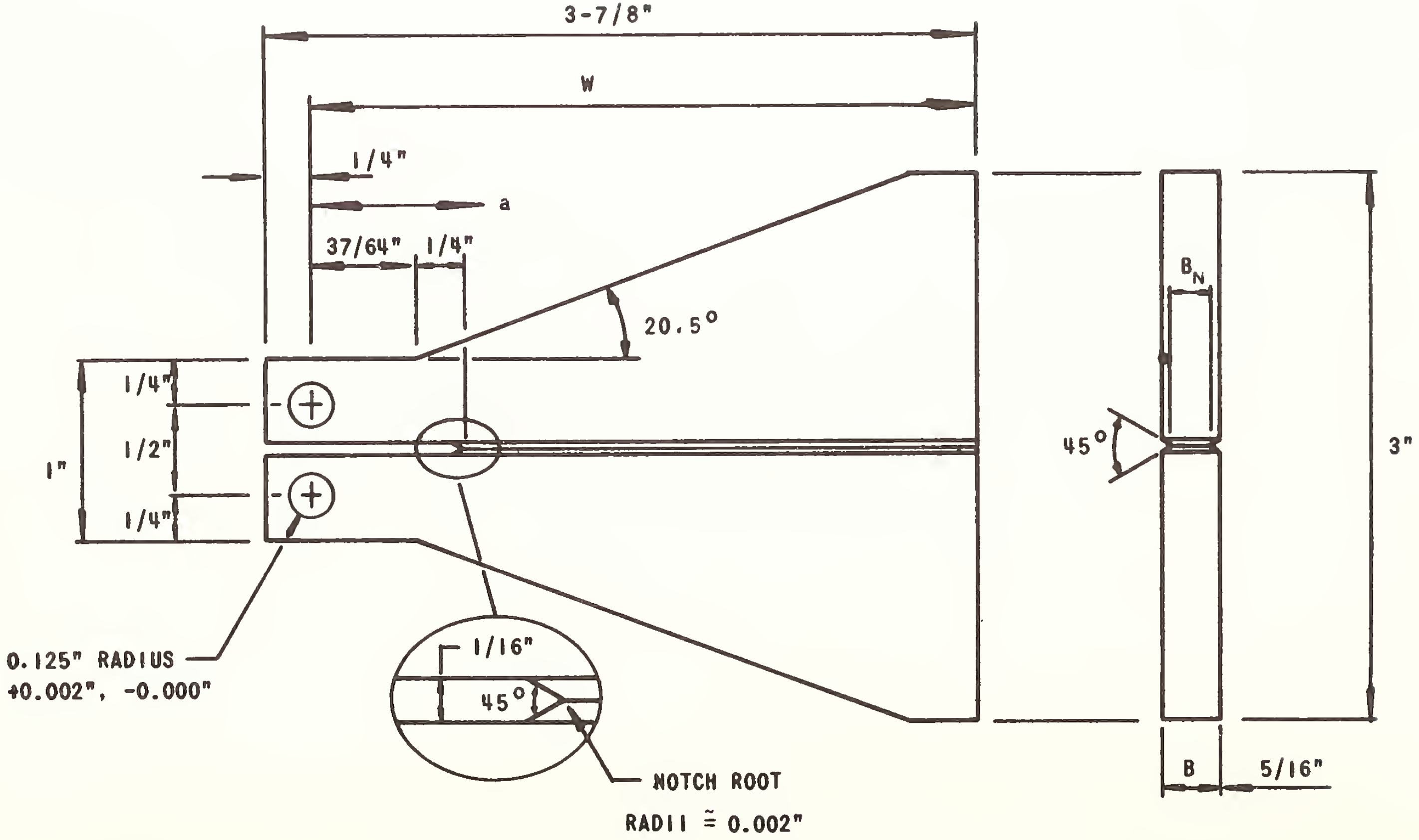


Figure 3. Constant Compliance Fatigue Crack Growth Specimen

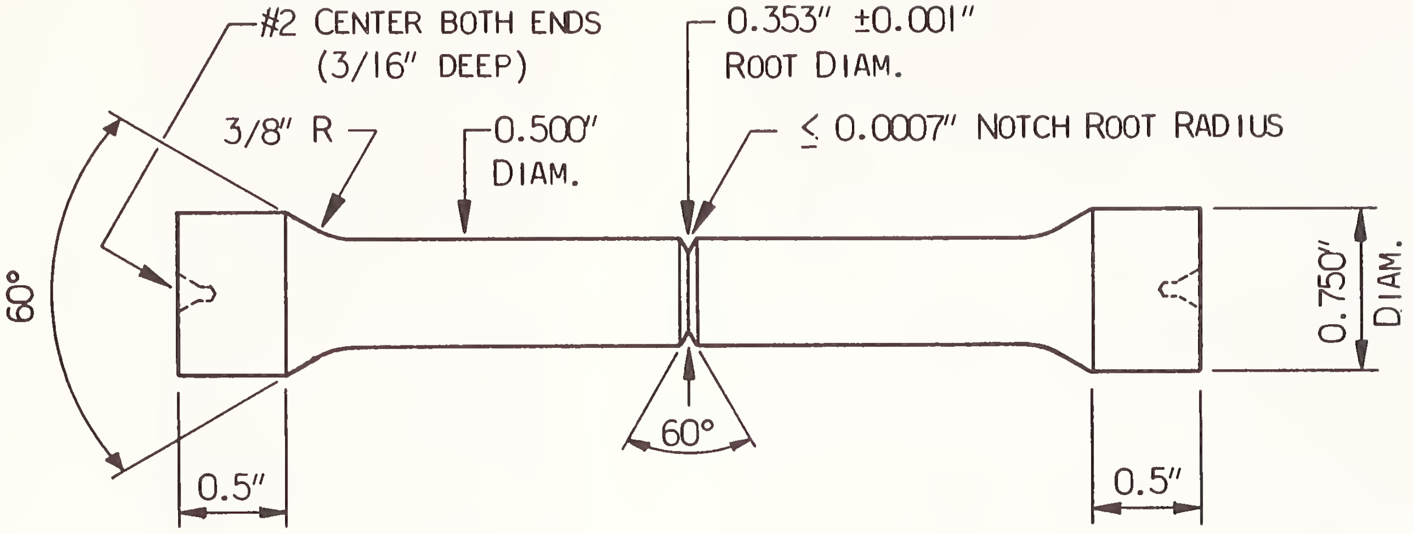
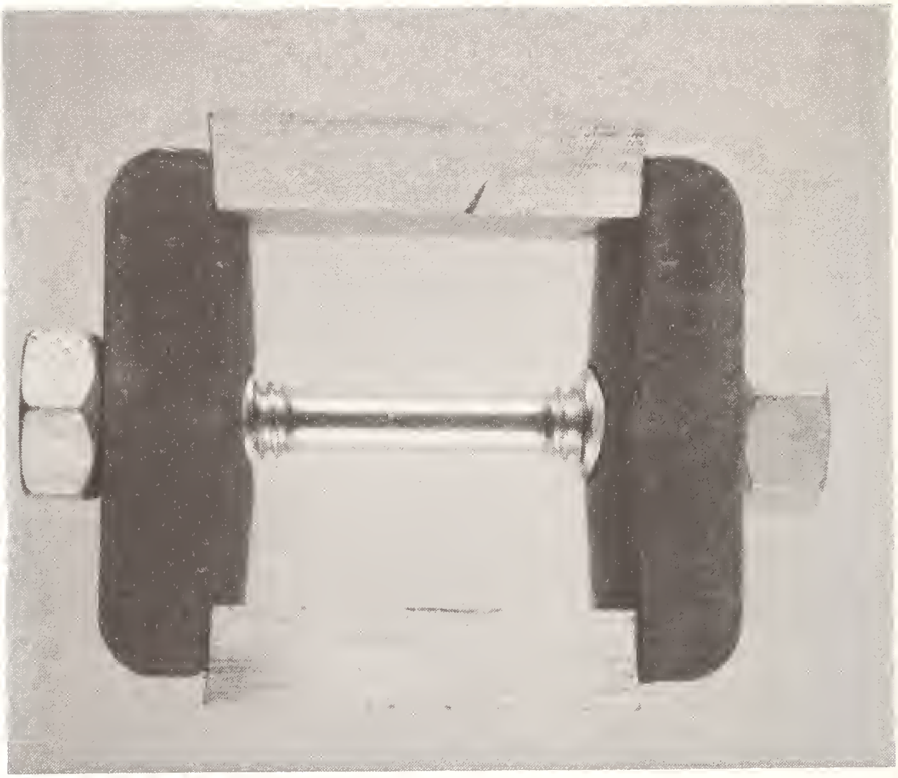
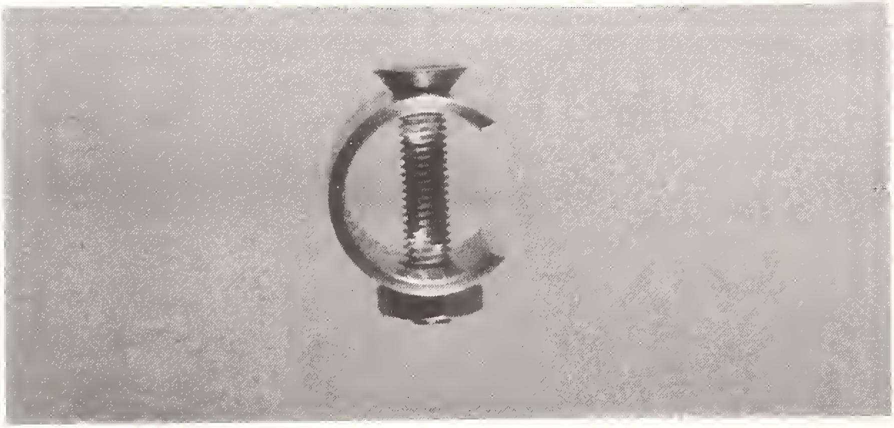


Figure 4. Notch Tensile Specimen



(a) Tensile Specimen Type



(b) C-Ring Type

Figure 5. Stress Corrosion Test Samples

(a) Olsen Cup

(b) Swift Cup

Figure 6. Formability Samples

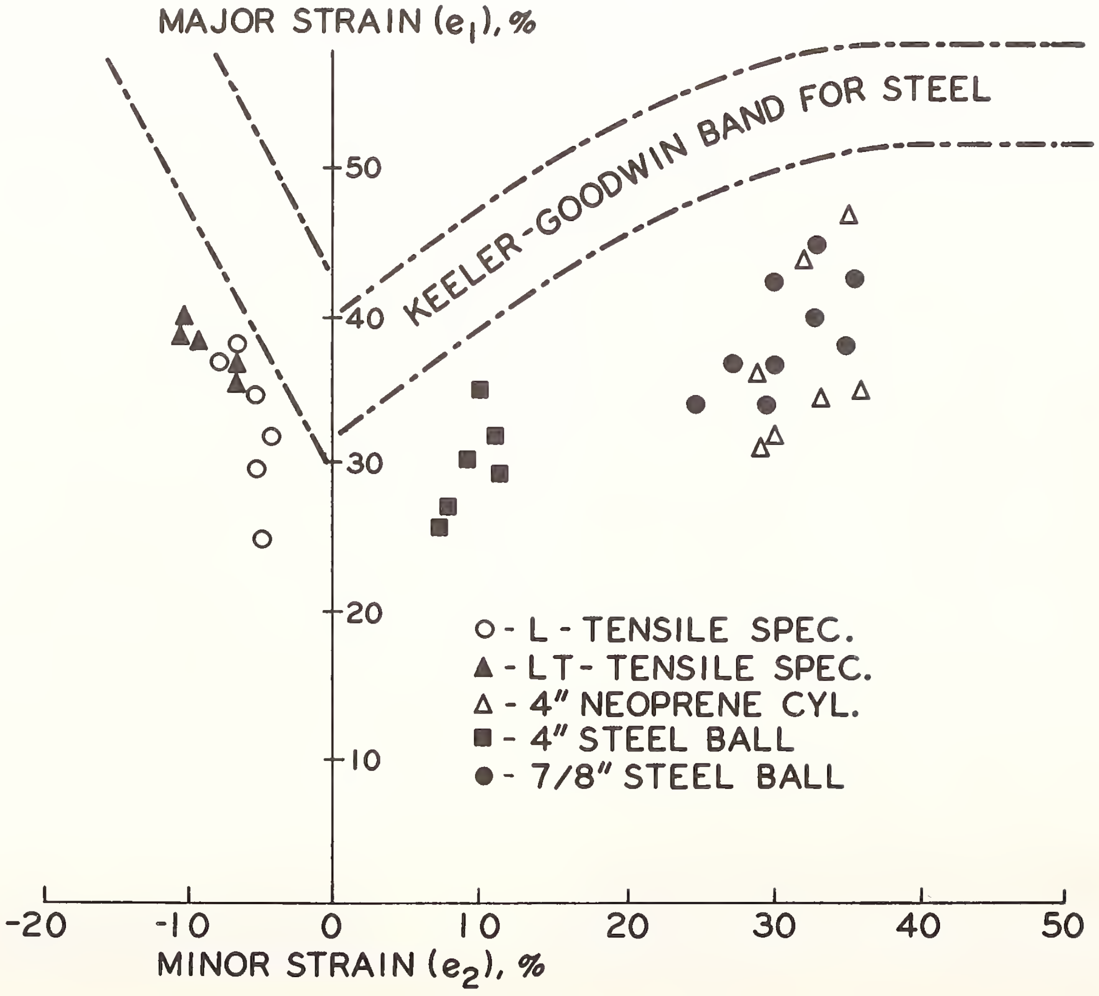


Figure 7. Forming Limit Curve for 2036-T4 Sheet

III. Quality of Welds

W.E. Lawrie

The use of standard reference materials in determining the quality of welds is extremely limited. In this country, welds are examined in accordance with codes established by the American Society for Mechanical Engineers and various organizations within the Department of Defense. These publications constitute "standards," but not in the sense of the title of the symposium. Standards are used for determining the sensitivity of examination techniques used for evaluating the quality of welds, but these standards are normally fabricated as necessary.

In determining the quality of welds, various nondestructive examination procedures are followed. Basically, each nondestructive examination technique depends upon the interaction of energy with the material under examination to provide a readout indicative of quality. Since quantative data is obtained from the energy-material interaction, some form of calibration is required.

The techniques commonly used for weld examination encompass one of the normal NDE methods: radiography, ultrasonics, magnetic particle, or dye penetrant. Eddy current techniques are not normally used for weld examination. In radiography, for example, the reference standard consists of a penetrameter, which is normally a small plate with a thickness of 2 per cent of that of the part being radiographed. Holes with diameter of 1, 2, and 4 times the thickness are drilled in the penetrameter as shown in figure 1. The penetrameter is placed on the object during radiography and as specified, one of the holes must be visible in the completed radiograph. In Europe, other types of penetrameters are used, one of which is the seven wire penetrameter. The assembly of seven wires of increasing diameter is placed on the object during radiography and a wire of specific diameter must be visible in the completed radiograph. In all cases, the penetrameters are made from the same or equivalent material as the test object.

Probably ultrasonic examination of welds requires greater use of references and currently greater changes are being made in ultrasonic examination techniques than in other NDE techniques. Again, fabricated references are used for adjusting the sensitivity of ultrasonic instrumentation. Ultrasonic techniques are based on the principle that a discontinuity in the weld reflects ultrasonic energy. The amount of ultrasonic energy returning to the transducer and displayed as a pulse on a cathode ray tube is the primary method of determining defect size. To correlate pulse height with defect size, a reference block with a known size hole or notch is used a calibrate the instrument, as shown in figure 2. This calibration is not always adequate. At a meeting on In-Service Inspection at Cleveland in April 1973, results of a Pressure Vessel Research Committee round-robin test indicated that Ultrasonic techniques were sensitive in detecting defects, but were less reliable in evaluating these defects. Part of the difficulty may be a lack of standardization of the instruments and transducers used for ultrasonic nondestructive examination.

As an example, figure 3 shows the frequency spectra of two transducers each of which is nominally 2.25 MHz. In one case, the transducer emits a relatively narrow band of frequencies around the nominal frequency. In the second case, the spectra exhibits peaks at 1.7 MHz and 3.1 MHz with a dip at the desired frequency.

Electronic amplifiers in ultrasonic instruments also require standardization. Figure 4 shows the response of an ultrasonic amplifier with a nominal frequency of 1 MHz. The maximum response actually occurs at 1.7 MHz.

If now we used the transducer whose spectrum is shown in figure 3b with the instrumentation that is shown in figure 4, we would have a system actually operating very effectively at 1.7 MHz. This actual frequency would not agree with either the switch setting of the instrument (1 MHz) nor the transducer nominal frequency (2.25 MHz). We would expect the relative response for different size defects for the 1.7 MHz system to differ from that of systems operating at either 1 or 2.25 MHz.

Another area where standards are required in weld examination is in the effect of ultrasonic attenuation. In general, ultrasonic attenuation varies with frequency as shown in figure 5. At low frequencies, attenuation is associated with hysteresis and increases linearly with frequency. At higher frequencies, attenuation is caused primarily by scattering and theoretically varies at the fourth power of frequency. Since the attenuation affects the amplitude of ultrasonic pulses, calibration blocks are used for setting instrument sensitivity to exhibit the same attenuation as the material to be examined.

For most applications, ultrasonic techniques provide an excellent assessment of the quality of welds. If a defect is either large or small, ultrasonic techniques will produce a reasonable evaluation of their importance. It is only when a defect is of borderline size, either acceptable or rejectable, that difficulties arise. These difficulties can probably not be resolved by the use of standards, but can be best evaluated by employing different techniques. One of the newer techniques with high potential is acoustic holography. The acoustic holography employs a scanning transducer as shown in figure 6. Ultrasonic data obtained from the transducer is used to generate optical holograms. The optical hologram is then used with the reconstruction of figure 7 to produce a series of 2-dimensional images of the defects. The hologram of a typical defect is shown in figure 8. The variation in optical density corresponds to differences in phase between the reflected ultrasonic pulse and an electronic reference signal; the light area indicates an in-phase condition and the dark area out-of-phase.

Those who are familiar with optical holography expect to see a three-dimensional image, however, the differences in wavelengths used for reconstruction causes a depth distortion. A cube with one inch edges would be imaged as a bar of one inch square cross section but very much longer than one inch. The depth distortion requires that we look at a number of planes at different depths, where each plane is shown as a 2-dimensional image, rather than one three dimensional image.

Standards are used to determine the resolution of the acoustic holographic system. The test block shown in figure 9 has 1/8" holes drilled in from each side with various spacings. In one side, the holes are at the same depth but separated by different amounts; in the other side, they are separated both vertically and laterally. The holographic image shown in figure 10 shows that at depth of 4-1/2" all holes are resolved. This corresponds to resolutions of about one wavelength. This is much better resolution than could be obtained using conventional ultrasonic methods.

The optical reconstruction unit is of adjustable focus so that any desired plane of the object may be imaged. The variable distance is displayed by a dial indicator. By adjusting for sharpest focus of the reconstructed image and reading the dial indicator, the depth of the image plane can be computed. The calibration block permits the constants used in the calculation to be determined.

The holographic technique has been applied to actual weld defects but primarily for evaluation rather than for detection. The image shown in figure 11 is of an actual weld defect in 10" thick material. The defect was detected with conventional ultrasonic techniques and was later ground out and repaired. During removal, measurements were made to which the holographic results could be compared. Excellent agreement in size, shape, and orientation was obtained between the holographic evaluation and measurements made during defect removal.

As has been shown, reference standards are used in a number of ways in weld evaluation. These standards, however, are generally not reflected to any primary standard but are fabricated to produce discontinuities of known size, shape, and orientation. The standards must be fabricated of material equivalent to that of the component under examination. The use of these standards permit the sensitivity and resolution of nondestructive testing methods to be determined.

Newer techniques of nondestructive examination are being introduced and may simplify weld examination. However, these newer methods will still require standards for calibration.

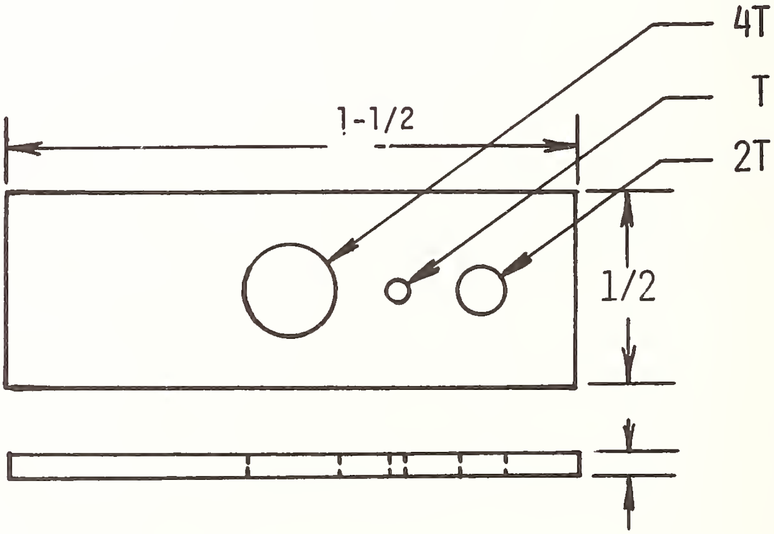
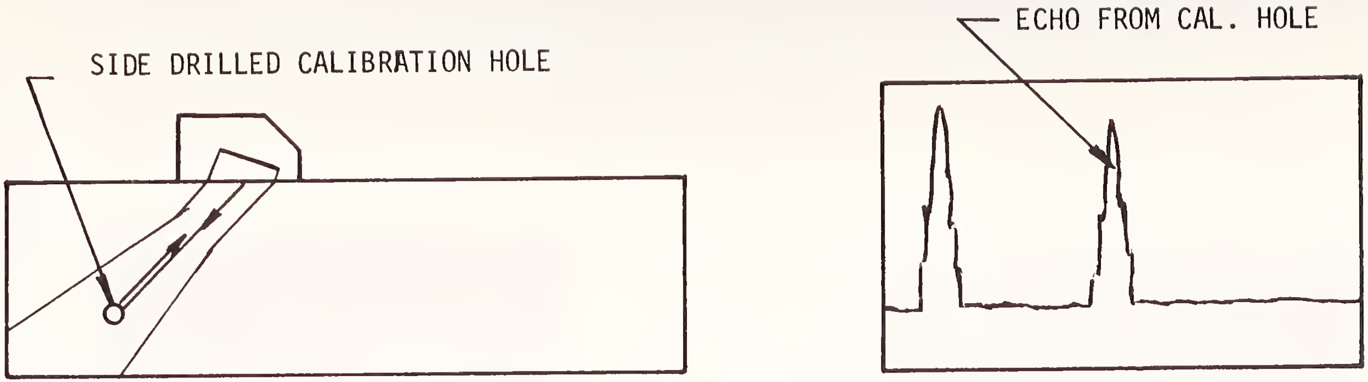
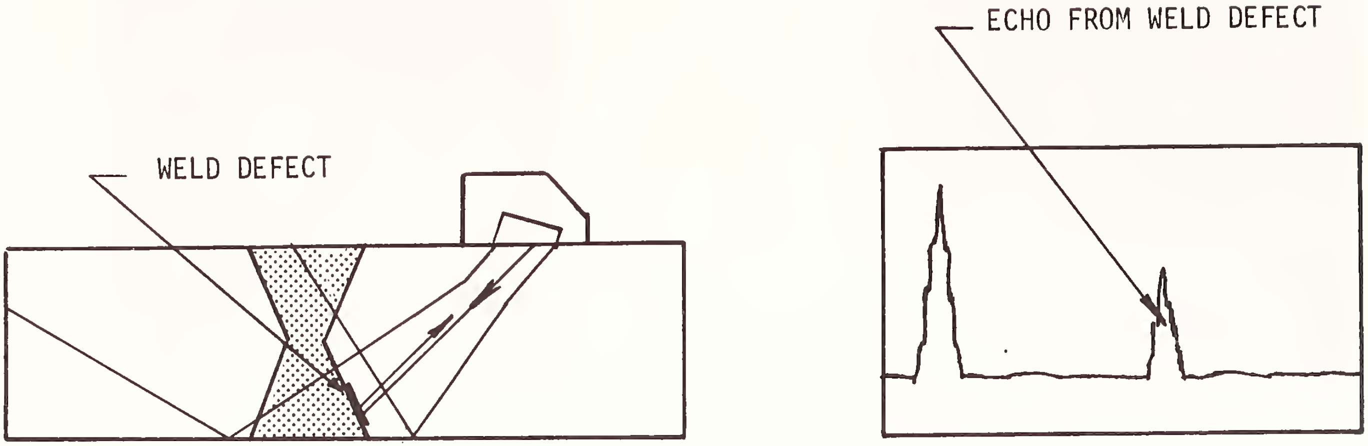


Figure 1. Penetrameter for Determining Sensitivity of Radiographs. A lead identification number is placed at the left end.



(a) Adjustment of Sensitivity Using Hole of Known Size



(b) Evaluation of Defect From Amplitude of Echo

Figure 2. Use of Calibration Blocks in Ultrasonic Examination

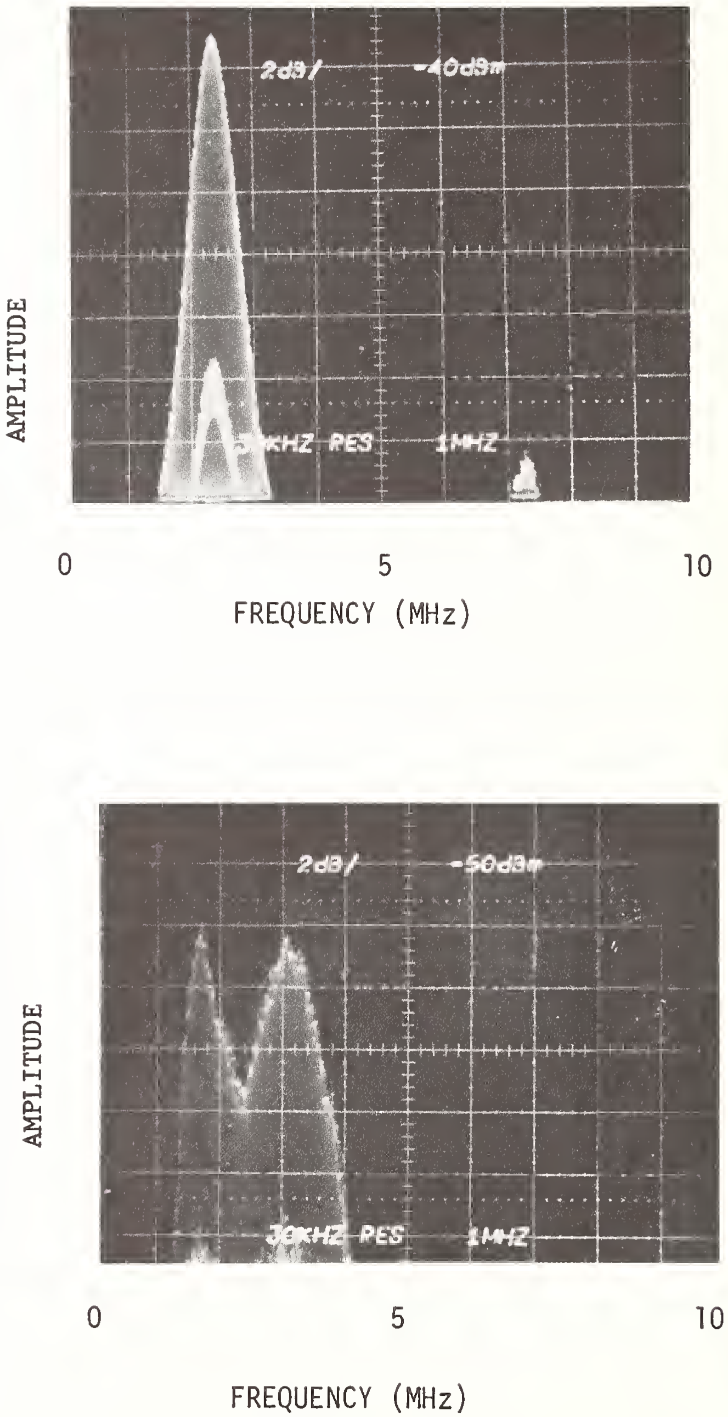


Figure 3. Spectra of Two 2.25 MHz Ultrasonic Transducers. Note double peak in lower photo.

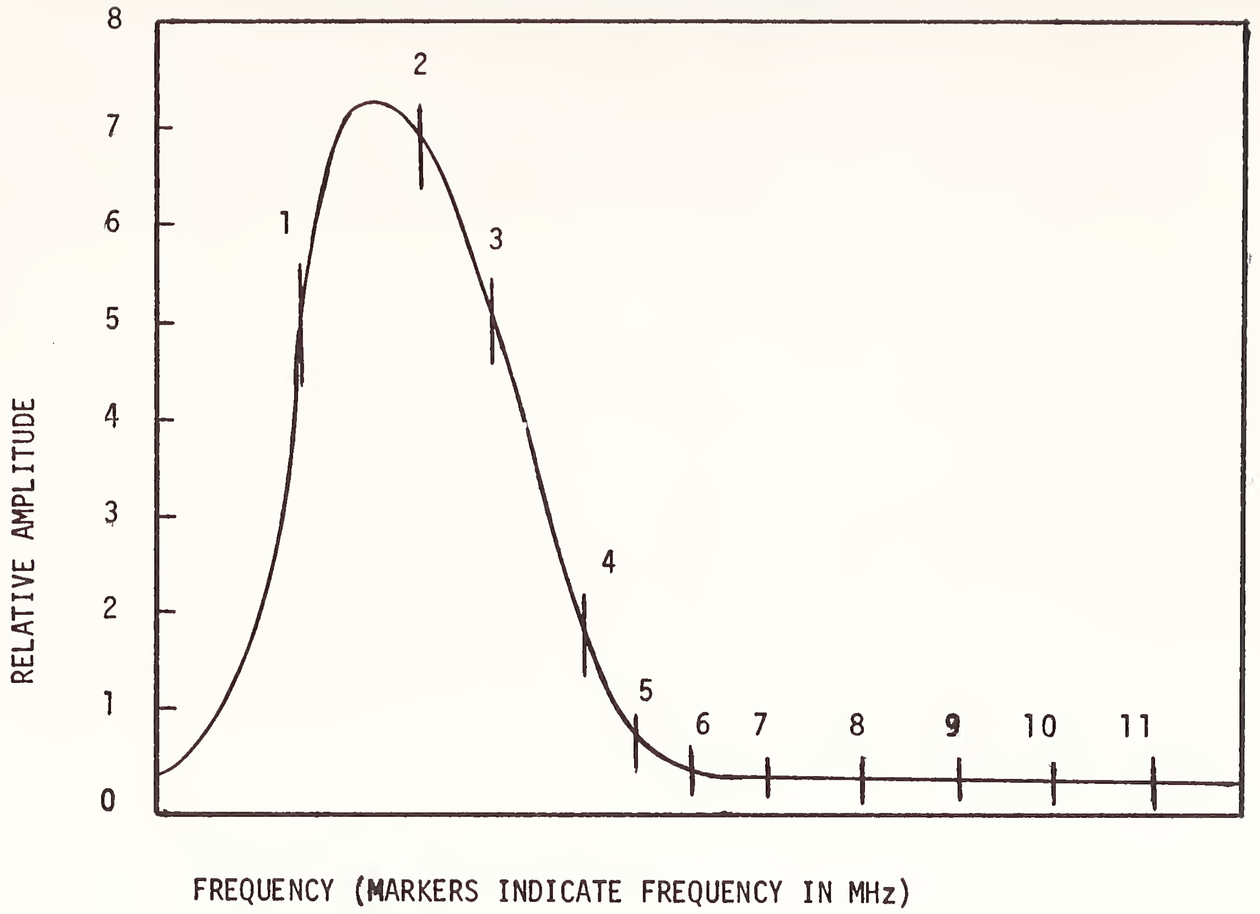


Figure 4. Frequency Response of Incorrectly Tuned Ultrasonic Amplifier

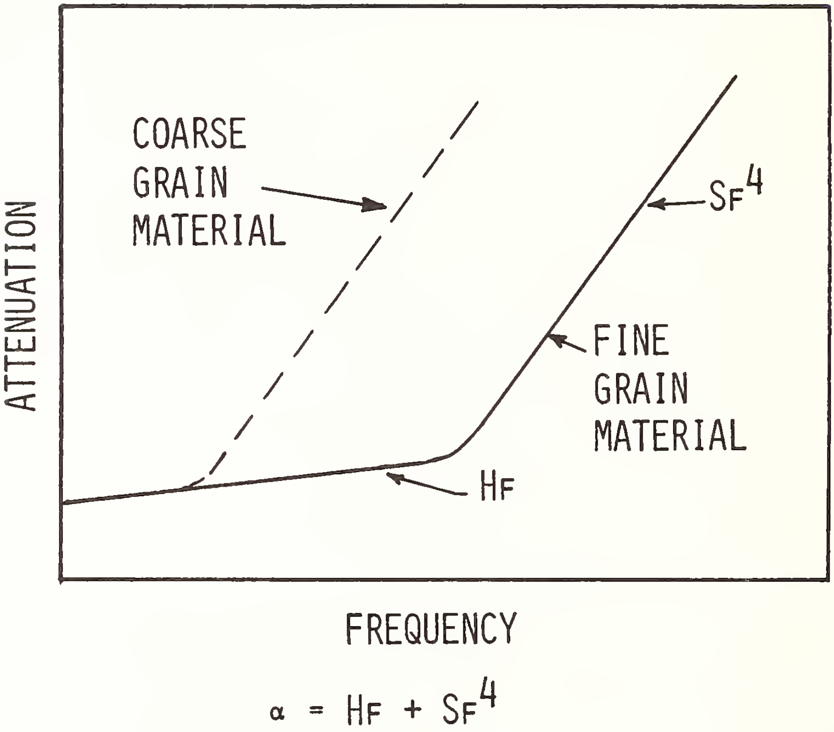


Figure 5. Ultrasonic Attenutation in Metals

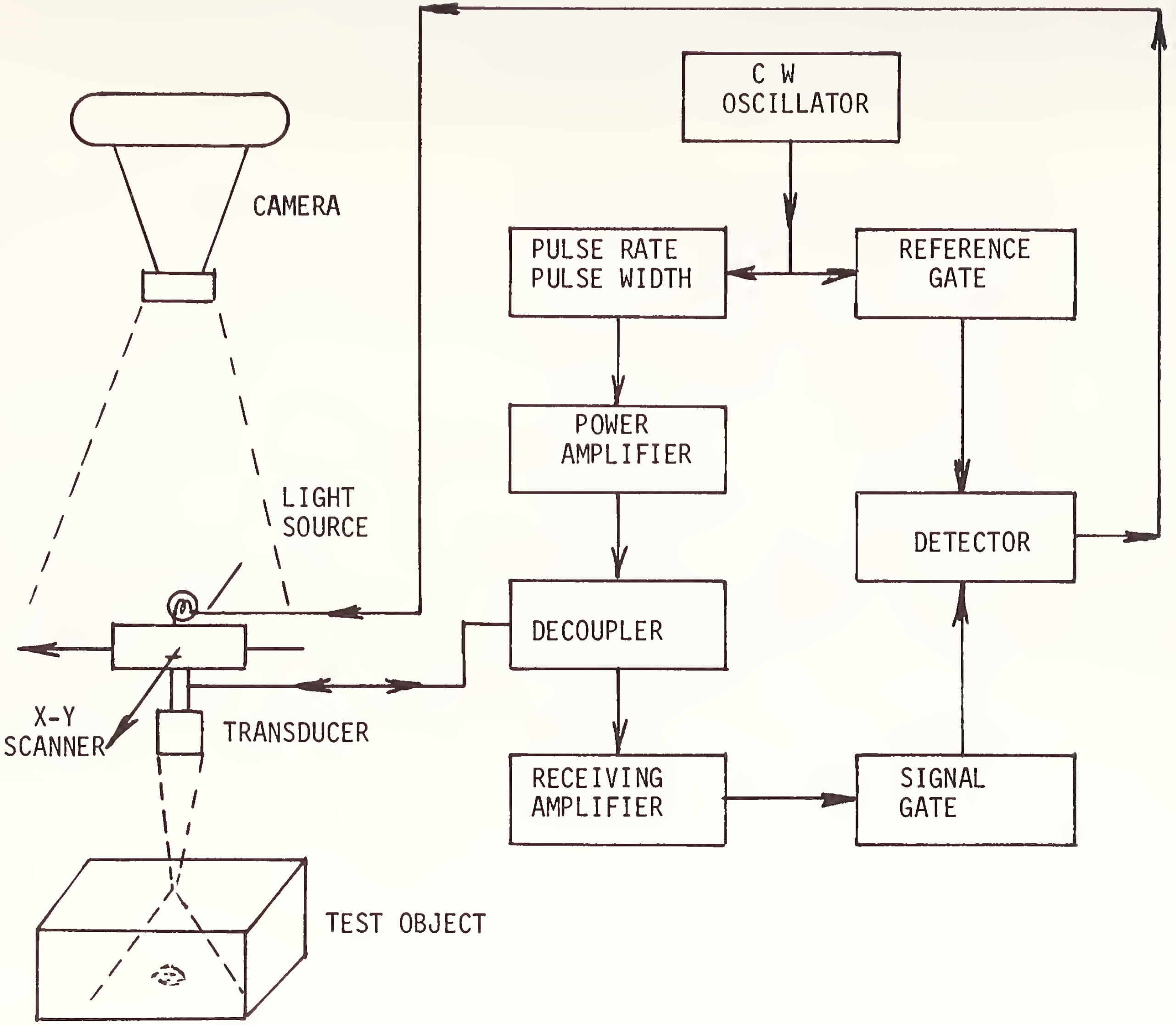


Figure 6. Acoustical Holography System

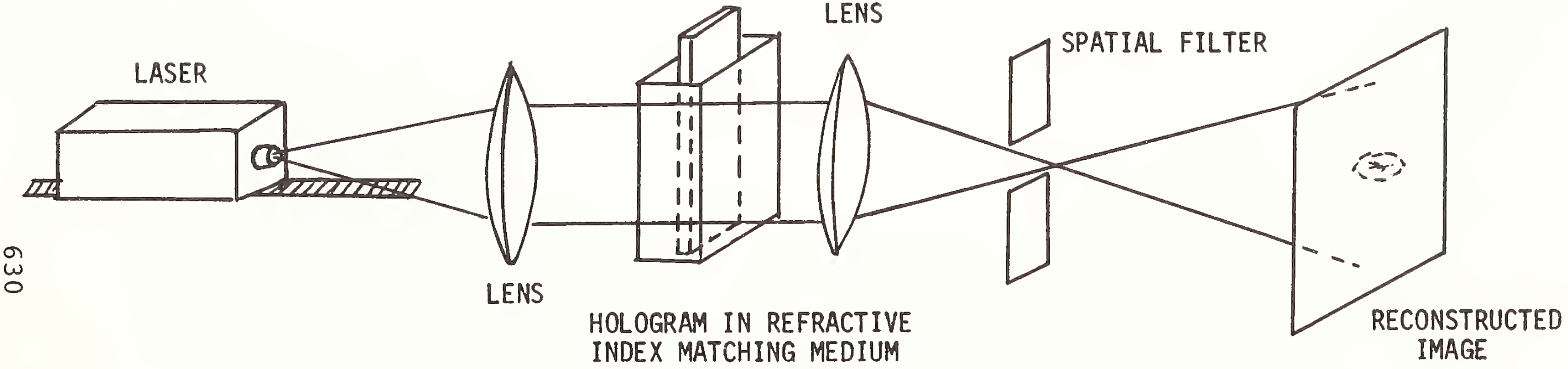


Figure 7. Holographic Reconstruction System

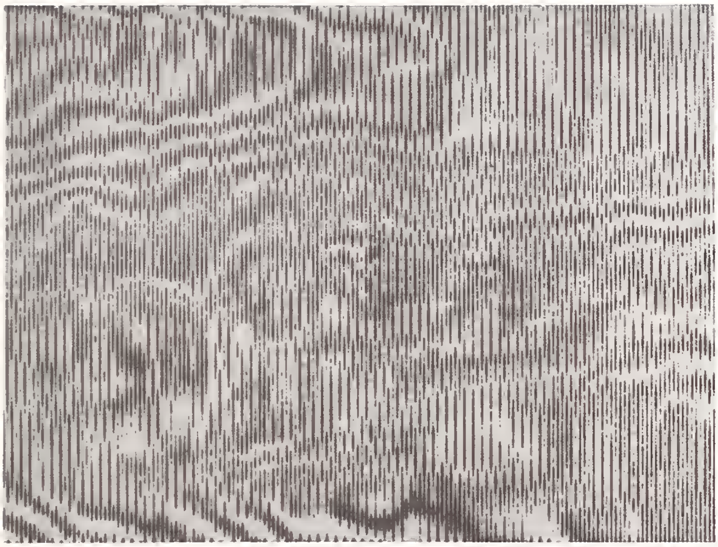


Figure 8. Typical Ultrasonic Hologram

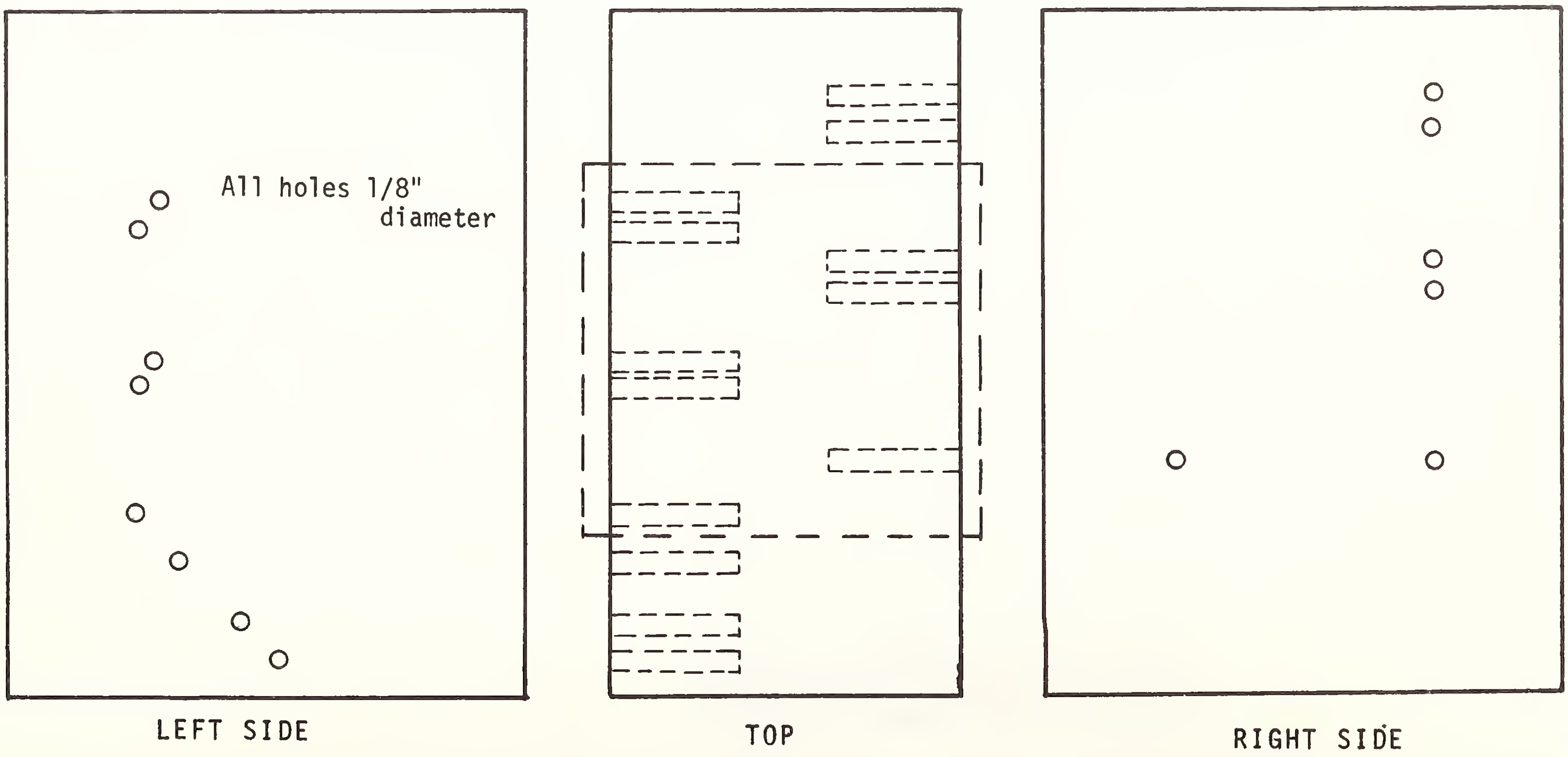


Figure 9. Acoustical Holography Resolution Test Block

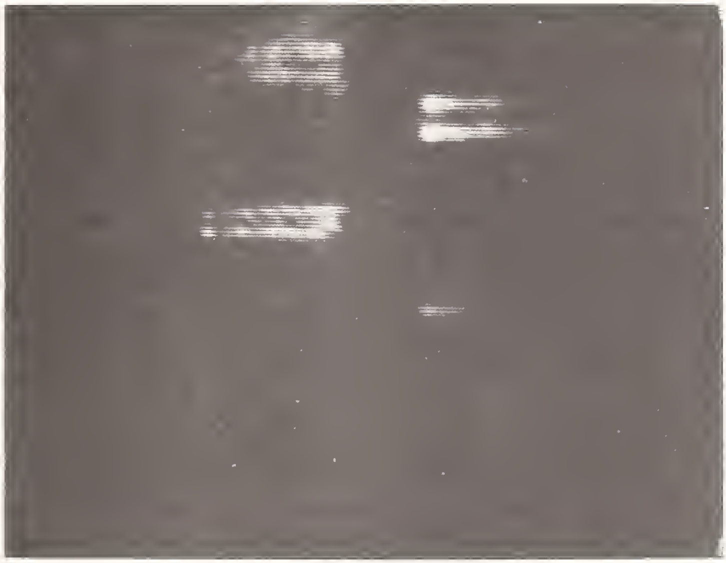


Figure 10. Reconstruction of Holes in Resolution Test Block

Figure 11. Reconstruction of Weld Defect

IV. Resolution and Magnification Standards for Electron Microscopy

A.W. Ruff

A. Introduction

No universally accepted, certified standard is presently available for the calibration of electron microscope systems. However, a number of working standards, including both specimens and measurement methods do exist and are used in electron microscope laboratories. There are several commercial sources for such reference specimens. At present, measurements that are accurate and reproducible to 10 per cent can be made in most cases. At the 1 per cent level or below such measurements can be made only rarely.

This paper considers electron beam image forming systems that involve a magnification range from 1x to 10^6x. Both surface and transmission microscopy are of interest. This large range of capability and application requires subdivision with regard to specimens and measurement methods. The present situation is described and considers the problems that exist and possible solutions. Significant instrument parameters are mentioned. Considerations of this kind would hopefully indicate areas where reference specimens and measurement procedures are required.

B. Transmission Electron Microscopy

We shall first consider the application of the transmission electron microscope. Figure 1 shows a replica of a thermally evaporated zinc single-crystal surface where certain step features and spacings required careful length measurements. Numerous other examples could be given. Two different microscope calibration methods are generally used. The first may be termed "operation with periodic calibration." In this method the operator refers to a tabulation of previous calibration data and instrument parameters when measuring a specimen photograph of interest. The instrument magnification is obtained from that periodically obtained calibration data. The second method involves "continuous internal" calibration where each sample is mounted in combination with a reference sample for examination within the microscope. Thus each photograph may contain a standard image having known dimensions. This latter method is less frequently employed, and is usually reserved for critical situations. Neither method is inherently superior provided that the entire measurement scheme is carefully considered.

What measurements and instrument parameters are crucial? In contrast to the light microscope, the focal length (hence magnification) of electron microscope lenses vary with the excitation potential and current. Hysteresis effects are significant. Thus the operator must measure and record several crucial parameters. These include lens currents (for four lenses or more), accelerating voltage, specimen position within the objective lens, and specimen tilt coordinates, to mention a few. A digital electrical meter is invaluable in this connection and gives more than sufficient precision. Systematic procedures for focusing are required to normalize the microscope lenses. Identical data must be recorded during the periodic calibrations. This is all in contrast to optical microscope procedures where only casual attention is required of the operator to record objective and photographic lens magnifications. It is not uncommon for a skilled electron microscope operator to realize too late that he neglected to record a crucial datum value associated with some photograph.

Magnifications in the range below 1500x can be calibrated using fine mesh screens that are commercially available and can be optically calibrated to accuracies in the range of 0.2 to 1 per cent. Such screens can be specimen supports for internal standardization. For intermediate magnifications up to 50,000x, replicas taken from ruled diffraction gratings are commercially available. An example is shown in figure 2. The accuracy of such grating replicas is affected by the production method. However, the replica can be calibrated itself by using laser illumination in an optical diffractometer. Measurements were made in this laboratory on a 28,800 lines/inch grating yielding an average line separation of 8,590Å. This indicates about 3% shrinkage in replicating the master grating whose average line spacing was indicated to be 8,830Å. With careful attention, the grating replica method can produce accurate calibrations to about 1 per cent and is then limited by nonuniform line spacings. Heckman has reported working at an accuracy level of 0.5 per cent using grating replicas.

Above magnifications of 100,000x, direct lattice resolution methods are employed. Labaw at NIH has described several dye substances having large lattice periodicities as determined by x-ray diffraction. Figure 3 shows a transmission photograph of Indanthrene Olive dye with a period of 24.9Å. Most modern electron microscopes could resolve this periodic structure. Wrigley recently described the use of bovine liver catalase with an 86Å periodicity. That material is now available commercially; however, reported variations in lattice spacings may exceed 2 per cent. Smaller lattice periodicities than these are available in many substances having the desired stability for use within the electron microscope. This leads into the area of resolution testing of the instrument. It is important to appreciate that resolution of image detail requires sufficient contrast and that this places additional requirements upon the specimen. Heidenreich recently showed that graphitized carbon black is an excellent resolution determining substance. It offers both lattice fringe separations of 3.4Å and textural detail for performing point-to-point measurements. Metal lattice images can be used, for example, gold (200) images having a spacing of about 2Å.

In summary, while no independently certified standard materials are available, commercial sources do offer specimens suitable for 1 per cent level calibrations. Greater accuracy may be possible with special precautions. While the modern transmission electron microscope is over 30 years old, significant problems remain with regard to proper measurement procedures and the control of significant microscope system parameters.

C. Scanning Electron Microscopy

This instrument is of recent origin and has very wide application to materials problems. It has been in substantial use since about 1966. Many of the previous remarks on instrument calibration apply here, such as a need for subdivision of the magnification range and the magnification variation with lens currents and accelerating potential. The magnification in this microscope is determined by electron drive signals applied to the scanning coils and the display device. It is important to realize that axial symmetry is no longer present in the image. In fact, the magnification in the scan line direction and the orthogonal direction is determined independently by adjustments. Linearity within the field is determined by the scan drive signals. Specimens are ordinarily tilted to angles of about 30° with respect to the incident beam and this leads to significant foreshortening. Tilt correction electronics are often provided; however, these also require quantitative calibration.

An example of a scanning electron microscope study of particulates is shown in figure 4. One aim of this investigation is to size the particles by accurate measurements, hence accurate calibration is required. What measurements and parameters of the instrument are crucial? As discussed earlier, lens currents (usually 2 or 3 lenses), beam voltage, and specimen tilt angle values are required. Further the specimen working distance from the final lens must be known along with values of internal voltage references that control display image sizes and drive signals. There are many more opportunities for uncertainity in magnification associated with the SEM that are inherent in the system design.

At magnifications below 1,500x a fine mesh screen can be used for calibration. Periodic measurements should be done over a range of working distance values, specimen tilt angles, tilt correction values, and electron beam potentials. At higher magnification up to about 15,000x, replicas of ruled gratings can be used; however, problems may arise with regard to obtaining sufficient image contrast. Improved specimen materials may be required at higher magnifications to obtain sufficient contrast in emissive mode imaging. The large depth of field of the microscope and the gross surface roughness of specimens produces special problems for the internal standardization method. Images from nonplanar grating replicas can be very distorted by magnification changes associated with local variations in working distance. The distortion can easily amount to 5 or 10 per cent.

Calibration at high magnification is not in a satisfactory state. Grating replicas produce very low contrast and are difficult to use. Efforts are underway to apply materials having large-period crystallographic structures. Brebrick has reported Bi-Te alloys having hexagonal layer priods of up to 500Å. Yakowitz at NBS intends to examine tantala-zirconia solid solutions that have ordered intergrowth periods of hundreds of Angstroms. Bhatacharya at Banaras University is examining polytypes of BiI and CdI, looking for repeat distances of 100-500Å. Presumably measurements of the characteristic distance in any of these materials could be made independently using diffraction techniques. However, it is not clear whether sufficient uniformity of period would be obtainable and whether sufficient contrast would be available.

In a round-robin measurement study, Ballard at NBS obtained measurements on the thickness of an electroplated gold thickness specimen from seven SEM installations. The results shown in table I indicate the problem associated with accurate measurements at about 20,000 magnification. While the reproducibility among operators of the <u>same</u> instrument was about 2 per cent, a maximum bias of nearly 20 per cent was found between different microscopes.

Table I

Comparison of Electrodeposited Gold Thickness Measurements

Instrument Operator	Thickness Measured (μm)	Average Thickness (μm)
A/1	3.63	
A/2	3.76	3.69 (±2%)
A/3	3.68	
B/1	4.32	4.38 (±2%)
B/2	4.44	
C/1	3.63	3.60 (±1%)
C/2	3.56	

In the area of resolution, a demonstrated need exists for a specimen to test SEM instrument performance. A survey conducted for ASTM-E4 Committee showed that many SEM operators desired some means for verifying day-to-day instrument performance. Such resolution verifying specimens have been proposed by several workers. Broers developed a GaAs-GaAsP deposited layer structure that contains nominal 150Å and 300Å layer spacings and these specimens are available commercially. Ballard at NBS proposed an Al-W dendrite structure having finely spaced, high contrast features. This material is available from the NBS, Office of Standard Reference Materials as RM 100. [Ed. Note: RM signifies Research Material, as opposed to SRM for Standard Reference Material.] RM 100 permits the SEM operator to establish optimum instrument conditions for critical studies. Since the resolution of modern SEM's is now well below 100Å, continual attention will need to be paid to the problem of providing an adequate test specimen, so that instrument parameters can be properly established. The appearance of commercial scanning transmission electron microscopes will push this resolution limit even lower.

In summary, no independently certified magnification standards are available at the 1 percent level for accurate application to the SEM. A few commercial standard specimens are available, the materials being related to previous transmission electron microscope reference specimens. A critical need exists for high resolution and high magnification reference specimens for the scanning electron microscope. Further it will be necessary to determine adequate measurement methods that control and specify all crucial instrument parameters.

Figure 1. Surface step features and spacings of a thermally evaporated zinc single crystal (M = 40,000X)

Figure 2. Replica taken from a commercially available ruled diffraction grating

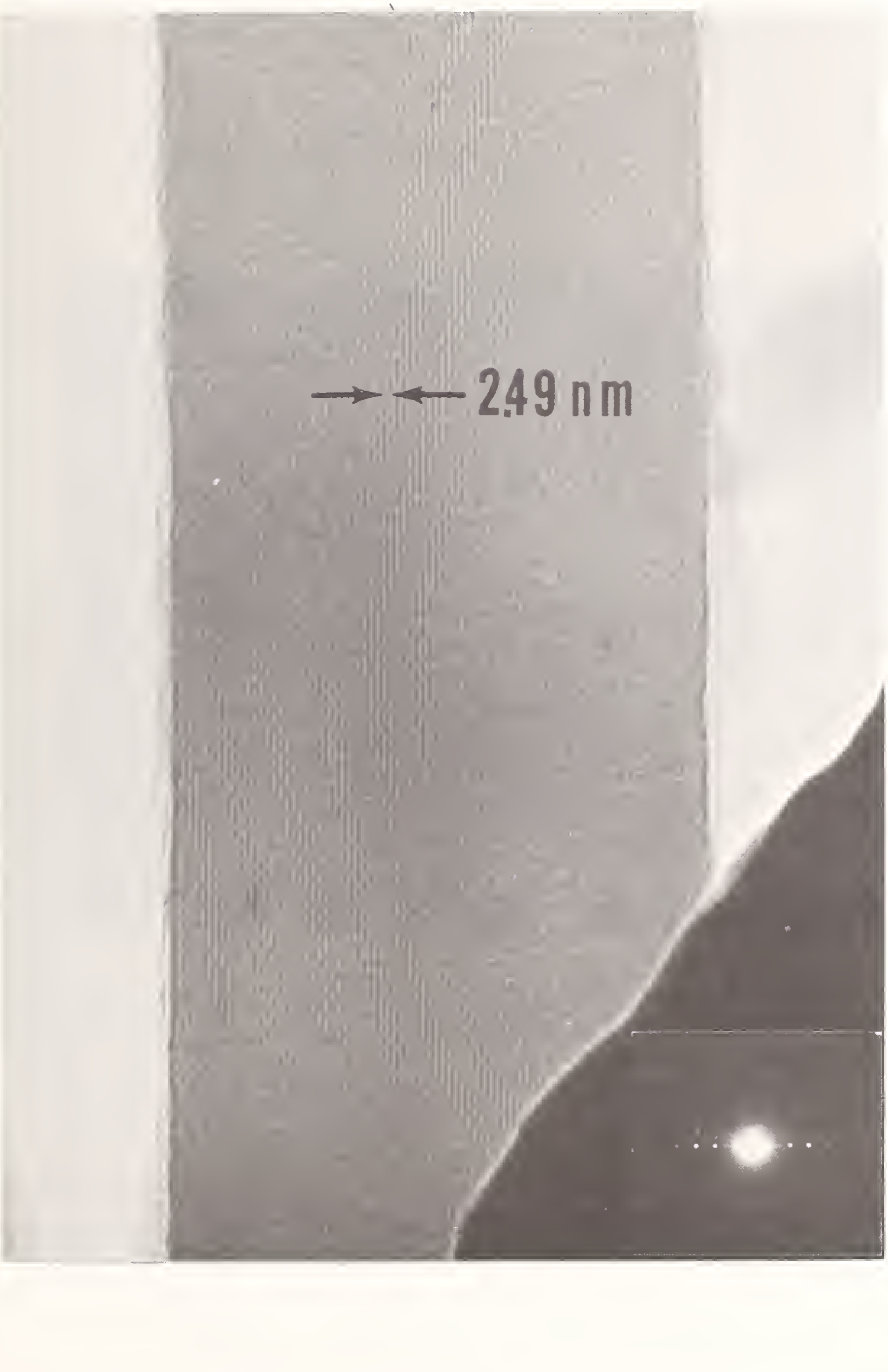


Figure 3. Transmission photograph of Indanthrene Olive with a period of 24.9 Å

Figure 4. Particulate as shown by a scanning electron microscope (m = 1000x)

NUCLEAR MATERIALS (FUELS)

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Early in the development of nuclear energy, there was an awakening to the needs for special Standard Reference Materials. Several of the SRM's available throughout the past 30 or more years have served some of the needs of the nuclear industry. Potassium dichromate, arsenic trioxide, and sodium oxalate have been among the oxidation-reduction standards that have been the reference points in assays of plutonium and uranium. The many SRM's certified for trace element contents, various of the high-purity metals and compounds, and several of the ferrous alloys were pressed into service. Good as these SRM's were, they did not completely fill the needs in one important aspect. They were not similar chemically to the reactor materials being analyzed.

Concern among knowledgeable scientists at NBS the U.S. Atomic Energy Commission, various AEC and contractor laboratories, and several laboratories in other countries working in the nuclear energy field resulted in a program to prepare and characterize special nuclear materials to be used as standards. Several of these are now included in the Special Nuclear Standard Reference Materials offered by NBS. In their latest catalog these materials are listed in four groups: Plutonium Assay Standards, Plutonium Isotopic Standards, Uranium Assay Standards, and Uranium Isotopic Standards. The materials included in these four groups are summarized in Table I.

With the availability of these plutonium and uranium reference materials, the assays and isotopic analyses of nuclear fuels could be referenced to standards containing the actinide isotopes themselves. Small differences were found in some cases between the results obtained using these Special Nuclear SRM's and the results referenced to materials that did not contain the actinide elements. The Special Nuclear SRM's have put the analyses of nuclear fuels on a firmer basis than was possible previously. In addition to this respectable list of Special Nuclear SRM's, many of the other standards offered by NBS are in continual use in the nuclear industry.

Probably no series of nuclear material SRM's is more widely used than the isotopic series: U-0002 through U-970. This series of eighteen samples of uranium oxide (U_3O_8) are certified for the abundances of ^{234}U, ^{235}U, ^{236}U, and ^{238}U. Noncertification of at least some of these for chemical composition prevents their parallel use as standards by which to calibrate ^{233}U spikes for uranium assay by isotopic dilution mass spectrometry (IDMS). In reprocessing and in fuel burnup analysis, this technique is being widely used. Observed interlaboratory differences in IDMS measurements are likely attributed to a lack of a common reference.

At the present time there are three plutonium SRM's ranging from 75 to 91% ^{239}Pu certified for isotopic content. These are available in the form of $Pu(SO_4)_2 \cdot 4\ H_2O$ and are certified for the five isotopes ^{238}Pu through ^{242}Pu. Unfortunately, these SRM's are not certified for chemical compo-

Yet another source of reference materials is the New Brunswick Laboratory of the AEC. These materials include spectrographic standards with added impurities in uranium, thorium, and beryllium oxide base materials, and metal and product materials to be used in referencing assays, isotopic measurements, uranium oxidation state analyses, and measurements of some other constituents. In addition, they offer various powdered ores for referencing uranium and thorium assays and for use as counting standards. Other Special Nuclear Materials are now, or soon will be available from other countries and from various international organizations.

The concern has continued as to the adequacy of the available reference materials; for some uses, available reference materials are definitely inadequate. A recent AEC questionnaire requests information about other standard materials needed and the relative urgency of the needs or the priorities. This questionnaire should be given very careful consideration and detailed information should be supplied to the U. S. Atomic Energy Commission to provide an adequate base to plan future additions to the available SRM's. NBS is also actively seeking information about needs for SRM's for nuclear materials, and the panel discussions at this Symposium are being used as one of the informational sources.

One type of reference material that is sorely needed is "working standards". It was the concensus that materials used as working standards were too diverse to be certified and offered by a single organization such as the National Bureau of Standards. It seemed preferable for each user laboratory to prepare its working standards or to have another responsible laboratory fill their specific needs.

This latter approach was followed, for example, at the LMFBF Fast Flux Test Facility (FFTF) now under construction at Richland, Washington, to be used to a significant extent in the development and testing of fast reactor core components. This requires that the materials used in the tests be exceptionally well characterized, and that standards, when available, be used to provide a common basis to characterize these materials. Various kinds of standards are used including, but not limited to SRM's, "working standards," calibration standards, and quality control standards.

A lack of adequate working standards was shown by an analytical chemistry development program for LMFBR/FFTF fuels in which two interlaboratory tests were conducted. In one series of tests, each laboratory was instructed to use the NBS plutonium metal and uranium oxide for calibrating its plutonium and uranium methods, respectively, and several working standards of mixed oxide powder spiked with known amounts of various impurities that were obtained at another laboratory (LASL) for distribution by HEDL. Needed standards were identified by these interlaboratory tests. Calibration and control standards were then prepared for use in qualifying and monitoring analytical laboratories involved in the production of fuel for the FFTF.

The value of interlaboratory tests or round robins has been significant in the FFTF programs. They have shown biases, problems with contamination from containers, and the need for standards. This information has led to prompt correction of problems; whereas, a single laboratory might have considerable difficulty in identifying such difficulties. The use of the various reference materials in these tests has contributed significantly to obtaining meaningful measurements.

The use of reference materials in a quality control program to obtain meaningful measurements is exemplified in the reprocessing of irradiated fuels at the Idaho Chemical Processing Plant. The important measurements from a nuclear fuel standpoint are (a) measurement of uranium input to the plant, (b) measurement of product output from the plant, (c) the measurement of impurities in the product, and (d) measurement of uranium in the lean waste streams. Uranium input is usually determined after the fuel assembly has been dissolved or after the fuel has been leached from the fuel assembly. Because of the highly radioactive nature of the resulting solutions, isotope dilution mass spectrometry is the preferred method for the simultaneous determination of uranium concentration and isotopic distribution. Plant product, in the form of uranium nitrate solution or uranium oxide, and in-process samples can be assayed by a number of methods. The lean waste streams are monitored by fluorimetry and mass spectrometry as required. Impurities in product materials are usually determined by emission spectroscopy, spark source mass spectrometry, or atomic absorption. All measurement procedures used in the processes are routinely monitored by analytical methods quality control program. The preparation and supplying of all reagents and standards is an integral part of this program to provide maximum control of method performance. Nuclear standards play a vital role in the quality control program and in the accounting of nuclear material passing through the plant.

Also of importance to reprocessing quality control has been the Umpire Laboratory Qualification Program and the ongoing Safeguard Analytical Laboratory Evaluation (SALE) Program. The preparation of working standards of typical plutonium and uranium materials actively handled by the nuclear industry is one of the major objectives of this program.

Nuclear materials safeguards requires an accurate knowledge of the quantity of special nuclear materials present in the fuel cycle. Increased attention being given to national and international safeguards has demanded that the nuclear industry sharpen its skills in the analysis of nuclear materials. To reduce LE(MUF) to a practical minimum, increased emphasis must be given to improved accuracy and precision in chemical and nondestructive measurements. Laboratories can refine techniques, make numerous repetitive measurements, and devote more effort to demonstrating the control of the quality of measurements being reported. Non of these efforts is cost-effective without an appropriate standard material by which one can determine any deviation from the "real" or "correct" value. A false sense of security growing out of improper or incorrect use of well-characterized standard materials is likewise not cost-effective.

Interlaboratory comparison programs such as GAE and SALE have generated materials whose composition has been determined by "consensus." These materials are available and have been used as secondary or working standards.

Some of these materials lack requisite chemical stability, however, once their sealed containers are opened.

Working standards for isotopic assay are used in the gaseous diffusion plants. Uranium hexafluoride samples are carefully prepared and cross-characterized against NBS material. These working standards become the basis for relative measurements on the gas instruments of UF_6 product material. Other highly accurate isotopic characterization of uranium and plutonium materials can be obtained on special request from BCMN (EURATOM).

Many of the chemical methods for determining uranium or plutonium for safeguards purposes have SRM traceability. Those methods should be standardized against uranium or plutonium. Quantities of standard and sample titrated should be of the same magnitude and of approximately the same chemical composition.

The influence that safeguards requirements are exerting on the nuclear industry is creating a clamor for additional standards. Of all the areas in safeguards research and development in which there exists a strong need for standards, the area of nondestructive measurement stands foremost.

During the past decade, interest at all levels in the nuclear community in improving measurement capabilities has resulted in development of a variety of nondestructive assay methods. These methods often are rapid, do not require sampling, do not affect the physical or chemical form of the material, and make possible accurate isotopic and assay measurements. Gamma ray spectrometry, neutron flux measurements, and calorimetry are typical techniques. Specific information, such as isotopic composition, physical positioning in the container, and significant impurities must be available for accurate assays by various of the techniques. A deterrent to the use of NDA methods involves the general inadequacy of nondestructive assay calibration methods and specifically, inadequate working, secondary, and primary calibration standards. For all practical pruposes, nondestructive assay standards do not currently exist beyond the working level, and the "working" standards are subject to justifiable criticism by virtue of their lack of traceability to certified source materials and confirmation based on independent measurements.

An appreciation for the complexity of the problem can be achieved by considering a wide range of configurations as exemplified in radiographs of typical geometric and loading variable waste assay standards (figure 1). These standards typify two unique attributes of nondestructive assay standards:

1. Inability to be verified directly, by sampling.

2. Reliance on chemical analytical standards for partial characterization bases.

In this regard, working level nondestructive assay standards can be said to be even more dependent on secondary or standard reference materials than their chemical analytical counterpart. For all practical purposes, the only way such standards can be confirmed nondestructively is based on a comparison to higher order standards. However, the current lack of such standards precludes this certification.

Another important point to consider is that all nondestructive assay methods depend on isotopic data. They rely on measuring one or more attributes of several of the isotopes, but none measures all of the isotopes. Because of this aspect of nondestructive standards, the need exists for reference materials certified for both isotopic composition and for fissile material content. For some NDA techniques, the standards should be relatively large. For example, for calorimetry of ^{239}Pu, the standard should be 4 g or larger.

The first step in mounting cohesive efforts toward satisfying the needs for NDA reference materials must include realization that nondestructive assay standards are related to, but still different from their chemical analytical counterpart. Areas of commonality include dependence on chemical attributes (e.g., form, isotopics, enrichment, impurities, and homogeneity) and certain physical attributes (e.g., mass and volume). Principal distinctions center around the dependence of nondestructive standards on certain physical attributes (e.g., matrix material, geometric loading, and dispersion) which by design simulate product and by-product materials subject to measurement.

Specific needs in the area of nondestructive assay measurements include at the working, secondary, and primary levels, the following:

1. Guidelines for preparing standards and mechanism for industrial exchange programs.

2. Methods for characterizing and certifying standards at all levels.

3. Primary and secondary measurement standards.

A coordinated industry wide attack on the problem is needed with government laboratory certification of working standards and development of mechanisms for providing primary and secondary standards.

At this point in time, standards for uranium and plutonium materials, either for chemical analyses or nondestructive assays, are most needed and used. Some interest was expressed in reference materials for neptunium and to a lesser extent for americium and even curium. Interest was also expressed in standards containing known levels of trace impurities, especially fluoride and chloride.

A particularly difficult type of standard to obtain and certify is that which must be used as a solid rather than in solution. Additional reference materials of this type are needed for methods calibration to measure oxygen-to-metal atom ratios, moisture, gas contents, and similar chemical characteristics of fuels and other material. The need exists also for isotopic spikes made from ^{233}U, ^{242}Pu, and ^{244}Pu that are of good isotopic purity.

The availability of reference materials is the important first step toward meaningful measurements, but adequate information about the standards must also be provided. More detailed certificates of analysis with detailed directions for use, suggested methods of standardization, and a list of impurities would promote more meaningful measurements. The analytical chemist needs to have as much information as possible on the makeup of the SRM, so that this information can be related to the wide variety of materials that must be analyzed. The SRM's are often of such purity or chemical composition that their behavior in an analytical method is quite different from the behavior of the materials to be analyzed. Perhaps some SRM's should be prepared that are not so pure, but yet well characterized, and this information be provided to the user. SRM's of the same chemical composition and physical form as the material to be analyzed are highly desirable.

In summary, the discussions indicated that much progress has been made during the past 30 years in providing special nuclear reference materials but that several needs still exist. The needs are most acute for nondestructive assay reference materials and for working standards. Nuclear materials certified for isotopic distributions and also for chemical assay would be valuable reference materials for NDA, but there are no ready answers for most NDA standards' needs. Working standards should be prepared by the using organization to best meet its needs, but confirmatory analyses by a government laboratory would add a measure of assurance and acceptance to the standard.

Interlaboratory analysis programs or round robins are of value in pinpointing analysis problem areas quickly. SRM's and working standards play important roles in these comparisons.

Increased attention given to safeguards has demanded better analyses of nuclear fuels and additional reference materials. These additional materials include neptunium, americium, curium, and standards containing known levels of impurities, oxygen-to-metal atom ratio, moisture, and gas contents. The status of uranium and plutonium reference materials, are summarized in Tables 2 and 3.

Meaningful measurements require adequate analytical quality control programs that include frequent methods calibration using certified reference materials. More information about the reference materials would be helpful in their use.

It was obvious that the nuclear industry is firmly committed to the use of reference materials, to improving nuclear materials characterizations, and to cooperation in safeguards programs. Much effort must be devoted to supplying the necessary reference materials to support this commitment and its growing needs.

Table 1. Special Nuclear Standard Reference Materials

Numbers	Description	Certified for
950	Uranium Oxide	Uranium Content, 99.94% U_3O_8
960	Uranium Metal	Uranium Content, 99.975%
949	Plutonium Metal	Plutonium Content, 99.99%
944	Plutonium Sulfate Tetrahydrate	Plutonium Content, 47.50%
945	Plutonium Metal, Matrix	Impurities, 99.9% Pu
946 947 948	Plutonium Sulfate Tetrahydrate	Plutonium Isotopes, At. %
U-0002 thru U-970[a]	Uranium Oxide (U_3O_8)	Uranium Isotopes, At. %

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[a] 18 materials

Table 2. Uranium Standards

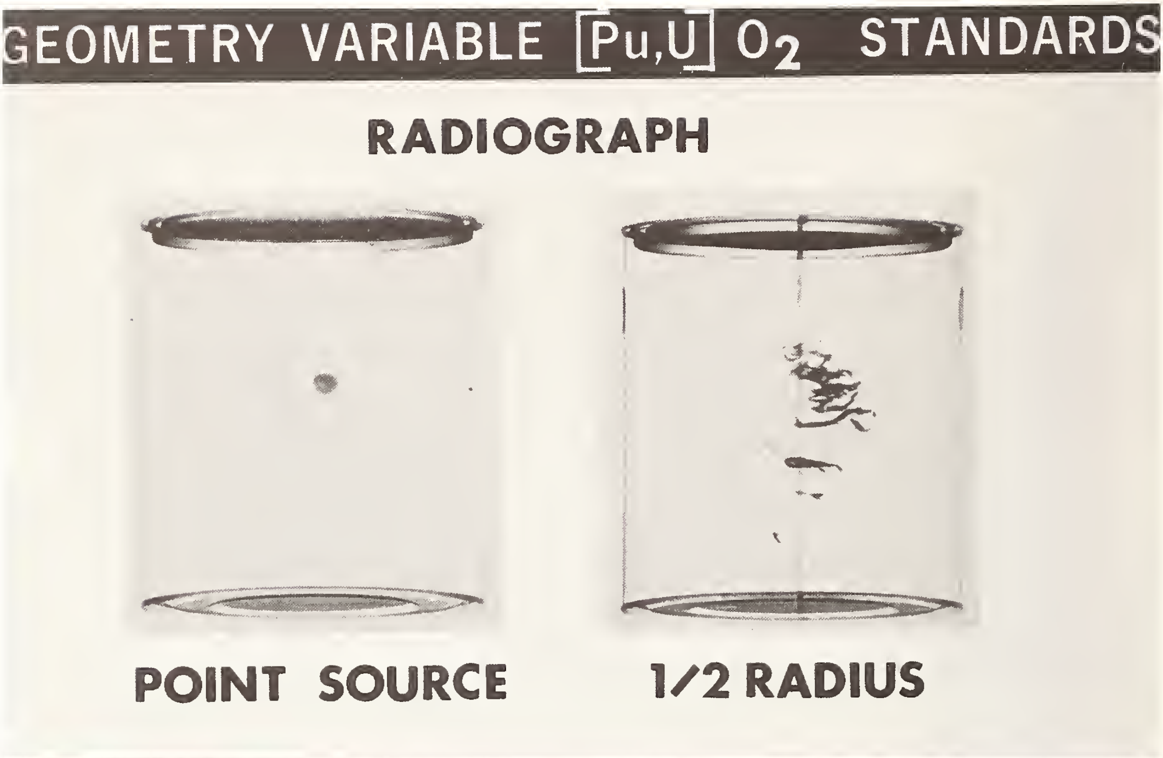
Material	Certification For	Availability
U-Metal	Conc	A
	Conc, Iso, Imp	N
U Metal 93% U 235	Conc, Iso	N
U Metal 97% U 233	Conc, Iso	N
U_3O_8	Iso	A
	Imp	A
UO_2 1-5% U 235	Conc, Iso	A
UO_2 (Large) 1-4% U 235	Conc, Iso	N
UF_6	Conc	N
UO_2 Pellets	Conc, Iso	N
(Pu, U)O_2 Pellets	Pu Conc, Iso U Conc, Iso	N
HTGR Beads	U Conc, Iso, Th Conc	N

A = Available N = Needed Conc = Concentration
Iso = Isotopic Contents Imp = Impurities

Table 3. Plutonium Standards

Material	Certification For	Availability
Pu Metal	Conc	A
	Conc, Iso	N
Pu Metal 99% Pu 242	Conc, Iso	N
Pu Metal 90% Pu 244	Conc, Iso	N
PuO_2	Conc, Iso	N
	Imp	N
$(Pu, U)O_2$	Pu Conc, Iso U Conc, Iso	N
	Imp	N

A = Available N = Needed Conc = Concentration
Iso = Isotopic Contents Imp = Impurities



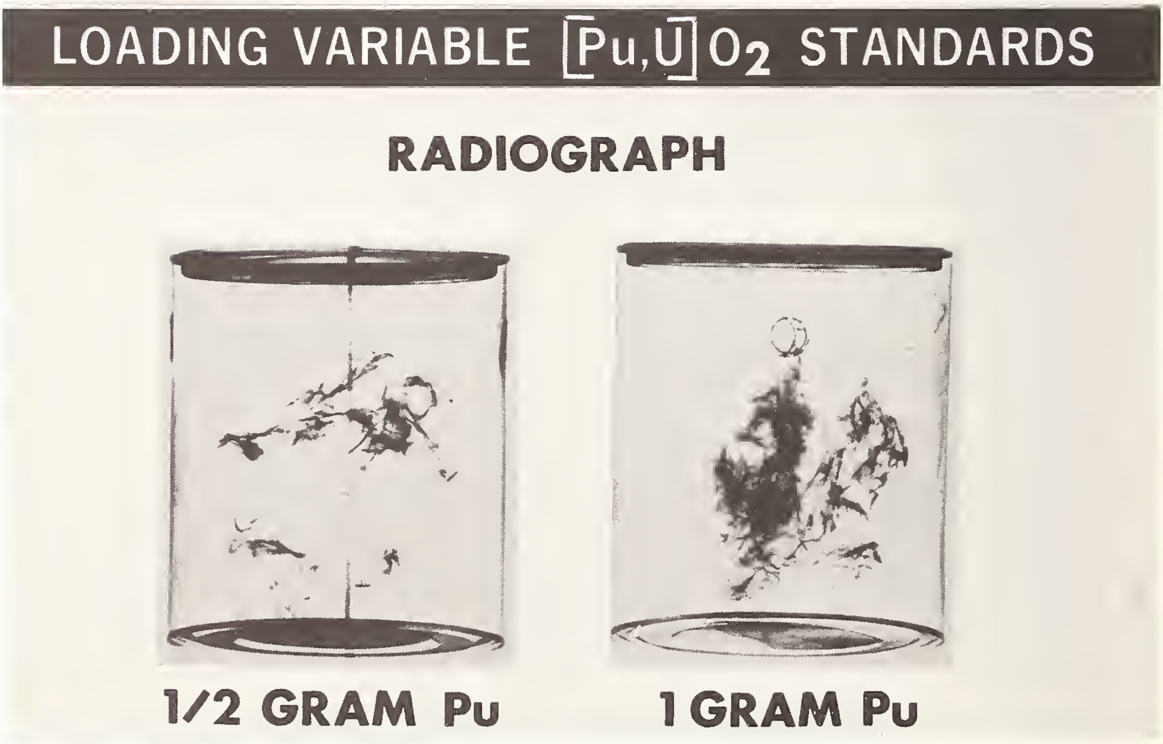


Figure 1. Radiographs of Typical Nondestructive Waste Assay Standards.

*Dark areas represent plutonium dispersed throughout matrix in a one-gallon waste container.

PETROLEUM

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I. The NBS Role in the Development and Certification of Primary Reference Fuels

C. L. Stanley

The measurement of engine knock in spark-ignition engines became an important economic as well as a technical parameter in the early 1920's. During this time, laboratory methods were developed to measure the knock quantity of fuels. However, the need for a defined scale by which the knocking tendency of fuels could be quantitatively interrelated still remained. Such a scale was proposed by Edgar in 1927. Edgar had noted that the straight-chain hydrocarbon, n-heptane, showed a strong tendency to knock in a spark-ignition engine. On the other hand, the branched-hydrocarbon 2,2,4-trimethylpentane (isooctane), was resistant to knock under such conditions. Using Edgar's suggestion the Cooperative Fuel Research Steering Committee, now the Coordinating Fuel Research Steering Committee, approved a preliminary octane number scale in 1930. This scale defined the octane number of a given fuel as the value equivalent to the number of parts by volume of isooctane blended with 10 parts of n-heptane, which give a fuel the detonation characteristics that matched those of the fuel being tested. The octane number was subsequently modified to the definition used today for both the ASTM Motor Method (D-2700 formally D-357) and Research Method (D-2699 formally D-908). The present definition is the whole number nearest the percentage by volume of isooctane in a blend with n-heptane that matches the knocking characteristics of the fuel when compared by either the ASTM Motor or Research Methods.

The scale as defined had one flaw. There was no single source of high-purity n-heptane or isooctane and specifications for them. In 1934 the CFRSC representing the automotive and petroleum industry requested NBS to develop specifications for these fuels. Samples of high-purity n-heptane and isooctane were prepared by Brooks and associates and the physical properties determined. Analytical studies of the foreruns and residues of commercial isooctane preparations were also made. This latter work gave, for the first time, good octane numbers for many of the hydrocarbon impurities. From these studies, specifications were developed that made it possible to prepare reference blends accurately to 0.1 octane number on the high end of the scale and 0.2 octane number on the low end.

Prior to 1947, the primary reference fuels were actually certified by NBS. This was possible since relatively small samples of the primary fuels were prepared per "batch." A sample of the bulk fuel was submitted to NBS for examination. If the sample initially met all specifications, the company was notified, and the "batch" was sealed in one gallon containers. One of these containers was selected at random and sent to NBS for testing. If this "check sample" met the specifications, the "batch" was certified and released. It should be noted that during this period, the primary reference fuels were not working standards, but were used to calibrate secondary working standards used in day-to-day calibration of CFR engines.

In 1946, it was decided to use blends of n-heptane and isooctane as direct working standards. This would, of course, require much larger quantities of high-purity n-heptane and isooctane. The petroleum industry responded by developing methods for preparing "lots" of up to 250,000 gallons of these hydrocarbons in very high purity. The NBS Automotive Section (which no longer exists) worked closely with ASTM and the petroleum industry in the development of these fuels. The development of means to prepare and store large amounts of these reference fuels marked the end of actual certification by NBS.

Since 1947, the practice has been to store the reference fuels in specially built, isolated tanks. The physical properties are still run by NBS on a submitted sample and reported to ASTM. Armed with NBS data and the storage facility inspection information, ASTM actually certifies the lot. To guard against lead contamination the prepared sample is stored under the specified conditions, and a specification of not more than 0.002 ml of tetraethyllead (later 0.002g lead) per gallon was instituted. This value is also determined by NBS.

Since the work by Brooks and associates, the physical properties of n-heptane and isooctane have been redetermined by workers associated with API Project 6 and by Pomerantz. The specification values were subsequently shifted to agree with the more recent values and these are the specifications used by ASTM today.

NBS discontinued the determination of octane numbers in 1961. At that time, it was pointed out that it was inconsistent with the philosophy of measurement to have the specification for a standard be the same property the standard was being used to measure. It was further suggested that the freezing point would be sufficient to evaluate the suitability of reference fuels for octane number standards. Because many members of Research Division I of ASTM Committee D-2 on Combustion Characteristics were concerned about the possibility of a few tenths of a percent of isooctane in n-heptane and vice versa, the Committee decided that the main producers should determine and report the octane numbers of their primary reference fuels when applying for certification. At the same time Research Division I on Combustion Characteristics requested Research Division IV, Hydrocarbon Analysis, to develop a gas chromatographic method capable of determining 0.1 percent n-heptane in isooctane and 0.2 percent isooctane in n-heptane.

After several years of cooperative work, in which NBS was involved, a tentative chromatographic method was issued in 1964. (This method was later approved and issued as ASTM Method D2268-71.) In the early part of 1969, Research Division I asked NBS to consider a program to evaluate reference fuels by this method and at the same time continue the present physical properties determinations. This would allow the comparison of the old and the new method over a period of time. The physical properties determinations have been continued; however, the evaluation program was never initiated.

The work at NBS relating to the certification of octane number primary reference materials has had several corallary benefits to the petroleum industry and the public.

1. At the request of ASTM, samples of extremely high-purity n-heptane and 2,2,4-trimethylpentane were prepared, purified and characterized. These are known as the "gold-plated" reference fuels. These samples are contained in sealed glass ampoules and

at present are considered the final arbitor in cases of disputes involving octane number.

2. The presence of the Automotive Section and of two altitude laboratories at NBS made it a logical place for studies of the variations of octane number with altitude. The accurate determination of these variations made it possible to intercompare engine results at widely differing altitudes.

3. In our studies of purity determination by freezing point and gas chromatography, it was found that the gas chromatography invariably gave higher purity values than the freezing point. At first it was assumed that impurity peaks were hidden under the main peak. However, about this time a paper by Broadhurst appeared that tended to support the idea that the freezing point is not completely free from bias at high purity. This problem has not yet been resolved.

4. For many years a mixture of n-hexadecane and 1-methylnaphthalene was distributed as a primary reference fuel for the diesel engines cetane number scale. This mixture perhaps contained a ratio as high as 2:1 of 1- and 2- methylnaphthalenes. Because the daily working reference fuels were large batches of stable secondary fuels, there was not a great deal of concern about this impurity. At NBS, we were aware of hydrocarbon mixture of three olefins, commonly mixnamed tetraisobutylene, which could be reduced, with some difficulty, to 2,2,4,4,6,8,8,-heptamethylnonane. This was done by a method developed at Pennsylvania University by Cosby. A large quantity of these olefins were prepared, hydrogenerated, and purified. The cetane number of this material was found to be very low and could be used as a primary reference fuel.

Cosby's paper appeared just about the time a new lot of secondary fuel was being calibrated. A rather good sample pf 1-methylnaphthalene was obtained at the same time; and upon calibration with it, the scale was found to have changed by nearly two units. This could have created serious economic problems. It was decided to set up a new cetane scale with n-hexadecane as 100 and the cetane number of the heptamethylnonane adjusted so that the earlier secondary scale would be maintained.

Finally, NBS is now in the process of certifying selected lots of n-heptane and isooctane as Standard Reference Materials. These SRM's are to be certified for the physical properties that we have been determining over the years. When these are issued, they are to be used by the individual manufacturer's laboratory or a laboratory selected by the manufacturer to run a comparison analysis.

Discussion: Does NBS have any present plans to supply certified reference standards for the measurement of cetane number of diesel fuels?

Not at the present time.

Are there problems associated with the use of pure hydrocarbons as reference standards for octane number when the actual fuel being compared contains tetraethyllead?

Only octane numbers are being compared and problems are minimal when the octane number of the calibrating mixture is matched closely with the fuel being used in the test engine.

II. The American Petroleum Institute Standard Reference Materials - 30 Years of Service to the Petroleum Industry

A. J. Streiff

This discussion of the background, preparation and some of the uses of the Standard Reference Materials of the American Petroleum Institute will provide an introduction to the statements of the three members of the panel representing the petroleum industry.

The API began to provide Reference Standards of hydrocarbons over 30 years ago. The total number of hydrocarbon reference materials, together with related compounds which are constituents of petroleum products, now includes in excess of 500 individual compounds.*

The initial reasons for this program were related to the outbreak of World War II. With the advent of war the petroleum industry soon became the largest single chemical enterprise in the country, its products comprising 60 percent of all the tonnage of supplies shipped to the armed forces. Manufacture of chemical products on such a scale required careful analysis in research and control.

For such products as aviation gasoline and monomers for synthetic rubber, it soon became apparent that the crux of

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*A complete catalog of American Petroleum Institute Standard Reference Materials can be obtained free by writing: API Standard Reference Materials, Attn: A. J. Streiff, Carnegie-Mellon University, Schenley Park, Pennsylvania 15213.

the matter lay in the development of fast and precise analyses. For this use, ultraviolet, infrared and mass spectrometers became invaluable tools. However, these early instruments required careful calibration, which in turn was directly dependent on the purity of the standards from which it was determined. At the beginning of the war it was not possible to obtain samples of the required purity of more than a dozen hydrocarbons.

An American Petroleum Institute research project on the composition of petroleum, then located at NBS, under the direction of F. D. Rossini, began to prepare standard hydrocarbons and certify their purities. In 1950 this activity was moved to the Carnegie Institute of Technology in Pittsburgh, now Carnegie-Mellon University.

From the beginning most of the starting materials that could not be readily obtained were synthesized by other API research projects.

Later, all of this work on hydrocarbons was consolidated into a single project designated Project 58 on the Synthesis and Purification of Standard Hydrocarbons. In recent years, that part of the project concerned with synthesis has been located at Oklahoma State University under the direction of Professor E. J. Eisenbraun. The purification and certification of purity was done at Carnegie-Mellon University and all API Reference Materials and distributed from there.

When the work on hydrocarbons was well under way, attention was turned to some of the non-hydrocarbon constituents of petroleum. Standard organic sulfur compounds and organic nitrogen compounds were prepared by API projects at laboratories of the United States Bureau of Mines in Bartlesville, Oklahoma, and Laramie, Wyoming.

All of these reference materials are of high quality. The target was 99.9 percent purity. Each compound was certified with respect to the amount of impurity. They are available in units of five ml, degassed and sealed under the compound's own vapor pressure in a Pyrex glass ampoule with internal break-off tip.

The new compounds synthesized in the past few years are available in one ml units, and though not certified with respect to purity are at least 99 percent pure and are useful for many calibrations.

Of particular interest to petroleum laboratories are six standards that are supplied with values for refractive index at seven different wavelengths at 20, 25, and 30 °C. Three of these hydrocarbons are supplied with refractive index values at 80 °C and 100 °C for five different wavelengths.

The methods used to produce these ultrapure compounds were physical methods which would be applied to make comparatively large amounts of pure material--of the order of a liter or more. The methods used were distillation, both regular and azeotropic, liquid-solid chromatography, crystallization (including zone melting) and clathrate formation. Gas chromatography and precise melting point measurements were used to enable selection of the purest material. Final purities were determined by the highly accurate calorimetric method or by precise time-temperature melting curves.

The requirements for the measurement of highly precise and accurate physical properties during the preparation of reference materials led to the development of excellent methods for the measurement of physical properties by the API projects. Hence, there resulted from the API program a vast amount of published property data from both our laboratories and those of many other laboratories in the United States and abroad who were provided with API materials.

Properties which have been measured with high precision and accuracy include boiling points over a wide range of pressures, densities at several temperatures, refractive index at many wavelengths and temperatures, freezing points, low temperature heat capacities, heats of fusion, combustion, vaporization and transitions in the solid. Critical constants and compressibilities of selected compounds have also been measured. Careful spectral measurements have been made in the categories of infrared, ultraviolet, mass, Raman and nuclear magnetic resonance.

From the basic physical property data other useful data have been derived. These include such values as the constants of the Antoine equation relating vapor pressure and boiling point, cryoscopic constants, entropies, heats of hydrogeneation and of isomerization. Correlations of these measured data have yielded calculated values of properties for other compounds which have never been made. Most of these data have been included in the Tables of Selected Properties of Hydrocarbons and in the catalogs of Spectral Data of the API Project 44 and Texas A & M University.

In recent years efforts have been made to provide compounds of higher molecular weight, particularly polynuclear aromatics for which there is much need in the research laboratories of the petroleum industry. These compounds are very difficult to synthesize and purify. Because of diminished financial support for basic work, progress in supplying them as reference materials has not been rapid. Continued financial support for research on these and related classes of reference materials is needed in order that the future requirements of researchers in this field can be met.

Discussion: Is the American Petroleum Institute continuing to support the standard reference materials program from budgeted funds?

A representative from the API indicated that in recent years most of the API budget for research has been used for applied environmental research. It is expected that support for basic research by API will be ended shortly. Supplies of existing reference materials on hand are large enough to supply the projected needs of the industry.

III. The Use of Standard Reference Materials In a Petroleum Analytical Laboratory

T. J. Mayer

A. Introduction

During data gathering I was amazed at all the places in the Laboratory where standards of some sort are used. Since I thought that even those from petroleum laboratories might be interested, I will survey a tupical R&D Analytical Laboratory and, at end of this survey, will discuss in more detail some different uses of "standards" to obtain meaningful measurements.

B. Survey of Use of Standards in a Petroleum Analytical Laboratory

The organization of the Analytical Section at Sun Oil R&D is shown in figure 1. This organization is probably fairly typical even though other laboratories may group their disciplines differently. I would like to tour this Section and mention how reference materials of some type are used in each Laboratory.

The first group, Elemental Analysis, contains the laboratories listed below the box in figure 1. This group, as the name implies, is concerned mainly with analyzing for individual elements, usually quantitatively. We use emission spectroscopy, x-ray fluorescence spectroscopy, and atomic adsorption spectroscopy mainly to determine metals in oils from the percent level down to trace levels. In many cases, we have not yet determined which of these three techniques is best for a particular analysis [1].

Until now, we have used the Conostan* Metallo-Organic Standards almost exclusively for trace metal analyses. These SRM's, sold by Continental Oil Company, are supplied in a constant metal free (less <0.1 ppm) base oil. Individual metals are available at 5,000 ppm in the base oil and 12 or 20 element blends are available in concentrations ranging from 10 to 900 ppm. We use these standards for both calibration and standardization although occasionally we have used the NBS Metallo-Organics in the Conostan base oil for additional standardization.

At this point, I should mention that NBS and EPA ARE cooperating with industrial and other laboratories to provide some fossil fuel standards. Four samples of trace elements in coal, fly ash, fuel oil, and gasoline have been cooperatively analyzed by several laboratories. The data are now being compared.

Microchemical analyses in our laboratory are generally concerned with C, H, O, and N determinations or molecular weights by vapor pressure osmometry. C, H, O, and N are done semi-automatically using a Perkin-Elmer Model 240 Elemental Analyzer. NBS acetanalide is used as the calibrating standard. NBS benzoic acid is sometimes used if a nitrogen calibration is not needed. A sample of squalane, which has been around so long that nobody knows its origin, is used for the molecular weight calibration.

Sulfur analysis can be done by many methods but we mainly use two, the LECO method and Dorhmann microcoulometric technique. We use NBS Sulfur in Residual Fuel Oil Standards to calibrate the LECO procedure for percent S. These standards range from 0.27 to 2.14 percent.

For ppm sulfur, in liquids, we prefer a microcoulometric technique for which we use Angstrom Company standards for samples ranging from 20 ppm to one percent. Below that level no good standards are available. SRM's in the 0.1 to 1 ppm range are needed to calibrate this microcoulometric procedure.

For sulfur in gases, the permeation tube, available from NBS and other sources seems adequate. For microcoulometric N analyses, no good standards are available.

The Materials Characterization Group is concerned with determining properties or composition of materials instead of elemental analysis.

*Registered Trade Mark of Continental Oil Company

X-ray diffraction is in this group because we use it to characterize catalysts and other solid materials. Generally, we are determining crystalline composition to study the changes in catalyst structure that occurred during preparation of the catalyst or during a reaction that is being catalyzed. When analyzing zeolite catalysts, for instance, we use Linde A, and alumina recommended by NBS to calibrate 2θ values. For other catalysts, such as metals or metallic oxides, we usually must resort to pure chemical reagents, e.g., 99.9 percent pure V_2O_5 for vanadium catalysts.

We have a microscopist in our Analytical Section, which may or may not be typical of other petroleum laboratories. Although much of the microscope work is particle size determinations and counting, we have some areas where SRM's are used.

Measuring the refractive index of solids is usually done on the microscope. Briefly, this is done by immersing the solid in liquids of known R.I. under the microscope. When the solid becomes invisible, its R.I. is then equal to the R.I. of the reference liquid. This method, therefore, requires a set of reference liquids with known refractive indices. In a like manner, if it is desired to measure the R.I. of a liquid under the microscope, a set of Standard Reference Solids are needed. Sets of both solids and liquids with Certified Index of Refraction are supplied by the R. P. Cargille Laboratories, Inc.

Melting points of very small samples are also done on the microscope using a Kohfler hot stage. The hot stage permits the microscopist to vary the temperature from 30 °C to 350 °C in order to determine melting points, transition points, sublimation points, etc. The hot stage is calibrated using standards supplied by Kohfler who state that they conform to NBS Standards. These materials are certified to melt within ±0.5 °C.

We also use a cold stage on the microscope to study waxes. The cold stage operates from +40 to -70 °C and at present no standards are available for calibration. We use pure compounds with known melting points.

The calibration of IR Spectrometers with polystyrene is well known so I need not describe this procedure. We use a potassium dichromate solution to calibrate UV spectrometers checking either transmittance or adsorbance at 10 to 20 different wavelengths.

In our Laboratory, NMR is used mainly for qualitative characterization so only routine materials like acetaldehyde or ethylbenzene are needed to tune the spectrometer. If quantitative measurements are required the standard reference solutions must be prepared from pure chemical reagents.

The Separations Group is the heart of most petroleum analytical laboratories. In this group, complex petroleum products are separated into fractions suitable for further analysis. Since we are usually dealing with hydrocarbon mixtures only, we use pure hydrocarbons, or blends of such, as reference materials. In the Distillation Laboratory, isooctane, n-heptane, methylcyclohexane, etc., are used to calculate column efficiencies and calibrate boiling point instruments. For liquid and planar (i.e., TLC and Paper) chromatography pure hydrocarbons are used to determine retention volumes.

Although, pure hydrocarbon standards are available from API and NBS, they are usually only in small quantities and expensive. For the large amounts of hydrocarbons needed in the Distillation and Chromatography Laboratories, we use the Phillips hydrocarbons mixtures almost exclusively.

In the Physical Properties Laboratory we determine refractive index, viscosity, API gravity, and other routine properties. Here, since better standards must be used, NBS isooctane (SRM 217b, 2,2,4-trimethylpentane) is used for both R.I. and density calibrations.

Viscosity standards, which are primary certified oils with known viscosity, are obtained from the viscometer manfacturer. (At one time these certified oils were available from NBS).

The Component Analysis Group is last because it is the group with which I am most familiar and I can discuss the use of reference materials in some of these disciplines in more detail.

I will depart from the sequence of laboratories shown in figure 1 and briefly discuss our Radiochemical Laboratory, which is confined to low-level tracer work. Most of the SRM's used in this laboratory are purchased from suppliers of radioactive materials, but many of these are referred back to an NBS primary standard. For example, a Certificate of Radioactivity Calibration for a toluene-C^{14} sample reads, "Found to give identical channel ratios (in liquid scintillation counting) to samples prepared from NBS Benzoic acid - 7-C^{14}, Sample No. 4925."

Mass spectrometry is used in our laboratory to determine the composition of hydrocarbon mixtures in terms of either individual components for lower molecular weight fractions or hydrocarbon type by carbon number for higher boiling fractions.

One mass spectrometer analyzes gases from refinery units. Usuaully we determine H and C_1 - C_6 hydrocarbons but we can also determine other gases such as He, COS, SO_2, H_2S, CO_2 and report N and CO together. This instrument is calibrated about once a year using 24 individual pure gases, obtained from Phillips Petroleum Co., to determine individual sensitivities. This procedure takes one to two days. In addition, two to three times a week a hydrogen check is run using pure hydrogen.

The other mass spectrometer is used for liquids analysis, such as gasolines, kerosines, gas oils, etc. Standard reference materials are used to derive M. S. analytical methods using the procedures described by Brown and others [2,3].

I would like to describe an application of some materials, which could hardly be called Standard Reference Materials, but which turned out to be useful because they were all that were available for a reasonable cost.

We wanted to develop a M.S. method for determining the composition of straight-run aromatic concentrates in the gas-oil range, boiling from 200 ° to 675 °F, which includes C_7 to C_{25} hydrocarbons. The method was to be a LIV procedure reporting seven major hydrocarbon types from alkylbenzenes to phenanthrenes by carbon number. For this carbon number range, 109 sensitivity constants were needed to report quantitative analyses in weight percent. Ordinarily these sensitivities would have been determined from pure compounds as described in References 2 and 3.

We did not have the necessary pure components. So for the C_{17} - C_{25} range we used extrapolated data published by Lumpkin and Aczel [4]. For the C_7 - C_{10} range, we used constants from gasoline analyses that were previously described. This left the C_{12} - C_{20} range for which we had 22 fractions of the API -6 crude oil as the only available reference materials. (These are available in 5 ml. vials from API.) These 22 fractions represent two large fractions each of which are subdivided into 10 fractions. Using an internal standard to inject constant weight samples and starting with estimated sensitivities for the different types from Lumpkin and Aczel [4] or previous company data, a series of trial and error determinations was made, adjusting some sensitivity constants each time, until the whole series of ten fractions produced the same weight.

In other words, we were injecting a constant weight of each fraction and when the sensitivities were correct the components would add up to same weight. Fortunately, the ten fractions in each group had enough differences in the hydrocarbon type composition so that changes in constants were significant.

As a final check, the analyses of the ten sub-fractions were used with a multiple regression analysis to find the proportion of each sub-fraction in the original source sample. Since the spectra were derived from constant weight samples, if the raw data were correct the sum of the fractions should add to 100 percent. The regression showed 102.3 percent, a reasonable check, we thought.

This illustrates the use of materials that could hardly be called SRM's, but since they were the best materials available, they were used as reference standards. Of course, if good SRM's had been available, at a reasonable cost, the job would have been much easier and probably more accurate.

In the Gas Chromatography Laboratory we use SRM's for both qualitative identifications and quantitative calibrations. An example of each will be shown.

Qualitatively, SRM's are used to identify GC peaks. Figure 2 shows a chromatogram of a synthetic mixture of C_9-isoparaffins. Peak identifications are shown for 35 possible C_9-isoparaffins. This synthetic mixture was prepared by starting with two to three components, adding components one at a time, and identifying the new peaks until 33 of the 35 components were added and identified. Retention times for the two unavailable components were assigned by boiling point and isomer structure.

At first small amounts of the API Standard Hydrocarbon Samples were used but they fairly pure C_9-isomers became available from Chemical Samples Company, Columbus, Ohio, at lower prices. Our experience with GC identification programs indicated that very high purity standards were generally not needed. A sample with 90 percent of the desired component was sufficient. Since the less pure samples can be purchased cheaper, they have found wide acceptance in GC work.

For quantitative GC work, one does need good accurate reference standards. Figure 3 shows the use of a SRM to calibrate a GC instrument. In this case we wished to transfer a gas analysis from the PE-154 Gas Chromatograph, which used a packed column, to a new PE-900 capillary instrument. Figure 3 shows the actual composition of the mixture and six replicate determinations for each instrument.

Although resolution of two components was lost, the accuracy on the PE-900 instrument was good enough to allow the analysis to be transferred. The resolution was regained later along with other advantages. The gas mixture used was Phillips ASTM Sample No. 6.

C. Work Done Without Available Reference Materials

I would now like to discuss a research problem where hardly any reference materials of any type or purity were available and what was done to obtain these materials.

Sun Oil has a Naphthalene Plant at its Toledo Refinery that produces high quality naphthalene and other products by extraction and demethylation of aromatics in gas oil streams. The plant was initially designed to extract naphthalene (C_{10}) from gas oil and produce additional naphthalene by demethylating the C_{11} isomers, 1- and 2- methylnaphthalene. Shortly after our Naphthalene Plant went on stream in 1962, we were asked to identify and determine the amount of the C_{12}- and C_{13}-alkylnaphthalenes in the feed to the Plant.

Determining the C_{12} isomers, which are ethyl- and dimethylnaphthalenes was not too difficult. From the results of API Research Project 6, Sun Oil and other investigators, we were able to gather either spectral or GC data or reference samples of good purity for all the C_{12}-isomers. Figure 4 shows the GC chromatogram of the reference mixture of C_{12}-alkylnaphthalanes that was used to calibrate our GC analyses. The chromatogram identifies 11 of the 12 isomers. One, eight - DMN is rarely encountered in our streams, but biphenyl, another dinuclear aromatic, is often observed.

Characterizing the C-13 alkylnaphthalenes was quite a problem, however. Here we had the possibility of encountering four propylnaphthalenes, 14 methylethylnaphthalenes, and 14 trimethylnaphthalenes for a total of 32 isomers. When the work was started, no spectral data or reference compounds were available for the propylnaphthalenes or methylethylnaphthalenes and data for only three of the trimethylnaphthalenes were available. It appeared that to provide the needed reference data we would have to synthesize our own reference compounds.

Fortunately, about that time, one of our co-workers found that ethylating 1-methylnaphthalene produced a mixture of methylethylnaphthalene isomers and using 2-methylnaphthalene produced another set of different isomers.

Figure 5 summarizes the procedures used to separate the mixture resulting from the ethylation of 2-methylnaphthalene (Mixture B). In the first step, two isomers were separated pure enough to characterize by spectral methods, but further GLC separation was needed to characterize the other four isomers. Figure 6 shows the GC identification of all the isomers found in this mixture. The 2-isomers predominate but some 1-isomers were present. Figure 7 shows the concentration of isomers found in Mixture A, which was made from 1-methylnaphthalene. We were expecting only 1-methyl isomers, which are in greater quantity, but we also obtained small amounts of 2-isomers.

The separation and characterization of 13 of the 14 methylethylnaphthalene isomers was described in detail in 1970 [5].

To obtain trimethylnaphthalene reference compounds more work was required. Five isomers were synthesized individually using dimethylnaphthalene starting materials. Another five isomers were separated in good purity from a petroleum fraction and three isomers were obtained from outside sources.

The description of the procedures used to prepare, separate, and characterize these TMN isomers was published in July, 1973 [6].

From the results of this work we were able to identify the C_{13}- alkylnaphthalenes and other components in two fractions to a gas-oil aromatic concentrate. We now use these two fractions as reference materials.

Figure 8 shows a GC chromatogram from the first fraction. This mixture shows the retention times for six dimethylnaphthalenes, two propylnaphthalenes, seven methylethylnaphthalenes and one trimethylnaphthalene.

Figure 9 shows a GC scan of the higher boiling fraction. Eleven MEN's and eight TMN's can be identified using this mixture. The other two TMN's found in petroleum can be identified from a still higher boiling fraction.

The work to prepare, separate, and identify the alkylnaphthalene isomers spanned three to five years. Had SRM's been available, it probably would have taken two to three weeks to produce the two reference mixtures shown in figures 8 and 9.

Conclusions: This author was somewhat surprised at the extent to which SRM's are used in a Petroleum Analytical Laboratory both as to the number and different types of materials that are required. It probably would be difficult, if not impossible, to operate an Analytical Laboratory without these SRM's.

In the future, this author would like to see the production of more, not less, SRM's. Higher molecular weight hydrocarbons, which would include polynuclear aromatics and condensed ring saturates, are particularly needed along with other materials that are going to become very imporant in our ecology-minded society. Many of these SRM's may not need to be of very high purity or available in large amounts. It would be nice if they were available, however.

Discussion: The fractions of petroleum of the API Research Project 6 used by the speaker for the analysis of aromatic concentrates in the gas-oil range were described. They are available from the API Standard Reference Materials office together with literature references.

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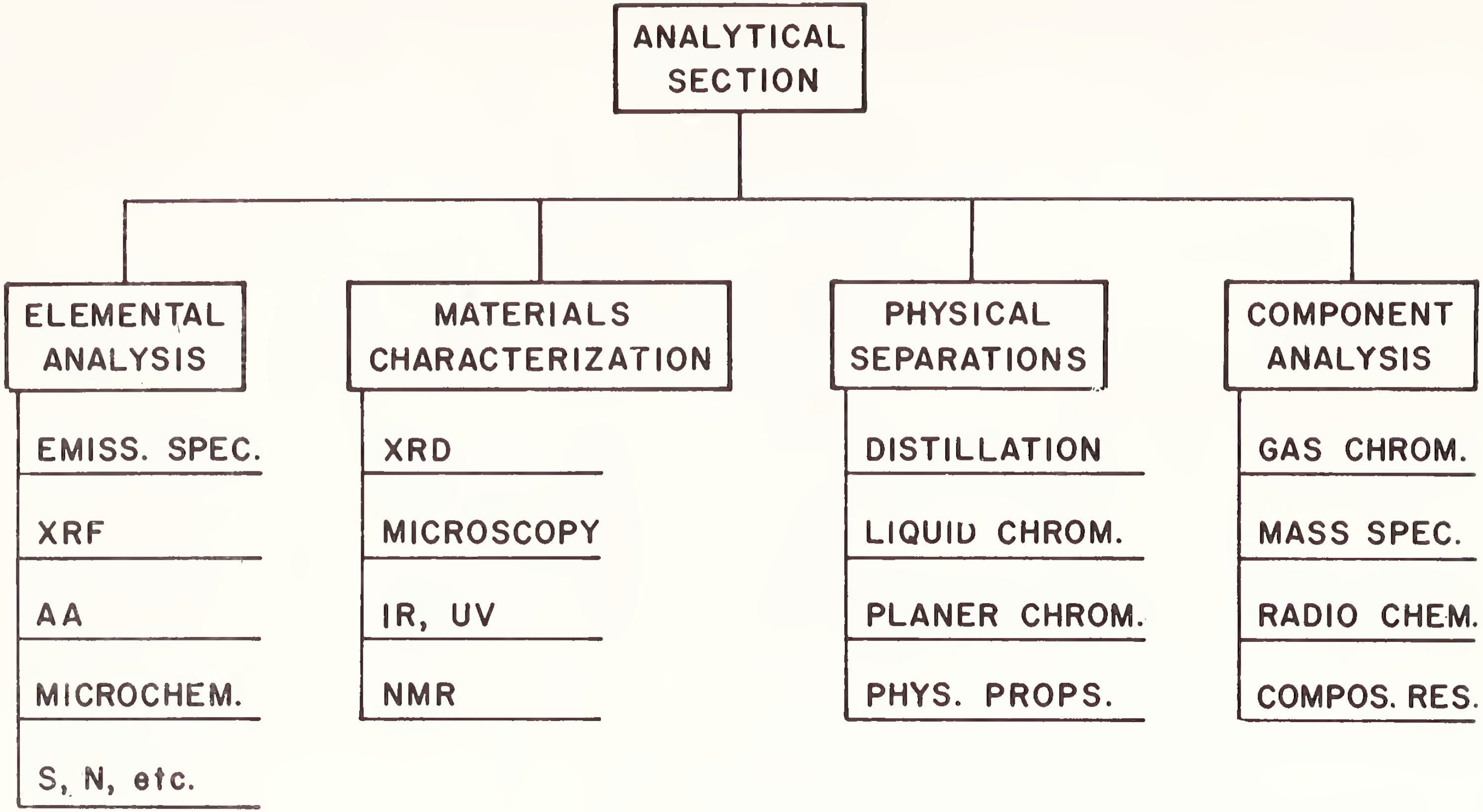

Figure 1. Organization Chart: Analytical Section

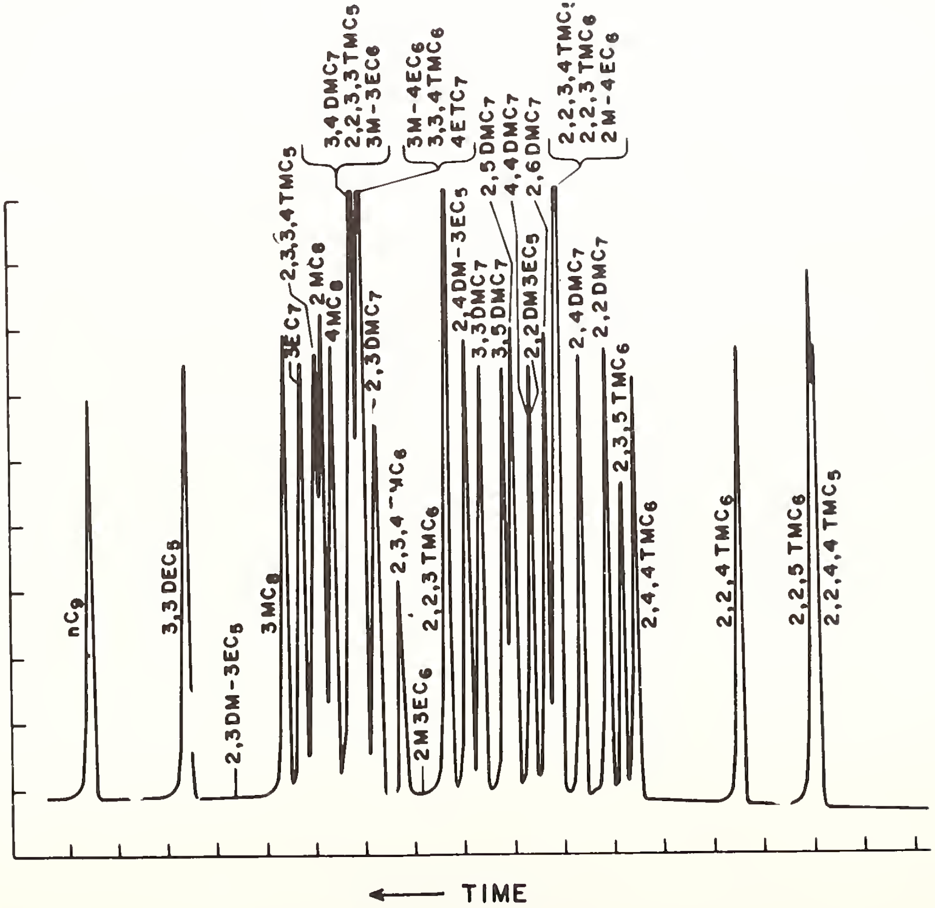

Figure 2. GC Scan of C_9 Isoparaffins

COMPONENT	ACTUAL WT.,%	MEAN WT.,% (6 RUNS - PE 154)	δ	MEAN WT.,% (6 RUNS - PE 900)	δ
$C_3=$	0.5	0.41	0.140	0.29	0.017
C_3	1.0	0.95	0.023	0.85	0.053
Iso C_4	36.5	36.26	0.074	37.35	0.761
nC_4	13.0	14.01	0.100	13.26	0.165
$C_4=1$	21.0	21.34	0.168	32.76	0.132
iso $C_4=$	12.0	11.44	0.103		
t $C_4=2$	7.0	7.39	0.062	7.15	0.081
iso C_5	1.5	1.60	0.014	1.79	0.264
c $C_4=2$	6.0	6.04	0.060	5.71	0.171
n C_5	0.5	0.53	0.022	0.55	0.103
$C_4=1,3$	0.8	0.75	0.009	0.70	0.015

Figure 3. Gas Analysis

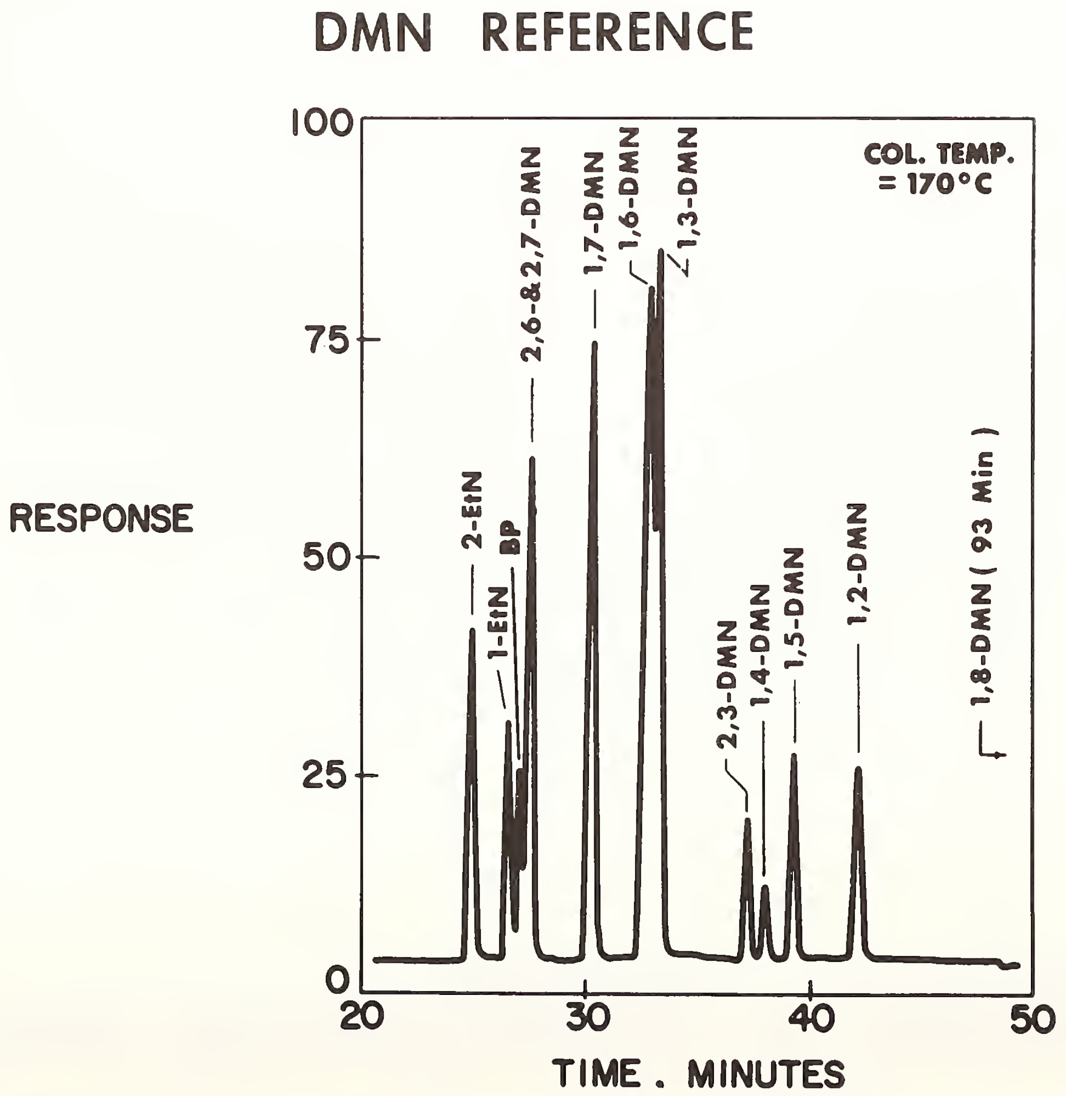

Figure 4. Reference Mixture: C_{12} - Alkylnaphthalanes

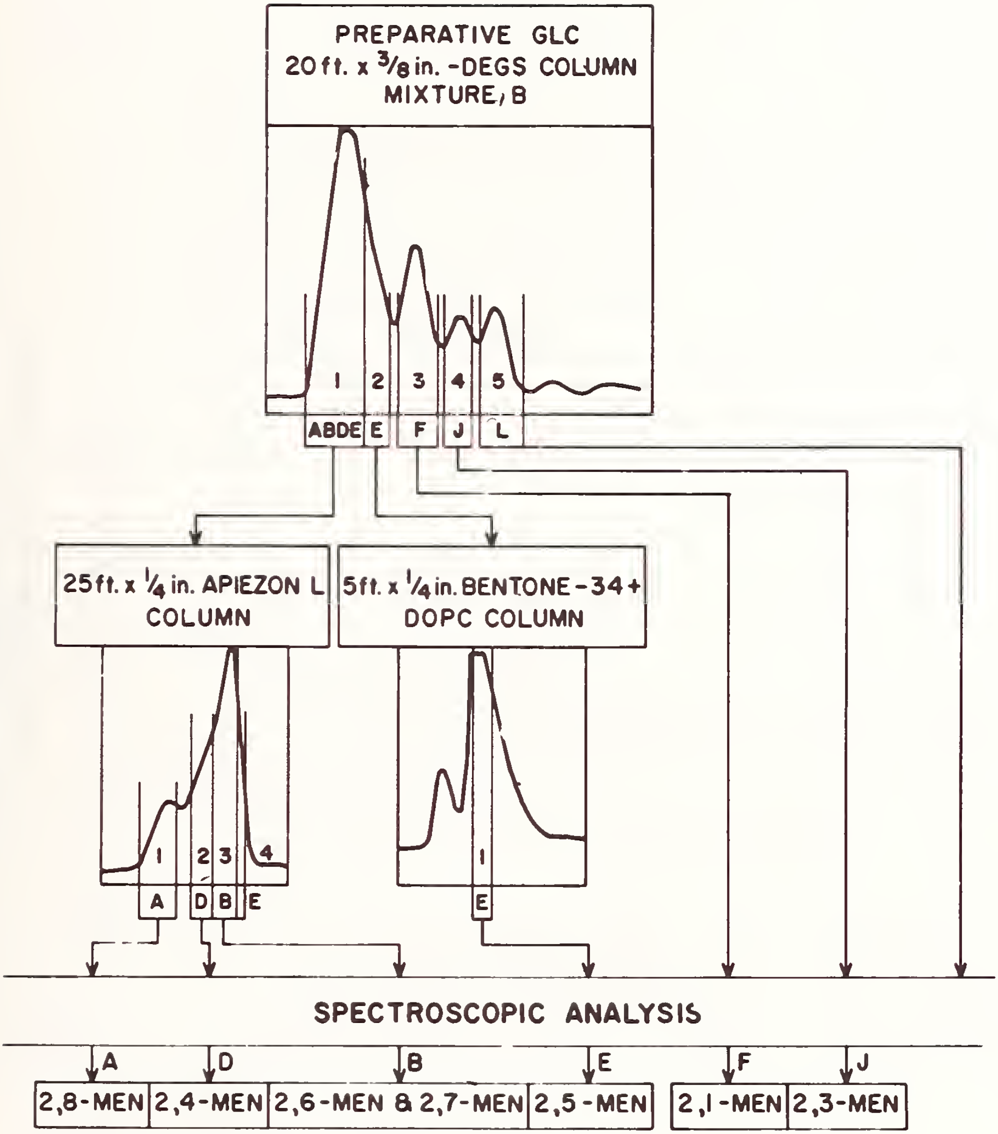

Figure 5. Schematic of Separation Procedures

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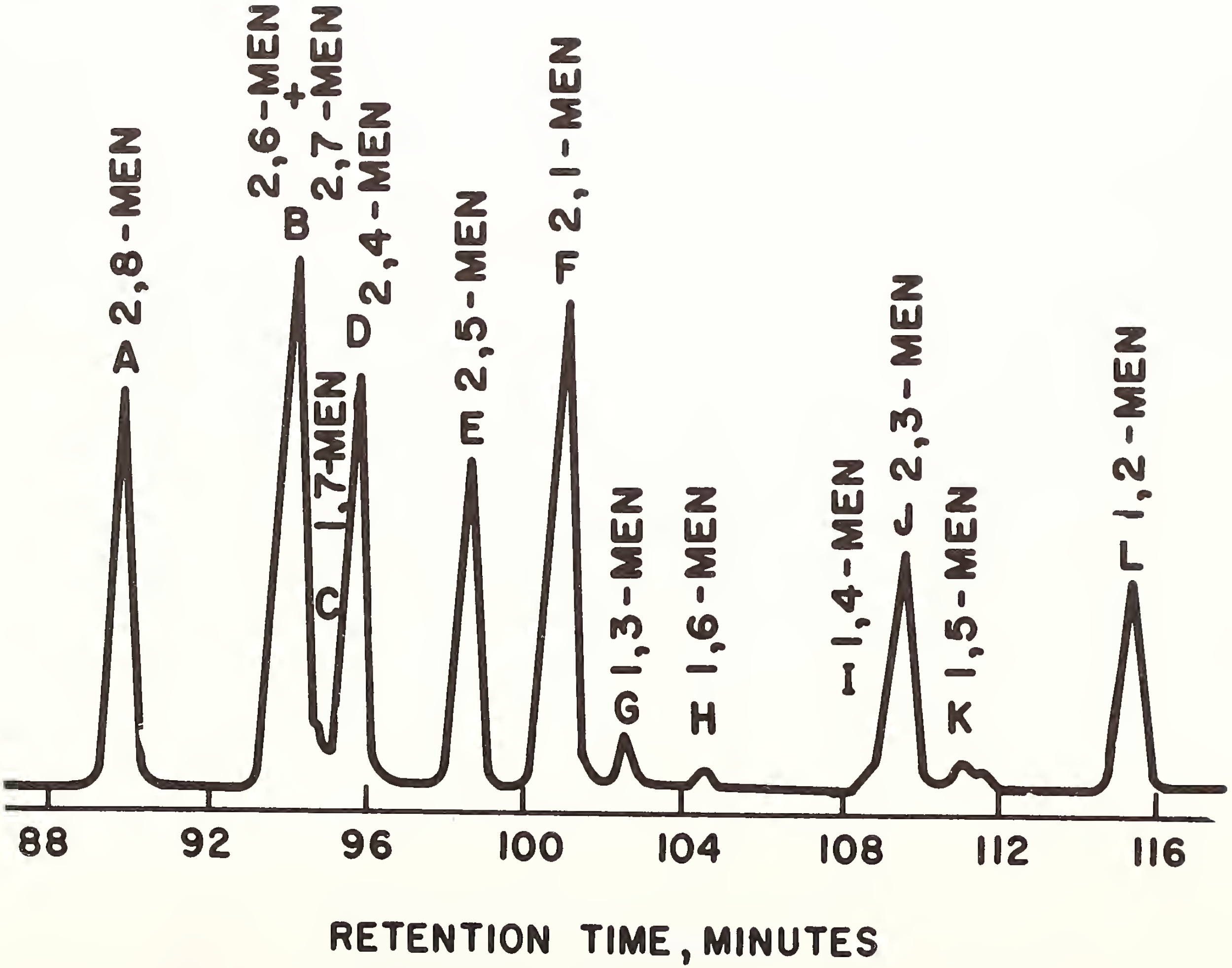

Figure 6. GC Identification of Isomers

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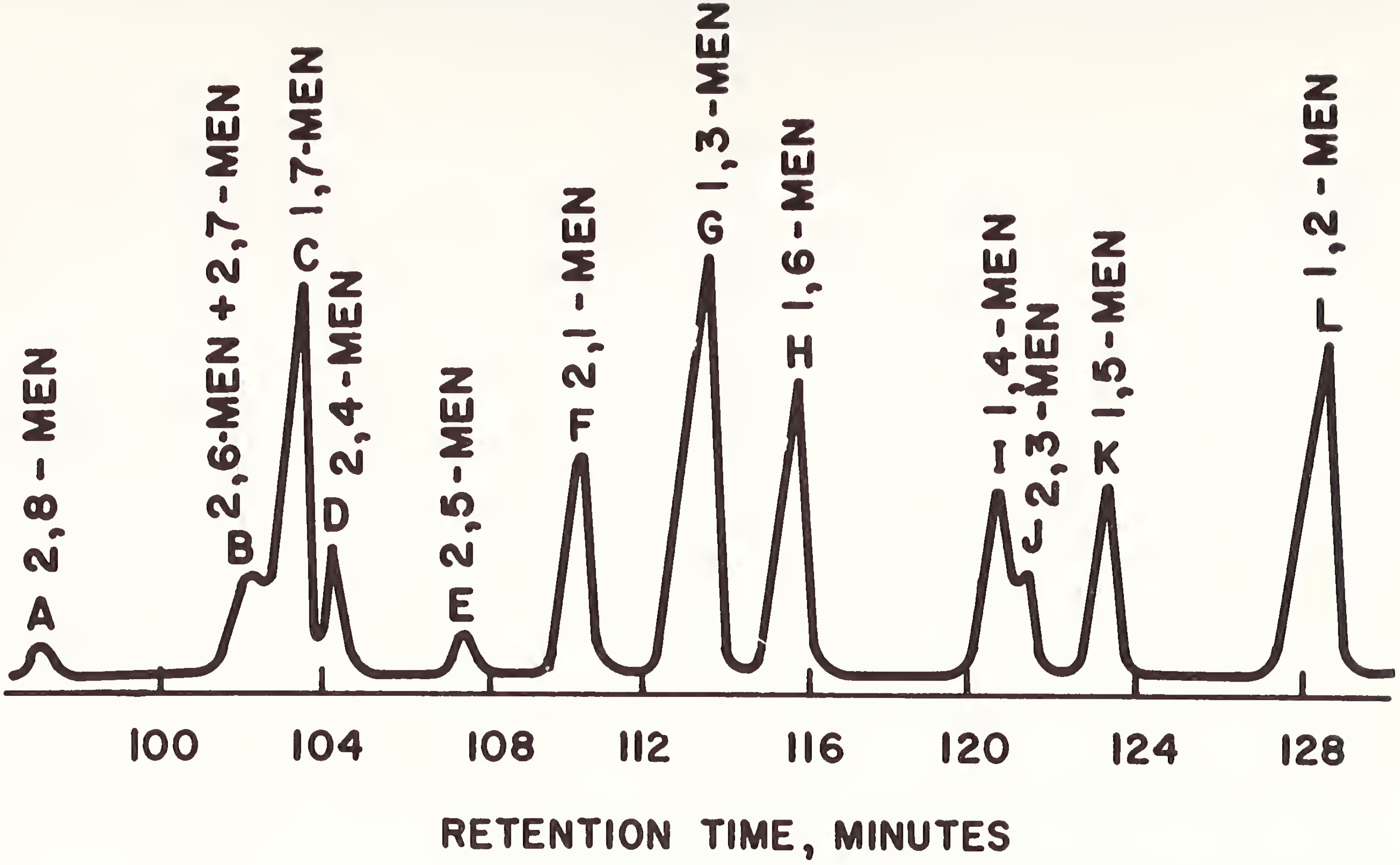

Figure 7. Isomers found in Mixture A

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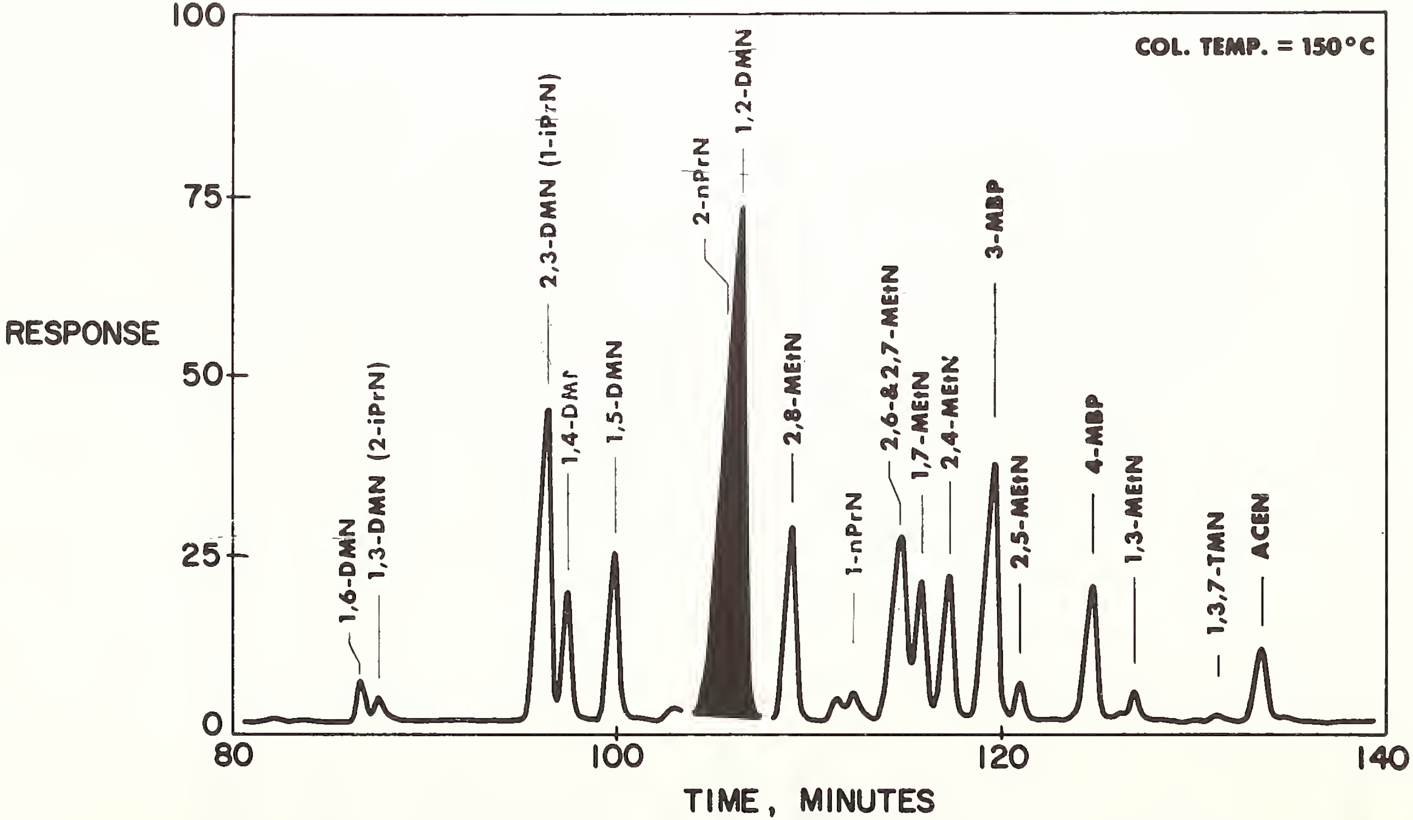

Figure 8. GC: 515 - 530 F Fraction

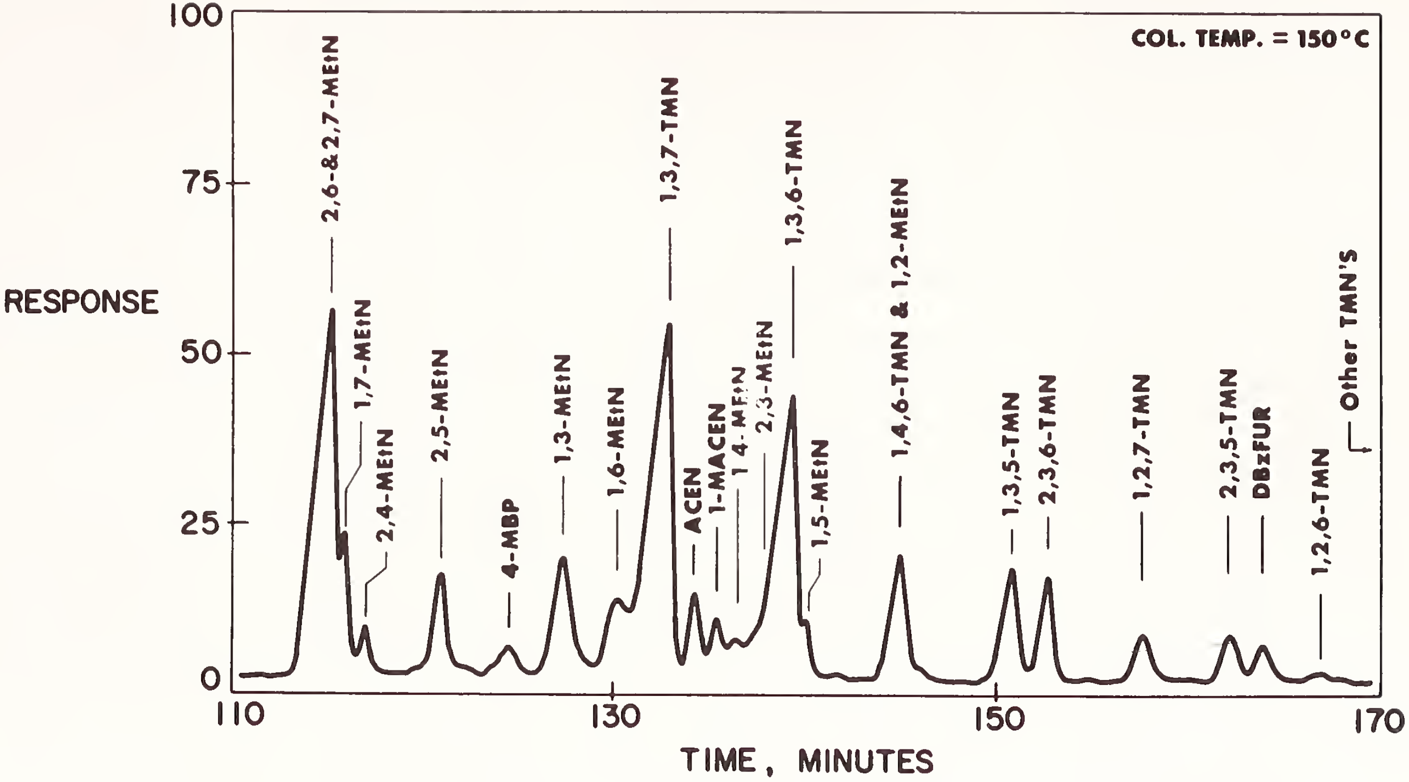

Figure 9. GC: 530 - 550 F Fraction

IV. Review of Uses of Standard Reference Materials to Determine Hydrocarbon Composition of Petroleum

F. P. Hochgesang

A. Introduction

This discussion is limited to the determination of individual hydrocarbons and hydrocarbon types in gasoline and higher boiling petroleum fractions such as kerosene, jet fuel and lubricating oil. The analytical determination of gaseous hydrocarbons (pentane and lower boiling) by gas chromatography and/or mass spectrometry is well known and is not reviewed herein. Other papers cover the determination of trace metals, sulfur, physical properties, spectral and thermodynamic properties, etc.

B. Determination of Hydrocarbon Types in Gasoline

1. PONA Analysis: The general method to determine Paraffins, Olefins, Naphthenes, and Aromatics by mass spectrometry is described in ASTM Method D-2789 [1]. Petroleum Laboratories often rely on NBS Hydrocarbon Blends (SRM's 592 through 599) for in-house determination of calibration patterns in the C_7 and C_8 range. Patterns for C_9 and heavier hydrocarbons may be obtained by extrapolation from C_8 and lighter, or other means. Olefins are determined in gasoline by analysis of the sample before and after olefin removal.

2. Molecular Weight Distribution: The general method to determine carbon number distribution of aromatic compounds in naphthas is described in ASTM D-1658 [2].

3. Typical Results are shown in tables I and II for a PONA summary and carbon number distribution from a catalytically cracked gasoline blending stock.

C. Determination of Individual Hydrocarbons in the Gasoline Boiling Range

Extensive use is made of the many high purity hydrocarbon isomers available from the API SRM Office at Carnegie-Mellon University. The determination of benzene, toluene, plus the specific isomers of C_8 alkylbenzenes, and C_9 alkylbenzenes may be accomplished relatively easily by gas chromatographic methods such as ASTM D-2267 [3]. Alkylbenzenes in the C_{10} to C_{14} range, naphthalene, and methyl naphthalenes may be estimated from mass spectrometry PONA results as mentioned earlier. UV absorption can determine naphthalene, also 1- and 2-methyl-naphthalenes in many cases.

Various methods are available in analytical literature [4,5] for GC determination of specific paraffins and monocycloparaffins (also most monoolefins) of molecular weight C_8 and lighter. High resolution gas chromatography is capable of resolving many C_9 and heavier paraffins, mono- and di-cycloparaffins. However, the lack of known reference materials for calibration prevents the determination of individual C_9 and heavier saturates. R. B. Callen, in a recent paper, extended individual cycloparaffin determination through the C_9 mol. wt. class by use of the methylene insertion reaction. This was possible because of the availability of many C_8 cycloparaffins of high purity (viz. API Standard Hydrocarbons). This work makes it possible to determine 273 hydrocarbon isomers in 360 °F endpoint hydrocarbon fractions.

D. Determination of Hydrocarbon Types Higher Boiling Than Gasoline

The mass spectrometry methods mentioned earlier for PONA determination in gasolines have been extended to include higher boiling petroleum fractions [7]. Typical results from application of the Cook-Robinson technique [8] to determine aromatic types present in a distillate fraction boiling in the lube oil range are shown in table III.

E. Determination of Individual Hydrocarbons in Petroleum Fractions Higher-Boiling than Gasoline

The published papers by J. G. Bendoraitis [9,10] demonstrate the extensive composition data that have been obtained by application of modern analytical techniques. In summary, the discovery of a series of isoprenoids (branched paraffins) in some crudes strongly suggests that chlorophyll was a prominent component which matured in a timespan of geologic age to form some portions of petroleum crude oil. The recent discovery of both an aromatic sterane series and an aromatic triterpane series strongly suggests that steroids and other materials of plant or animal origin also are involved.

Such conclusions result from the application of the combined techniques of gas chromatography, mass spectrometry, nuclear magnetic resonance, and ultraviolet and infrared absorption spectrometry to isolate and identify the major components. The ability of gas chromatography to resolve various isoprenoids and triterpanes from n-paraffins in crude oil is demonstrated in figure 1. A major source of the isoprenoids is believed to be chlorophyll, as shown schematically in figure 2. The distribution of isoprenoids found in an east Texas crude oil is shown in figure 3. The probable structures of monoaromatic sterane and triterpane derivatives believed to have been found are shown in figure 4.

F. Continuing Needs for Standard Reference Materials

1. Gasoline Boiling Range: High purity standards to identify and quantitatively calibrate instrumentation to determine hydrocarbon constituents through the C_8 compounds largely are available from the API-SRM Office at Carnegie-Mellon University. The most notable exceptions are some monoolefins. C_9 and higher mol. wt. hydrocarbons are needed. An especially obvious absence of HC's in this boiling range involves the bicycloparaffins and their methyl derivatives; viz, methylbicyclooctanes, methylhydrindanes, and methyldecalins.

2. Higher Molecular Weight than Gasoline: Except for a few n-paraffins, known hydrocarbons of mol. wt. greater than C_{12} mostly are not available. Especially needed are the ring structures (both cycloparaffinic and aromatic, including combinations of these in fused ring systems), which may result from degradation (either natural or "man induced") of biological precursors.

3. Who Needs? Petroleum research obviously is stymied for major compositional knowledge. Further, the availability of ring compounds of the type mentioned above surely would aid important current and future problems encountered in oceanography, geochemistry, biochemistry and related disciplines.

References

1. ASTM D-2789 "Hydrocarbon Types in Low Olefinic Gasoline by Mass Spectrometry."

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3. ASTM D-2267 "Aromatics in Light Naphthas and Aviation Gasolines by Gas Chromatography."

4. Schwartz, R. D. and Brosseaux, D. J., Anal. Chem., 35, 1374 (1963).

5. Polgar, A. G., et al, Anal. Chem., 34, 1226 (1962).

6. Callen, R. B., "Applications of the Methylene Insertion Reaction to Composition Studies: High Resolution

Gas Chromatography of the C_9 and C_9 Naphthenes," Presented at ACS Meeting, August 1973. (Paper scheduled to appear in Petroleum Division Preprints for Spring 1974 ACS Meeting.)

7. ASTM D-2425 "Hydrocarbon Types in Middle Distillates by Mass Spectrometry."

8. Robinson, C. J. and Cook, G. L., Anal. Chem., 41, 1548 (1969).

9. Bendoraitis, J. G., et al, "Isoprenoid Hydrocarbons in Petroleum: Isolation of 2,6,10,14-Tetramethylpentadecane by High Temperature Gas Chromatography," Anal. Chem., 34, 49 (1962).

10. Bendoraitis, J. G., "Hydrocarbons of Biogenic Origin in Petroleum: Aromatic Triterpenes and Bicyclic Sesquiterpenes," presented on September 18, 1973, at the 6th International Meeting on Organic Geochemistry, Rueil-Malmaison, France. This paper is scheduled to appear in the published proceedings of the Meeting. Contact Comite D'Organisation 6e Congres International de Geochimie Organique, c/o Institut Francaise de Petrole, 1 et 4 Avenue de Bois Preau, 92502 Rueil-Malmaison, France.

Discussion: In response to questions the speaker said the data he reported regarding the composition of crude oil strongly suggests steroid precursors for petroleum and is potentially important for future environmental studies.

Table 1. Catalytic Cracked Gasoline Stock

Component Types		Volume, %
P	Paraffins	31.1
O	Monoolefins	14.3
	Cycloolefins & Diolef.	3.5
N	Monocycloparaffins	9.7
	Dicycloparaffins	0.3
A	Alkylbenzenes	35.6
	Indanes & Tetralins	3.7
	Naphthalenes	1.8
	Total	100.0

Table 2. Alkylbendene Distribution Catakytic Cracked Gasoline Stock

	Volume, %
C_6 (Benzene)	0.3
C_7 (Toluene)	4.2
C_8 (EtB + Xylenes)	9.4
C_9	10.7
C_{10}	5.5
C_{11}	4.1
C_{12}	1.1
C_{13}	0.3
Total	35.6

Table 3. Lube Stock Aromatics

Component Types	Volume, %
Monoaromatics	36.5
Diaromatics	22.8
Triaromatics	11.3
Tetraaromatics	7.5
Pentaaromatics	3.3
Benzothiophenes	2.1
Dibenzothiophenes	1.8
Naphthobenzothiophenes	1.9
Unidentified Aromatics	12.8
TOTAL OF ABOVE	100.0
VOL PERCENT OF SAMPLE	37.2

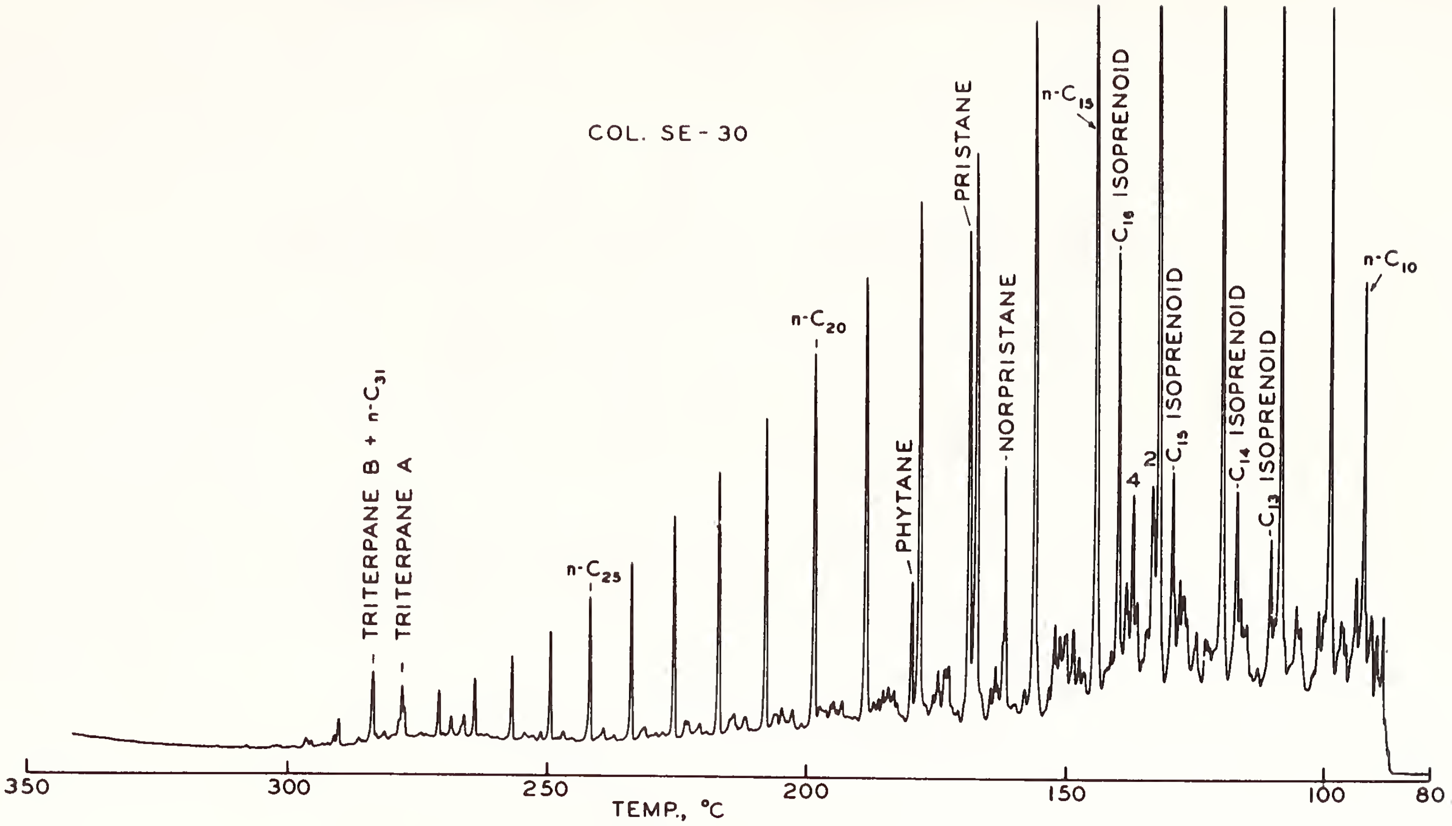

Figure 1. West Ranch Crude

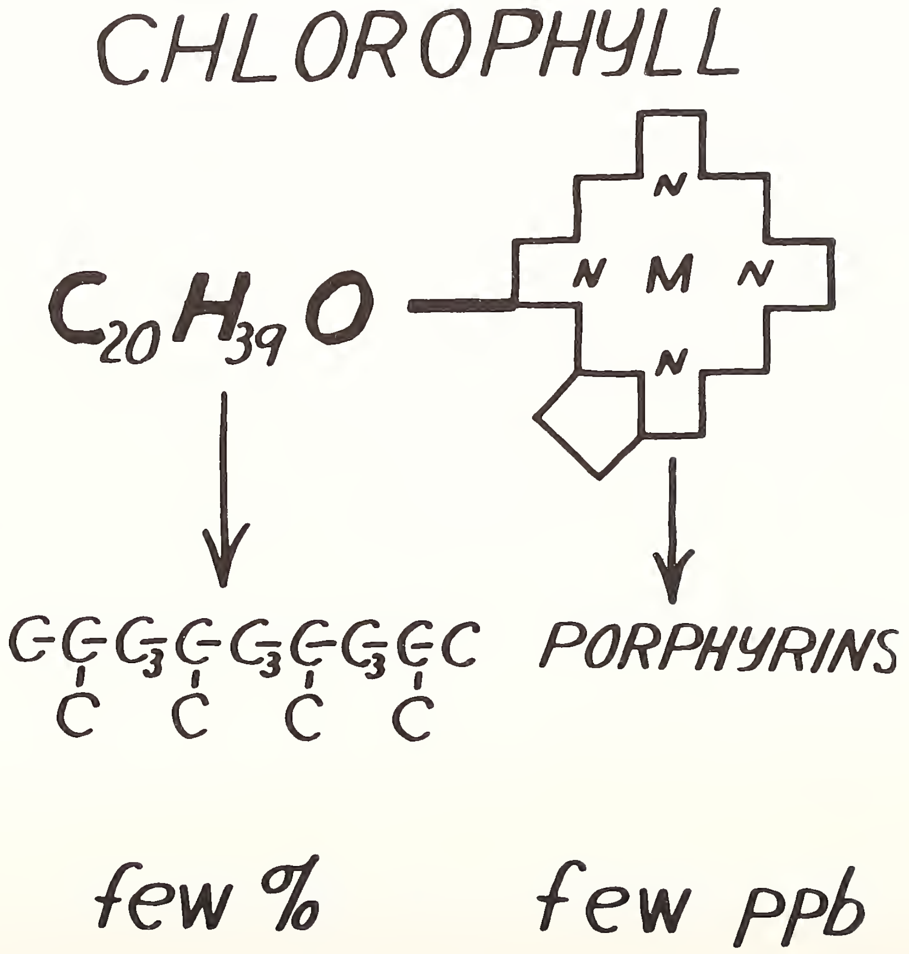

Figure 2. Isoprenoids from Chlorophyll

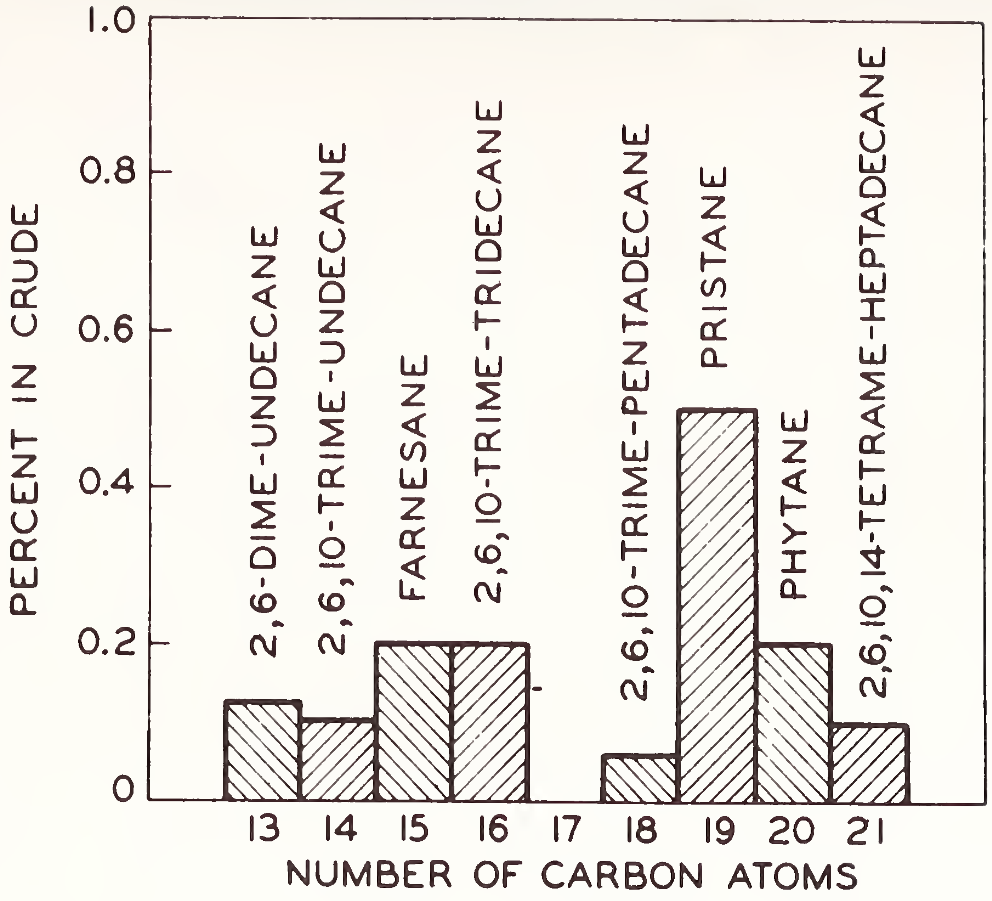

Figure 3. Distribution of Isoprenoids Isolated From East Texas Gas Oil

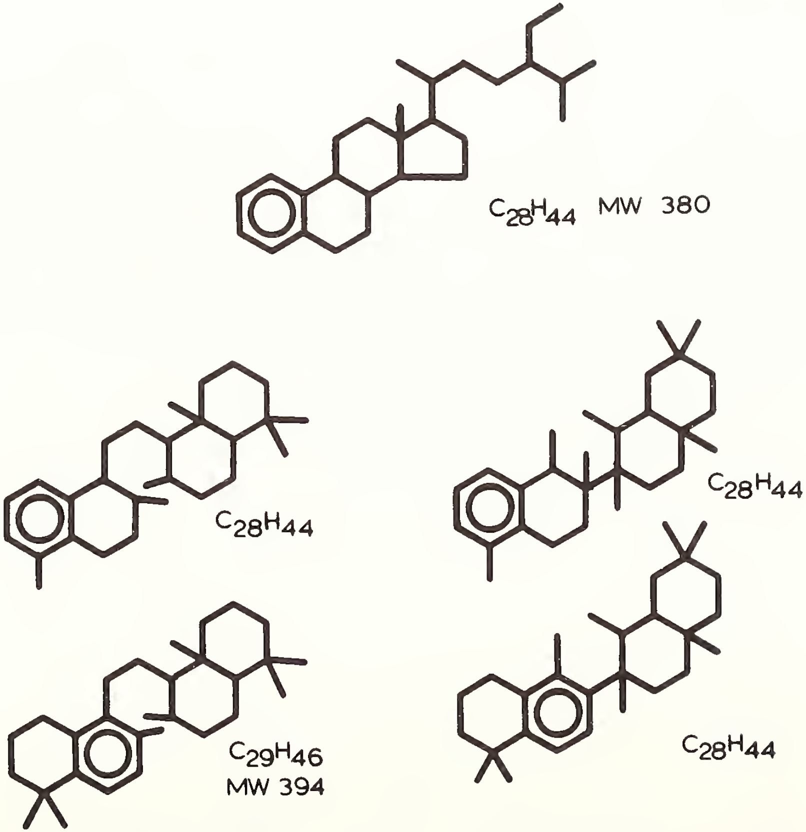

Figure 4. Probable Structures of Monoaromatic Sterane And Triterpane Derivations

V. Elemental Analysis of Petroleum and SRM's

Elwin N. Davis

By comparison to other industries the petroleum industry was a late-comer to having available and making use of SRM's. Until the days of World War II, the industry gave only cursory attention to the precise elemental composition of crude petroleum or its products. We were primarily defining our products by boiling point or other physical properties. Products were generally made by simple distillation procedures. Automotive and home heating fuels were subjected to some degree of treatment principally to remove corrosive sulfur compounds, but in most cases, the sulfur in the fuel was measured not by the actual sulfur content, but whether there was corrosive staining of a copper strip. Lubricants, for the most part, were straight-run products that were only dewaxed or deasphalted and contained no significant additives.

World War II demands for a large volume of petroleum products, especially high-octane aviation fuels, brought about some rather significant changes to the industry and to our refining technology. Chief among these was the fluid cracking process, which greatly increased the yield of gasoline and light fuels obtainable from a barrel of crude. After the process came into use it soon became apparent that some of the hydrocarbon material being fed to the cracking units significantly reduced the activity or efficiency of the catalyst resulting in much lower yields of the desired products. The reason for this reduced activity or poisoning was determined to be the naturally occurring nickel or vanadium compounds that were found in that portion of the crude that was being introduced into the cracking unit. The industry had long been aware of the presence of nickel and vanadium in crudes and the concentration might vary from a few parts per million to several hundred parts per million. These elements had not previously been a significant problem in the processing of the crude or in the use of the products made from it.

With the introduction of the catalytic cracking process the industry was faced for the first time with the necessity for elemental analysis with concentration levels in the parts per million range. In those days this was considered trace metal analysis. I guess today it is almost a gross quantity. In about the same era the quality requirements of lubricants for internal combustion engines -- automotive, aircraft and all classes of diesels -- became more demanding. Closer engine tolerances, bearing materials, and devices such as hydraulic valve lifters required that the lubricant resist oxidation and exhibit considerable detergency or the ability to carry away the undesirable materials formed in the combustion process. Straight refined oils, no matter how carefully made, did not possess these properties. It was therefore necessary to supplant the oils' natural characteristics with other materials to improve their detergency and resistance to oxidation. A large number of compounds have been used for this purpose over the years, but the first, and by far the most persistent, have been the alkali metal sulfonates. Various zinc compounds are in use today. So the need for elemental analysis presented itself to the industry.

The demands for another application of elemental analysis of petroleum products came from outside the petroleum industry, from one of the users of our products. Railroads were operating increasing numbers of very large and expensive diesel locomotives and found that by analyzing engine lubricating oil at frequent intervals for the elements that were present in the engine's components, such as pistons, rod bearings, wrist pins, crankshafts, valves, engine coolants, etc., it was possible to predict, with a fair degree of confidence, the imminent failure of some component engine part. Protective measures had to be taken and catastrophic failure avoided. Although this application of elemental analysis did not directly concern the production or quality control of petroleum products, the industry did consider it to be one of its problems since we had cooperated with the railroads in developing the necessary analytical techniques and the correlations that were involved. We continued for many years to perform these analyses for some of the smaller railroads. We now find that we have 19 elements that we need to determine in petroleum or its products and again we are looking at the low parts per million range. Elements involved in this work were aluminum, barium, boron, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, nickel, phosphorus, silicon, potassium, silver, sodium, tin, and zinc. This technique has been applied to other areas of transportation such as in the aricraft and trucking industries; for buses and military vehicles to some extent.

The fifties and sixties brought further advances in refining technology and additional demands for elemental analysis. The catalytic reforming process, for example, utilizes a catalyst of platinum generally impregnated on an aluminum carrier. The value of catalyst of a single charge to a processing unit can be in excess of one million dollars. These catalysts can also be poisoned by elements that occur naturally in petroleum. Arsenic and lead are two of the principal poisons to the platinum reforming catalyst and their presence at a level of even a few parts per billion can be a serious problem.

New requirements were placed on many of our products because of the sensitivity of some of the new machines and equipment in which they are used. Gas turbines, for example, were found to be severely damaged by the vanadium component of fuel that they burn. Silver bearings in railroad diesels were sensitive to even trace concentrations of zinc in the lubricant.

The mid-sixties brought about the start of a new series of elements with which to be concerned at lower concentration ranges. This refers to our belated concern for the environment and what our products have been doing to it these many years. We now find ourselves looking for elements in the part per billion or fractional part per billion range that may be emitted to the atmosphere via a combustion process and may be harmful and present a hazard when so emitted. The Environmental Protection Agency at this point has defined about 15 elements in this category and because of the widely varying origin of crudes processed in this country, I don't believe that any of them can be positively identified as not being present in some fuel that's being burned in the country today.

All the foregoing remarks are intended to be a rather hurried view of the development of the industry's needs for elemental analysis and to show that the scope of the work of the petroleum analytical chemist extends somewhat beyond the compounds of carbon and hydrogen. In thinking about this I went back to a 1940 ASTM book. It really has nothing to do with SRM's, but it seems that as late as 1940 our products were defined essentially by nothing but physical testing procedures and only in the case of sulfur and tetraethyllead will one find any reference to elemental analysis in the manufacture and quality control of petroleum products. I don't really mean to imply that the industry wasn't aware of these things back in those days. It was aware, but not really concerned, because elemental analysis was not really important as far as the day-to-day problems of the manufacturing and control of petroleum products. Having shown the present needs of the industry for elemental analysis, I belive it goes without saying that the need also exists for SRM's.

Our products and the crudes that we produce or buy are articles of commerce and are bought and sold on the basis of specifications, and specifications often describe the elemental composition as well as the physical properties. Thus it is desirable to have a common point of reference for calibration or checking the analytical techniques being employed. This is especially important when working with petroleum. Since the element to be determined is, in general, in solution at very low concentration levels in the hydrocarbon matrix, many of the analytical techniques will require some method of removing (possibly concentrating) the element of interest from the hydrocarbon material and we find that the preparatory step is very important in the final method of determination. In other cases where the elemental determination is made directly from the hydrocarbon material itself, the hydrocarbon can present itself as an interferring substance in the elemental analysis. It is readily apparent then that it is desirable or necessary to have a SRM available with the element of interest in a matrix material bearing a close resemblance to the material under study. This often extends to having the same hydrocarbon type or material of the same boiling range.

Having established the need for SRM's, let us see what is available. Prior to 1960 there were no elemental standards in a hydrocarbon matrix available as SRM's. During the mid-fifties a committee of the American Petroleum Institute, known as the Committee on Analytical Research, had been wrestling with the problem of finding suitable oil-soluble metallo-organic compounds to be used principally as calibration materials for optical emission spectroscopy. There were to be applied primarily to some of the problems which I discussed previously. At that time there were a very limited number of suitable compounds available. There were numerous problems with the purity solubility, and compatibility of the materials. There was always that nagging doubt about the true assay value of the element in question. The API felt that the problem was great enough that they were willing to fund a project for development of suitable compounds. The Committee made contact with NBS and found that NBS had been looking into this problem and had done some work on the subject back in 1957. They were willing to undertake an assignment with a partial funding from the API. I am not sure of the total provided by API for the project, but I believe it was near $80,000 before completion. I am also not sure about the NBS investment, but I believe that it was on a matching basis, which would make the total cost of the project in the neighborhood of $160,000. This was a pretty big chunk of money back in the fifties and certainly bought more manpower than it would today. So it is obvious that this was a sizeable project and it did produce oil-soluble compounds for some 24 elements.

These compounds resulting from the joint NBS-API program were first made available in 1960. They have had extensive use within the industry and also by others using petroleum products. They were the first elemental SRM's available from NBS specifically for use with petroleum products. Their use will be discussed later.

Other useful reference materials available from NBS include four fuels containing sulfur. Three of them are residual fuels with varying sulfur content. The fourth is a distillate fuel with a sulfur content of 0.2 percent. Also available from the NBS is a "General Material," which is a residual fuel containing nickel and vanadium at the 93 and 79 parts-per-million level, respectively.

How have these NBS-SRM's been used in industry? Several years ago, Research and Development Division 3 (on Elemental Analysis) of ASTM Committee D-2 submitted a questionnaire to its members on the use and satisfaction that had been experienced with the NBS metallo-organic SRM's. Twenty-three of the approximately 40 questionnaires sent to members of Division 3 were returned. All but three of these were returned from petroleum company laboratories. Fifteen laboratories reported that they had used the NBS metallo-organic SRM. My feeling is that this questionnaire did show that these SRM's are being used in the industry in a variety of analytical techniques and it also indicated that there are some problems. Principally the problems are with solubility and there are probably some problems of compatibility especially when they are used in complex mixes. One also has to remember that these compounds were designed and first made as SRM's for the optical-emission spectrograph back in the late fifties and, in general, they were probably intended for ashing techniques where the sample was ashed in some manner, either wet ashing or dry ashing, before being burned in the spectrograph. In recent years, laboratories were attempting to use the standards with a number of techniques which, 15 years ago, we didn't dream were going to be available. Problems have been encountered due undoubtedly to the interference of matrix materials.

What do we see as needed now and in the future? As we have been talking about the metallo-organics, let us consider these first. The need does exist for this type of material and the present selection of elements is good. We do not see any need for an extension to other elements--in this concentration range anyway. Solubility does need to be improved. Stability needs to be improved. Compatibility needs to be improved. Also, it would be desirable to remove as much of the foreign material of the solution as possible. I don't mean other elements, but primarily the materials that are used to solubilize the metallo-organic, i.e., the matrix should be kept as closely as possible to a petroleum hydrocarbon matrix. We also would recommend that the concentration of the element be kept as high as possible. Turning to the SRM in a specific hydrocarbon matrix, such as the sulfur in residual and distillate fuels, these have been extremely valuable at this point. But the range needs to be extended, revised, and especially include lower values of sulfur. In the future there should be included a motor fuel or gasoline probably supplied in a sealed ampoule. The vanadium-nickel sample now offered as "General Material" should be made available as a SRM and several more, both higher and lower concnetrations need to be made available for these materials. Lead in low-lead or no-lead gasoline will soon become an industry problem and we would like to see SRM's made available in the form of gasoline samples, again in sealed ampoules, containing several levels of lead, both as TML and TEL, or possibly mixtures of the two at the .03, .05 and .07 grams per gallon level.

Just a little further down the road we see a need for a new level of SRM's for trace elements that may be present in fuels and reach the atmosphere after combustion. Elements of potential interest here include arsenic, selenium, mercury, beryllium, manganese, cadmium, chromium, cobalt, vanadium, nickel, zinc, and molybdenum. At this point it is difficult to define levels for any of them from possible presence in fuels that are burned in this country. However, I believe that the concentration level for all except the vanadium-nickel should be something less than 100 parts per billion. We believe that these should be the naturally occurring materials in a natural matrix.

It is imperative that SRM's for this last group of elements listed become available in the near future because they are going to be important as far as the petroleum industry is concerned. The Environmental Protection Agency has indicated that they are looking at these elements. In the very near future we expect to have to look at our fuels from the standpoint of the presence of these elements at concentrations of one to 100 parts per billion. The analytical methods are themselves very difficult and without SRM's it will be a very difficult project to handle.

Discussion: There was a lively discussion regarding the need for work on standard methods of analysis as well as SRM's. No conclusions were reached regarding standard methods of analysis; however, it was generally agreed that some updating of the NBS Metallo-Organic SRM's should be undertaken along the lines suggested by the speaker.

ORES AND GEOLOGICAL MATERIALS

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I. Meaningful Measurements with Rock and Ore Standards

F. J. Flanagan

One aspect of meaningful measurements--accuracy--conveys the idea that a value is very close to the truth, but truth must be defined rather carefully. The question of how meaningful a measurement is, involves not only the problem of definition, but also the reason why the analysis was requested. A determination answers the question, "How much?" but the quality or meaningfulness of a determination depends on the underlying inquiry, "Why do we wish to know how much?" The question "Why?" is not novel, as Lundell [18] used it to introduce his paper, "The chemical analysis of things as they are."

Differing answers to the question "Why?" may be seen from the history of G-1 and W-1, which shows that they were originally prepared for three separate reasons. G-1, the granite from Westerly, RI, was collected by Felix Chayes of the Geophysical Laboratory for modal analysis. Chayes was soon joined by H. W. Fairbairn and L. H. Ahrens of the Massachusetts Institute of Technology, who wished to determine whether the spectrograph might play a useful role in quantitative work on the major elements of rocks. Meanwhile, the U.S. Geological Survey collected diabase, W-1, from the Bull Run quarry, Centerville, VA, and prepared the sample for control purposes in chemical work on rocks. By mutual agreement, the three groups joined in a collaborative effort on the two rocks. In his summary of results Fairbairn [11] noted that further collabaration by chemists a need clearly indicated by the study, was possible now that there was an adequate stock of the two rocks, thus giving a fourth reason for the existence of the two samples.

After a rock has been selected as a reference sample--a procedure that involves answering why one rock is preferred to others--at least one other question must be answered before preparation. Do we wish to prepare a sample of *a* granite, or a sample of *the* Westerly Granite? USGS believes that the sample should represent *the* Westerly Granite, thereby serving two purposes, and the choice made will govern details of the method of preparation. One can gauge the amount of care taken during the preparation of rock reference samples of several organizations from the study of the free iron content of such samples by Ritchie [23] and the published methods of sample preparation used. It is reasonable to assume that the granodiorite GSJ-JG-1, Ando [1], prepared by crushing in a large granodiorite mortar and by rolling in a granodiorite rolling mill, was processed with a minimum of undesirable contamination.

Although G-1 and W-1 were originally prepared for major- and minor-element analysis, they developed into useful samples for many trace elements, as scientists soon started to report such data. In the last decade, a number of papers: Turekian and Carr, [27] Clark and Swaine, [8] Filby, [12] Ball and Filby, [2] Compston et al, [9] were published on the trace-element contents of several NBS-SRM's: limestones, feldspars, refractories, clays, and rock-radium standards, again a purpose for which the samples were not prepared.

Scientific inquiry is obviously not inhibited by the purpose for which reference samples were prepared, and I believe that we will no longer see reference samples of rocks, ores, or minerals prepared for a single purpose. The preparer of such samples should try to anticipate future needs by conforming to the requirements for the most sensitive, accurate, and precise methods available now or in the foreseeable future. If reference materials are prepared carefully for these refined methods, they should be satisfactory for those with less stringent requirements.

A sample of rhyolite obsidian prepared for the determination of gold at or below the 1 ppb level may not be satisfactory for rock analysis if the method of preparation caused changes in the H_2O^+, H_2O^-, or FeO contents. If the ground sample is to represent the parent rock, then such changes will alter the chemical composition. If we are interested only in a rhyolite, such changes may be immaterial. Thus, the method of preparation may reduce the meaningfulness of a sample prepared as a general rock reference sample.

The subject of meaningful measurements reminds me of the informal discussion following formal presentations at a symposium on spectroscopic rock and ore standards during the 1972 International Geological Congress. The main topics were the most precise and accurate methods of analysis, but the recurring question "What is good (=meaningful) data?" was normally answered by, "Those data furnished by a good analyst." The "good analyst" was then defined as one who furnished "good data." There is at least one technique available to break this circular argument.

The question of who is a good rock analyst has always generated a subjective and comparative answer that depends on the one answering the question. The adjectives, "bad, fair, good, or excellent," used to describe an analyst are subjective; what is needed is an objective test.

A commonly used method of judging the ability of a rock analyst is to take his analysis of G-1 or W-1 and make a series of subjective judgments about how well or badly his data agree with the published averages for the oxides. Then the judge somehow sums perhaps a dozen subjective judgments for as many oxides and finally gives a summary subjective judgment of, say, "a fairly good analyst."

While considering the data by an analyst and the published means and standard deviations for G-1 and W-1, I remembered the χ^2 test that is used to determine if a set of data adequately fits a specified distribution. A deviation of a single datum from the average of all data, when normalized by dividing by the population standard deviation and then squared, is distributed as χ^2 with one degree of freedom. We can sum such normalized squared deviations for each of the n oxides in a rock analysis to obtain a value of χ^2 with n degrees of freedom and thereby obtain a numerical index of the value of the data or of the ability of an analyst. An example of the calculations is shown in Table 1.

Table 1. Computation of χ^2. (From Flanagan [13])

	1 Analyst 17 (Stevens and others, 1960) (weight percent)	2 Mean (Stevens and others, 1960, table 3, all analyses, p. 31) (weight percent)	3 (1-2)	4 Standard deviation (Stevens and others, 1960, table 3, all analyses, p. 31)	5 (3/4)	6 (5^2)
SiO_2	72.45	72.35	+0.10	0.48	0.21	0.0441
Al_2O_3	14.18	14.32	-.14	.37	-.38	.1444
Fe_2O_3	.75	.95	-.20	.30	-.66	.4356
FeO	.98	.99	-.01	.11	-.09	.0081
MgO[a]	.35	.40	-.05	.13	-.38	.1444
CaO[b]	1.36	1.40	-.04	.12	-.33	.1089
Na_2O	3.28	3.31	-.03	.23	-.13	.0169
K_2O[c]	5.54	5.42	+.12	.39	.31	.0961
H_2O^-	.03	.06	-.03	.05	-.60	.3600
H_2O^+	.26	.36	-.10	.18	-.56	.3136
TiO_2	.26	.26	0	.04	----	----
P_2O_5	.09	.10	-.01	.06	-.17	.0289
MnO	.02	.03	-.01	.01	-1.00	1.000
CO_2	.08	.08	0	.01	----	----

$\chi^2 \overset{\sim}{=} \Sigma = 2.7010$

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[a] Plus 0.63 BaO.

[b] Plus SrO.

[c] Plus Rb_2O.

At least three factors make the technique less than rigorous:

A. The means and standard deviations should be population estimates. We can qualify population by specifying data published within a time interval or in a specific article.

B. We generally do not know whether the data are single determinations or the averages of two or more.

C. The determinations should be independent. This criterion is not met in the determination of Al_2O_3 in the classical methods of rock analysis or in the determination of the Fe_2O_3 contents of rocks by any method presently used.

Except for the Fe_2O_3 content that must be obtained by subtracting the Fe_2O_3 equivalent of FeO, determined separately, from the total iron as Fe_2O_3, the trend during the last two decades has been to use spectrophotometry, atomic absorption, and other methods in rock analysis. Independent determinations so obtained will allow us to calculate a slightly more rigorous estimate by which we can judge the goodness of data or the ability of an analyst.

The title of this panel might have been "Ores, Soils, and Geological Materials." Soil standards are of interest to agronomists, to environmental geochemists for obvious reasons, and to exploration geochemists in their search for geochemical haloes of an element. Soil standards present special problems, as the quantities must be large and the collection, shipment, and preparation of the samples must be in conformance with the Plant Pest Quarantine Regulations of the Department of Agriculture.

If an analyst is to use standards to make meaningful measurements, the methods for standardization and certification should be of the highest quality, as the cost of the analytical time of potential users will greatly exceed standardization costs. Such methods might well possess the properties of good estimators in the statistical sense (Mood [21]).

The methods should provide unbiased estimates--the estimate of the element to be certified should not differ significantly from the true but generally unknown value. The average is an unbiased estimator, but one can use a biased estimator if the difference between it and the true value is small. However, one should know the extent and direction of the bias.

The next important quality is consistency. If the value we are estimating nears the true value with a probability approaching one as the sample size in the statistical sense increases, the estimator is said to be consistent. A consistent estimator may be biased for finite sets of data, but the bias may approach zero as the number of determinations in a set of data becomes large. Consistency in this sense should not be equated with "reproducibility," as many of us have seen reproducible analytical schemes that consistently yield the incorrect answer with remarkable precision. This situation may be the fault of both the method and the analyst, of the former because it was not designed to eliminate a possible interference, and of the latter because he did not test for the absence of the interfering element.

The method should yield an efficient estimator--that which has the smallest limiting variance. For samples drawn from a normal population, the sample mean, $\bar{x}$, is an efficient estimator of μ, the population mean. If the estimator contains all the information in the sample regarding the parameter, it is said to be sufficient, but sufficient estimators exist only in rather special cases.

As most of us are pragmatists, we generally use the average of our determinations, and the average possesses the qualities above. However, the use of the average is no panacea for all our problems as the complexity of many rocks, ores, and minerals introduces further complications. The literature contains many papers for the determination of the elements that are valueless for our sample. Nature operates in diverse ways to form the materials of our earth, and schemes based on calibration lines made with pure substances or solutions, or on the analysis of a single rock or ore type, may not be adequate for all rocks or ores. The analyst must ensure that interfering elements are absent in his rocks or ores or make suitable changes in the procedure if interferences are present.

Before we make our meaningful measurements, we should ensure that the standard itself is meaningful. We again face the problem of a definition. One frequently used is that the standard should be as close a match to the unknown as possible. Those of us in geochemistry will immediately recognize the physical impossibility, not only of preparing large quantities of an infinite number of standards, but also of storing one bottle each of such samples in a laboratory.

Those preparing ore standards must ask themselves such questions as (1) should one or more samples of the same ore be prepared; (2) at what levels of concentrations for the elements; (3) should samples be from the same or different locations; and (4) if present, do the amounts of interfering elements differ in samples from differing locations? Those preparing rock samples must ask almost the same questions, but whereas a limited number of elements are determined in an ore standard, geochemists may soon ask for rock standards with data for every element in the periodic table. As an example, approximately 65 trace elements have been determined in the USGS rocks W-1 and BCR-1. For either rocks or ores, many samples selected for preparation may be the result of compromise--those samples that will do the greatest good for the largest number of analysts. Other samples may be prepared because of an immediate and overriding urgency, such as the NBS SRM's for sulfur and for mercury in coal, or the four recently analyzed NBS-EPA samples.

The most important quality to be possessed by any standard is that of homogeneity, for if we have no assurance that our portion of a standard has the same composition, within limits, as all other portions, we may not be able to obtain meaningful data for eventual comparison with data by others. Disregarding the analytical methods, there are at least two general methods for determining the homogeneity of standards. Serious differences exist between the two methods, and both methods will be discussed.

The method generally found in the literature for declaring homogeneity is to make a series of measurements of some element and then to calculate the coefficient of variation of the measurements. The analyst then makes a statement such as, "As the coefficient of variation of the data is less than X percent, the standard is homogeneous for element Y." The critical reader might ask if the upper limit for the coefficient was set *a priori*, or after the data were obtained and the calculations made. In either event, the criterion is subjective, and an objective criterion would be better. The more curious reader might wonder if the determinations were made on portions from only a single bottle. Ideally, the statement might also include "by the method used," as the sample might not be homogeneous by a more refined method.

Assuming that the determinations were made on portions from one bottle, what do they mean? Each determination is composed at least of the true value, plus some effects due to the analytical method and to sampling the material, plus some random error. If we make the usual calculations for the average and standard deviation, we cannot separate the variation due to these different sources. For data on portions from a single bottle, the calculated standard deviation is only a measure of the spread of the data and should not be equated with "error." The mean and standard deviation adequately summarize the set of data, but we cannot extrapolate the estimate and possible conclusions to any other bottle in the prepared lot of the standard.

The criterion of homogeneity that the coefficient of variation should not exceed some arbitrary limit may also be a scientific boobytrap. The analyst should be careful that his zeal to obtain a low coefficient of variation does not result in a search for mere consistency of data. His sets of measurements must be random samples from populations of all such conceivable measurements if he is to use his data for prediction--the primary purpose of standards. Eisenhart [10] discusses this and other problems concerned with the evaluation of precision and accuracy.

New analysts in the Geological Survey may be introduced to the concept of homogeneity early in their careers. It occasionally happens that the ground portion of a rock may be consumed in the analyses or may be lost and that determinations on a new portion may not agree with those made previously. On such occasions, some may use the excuse of a different sample, not realizing, or forgetting, the nature of the sample with which they deal. Rocks and ores differ from chemical compounds in that they are generally fine-grained mixtures of several impure compounds. It is the principal duty of the one preparing the rock sample or ore standard to ensure that even minor differences resulting from these impure compounds do not invalidate the final product.

Several techniques are available to the preparer by which he can determine whether he can prepare a homogeneous standard. For those who need worry only about the homogeneity for major and minor oxides in a rock analysis, Chayes [5] determined by the grain counting of several thin sections of the rock that USGS G-2 should be homogeneous for these oxides. For those who must prepare a rock that is homogeneous for trace elements --the rule rather than the exception for the last decade-- methods in the literature, based on the Poisson or the binominal distributions, will allow one to calculate either (1) the error due to particle size that one may incur in a trace-element analysis, assuming a specified weight of sample; or (2) the weight of sample necessary so that the error will not exceed X percent at some probability, assuming a given particle size.

These latter calculations may also be applied to elements at the major and minor levels. Reiss et al, [22] and John et al, [16] discussed the amount of sample necessary for an analysis to be within X percent of the mean and give nomographs showing the relation between the number of particles, the percent composition, and the percent relative sampling error, plus a formula for calculating the number of particles of a given size necessary, or by a simple conversion, the weight of sample necessary. Among others who have discussed the problem of sampling error and rock analyses are Wickman [30], Wilson [31], and Kleeman [17].

Behre and Hassialis, in the 1947 edition of Taggarts Handbook of Mineral Dressing, [3] published a method of calculation based on the binomial distribution; this method is more rigorous than that found in many papers because Behre and Hassialis included the covariance term that others may neglect. Their technique, with several examples shown in tabular form, may be used to calculate either the errors that might occur or the weight of sample necessary so that a specified error will not be exceeded.

Most methods require some preliminary knowledge of, or work on, the distribution of the minerals in the rock and the trace-element contents of the minerals. All methods, including the size-weight ratio discussed by Bennett and Franklin, [4] should yield the same approximate conclusion that, when determining trace elements in the low ppm range, the error due to the distribution of the trace elements in the sample grains will not seriously affect the error of the determination if the rock is crushed to pass a 200-mesh screen.

For samples of larger grain size, there have been difficulties in determining Zr in granitic rocks for which zircon constitutes about 0.02 percent of the rock. The problem is much worse for the determination of Hf which constitutes about 1 percent of the zircon. One can also avoid the assumed problem with G-1 and W-1 of grains settling out of a powdered mixture by selecting a glassy rock for a standard, Chayes [6,7] vs. Vistelius [28,29].

As a general rule, we will reduce such sampling error and be more certain of homogeneity as the grain size decreases, until we reach a particle size where the powdered material absorbs atmospheric moisture and tends to form balls. Fortunately, these balls will not always result in heterogeneity.

Recent work in our laboratory has been done by Gottfried, Rowe, and Tilling [15] to establish background levels of the abundance of gold in volcanic rocks. Using a fire assay concentration following neutron activation, they have shown that USGS RGM-1, a rhyolite obsidian from Glass Mountain, Calif., Tatlock et al, [26], prepared so that 97 percent passes a 200-mesh screen, has a homogeneous gold content at the 0.6 ppb level by a technique that will be discussed below.

Because granular rocks are generally heterogeneous mixtures of minerals of widely differing compositions, we may expect some differences among units of issue of the same standard regardless of the manner of preparation, provided that the method of measurement is sufficiently sensitive and precise. If there is the possibility of some finite detectable difference among the bottles of a standard, then any process of standardization should provide some estimate of this bottle-to-bottle variation. The estimate should be so obtained that it may be extrapolated to the entire lot of bottles of the standard. Without such an estimate, the analyst might not know if his slightly aberrant value could be expected, or if he will lose some of the meaning of a measurement when he uses the certified or average value as a reference point on a calibration line.

As each analyst may have his own bottle of standard, and as each bottle may conceptually have a content of the element that differs slightly from that of all other bottles, there is an obvious need for some measure of the bottle-to-bottle variation. One of the least costly ways of achieving this objective is to use during standardization a simple experimental design with a single variable of classification.

The variable of classification is the number of bottles used in the test; these should be randomly selected from the stock. To extrapolate estimates and conclusions from a small number of bottles of a sample to the entire lot of bottles, preparation and standardization should involve the process of randomization whenever the choice of alternatives is presented. Not only should the bottles be randomly selected from the stock, but the determinations on n portions from each of the k bottles should also be made in random order. For bottles of older stock that had not been numbered in some orderly sequence and cannot therefore be randomized, selections may be made from randomly selected batches of haphazardly stored bottles.

The experimental design with a single variable of classification, usually called a one-way design, has been used almost exclusively in a report compiled and edited by Flanagan [14], which contains about 15 papers contributing data for the standardization of new USGS samples. For those papers, each analyst was furnished three randomly selected bottles of a specific sample, and he was requested to make determinations on two or more portions from each bottle (but the same number per bottle to preserve the simplicity of the arithmetic). Several analysts who made determinations on two portions from three bottles for all samples used one single random order encompassing all 48 determinations, a procedure that effectively relates all determinations to each other.

The analysis of variance for this design allows us to calculate an average and two mean sums of squares: (1) a mean sum of squares for the variation within bottles which we equate with analytical variance, but which also contains, in addition to random error, some measure of our inability to sample powders perfectly; and (2) a mean sum of squares for the variation due to bottle means. We can partition the components of this latter mean sum of squares so that we can estimate a bottle variance. Of at least equal importance, the F test involving the two mean sums of squares affords us an objective test of the homogeneity of an element in the bottles of sample, and because of the random selection of the bottles, we may extrapolate our estimates and conclusions to the entire lot of bottles.

The estimation of bottle variances is not without problems. Many such estimates are negative, and these negative estimates are clearly embarrassing, as variance components are, by definition, positive. The problem of negative variances has been discussed by several statisticans; among those, Searle [24] listed several possible steps, few of them satisfactory to him, that may be taken when such estimates occur.

Bennett and Franklin [4] stated that one can expect such negative estimates in about half of the tests on data for which our hypothesis ($\sigma_\beta^2 = 0$) is true, and that these negative estimates may be attributed to sample fluctuations about an average value of zero. As a temporary expedient, we might rewrite a negative bottle variance, $-\sigma_\beta^2$, as $\sigma_\beta^2(-1)$, or as $\sigma_\beta^2 i^2$, and table the negative estimate as a bottle standard deviation $\sigma_\beta i$, where i is equal to $\sqrt{-1}$. The i, especially if italicized, should be a sufficient warning that the tabled standard deviation was obtained from a negative variance. We would then have a numerical but partly imaginary estimate that might be useful until a rigorous statistical solution to the problem is available.

Another aspect of the bottle variance might be mentioned. The usual hypothesis--that the bottle variance is zero--is tested by comparing the F ratio from the analysis of variance with the fractile of the F distribution in tables at some signifiance level and with the appropriate degrees of freedom. If the computed F equals or exceeds the tabled value, it is a practice in texts to declare that there is a significant bottle variance and then to calculate this estimate. Alternately, if the F ratio is not significant, the hypothesis is not rejected, and the calculations are halted.

Perhaps we can do a little better than not to reject the hypothesis by posing equivalent questions: "Is there a significant bottle variance?" or, alternately, "Are the observed bottle means significantly more dispersed than we would expect if they were all obtained from the same population?" If the bottle variance is not significant, we may wish to use this estimate just as much as we wish to declare a standard to be heterogeneous when we obtain a significant F ratio. However, if the standard is declared heterogeneous, the calculation of a significant bottle variance may be academic only.

Having been assured that the standard is homogeneous, the analyst plots the average response of his determinations against the certified, average, or best value given. If these values are given only as a mean and a standard deviation, with the latter not always clearly defined, the analyst must accept the given value unless he wishes to undertake his own program of standardization. He may have evidence from his own work that the given value for a standard does not conform to a linear response obtained with similar values from a number of standards. In this case, having exhausted the possibilities of error in his technique, he may need to use his average for the calibration line, provided that his estimate fits the linear response.

If the analyst is using portions from a single bottle for which a mean and a bottle standard deviation are given for an element by a specified method, he can at least have some assurance about his measurements. He can form a confidence interval at some predetermined level from the given mean and bottle standard deviation and determine whether the average of his determinations is included in the interval. If it is included, he will be safe in using the certified value. If it is not included, his average is significantly different from the mean given, and he has at least two choices: (1) recheck his method to see if he can improve his data; or (2) use his average rather than the value given.

One generally sees in the literature three types of linear calibration lines: (1) no points, (2) averages of some unknown number of determinations, or (3) all data plotted. Most of us realize that the last is the truest picture of "the chemical analysis of things as they are." Mandel [19] has discussed the linear calibration line.

Plotting all our estimates will not necessarily solve the problem of obtaining meaningful data. Many methods have upper or lower limits of estimation, or both, and together with the frequent scatter even in the center of the useful range, the analyst might wonder how much confidence he could place in his estimates. If he plots all of his estimates within the range, it is obvious to him that a standard deviation of points at mid-range cannot be used for the entire range.

Statisticians have other techniques available so that we can estimate errors in our measurements. The method of least squares by which we calculate the calibration line allows us to calculate the standard deviation of the slope of the line. Bennett and Franklin [4], among others, discussed the erection of confidence limits around the line of regression, and Mandel and Linnig [20] discussed both the two branches of a hyperbola forming the confidence band around a calibration line, and the joint confidence region for the slope and intercept (that part of our calibration line where our estimates are generally most imprecise).

We can make our best estimates at the point $\bar{x}$, $\bar{y}$, the average concentration and response, respectively. The slope becomes less variable as the number of values, x_i, for which an observation, y_i, is made, increases. To best estimate the slope, we should choose points x_i as widely scattered as possible. In the extreme case, if we have convincing *a priori* evidence that the relation between response and concentration is linear, we can get the best estimate of the slope if we concentrate half of our 2n measurements at each end of our usable range of concentration.

As a closing subject we might ask a question designed to elicit comment. Are certificates or compilations of data preferable for reference materials? Many geochemists use compilations to select data by a specific method and by an analyst they trust and then use these data for comparison. Because of the rather large interlaboratory variation in data found in the literature, geochemists can also use compliation to furnish convenient, if somewhat tenuous, ties between studies throughout the world on a specific rock type, provided such studies include data determined on the same rock reference samples. Compilations can furnish the user with a subjective idea of the ability of his scientific competitor, and they may also be useful for selecting analysts to participate in analyses for standardization.

Compilers and those who prepare certificates have common problems that differ mainly in degree. The most obvious difference is the amount of data available to either. The compiler has the advantage that he can correct his mistakes by hopefully publishing another compilation, whereas correcting an error on a certificate, when the error has been demonstrated unequivocally, would seem almost an insurmountable clerical problem.

I am not certain that the ideas presented here will help us make more meaningful measurements, but if they provoke our considered thoughts about the nature and composition of the ore and rock standards, the measurements, and how we will use them, then the session might not have been held in vain.

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Discussion

Q. I noticed that you said nothing about blanks.

Flanagan:

The subject is adequately covered in John Mandel's book.

Norton:

Do you specify the methods and how many determinations for standardization, or do you send the samples to any analyst who requests them?

Flanagan:

For the last set of samples, I tried to pick the analysts, but one cannot always tell if an analyst is the best in his field. I tried to pick the analysts so that techniques, universities, and several geological surveys were represented. I generally prefer IDMS data above all others. IDMS data for Ba is excellent whereas analysts using most other techniques still have trouble determining Ba in rocks.

Shields:

I cannot see averaging IDMS data with data by all other techniques. One should not average emission spectrometry data for Rb and Sr with IDMS data.

Flanagan:

For the last compilation (in press), the averages for Rb and Sr by other techniques approach the IDMS average. Such averages for Ba are not quite as good.

Shields:

We have never published our BCR-1 data. We have found BCR-1 to be heterogeneous for Th.

Flanagan:

By what qualification?

Shields:

Heterogeneous in that the data on sample portions range between bottles by more than an order of magnitude beyond the capability of the method.

Flanagan:

I would like to see that data.

Q. Do you have any information on USGS soil samples?

Flanagan:

Our Branch of Exploration Research in Denver has prepared three soil samples. Several other organizations have prepared, or are preparing, soil samples and they are in the list, "Reference Samples for the Earth Sciences."

[Editor's Note: At press time, Mr. Flanagan planned to have this list published in Geochimica et Cosmochimica Acta.]

Steele:

Could you comment on round-robins?

Flanagan:

Unless one preselects those to participate in round robins, one frequently finds an analyst who wishes to try his new method. Such procedures tend to widen the spread of the entire set of data beyond the limits of the normally wide interlaboratory (or interanalyst) variation usually found in such studies. One can predict, as a result of numerous round-robin studies in the past, that the interlaboratory variation will be very much larger than any other source of variation and I prefer to avoid round-robins.

Shields:

At the Bureau, we use round-robins to evaluate interlaboratory variation.

Flanagan:

Right. There is more interlaboratory variation than variation from any other source.

Steele:

This has been our experience in a round-robin on a precious metal ore sent to laboratories throughout the world. One might expect that some laboratories, because of their experience in precious metal analysis, might yield good data. It happens occasionally that such a laboratory yields data outside of the distribution of the data by all other laboratories. This creates a problem. If one selects laboratories, one selects a bias.

Shields:

We are our own bias. The Bureau selects analysts for our steel samples from the steel companies that use the samples. Every NBS-SRM certified in the last five years has been analyzed by one of three routes; a reference method, two independent methods, or a round-robin of selected laboratories.

Canadian Standard Reference Materials

A. H. Gillieson

Action to meet the industrial need for Standard Reference Materials (SRM's) in Canada began in 1955, when six Canadian spectrographers, representing the Mines Branch (Department of Energy, Mines, and Resources) and industry, laid plans to produce copper and copper-alloy spectrographic standards. A year later this group was incorporated with the then Canadian Association for Applied Spectroscopy, who agreed to sponsor the standards program and to provide an initial financial loan. The first three certificated standards - phosphor-bronze cast discs - were available for issue by 1962 and the Mines Branch undertook responsibility for sales and distribution.

To avoid duplication in the production of standards, the embryonic Canadian effort had maintained contact with and consulted the National Bureau of Standards, who, in 1962, encouraged the Canadian group to implement their original plans for the production of commercial-purity copper-rod standards. With the cooperation of five American, one French, and four Canadian laboratories in the analyses for certification, the four standards fabricated by the Mines Branch and Canadian industry became available for issue in 1967.

In 1957, a parallel group also sponsored by the CAAS undertook the production of powder standards for geological and mineralogical needs, and, by 1961, two standards - a Sudbury sulphide ore and a Bancroft syenite rock - were issued with preliminary analyses. During the subsequent eight years, further analyses by some 40 laboratories spread over 12 countries, amplified and reinforced the original analysis, and indicated that these two standards were of the same order of homogeneity as the famous G-1 and W-1 of the U.S. Geological Survey. Although these two standards had not been produced primarily to meet industrial needs, sales to industry by 1969 were one-third of the total, and it was clear that there was an industrial requirement for non-metallic powder standards.

As a result, and bearing in mind that Canada is one of the major resource countries of the world, the Mines Branch began a program in 1968 for the production of Standard Reference Materials typical of Canadian ores, and today has on sale 3 platinum-group ores, a molybdenum ore, a complex zinc-tin-copper-lead ore and a low-grade copper-molybdenum ore. The Geological Survey of Canada has produced three ultramafic rock SRM's, which are available through the Mines Branch. Thus, at this date, Canada has available for issue, 19 SRM's - 7 metallic, 7 ore, and 5 rock SRM's.

Since its origin, the Canadian effort has had changes in organization. Until early 1973, SRM production was sponsored by the Canadian Association for Applied Spectroscopy which in 1967, changed its name to Spectroscopy Society of Canada, but it had long been realized that the Mines Branch had been the major collaborator in the work, and it was felt that SRM production lay most appropriately in the domain of the Federal Department of Energy, Mines and Resources. The transfer was effected on January 18, 1973, and the Director of the Mines Branch is responsible for the Canadian Standard Reference Materials Project.

Under Government sponsorship, work is proceeding on the production of further Canadian SRM's: six radioactive ores, three iron spectrographic "setting-up" SRM's, and one zinc-lead ore are nearing completion; work is in hand on a gold ore, an iron ore, a copper-nickel-iron ore, on five commercial-purity copper discs and, through "Agriculture Canada," four SRM's typical of Canadian soils. It is planned to produce SRM's for a blast-furnace iron, a cerium-iron alloy, a blast-furnace slag, and two tungsten ores (or concentrates).

To meet internal needs, Canada has produced 19 SRM's; a further 10 will be available shortly; 8 are in hand, and the production of 5 is in the planning stage - a total of 42 SRM's. This total is only Canada's present goal and, without doubt, Canada will continue to increase the number of SRM's available to assist industry in Canada and throughout the world.

An SRM must be similar in composition to the material being processed but not necessarily identical; in addition, sufficient funds must be available to underwrite its production. At the Mines Branch we are very fortunate that several divisions have conventional size-reduction, blending, and sampling equipment, and supporting analytical laboratories.

We began our project with two basic raw materials, the first being a typical Sudbury ore characterized by its copper, nickel, and iron content. We still have a supply of this standard (original weight about 500 lb) and we have extended its analysis.

The second material prepared and assayed was a syenite rock from the Bancroft area. Although initially it was designed to appeal more to geologists than to chemists, it has also been much sought after by mineral analysts.

The 150-lb supply of SRM from this rock was exhausted in four years and, within six years of the first sampling, another rock lot was taken. Mines Branch mineralogists were quick to point out that the replacement rock was a most inferior mineralogical specimen indeed. We replied that our primary interest was in its chemical analysis and, hence, its suitability as an SRM. The standards are to be used to establish the accuracy of analytical methods, and this criterion is the primary measure of their worth and their effectiveness in mineral and metallurgical chemical analysis.

When a rock or ore judged to be suitable for an SRM is first obtained, a major matter of interest from the standpoint of chemical analysis is its trace-element content. The material must be prepared in such a way that the absolute minimum of these same trace elements be added to the sample.

The research scientists in the Mineral Processing Division suggested that we grind the material autogeneously; i.e., that the ore be used as its own grinding medium. In most instances, fist-sized chunks of ore are loaded into a Teflon-lined mill and, as they collide with and abrade one another, are ground. The amount of contamination is thus kept to a minimum, but it is a wasteful method of grinding as unavoidably, about a quarter of the material is left oversize.

Size of sample is our next consideration, i.e., the particle size to which the bulk sample is ground. In general, we agree that the ground pulp should pass through a 200-mesh Tylor screen. This particle size is small enough for good homogeneity, minimum electrostatic agglomeration, and easy dissolution of sample.

Homogeneity is all-important in the preparation, handling, analysis, and ultimate use of SRM. Initial consideration of the homogeneity of a sample with respect to trace elements, is best forgotten about entirely. The sample material, especially if it is a rock, usually contains a wide variety of minerals in several states of distribution. A check is therefore on the distribution of one or more of the major constituents of the sample material. The method of analysis is usually non-destructive (e.g., x-ray fluorescence), which permits accurate determination of major constituents in a large number of samples. In some instances, such as in the preparation of SRM to be used in the calibration of an optical emission spectrometer, each SRM-unit block has been analyzed to ensure accuracy. Such an individualized procedure is not normally possible with most types of SRM. To minimize segregation effects, the SRM must be sampled for homogeneity analysis as soon as possible after preparation for use.

To establish analytical values for the elements of interest, certain laboratories were invited to collaborate. However, such an undertaking is becoming increasingly more difficult. The number of laboratories in the world that are interested, capable, and have the time to spare is limited. In addition, the number of SRM's in preparation in the world is increasing; we are, therefore, beginning to reach a state of diminishing returns as far as collaboration on analysis is concerned.

Discussion

Q. How do you blend your samples?

Gillieson:

By a double conical blender. One company calls theirs a Rota-Cone Blender.

Q. On your Pt ores for which you use concentrates, have you tested for segregation?

Gillieson:

All samples are tested for homogeneity, generally on a large number of bottles and chiefly by x-ray fluorescence. We usually try to test about 10-20 percent of the bottles by non-destructive methods. For some ores and other non-geochemical samples, we have tested 100 percent for homogeneity.

Q. Testing for homogeneity is a problem for Pt and Au ores.

Flanagan:

You have an alluvial Pt sample that yields data with a large variation within a bottle but considering the entire lot of bottles, the sample is fairly homogeneous. Chemists are usually hesitant to analyze a material giving such a wide spread of data from a single bottle, probably because they do not realize that the entire lot of bottles is homogeneous. They may also fail to appreciate the fact that we might have no Pt if we did not have such sources of supply.

Q. One encounters the same problem in the field--trying to get a representative sample when the ore metal is distributed heterogeneously in the rock.

Gillieson:

We will be testing our W ores for homogeneity, especially to determine whether the heavier minerals settle to the bottom of the bottles, even during storage. The chemist should always mix the contents of a bottle before sampling for analysis.

Shields:

We have had a similar experience with NBS-SRM 70a (K-Feldspar). The Rb and Sr contents of the sample in the -200 +325 mesh size differ by about 5 percent from values determined on samples taken directly from bottles.

Q. Do laboratories from other than Canada join in your analytical programs?

Gillieson:

We have quite wide participation, depending on the material. For our soils, three or four European laboratories have offered to analyze the samples, plus laboratories in the U.S. and Canada. However, most laboratories are in North America.

Reference Sample Programme of the National Institute for Metallurgy

T. W. Steele

South Africa's modest endeavours in the field of SRM's can be said to have begun in 1966, when I suggested to our analytical staff at the National Institute for Metallurgy (NIM) in Johannesburg that we should prepare six samples of South African igneous rocks for use as standards. The six samples chosen ranged from acidic to basic rocks and included a lujavrite that is interesting because of its suite of trace elements. It was not then anticipated that we would go any further in this field than the preparation of these rock samples.

We soon realized that the work involved in the preparation and standardization of the samples was much more than we had anticipated and we enlisted the cooperation of the South African Bureau of Standards (SABS). Both bodies undertook those aspects of the work best suited to their experience and available facilities. NIM did the crushing and subdividing of the samples. SABS received the 100-gram portions in bottles, had them suitably labeled, and distributed them to analysts throughout the world. NIM received the results, did the statistical analysis, and wrote the report.

The six rocks, now known as the NIMROC samples, have reached the stage of what may be termed "maturity" and the SABS is now preparing certificates that give recommended values for major and minor elements and, because of the relatively fewer number of results, orders of magnitude for the trace elements. A small charge is now made for the samples but they are available free of charge to those analysts who can supply us with more trace element data.

When it was felt desirable to continue our work in preparing reference samples, the cooperation between NIM and SABS was placed on a more formal basis by the establishment of a committee known as the "South African Committee for Standard Reference Materials." Apart from its direct involvement in the preparation of standard samples, the functions of this committee are to explore the need for new SRM's in South Africa and to give advice and guidance to any other industrial or scientific organization that wishes to undertake the preparation of reference samples. We are presently trying to systematize procedures for the preparation of reference samples.

The second major project of this committee was the preparation of a precious metal ore for which the sum of the precious metal contents is about 7 ppm. The sample was taken from the Merensky Reef in the Bushveld Igneous Complex in the Northern Transvaal. The original weight of the sample was 7000 kg and the final sample portions weighed 2 kg.

We sent two 2-kg portions to a number of laboratories for the analysis. We selected laboratories that had some experience in the analysis for precious metals.

Of the 45 laboratories who received the sample, 37 have submitted results. Approximately 400 results each for platinum, palladium, and gold have been received, about 300 each for rhodium and iridium, and about 100 for ruthenium, osmium, and silver. The statistical analysis of these data is well under way and the report should be issued early in 1974.

We are currently undertaking the preparation of two samples of chromite and two samples of ferrochrome alloys. The chromite samples were chosen as there appeared to be no chromite SRM's available with values for other than a few elements. The two ferrochrome alloys were prepared because South Africa now has a growing ferroalloy industry. We hope to produce a series of ferroalloy samples.

I have been referring to what we call our international standards-so called because the samples are of large size and have been analyzed on an international basis. I should also mention our other programme which is the collection and preparation of a large number of ores and minerals of a relatively small size--usually about 20 kg. Since the inception of the program five years ago we have a total of 450 samples representing 105 different types of minerals and ores. More samples are being added to the collection each year.

These samples are analyzed by our own laboratory preferably by more than one method and, as the opportunity arises, by external laboratories in South Africa and overseas. For example, during the past five years, five samples of rare earth ores (three of monazite and two of carbonatite) covering a range of .02 - 50 percent total rare earths were submitted to 15 laboratories (more than half of them were overseas) who were chosen for their experience in this field of analysis. The main purpose of these samples is for use as quality control samples for our service work at NIM, but a limited amount of these samples may be given to laboratories who have a real need for them.

In support of our SRM programmes, we are investigating the best ways of handling large numbers of results and the development of computer programmes for the statistical analysis of such data.

The time is appropriate for organizations involved in SRM programmes to pool their knowledge so that other organizations preparing similar samples might be warned of pitfalls. Among possible items for discussion are the methods and the elements that should be chosen for tests for homogeneity. Should we choose a heavy mineral likely to segregate in rocks and ores and use the elements in this mineral to determine homogeneity by x-ray fluorescence? Should there be some standardized method of reporting data? For example, if eight results by x-ray fluorescence were reported, it is not always stated whether the results were obtained on eight portions of the sample, or whether the results were obtained from eight counts on the same portion. Among items for consideration might be a method to indicate non-significant zeros in data, and some agreement on a method for the rejection of outliers. A collection of answers to these and similar questions may help us make more meaningful measurements.

Reference Materials and the Analysis of Geological Materials in the U.S. Geological Survey

D. R. Norton

This paper describes some methods of analysis used in the U.S. Geological Survey and how they relate to reference samples issued by NBS and other organizations.

Lundell [12] pointed to the complexity of natural materials and to the need to maintain the analytical viewpoint in a world of increasing specialization. The purpose of the analysis, sampling problems, chemical interferences, the choice of equipment, the training of the analyst, accuracy and precision required, calibration procedures, and the cost of the analysis were considered as pertinent to the choice of the analytical methods then as they are today.

NBS uses a similar analytical viewpoint in developing SRM's certified for chemical composition. These well-known reference materials are used both to establish the accuracy of methods of analysis and to calibrate analytical procedures. Reference sample programs of other organizations, however, usually fall short of the goal of standards for certification, as such programs generally are directed toward interlaboratory comparisons of results and methods. However, the common goal of these programs is to provide a means of estimating the accuracy of analytical methods.

A status report of a committee of the National Academy of Sciences, White, et al [23] evaluated questionnaires returned by laboratory supervisors in industry and government. The categories selected for study were materials tested, elements determined, concentration ranges, and analytical techniques. As rocks and ores were not included among the materials selected, our experience with the analysis of earth science materials may be of interest.

The analytical methods used in our laboratories range from neutron activation analysis to the classical methods of rock analysis. The latter methods have been described by Peck. [15] The determinations of fluorine, Peck and Smith, [16] and chlorine, Peck and Tomasi, [17] are now included with the rock analysis when the need to determine these elements is indicated. Peck directed special attention to the design of the laboratory equipment and to the procedural details. His laboratory is widely known for the high accuracy and precision of its analyses of silica rocks and has contributed data by conventional rock analysis to the certification of NBS-SRM's 1b, 88a, 97a, and 98a.

A classical rock analysis of a sample, together with a rapid rock analysis of the same sample for comparison, is shown in table 1. The determinations of the first fourteen constituents are referred to as a conventional rock analysis. If fluorine and chlorine are determined, the summation is corrected by subtracting the oxygen equivalent of these elements. Summations outside of the range 99.50 to 100.25 indicate a silicate of unusual composition, the presence of interfering elements, or operational errors. A summation near 100 percent is not in itself a guarantee of accuracy as some constituents are determined by difference, which may result in compensating errors.

Table 1. Silica Rock Analysis by Conventional and Rapid Methods

Constituent	Conventional (%)	Rapid (%)
SiO_2	70.48	70.5
Al_2O_3	14.78	14.8
Fe_2O_3	0.33	.33
FeO	3.03	3.0
MgO	0.49	.49
CaO	0.98	.98
Na_2O	3.23	3.2
K_2O	5.62	5.6
H_2O +	0.60	.60
H_2O -	0.06	.06
TiO_2	0.25	.25
P_2O_5	0.10	.10
MnO	0.04	.04
CO_2	0.10	.10
Cl	0.01	---
F	0.06	---
Subtotal	100.16	---
Less 0	0.03	---
Total	100.13	100.

The conventional methods used for determining constituents are shown in table 2, together with the chemical species determined. Gravimetric and volumetric analyses are the principal methods used in this scheme; four constituents are determined by spectrophotometric methods. The gravimetric methods obviously do not require standardization, as they are primary methods. Only one standard (NBS-SRM 154b, TiO_2) is used for calibration; other standards are pure metals or reagent-grade chemicals. The phosphorus solution is standardized gravimetrically.

The four constituents determined by difference are also listed in Table 2. The determinations of H_2O^+ (combined water), Fe_2O_3, and Na_2O require two separate determinations each to arrive at the calculated value, whereas five separate determinations are necessary to estimate the amount of alumina. The need for high accuracy in all determinations is apparent.

The development of rapid methods of silicate rock analysis satisfied the demand for less time-consuming and less costly methods of analysis. Maxwell [13] of the Geological Survey of Canada notes that such methods are largely photometric, free of the involved separations necessary in the conventional scheme, generally independent of each other, and less subject to accumulated errors. On the other hand, sampling errors may be greater due to the smaller sample size used and operational errors may be a problem unless personnel adhere rigidly to procedural details.

The development of rapid methods of rock analysis by USGS was initially carried out by Shapiro and Brannock [20] and the procedure was revised later by Shapiro. [19] The use of spectrophotometric, atomic absorption, and x-ray fluorescence procedures predominate in the rapid methods of analysis by USGS and the Geological Survey of Canada (Table 3). The methods reported by Maxwell [13] rely principally on x-ray fluorescence analysis, while Shapiro and Brannock [21] and Shapiro [19] use atomic absorption and photometric methods. Some variations of conventional methods are still used for the determination of H_2O^+, H_2O^-, CO_2, and FeO. USGS also uses variations of several x-ray fluorescence procedures, including those of Rose, Adler, and Flanagan [18] and of Fabbi. [3]

Table 2. Conventional Methods of Silicate Rock Analysis

Sample Portion	Constituent Determined	Method Used	Specie Determined
		Peck (1964)	
1	H_2O-	G	H_2O
	SiO_2	G	SiO_2
	CaO	G	CaO
	MgO	G	$Mg_2P_2O_7$
	TiO_2	S	Ti-peroxy complex
2	FeO	V	Fe++
3	K_2O	G	K_2PtCl_6
4	MnO	S	MnO_4-
	P_2O_5	S	Vanadium molybidphosphate complex
5	CO_2	G	CO_2
7	F	S	Zr-SPADNS Complex
8	Cl	V	Cl-
1,6	H_2O+	Difference	Total H_2O - (H_2O-)
1,2	Fe_2O_3	Difference	Fe_2O_3 (Total Fe) - Fe_2O_3 (FeO)
1,4	Al_2O_3	Difference	R_2O_3 - (Fe_2O_3 (Total Fe) + TiO_2 + P_2O_5 + SiO_2 recovery)
3	Na_2O	Difference	(NaCl + KCl) - KCl

G = Gravimetric; V = Volumetric; S = Spectrophotometric

Table 3. Rapid Methods of Silicate Rock Analysis

Constituent	U.S. Geological Survey Shapiro and Brannock (1962)	U.S. Geological Survey Shapiro (1967)	Geological Survey of Canada Maxwell (1968)
SiO_2	S	S	XRF
Al_2O_3	S	S	XRF
Fe_2O_3	S	S	XRF
FeO	V	V	V
CaO	V	AA	XRF
MgO	V	AA	XRF
Na_2O	FP	AA	FP
K_2O	FP	AA	XRF
H_2O+	C	C	C
H_2O-	C	C	C
TiO_2	S	S	XRF
P_2O_5	S	S	S
MnO	S	AA	XRF
CO_2	C	C	C

S = Spectrophotometric; AA = Atomic Absorption; XRF = X-ray Fluorescence; FP = Flame Photometric; V = Volumetric; C = Conventional

The recent methods of rapid rock analysis, [19] are based on the single solution of the sample after fusion with lithium metaborate. This procedure originated with Ingamells [7] who later suggested its use with atomic absorption spectrometry, Suhr and Ingamells, [22] and with spectrometric procedures, Ingamells. [8]

Reference materials used for the rapid rock analysis are shown in table 4. Shapiro and Brannock [21] used NBS-samples extensively whereas Shapiro [19] used USGS samples G-1 and W-1 in the determination of SiO_2, Al_2O_3, Fe_2O_3, and TiO_2, and reagent-grade and high-purity materials for the standardization for other constituents.

Table 4. Standards for Rapid Methods of Silicate Rock Analysis

Constituent	Standards Brannock and Shapiro (1962)	Standards Shapiro (1967)
SiO_2	NBS-SRM 99 (feldspar)	USGS-G1, W1
Al_2O_3	NBS-SRM 99 (feldspar)	USGS-G1, W1
Fe_2O_3	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	USGS-G1, W1
FeO	NBS-SRM 136 ($K_2Cr_2O_7$)	NBS-SRM 136 ($K_2Cr_2O_7$)
CaO	NBS-SRM 88 (dolomite)	$CaCO_3$, reagent grade
MgO	NBS-SRM 88 (dolomite)	Mg ribbon, high purity
Na_2O	NaCl, reagent grade	NaCl, reagent grade
K_2O	KCl, reagent grade	KCl, reagent grade
TiO_2	NBS-SRM 154 (TiO_2)	USGS-G1, W1
P_2O_5	NBS-SRM 56 (phosphate rock)	NBS-SRM 56 (phosphate rock)
MnO	NBS-SRM 25 (manganese ore)	Mn soln., analyzed, comm.
CO_2	$CaCO_3$, reagent grade	$CaCO_3$, reagent grade

USGS chemists use NBS-SRM's to calibrate and to establish the accuracy of their methods, but USGS has its own rather extensive reference sample program. Flanagan [4] discussed the petrography, sample processing, chemical analysis, spectrographic analysis and homogeneity of USGS silicate rocks G-2, GSP-1, AGV-1, PCC-1, DTS-1, and BCR-1. These samples fill a need for reliable reference materials for the determination of major, minor, and trace elements in silicate rocks. Another report that presents preliminary analytical data, norms, petrography, and geology for seven other USGS samples is now in press.

Worldwide sources of geochemical standards are listed by Flanagan [5] and usable values for several of these samples are given by Abbey. [1] Flanagan lists rock, mineral, and ore standards including some industrial products, radiometric standards, and isotopic standards of interest to the geochemist and geologist. Abbey notes that NBS-70a (potash feldspar) and NBS-99a (soda feldspar) are the only SRM's available from NBS that are suited for the determination of major and minor constituents of silicate rocks. The several refractories available from NBS and their two replacement clays may also be suitable for rock analysis.

Glass reference samples for the trace element analysis of geological materials were prepared and analyzed spectrochemically under the direction of Myers, Havens, and Niles. [14] Four glass samples were formulated by Corning Glass Works by adding 46 trace elements at the 0.5, 5, 50, and 500 ppm levels to melts of a matrix that approximates the composition of an igneous rock. A fifth batch of the matrix was prepared with no trace elements added to serve as a "blank." These materials were powdered and are used for quality control in some USGS laboratories.

A similar set of silicate glass standards including a "blank" were prepared by Corning for NBS by adding 61 trace elements at the 0.02, 1, 50, and 500 ppm levels. These SRM's are available in wafer form from NBS. Barnes, et al, [2] describe the chemical and the mass spectrometric procedures, and give data for lead, uranium, thorium, and thallium.

USGS is concerned with a multitude of new problems in environmental geology and in the search for energy resources. The ever increasing numbers of samples of sediments, soils, plants, marine organisms, shale, coal, and coal ash, submitted for analysis frequently require new methods of analysis, such as that for the determination of mercury in coal, Huffman, et al. [6] We have recently participated in an EPA-NAS study to evaluate methods for the determination of arsenic, mercury, manganese, selenium, uranium, lead, thorium, and sulfur in coal.

Our laboratories furnished determinations for a study by the Institute of Geological Sciences, London, Lister and Gallagher [11] to evaluate data from laboratories for copper, molybdenum, lead, tin, and zinc in materials ranging from low-grade ores to high-grade concentrates. USGS undertook a reference sample program for the Association of Exploration Geochemists and Lakin [10] presented an evaluation of questionnaires sent to laboratories to determine, among other factors, the methods of analysis most frequently used and the materials most frequently sampled. Samples distributed for the association consist of three soils, a jasperoid, an Fe-Mn-W-rich hot spring deposit, and a porphory copper mill head. Data have been returned by more than half of the 157 laboratories receiving the samples.

USGS is represented on the ASTM Task Group on Standardization of Methods for Determining Trace Elements in Coal and on the Subcommittee for the determination of mercury in coal.

We also support the functions of the ACS Committee on Environmental Analytical Methodology of the Division of Analytical Chemistry, the aims of which were discussed by Laitinen. [9] Our rock analysis laboratory is presently analyzing several clay minerals prepared for the Source Clay Minerals Repository of the Clay Minerals Society.

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Discussion

Andersson:

I would like to mention some cooperative work in Sweden, Norway, and Denmark. We have analyzed three reference samples for about 16 elements by several different techniques. I can furnish the address from which the samples may be obtained.

Flanagan:

I would like to include the information in the list, "Reference samples for the earth sciences."

Q: Do you know if there is work undertaken to characterize phases present?

Flanagan:

Microprobe work?

Q: No. Quantitative diffraction work for the phases present in rocks and minerals. What are the phase compositions? This is important in bauxite processing for the aluminum industry. (No one at the panel knew of such work.)

May:

The Survey samples were prepared because of the analytical chemist rather than the mineralogist. Samples prepared as reference materials depend on what samples are being pushed by whom. Any time an organization commits itself to the preparation and subsequent analysis of a standard, it is committing itself to a large expenditure of funds. We must decline requests to analyze standards when such commitments exceed our estimated capacity for such work.

Gillieson:

The speaker mentioned summations in a rock analysis. In normal silicate samples, the assumption that the elements are present as the oxides is reasonable. When we have a non-silicate sample such as a sulfide, or a sample with a large content of an element in more than one valence state, who is to say, for example, if the element is present as V_2O_3 or V_2O_5? We do some oxygen determinations by neutron activation to obtain accurate figures, especially in sulfides. The equipment is not common and I do not know how many people use it.

Flanagan:

There have been at least four papers on oxygen in rocks: (1) Volborth, A. and Banta, H. E., Oxygen Determination in Rocks, Minerals, and Water by Neutron Activation, Anal. Chem., 35, 2203-2205 (1963); (2) Volborth, A. and Vincent, H. A., Determination of Oxygen in USGS Rock Standards by Fast-Neutron Activation, Nucl. Appl., 3, 701-707 (1967); (3) Huysmans, K., Gijbels, R., and Hoste, J., Determination of Oxygen and Silicon in Rocks by 14 MeV Neutron-Activation Analysis and Its Precision, Talanta, 20, 843-854 (1973); and (4) Volborth, A., Dayal, R., McGhee, P., and Parikh, S., Method for Ultra-Accurate Oxygen Determination for Rare Reference Samples, Analytical Methods Developed for Application to Lunar Samples, ASTM STP 539, American Society for Testing and Materials, 120-150 (1973).

May:

Several years ago our chief geologist asked about our facilities for the direct determination of oxygen. We can determine it at our reactor in Denver but there have been no requests. The assumption that the elements in rocks are present as oxides seems quite valid. The direct determination of oxygen might be more meaningful to us for minerals with elements in different valence states.

Gillieson:

May I raise the question of ferrous and ferric iron? How is one to determine ferric iron in pyrite? One possible method is the Mossbauer effect.

Flanagan:

Groups at both the Oak Ridge National Laboratory and the Illinois Institute of Technology have done Mossbauer work on USGS samples in preparation for the lunar samples.

Geological Samples and SRM's from NBS

I. L. Barnes

During the past half century, NBS has provided reference materials of geological interest--principally ores and other materials of economic interest. More than a decade ago, our laboratories started to provide SRM's directly related to the interests of the U.S. Atomic Energy Commission in uranium ores. Work since then has continued on uranium SRM's with the natural extension to SRM's for plutonium, and we have simultaneously branched into the general area of SRM's for geochronology, primarily the uranium-thorium-lead and the rubidium-strontium systems. We have also prepared several SRM's of interest for their trace element contents. NBS has recently supplemented those SRM's of interest to the mining industry with the issuance of copper and molybdenum SRM's. Our laboratories are now supplementing our original efforts on uranium ores by a project to redetermine, with the increased accuracy available, the isotopic composition of natural uranium. Some potential applications may be seen by examining these groups of SRM's in greater detail.

We have now completed certification of 18 different uranium isotopic SRM's with extreme U-235/U-238 ratios ranging from 186.77 to 0.000176. There are also available two SRM's prepared as assay standards--a uranium metal and a uranium oxide. There is no difference between the uranium assay in the isotopic SRM's and in the assay SRM's, except that the isotopic SRM's are not certified for assay. The isotopic SRM's have been used in studies of the formation of ore bodies in the Colorado Plateau by Rosholt and co-workers in the USGS.

There are also three plutonium assay and three plutonium isotopic SRM's available. These are important to nuclear reactor or nuclear fuels programs.

The next group of important SRM's are those assay and isotopic SRM's for a variety of elements that are a direct result of the atomic weight program at NBS. These materials are used as SRM's in the determination of the atomic weight of a specific element and are absolute standards. Assay and isotopic SRM's are currently available for the elements boron (2), copper, lead (3), rubidium, strontium (normal and Sr-84 spiked), and rhenium. The elements for which work is currently being conducted include: silicon, lead-206, thorium-230, uranium-235, potassium, and nickel. Isotopic SRM's are available for chlorine, bromine, silver, chromium, and magnesium. These SRM's are useful not only for the assay of various ores and minerals, but they also form the complete basis for absolute U-Th-Pb and Rb-Sr dating systems.

The most recent SRM's to become available are those for trace elements. Most of you may be familiar with the Trace-Elements-in-Glass SRM's, which are silicate glasses doped with 500, 50, 1, and 0.02 ppm of 61 elements. We predict that these materials will become the most widely used SRM's ever produced for establishing trace element methodology. It is a fact that, if you can analyze these successfully, you can analyze anything. A potassium feldspar and a pure calcium carbonate, both certified for several elements, are also included among the trace element SRM's.

The last group of SRM's to be mentioned include those intended to be of direct and immediate interest to the mining industry. We have recently issued several such SRM's: copper mill heads, mill tails, concentrate, and molybdenum concentrate.

The SRM's mentioned include some 63 different SRM's concerning 62 different elements. It might seem to the unitiated that these should satisfy nearly everyone, when in fact they satisfy very few. That the rock analyst wants an SRM whose composition approaches that of the rock he will analyze today is a truism we have come to accept.

It is impossible to produce every SRM that everyone wants. Not only would the cost be prohibitive, but I doubt if there are enough analysts in the world, let alone at NBS and at other agencies that produce SRM's, to accomplish this goal.

It is hoped, however, that those SRM's of the greatest need, not only today but in the future, may be produced in the quantity and at the time needed. This can only be done if the communication channels such as this conference are both effective and, most importantly, continuous.

Discussion

Q: Do you use the term natural or normal uranium?

Barnes:

We use the term natural uranium.

Q: I assume that you will analyze samples from different parts of the world.

Shields:

No. We certified the composition of a naturally occurring uranium sample. Several groups have previously made surveys of uranium mineral samples for their isotopic composition.

Q: We know they are not the same.

Shields:

They differ, depending on the location and type of sample.

Barnes:

In calculating the Pb-U-Th ages one major concern is the U-235/U-238 ratio. We think this ratio should be determined for each sample. We chose one sample that we called natural uranium and certified it.

Norton:

Would you compare the relative ease, costs, etc., of your method with other methods?

Barnes:

We are both expensive and slow, but accurate. The first time we analyze for an element we are relatively expensive, but after that we are about as expensive as other techniques, and we do not need to make quantitative separations. We rarely need to repeat a sample.

Q: Do you use IDMS to characterize high purity metals, in addition to the work on the glasses?

Barnes:

We have not used thermal-emission IDMS but we have used spark-source IDMS for a few metals such as Fe, Pt, Au, and Zn.

Shields:

For our Mo standard (about 55 percent Mo) we get 0.08 percent precision (absolute) for Mo. The IDMS technique is unambiguous for Mo and Re.

May:

Can you comment on the relative cost of setting up IDMS?

Shields:

About one percent of that for a reactor. A decade or so ago, a mass spectrometer cost about $100,000 and the method was almost prohibitively expensive. The cost is about the same today, but ion probes and microprobes cost two or three times as much. Computer time for our NAA group costs more annually than the money devoted to mass spectrometry.

May:

The reactor can handle a larger number of samples.

Shields:

But we would furnish a thousand times more information per analysis and our data are fundamentally free of interferences. We will certify several elements in a sample and our neutron activation group can then use these as keying elements for their standardization, including studies of homogeneity.

Gillieson:

Do chemists or physicists operate your mass spectrometers?

Barnes:

Mainly analytical chemists, but we have several physicists.

PLASTICS

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I. Introduction

The purpose of this panel was to evaluate the present utility of SRM's -- as they now exist for plastics -- and to examine possibilities for improving the value of this reference system in the future.

The panelists reflected a large portion of the plastics spectrum, representing chemical manufacturing, large-scale fabrication, a major consulting laboratory for the plastics industry, a university center for academic research and education, and NBS. The interests of other important disciplines, such as medicine, pharmacology, toxicology, and biology, were recognized as important but were not represented on the panel.

Discussion among panelists and the audience developed a variety of views and proposals for enlarging and otherwise changing the plastics SRM system to be of greater value, particularly to industry, domestically and internationally. Three general recommendations were produced during this panel:

1. NBS should create, or expand the existing, "Polymeric SRM Advisory Board" to include representatives of polymer industries, including testing, standardizing, research, and educational associations and institutions dealing with polymers --

not restricted to plastics. A function of this group should be a consistent effort to publicize effective uses of SRM, including details of experimental plans, but avoiding proprietary references.

2. The Advisory Board should consider expansion of the polymeric SRM program to include a broader system of additional materials larger in mass, initially less completely defined than, but ultimately as well characterized for specific uses as, present SRM's. In this system, a larger "clearing-house" role should be examined for NBS, which could link other laboratories and list sources of SRM's and standardizable materials, both nationally and internationally, through IUPAC and/or ISO. More specific proposals of this nature are in the speakers' presentations.

3. The NBS should establish a more flexible accounting system that would treat the present and recommended expanded SRM program as a whole, not as a collection of materials, each of which must individually satisfy criteria for zero-profit-loss. The same criteria should provide for contribution of funds and contributions of or charges for services, or materials, by industrial and other interested groups. [Editor's Note: Of these two suggestions, the latter is already incorporated in the accounting procedures, while the former would necessitate substantial changes in the regulations governing the use of federal funds.]

II. Polymer Standard Reference Materials at the National Bureau of Standards

H. Wagner

NBS now distributes four Polymer* SRM's: two polystyrenes (narrow and broad distribution) and two polyethylenes (linear and branched). These SRM's have been characterized for two or more properties such as: molecular weight, limiting viscosity number, melt flow, and density. They are used in many laboratories, both industrial and academic, to check the rather difficult and complex procedures and instrumentation employed in polymer characterization. The linear

*Here and elsewhere in this report the word "polymer" is used but "plastics" would be more appropriate for the specific polymers most frequently mentioned in this Symposium. These few "thermoplastics" polymers are not representative of, but ultimately must be expanded in number and type to include, all synthetic fibers, elastomers, etc., which are certainly equal in industrial importance to the polymers identified here.

polyethylene SRM, for which the molecular weight distribution is certified, is particularly useful for the calibration of liquid exclusion chromatography (GPC) columns. [Editor's Note: NBS issues several other plastic SRM's, some of which are certified for permittivity and related dielectric quantities and some as light sensitive plastics.]

At present, NBS is engaged in preparing and characterizing linear polyethylene fractions for certification and in providing background molecular weight data for a bovine serum albumin SRM to be certified by the Analytical Chemistry Division as a clinical chemistry SRM. Several other polymers are being considered for future SRM's, and the suggestions and advice of polymer scientists will play an important role in deciding which of these will be chosen. The criteria for selecting a polymer for SRM status include definably high chemical purity, long-term stability, as well as the criteria applicable to all SRM's such as we need for accuracy of analysis, the need for an industry-wide standard from a neutral source, and the need for a continued availability of a highly characterized material from a common source. Among polymers now under consideration for future SRM status are polystyrenes of very high and low molecular weights, with very narrow molecular weight distributions, primarily for GPC calibration. A narrow molecular weight distribution, water-soluble polymer, is also being considered. Overall, the most critical consideration is that the proposed materials be the materials that are most needed as SRM's.

III. The Importance and Limitations of NBS-SRM's to Consulting Plastics Laboratories

M. Ezrin

The use of NBS-SRM's as standards provides the best possible basis for ensuring clients, concerned with patent-infringement, compliance with purchase-specifications, etc., that molecular weights and other properties determined on unknowns are reliable. NBS is to be applauded for the very high quality job it has done with existing standards. The high cost, $100 for 50 grams, of the linear polyethylene SRM is enough to prevent some potential users from buying this SRM. Should the cost of SRM's increase still more, there is the danger that they will not be purchased widely enough to be useful on a broad basis. Possibly smaller quantities can be sold at lower cost. In the interest of keeping cost within reasonable limits and at the same time making a greater variety of SRM's available quickly, possibly the number of determinations of each property measured can be reduced.

A low molecular weight component of the polystyrene (SRM 706), apparently is a cause for some lack of agreement between GPC and solution methods.

Some possible new SRM's that should be considered are:

1. A low molecular weight polymer in the range 5000-10,000 measured for number average molecular weight by vapor pressure osmometry;
2. A glass transition temperature SRM measured by DTA or DSC -- this could be done with the existing polystyrene SRM's;
3. A polymer latex particle size distribution SRM's;
4. A strength properties SRM's;
5. A series of water-soluble polymer molecular weight SRM's, possibly by sulfonating the present polystyrene SRM. At present, for this purpose, there appears to be available only the Pharmacia Company's dextran standards, and Mann Research's protein molecular-weight standards.

In addition, the availability of reference standards (other than NBS-SRM's) should be stressed, with the caveat that their quality may be lower in one or more respects. Pressure Chemcal Company, Pittsburgh, Pa., is one such source. It supplies the series of polystyrene standards used universally for GPC calibration. This method is so important and the accuracy is so dependent on the reliability of the values claimed for the standards that consideration should be given by NBS to taking responsibility for certifying the molecular weights and even possibly supplying them to ensure their continued availability.

An important but little publicized use of SRM's is in court proceedings dealing with, for example, cases of alledged patent infringement or of product-liability involving alleged noncompliance with specifications.

There is a trend of de-emphasizing polymer characterization by major plastics raw materials suppliers. On the other hand, there is evidence of growing need by processors and fabricators for such information to establish effective quality control systems. Too often, the polymer processor or fabricator, with smaller laboratory facilities, is not closely familiar with the NBS-SRM program and thus depends on consulting laboratories for guidance.

The Joyce Loebl Disc Centrifuge is particularly effective for determining the particle-size distribution of polymer latices. The importance of this, in its field, is similar to GPC in determining molecular weight distributions. This new centrifuge could provide the basis for SRM's certified for latices of defined particle-size and particle-size distribution.

IV. An Industry View of the NBS Polymer SRM's

C. Howard

The most widely used SRM's are the two polystyrenes for molecular weight calibration. These SRM's 705 and 706, have been in general use since the early 1960's. Most laboratories have found them most useful for calibration of light scattering and osmometry equipment. They have not served to fill the need in calibrating gel permeation chromatography. The polyethylenes, SRM's 1475 and 1476, available in 1969, have been useful for this later method as well as metal viscosity calibration. One additional narrow molecular weight polyethylene fraction may be available in 1974 or 1975.

The need, as defined by many in ASTM D-20, is for larger quantities of material for larger scale calibration and referee testing. Some progress has been made outside the current NBS program, but most industry representatives feel there is much room for NBS entry.

In summary, the SRM program in the area of plastics standards has not moved as fast as the growth of the industry warrants. The need for SRM's must be evaluated, and the cooperation of industry solicited. While all types of SRM's cannot be maintained at NBS, this seems to be the best starting place.

The desired larger quantities of present and future SRM's need not be as exhaustively characterized as present supplies of present SRM's. Perhaps there is justification for another category, as "provisional," for such materials; with further characterization these could be advanced to the fully certified SRM stage. Polycarbonate, PVC, and nylon were identified as plastics for which reference samples are needed by industry, as well as means for characterizing smaller molecular compounds useful in plastics, standards for morphological evaluation, and also for DTA and DSC analyses. (The present SRM's are satisfactory, but more -- offering a full-range of values -- are needed.)

V. The Utility of SRM's and Meaningful Measurements in the Plastics Industry

S. Newman

A. The Broad Look

In exploring the utility of SRM's and Meaningful Measurements in the Plastics Industry, three major (overlapping) elements comprise this technology: (1) the scientific community; (2) the material supplier, who converts feedstock into resin; and, (3) the fabricator, who combines engineering and processing skills to produce a useable article. The first two elements seem already well supported. They are concerned primarily with molecular structure and properties to establish scientific principles, develop new material concepts, and control the nature and consistency of the polymers produced. To this end, SRM's are frequently needed in small quantity to verify analytical procedure and measurements in the determination of variety of basic molecular parameters, e.g., molecular weight and distribution, chemical purity, long-chain branching, unsaturation, tacticity and geometrical isomerism, and crystallinity. SRM's and procedures for the analysis of such quantities should be on hand if they are not already available.

The processor may also be concerned with some of these parameters, but largely for the purpose of quality control and to ensure the uniformity of his "raw materials" of manufacture. While the chemical manufacturer is increasingly oriented toward "tailoring" his products for specific end-uses, product fabrication and performance lie principally within the domain of interst of the designer and processor of end-products. It is the problems of this segment of the industry which has been most neglected, and therefore, needs attention.

The need for SRM's by the scientific community and the chemical manufacturing element of the plastics industry is acknowledged, but the major segment of the industry, processing, has little need for SRM's in small quantity. For processors and converters, for instance, interested in checking die characteristics, machine performance, mold finish, throughout, or any of a variety of processing variables, commercial grades of resins are suitable and available in large quantity. Moreover, some commercial resins are sufficiently consistent and well characterized as regards molecular weight and rheological behavior to effectively function as SRM's.

As far as engineering design is concerned, a wide range of use properties are, of course, of vital interest to the user: mechanical, thermal, electrical, dielectric, surface characteristics, flammability, optical, thermal, etc. There is no need to construct a "laundry list" of the vast number of use properties of importance to the engineer and designer. Again, SRM's in small quantity are generally of little significance. Of greater value are test methods that can provide information important to design considerations, performance requirements and use behavior.

The need for meaningful measurements of major significance to the plastics industry, which will require new and broad characterization of new and different SRM's, has been illustrated by the studies of Drs. G. Alers, K. Rusch, H. Van Dene and others.

B. Materials Testing and Selection

1. Non-Destructive Testing

Non-Destructive Testing (NDT) of plastic materials and components (during and after fabrication) must be expanded as a significant field of endeavor, if productivity, reliability, and quality control are to be improved. The overall objective of NDT is to detect deviation of a part from the laboratory prototype on which the design was based. Much current NDT simply detects deviations from homogeneity, by responding to discontinuities in physical properties. This limitation has lead us into four problem areas.

(a) Detected discontinuities must be characterized as to their size, shape, origin, etc., so that a decision can be made concerning their effect on the ultimate use of the part. An obvious example is determining the size and sharpness of a crack so that fracture-mechanics design-criteria can be applied.

(b) With increased use of composites and protective layers, test instrumentation that responds only to discontinuities cannot always detect cracks or regions of poor bonding at the interface between different materials. The most serious problem is the non-destructive measurement of the strength properties of an interface-region whose thickness may have atomic dimensions. Plastic-to-adhesive bonds, or electro-deposited interfaces are typical boundaries requiring characterization.

(c) In many cases, a serious flaw may not be associated with a discontinuity in properties. For example, residual stresses are by nature diffuse, but they can lead to stress-cracking failure in service or dimensional instabilities during the manufacturing process. There are also intentional gradients in properties that require quality assurance such as the depth of density-gradient or the contour of a chemical-composition change.

(d) In addition to these defect-location and characterization problems, there is the more general problem of devising a non-destructive test that yields quantitative measures of important material properties. These include non-destructive measures of the yield strength, fracture toughness, and ductile-to-brittle transition temperatures in various materials.

A significant research effort is needed to bring these types of measurements into the NDT inventory.

2. Computer Assisted Selection of Plastic Materials

The proliferation of plastics, and the seemingly random methods of publishing data on properties and processing techniques, has complicated selecting an optimum material by an increasingly sophisticated industry. In fact, this may dictate a computer service to scan extensive data banks and select candidate materials. This could revolutionize plastics design and materials selection by both government and industry. An appropriate program could offer:

(a) rapid access to comprehensive information on materials' properties and previous service experience, and

(b) a uniform and consistent logic sequence to define material specification, component design, and fabrication method.

Material selection and component design may comprise three steps. First is problem definition, which requires the full knowledge and experience of the engineer. Second is the spectrum of available materials, which involves the retrieval and comparison of large quantities of data. The third step is selection, which may be entered efficiently and confidently by freeing the engineer from serving as a memory bank.

Computerization of step two has several advantages. First, the computer program would encourage applying a <u>systems</u> approach to material specification and component design, by requiring key input-parameters to be identified in a uniform logic sequence before entering the selection-process. Second, the experience and knowledge of the best materials engineers would be open to all engineers, thus continually upgrading materials utilization and component design. Later in its development, the computer facility could further upgrade industrial plastics design by providing sophisticated analytical techniques to the engineer. For example, important engineering parameters such as maximum and minimum use-temperatures and toughness could be computed from basic material properties, rather than from less-precise data such as heat deflection temperature, izod impact, or falling-ball impact tests. Design parameters proven valuable in component-design, but not widely used could be introduced; e.g., fatigue damage analysis, environmental stress-cracking, and fracture toughness. Another capability is extra- and inter-polating experimental data using established theoretical relationships. Examples are: (a) the rate and temperature dependencies of mechanical properties, (b) influence of fibers, particulate fillers, voids (foams), or plasticizer or mechanical properties, and (c) ultimate service life under known loading and environmental conditions.

The following list outlines the type of information that would be necessary in a computerized scheme.

Exemplary Property Information Required for
Materials Selection Test Methods and Possibly Selected SRM

I. Physical Properties:

   A. Mechanical (-40 °F to the maximum service temperature--(need not be listed in detail).

   B. Chemical, such as:

      1. Resistance to (a) organic solvents, aqueous acids/bases/salts; (b) solvent-induced stress-cracking (crazing) as several stress levels.

      2. Absorption of moisture, organic solvent permeability.

   C. Miscellaneous, such as:

      1. Flammability (burning rate),

      2. Paintability, and

      3. Frictional characteristics.

II. Manufacturing Considerations:

   A. Fabrication Processes

      1. Suitable processing/forming operations (injection molding, compression molding, sheet forming, etc.).

      2. Typical processing conditions (pressure, temperature, cure time, etc.).

      3. Mold shrinkage.

4. Machining qualities (grinding, drilling, punching, shearing, etc.).
5. Dimensional reproducibility, stability.
6. Suitable post-molding operations (friction welding, plating, adhesive bonding, etc.).
7. Surface appearance/"feel."
8. Occupational toxicity of ingredients.

B. Suitable Fastening Techniques

C. Influence of Processing Conditions on Mechanical Properties

1. Disperation of fillers, fibers, rubber particles, etc.
2. Crystalline morphology.

III. Approximate Costs:

A. Price by weight

B. Price by volume.

Prediction of LongTerm Properties as Exemplified by the Evaluation of the Weathering Performance of Paints

Final judgment of weathering is now made after two years outdoors exposure (usually in Florida). If this period were shortened significantly, development of new paint systems could be speeded accordingly. Unfortunately, so-called "accelerated" testing, i.e., subjecting the paint film to an artificial severe environment, as in a weather-o-meter, does not always correlate with a longer exposure outdoors. It is probably not that a reliable "accelerated" test cannot be devised, but rather that the causes of poor weathering performance are not understood sufficiently to devise such a test beforehand. Also, testing procedures used to evaluate weathering are such that only relatively gross changes are detected; hence slow erosion must proceed for an extended time before it is detected.

The aim, thus, would be to develop more sensitive test methods to make judgments earlier. At the same time, the physical and chemical changes during weathering should be identified, to understand the process itself. In other words, the tests should identify the cause of poor weather performance, not merely correlate to poor weathering.

The methods used should detect small changes in properties and composition, and yield an interpretable number or set of data. The tests should encompass means to evaluate changes that occur at the free surface and the paint/substrate interface, as well as overall film properties, erosion, migration, embrittlement, and corrosive failure. These methods divide into two parts: (a) evaluation of physical changes, and (b) chemical analysis of possible composition changes.

A. Physical tests may include:

1. Surface properties; surface roughness, including electronmicrographs of surface topology; and surface wettability, by Zisman analysis of the dependence of contact angle of a series of non-wetting liquids on surface tension of these liquids. As most paints comprise surfactants, to provide a low energy surface of the final film, one should find if the surfactant remains on the surface or gradually disappears, hence changing the wettability of the surface, in turn opening it to chemical attack by polar materials.

2. Interfacial properties: paint/primer and primer/substrate interfaces must be considered. Loss of adhesion is checked by standard methods. Small flaws can be detected by determining the ultrasonic scattering coefficient (analysis for corrosion by microprobe).

3. Film properties such as determination of the modulus, and embrittlement. An adverse environment may lead to stress-cracking or initiate sharp microcracks, which will propagate on stressing. Their influence may be detected by either a standard mandrel bend test, or by a three-point bend test.

B. Chemical analysis should include:

1. A thermal gravimetric analysis (TGA) to determine the thermal decomposition profile as a function of outdoor exposure.

2. An analysis by gc/mass spectrometry to identify decomposition products. As low molecular weight additives tend to migrate to the surface and exhibit greater volatility than the paint matrix, these additives may be collected and identified before the matrix itself decomposes.

Further chemical information, such as the total loss of material, could be studied by incorporating labeled compounds in a control formulation. Specific information as to the chemical reactions, which accompany weathering, could also be assessed by the specific method of incorporation of the label.

VI. Polymer SRM's of Interest to the University

T. G. Smith

The university interest in polymeric SRM's in terms of the utility and limitation of the present polymeric SRM program is discussed as applied to research in, and teaching of, polymer chemistry and chemical engineering. The uses may be divided into two categories: calibration materials (light scattering, osmometry, GPC, and viscometry); and well-characterized research materials for use in morphological studies, and in studies where molecular weight distribution must be known, as in research on the mechanism of separation in GPC, hydrodynamics of molecules in solution, etc.

The objective of this discussion is to indicate how the university community employs polymeric SRM's; what their needs are and the means that might be taken to meet the needs. A university professor has two callings -- one involves the training or teaching of students and the other involves research. These two broad areas usually overlap. In the teaching area, SRM's are used:

1. To make students aware of the need for calibration standards;

2. To train students in instrumental analysis and calibration; and

3. To train students in error analysis and the design of experiments.

The research area finds the greatest use for SRM's. This use of SRM's is no different from that of the NBS or any industrial research laboratory as far as their use as calibration standards go. They are used for calibration of molecular weight determination equipment, for training graduate students in methods of using molecular weight determining instrument, and for cross-checks on experimental methods among students.

Interest exists in the use of polymeric SRM's as test materials for use in the development of new molecular weight determination apparatus, as well as in modifying methods of determining molecular weight and molecular weight distribution. There is also interest in their use as standards in experiments to broaden our understanding of the mechanism of separation in GPC. Further, they serve a useful purpose in the development of new GPC resins and in the development of methods to analyze GPC data.

A third area where SRM's find use in the academic world is as well characterized research materials. The use of an SRM as a research material has the advantage that the molecular weight, and sometimes the molecular weight distribution are known to a high degree of accuracy. This can provide several benefits:

1. The researcher can rely on the measurements and save himself time and money.
2. The reporting of the SRM values can be done with confidence.
3. The entire NBS experience with the material becomes available.
4. Modifications of the polymer during an experiment can be made with greater confidence as the base line is well established; such as in the study of cross-linking or shear degradation.

One of the purposes of this meeting was for NBS to get feedback from SRM users to obtain a measure of what future needs are. Dr. Wagner provided the results of a questionnaire sent to users of SRM 705 and 706 in 1970, which reflects NBS' concern in this area. The number of responses from universities was not great, but then the number of universities with active polymer science programs is not great.

NBS should consider providing polymer SRM's of the following types:

1. A water soluble polymer;
2. Sharp polystyrene fractions over a range of molecular weights;
3. A polymer for vapor phase osmometry;
4. A polymer with polar groups or tagged groups; and
5. A high molecular weight polyethylene.

Also, NBS should provide GPC results for the current polystyrene SRM's and provide, but not necessarily certify, other data that may have been obtained at NBS on the SRM's. These results from NBS research studies on SRM's might be attached to the certification. Publications similar to NBS Special Publication 260-42, which concerns linear polyethylene, would be helpful for each of the SRM's. This publication is an excellent summary of experimental method and analysis of results. It is recommended to students as an example of an outstanding piece of work to characterize a polymer.

With respect to cost, the existing SRM's are considered inexpensive because of their extensive completed characterization, with specified levels of precision and reliability.

VII. Discussion

The discussion period was wide-ranging and covered several topics in response to questions raised by the Chairman and others. These comments are summarized and are not necessarily in the order presented, but grouped around the major questions raised.

Question 1. To what extent does NBS have a "Master Plan" for the growth of the SRM program?

NBS representatives indicated that, as a part of the Department of Commerce, commercial importance must be stressed, as it is in the current inclusion of the polystyrene and polyethylene SRM's. This importance has been expressed through ASTM (D-20 and other committees) in terms of its selection of materials and evaluation techniques beginning in 1965. The SRM program, by OMB requirement, must be self-supporting -- sales for each SRM must cover its cost. For these reasons, NBS canvassed industry -- manufacturers fabricators, and users -- to determine broad industry needs. In this survey, it must be recalled that plastics SRM's are very few among the total of over 850 SRM's of all types.

While these constraints must be recognized as realistic and strict, one wonders if greater publicity might be effectively given to NBS inquiries to polymer-concerned industry. Are other fields of science, education, medicine, toxicology -- all with interests in polymers, also queried? Is ASTM a broad enough source for guidance to NBS? Should other trade groupings such as the Society of the Plastics Industries, Society of Plastics Engineers, Plastics Institute of America, etc., be included to emphasize other dimensions? Are there non-polymeric materials that might be worthwhile as SRM's to satisfy specific polymeric needs -- as in the very wide range of additives to polymers? To what extent might these or other industrial, educational, or research groups support cost elements in SRM programs?

If as reported, 20-25 percent of NBS-SRM's go overseas, what is the feedback from these users? Are present and future domestic users to benefit from these activities?

In the rubber field, the existence of substantially-larger (30 kg) quantities of a polyisobutylene SRM, with well controlled curing and reinforcement characteristics, suggests a more responsive activity by ASTM D-9, as opposed to that by ASTM D-20. Is there a sufficiently continuous and active assessment of the needs for plastics SRM's by ASTM D-20, on its own, and in possible coordination with other groups identified above? These questions lead to another broader one.

Question 2: To what extent should there be a SRM "system," linking the NBS with other laboratories (not limited to the U.S.) and incorporating larger and different samples?

One can visualize the NBS in a "clearinghouse role," associated with other industrial and national laboratories worldwide. In this sense, the NBS would list sources, identities, levels of characterization (numbers of laboratories examining one material with standard methods and with results statistically qualified as to average, standard deviation, etc.), masses of materials available, costs of each, etc.

A hierarchy of samples would appear feasible. The present certified SRM represent the epitome of quality. Larger quantities of more recently chosen "research sample" materials would necessarily be qualified by various laboratories using standard methods, but initially with fewer determinations, thus larger standard deviations, and for fewer parameters. (Those samples earlier available from Brooklyn Polytechnic Institute and more recently transferred to the Macro Molecular Institute, Midland, Michigan.) In time, with additional measurements, such lower ranked materials would advance to certified SRM's. Regardless, at whatever stage of refinement, such materials would be available from the originating source, in selected quantities at appropriate costs. To the extent that less characterized materials would be available in larger quantities, it is possible that greater industrial and other usage and support would result.

Because of the extremely large potential variety of materials characterized by specific parameters that could be envisioned, the "system" should include the identification of facilities to prepare such materials and to characterize them to different levels of refinement. Engineering properties should receive greater emphasis, especially dynamic as opposed to static modes. Also, the inclusion of SRM's defined as to chemical composition should be considered, for example, contents of constituent monomers in co-polymers.

An example cited for such larger scale purposes and materials included the optimization of extruders as to throughput and product quality, with materials of well-defined heat capacity, molecular weight stability, and viscosity as a function of temperature.

Such an arrangement would require an administrative group centered at NBS, possibly within the Polymer SRM Advisory Board representing the different concerned organizations and disciplines. This group could set policy as to publicity, and international linkages, possibly through IUPAC and ISO/TC-61.

A National Academy of Sciences Report* was mentioned as possibly relevant to this concept. This report requested another staff scientist to expand SRM activities. But more aggressive and broader, industry-oriented publicity seems needed. One such illustration, with several specific examples was included in a report of an interview with the Director of the NBS Institute for Materials Research.** This is helpful, but further detail for each of the cited cases, in journals relevant to each, would reach a much broader, perhaps more concerned audience.

Clearly, there may be Congressional, OMB or other Federal restrictions, inhibiting such a broader SRM concept; these will have to be evaluated. Apparently in the EEC field, as reported by Dr. Lauer, it has been found easier to "internationalize" the less proprietary, less competitive SRM's, for more scientific and educational purposes, which are freer of economic problems.

On the other hand, if limitations in petrochemical feedstocks force plastics' prices to increase, then competition with other materials may be expected to stress engineering properties (rather than relatively frivolous uses) for more meaningful measurements, more reliable methods, and in turn, greater dependence on different types of, and more broadly characterized SRM's. Ultimately, this might lead to greater industrial use of, and support for the plastics SRM program.

Question 3: To what extent should medicine, toxicology,

*"Molecular Properties and Characterization Section" in 1970-1971, 1971-1972 NAS-NAE-NRC Annual Reports of the Panels for the Evaluation of the Research Development and Technical Service Activities of the National Bureau of Standards.

**Materials Research and Standards, 12:5 (1972).

and other investigational fields participate in the SRM program?

Plastics are very heavily involved in health-related uses -- food packaging, organ-replacement, and other surgical uses. In evaluating plastics for these uses, there appears to be a lack of understanding of polymer-chemistry and physics by toxicologists, pharmacologists, physicians, etc. Critical experiments with selected SRM's could provide the needed information.

For example, in food-packaging, FDA necessarily concerns itself with the safety of extractable moieties, including oligomers. Preparation and toxicological testing of these fractions are costly and time-consuming. In all the many commercial polymers so far tested for oligomers, the record shows physiological inertness. The conclusion is growing that these oligomers do not undergo metabolism or pass through the intestinal wall. A careful evaluation of these factors for SRM quality oligomers could well elucidate mechanisms involved, minimize concern for these materials in such uses, and redirect scarce expertise to more fertile areas.

Related to this is growing international interset in plastics for food packaging, especially in Eastern European countries. Unfortunately, these are frequently guided by medical and toxicological principles that show extreme East-West variations. For example, most USSR limitations on extractable mono-molecular and oligomeric moieties are far more strict than USA and Western European regulations. To resolve these basic differences, critical experiments with well-characterized materials in these categories are as necessary as expertise, interest, and financial support in using them.

Much the same situation appears to exist in evaluating polymers for implantation for various surgical reasons. This field is of interest to ASTM F-4 on Surgical Implants. The literature suggests that too often medical and toxicological workers seem to accept an uncharacterized commercial material as representative of all materials in the same generic category, and, perhaps worse, as acceptable, as to chemical and physical composition, for the intended analyses. Distinctions need to be made between "medical grade" and other less critical grades of a material. The need for SRM-quality materials for effective research in this field seems evident.

Perhaps a greater need is for more effective liaison between representatives of "health" uses of plastics and those plastics experts close to the SRM program. At the same time, it must be recognized that the polymers of interest are not limited to plastics, but must also include synthetic fibers, rubbers, and selected natural polymers, including those further modified chemically and physically.

RADIOACTIVE MATERIALS

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I. Introduction

Because radioactive materials can seldom be maintained as long-lived standards, such as may be done with other materials, the production and use of radioactive reference materials involves a three-phase operation:

A. The production and periodic reproduction of national primary standards of specific radionuclides.

B. The production of working-level reference materials at lower levels of accuracy by industrial and other non-national laboratories on a more frequent schedule.

C. A program of periodic intercomparisons between the national laboratory and the producers of working-level reference materials to establish "traceability" to the national laboratory.

These principles apply to reference materials of radioactive nuclides in all areas but are particularly important in the pharmaceutical and environmental areas because of their involvement with public safety and regulatory functions.

II. Summary of Panel Discussions

Earl L. Meyers, Director of the Division of Oncology and Radiopharmaceutical Drug Products of the U.S. Food and Drug Administration, opened the discussions by reviewing the role of reference materials in determining the safety and effectiveness of radiopharmaceuticals. The availability of national standards and readily available reference materials are required to control identity, strength, and purity of radiopharmaceuticals. The responsibility for providing national standards of radioactivity and purity for radionculides used in medicine should be assumed by the National Bureau of Standards.

Availability of reference materials is not sufficient to control safety and efficacy unless a system of methods validation is established. The supplier of radiopharmaceuticals must prove the validity of the methods that are used to control the quality of his products. These methods will be verified by laboratory tests of the products of a supplier. In later discussions it was pointed out that participation by a supplier in an intercomparison procedure between NBS and industry would provide the supplier with a constant reverification of his procedures for quality assurance.

Wilfred B. Mann, Chief of the Radioactivity Section, National Bureau of Standards, described the availability of radioactive SRM's that are provided by NBS. He pointed out several gaps in the availability of national standards for radionuclides that are of importance in radiopharmaceuticals and environmental control activities. The identification of such gaps is done by liaison between NBS and various governmental agencies such as AEC, DOD, FDA, and EPA. In many cases this liaison is strong and continuous, but in others, it is too weak.

Again, W. B. Mann suggested that the availability of SRM's is not sufficient. The term "traceability to NBS" cannot be defined only in terms of the use of available standards, but must involve a constant program of intercomparisons among laboratories to establish that a specific laboratory has valid methods and techniques to analyze radioactive materials. He then described ongoing programs of intercomparisons that have been established between NBS and users of their SRM's in which the AEC, the Atomic Industrial Forum, the College of American Pathologists, and the Department of Defense act as coordinating agencies. Expansion of such programs through the Food and Drug Administration and Environmental Protection Administration would be highly desirable.

Yves Le Gallic, Head of the Ionizing Radiation Laboratory of the Bureau de Metrologie Nationale in France, described the calibration chain as used in France. Primary and secondary standards are produced by a national primary laboratory. Tertiary standard reference materials are produced by calibration centers through reference to the secondary standards. The last stage involves approved industrial laboratories that distribute quaternary reference materials that are used in routine measurements. All laboratories in this chain must periodically prove their capabilities by intercomparisons up and down the chain.

Y. Le Gallic agreed with the earlier speakers in tying SRM's to a testing program of the various steps in any calibration chain. By the use of the words "official guarantees" and "official seal" he appeared to propose a more formal chain of calibration approvals than the speakers from the United States.

This lack of formality in the U.S. program was emphasized by Carl Seidel of New England Nuclear Corporation and Chairman of a Subcommittee of the Atomic Industrial Forum made up of industrial manufacturers of radioactive reference materials. In the United States, NBS is the national primary laboratory, but the next and only level is the industrial manufacturer. Only in the last year has a program of intercomparisons been established to allow industrial laboratories to prove their capability and traceability to NBS. This program is voluntary and supported financially by the industrial participants.

This group of industrial laboratories is now working to establish a more formal program by seeking to form a recognized committee within the American National Standards Institute. The proposed program would include standard procedures for various counting and analytical instruments, standards for reporting accuracy and precision, and a formal program of intercomparisons with NBS that would include industry, governmental laboratories, and users.

The discussion period following the presentation by panel members strongly supported the need for more standards at the national level in all use areas and the requirement for methods and performance evaluation. The environmental participants particularly noted the need for gas standards for environmental atmospheric analysis and for SRM's of several radionuclides in various matrices, such as milk and lake sediments.

RUBBER AND RUBBER COMPOUNDS

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Reference materials for testing rubber had their inception in 1944 when commercial lots of five materials were distributed by their suppliers to Government synthetic rubber plants for testing production to assure uniform rubber from 16 facilities. The problems encountered with these materials led the Office of Rubber Reserve in 1948 to request the National Bureau of Standards to assume responsibility for them. Shortly thereafter ASTM Committee D-11 appointed a special committee on standard materials, the forerunner of Subcommittee D-11.20 on Compounding Materials to work with NBS. This committee advised NBS on materials needed. Today, 20 SRM's for rubber compounding have been established including 5 rubbers. They are listed on page 73 of the 1973 Catalog, NBS Special Publication 260. They are used somewhat differently than other SRM's. A rubber is mixed with several compounding materials in order to evaluate its vulcanization characteristics. The results depend both on the rubber and the particular materials used, including the proportion of them in the compound. A small amount of impurity can have a pronounced effect. Therefore, SRM's must be used in quality control of synthetic rubber production. NBS SRM's for rubber compounding are used in many countries for this purpose. They are also used in the same manner other NBS SRM's are used--to standardize testing procedures among laboratories.

These SRM's must fulfill the following requirements: (1) uniformity, (2) stability, and (3) reproducibility. The first two requirements apply to any SRM. The third requirement is unique for compounding materials and stems from their use in quality control of production. Successive lots of an SRM for rubber compounding must be essentially equivalent in rubber tests. Chemical tests are not reliable for determining equivalency. For example, NBS SRM 370 is a reagent grade zinc oxide that meets the requirements of the American Chemical Society and has a surface area of approximately 3000 m^2/kg. Yet, differences in vulcanization characteristics of rubber are found using different lots of this zinc oxide. Apparently impurities in the atmosphere in which high-purity electrolytic zinc is burned affect the composition of the zinc oxide sufficiently to influence vulcanization, although the amount of impurity is well within that permitted in the ACS specification.

A similar experience was experienced with stearic acid. A small amount of impurity in a high-purity stearic acid had a pronounced effect on vulcanization. The nature of the impurity has not been determined. Recent lots of NBS SRM 372 have been equivalent to chemically pure stearic acid made by recrystallization. Therefore, the highest purity materials commercially available have been selected when possible.

Some materials like carbon black used in rubber cannot be obtained without significant amounts of impurities. The reproduction of lots of such materials is much more difficult. The blending of two lots is sometimes required to obtain the desired effect in rubber. Obviously, these lots are heterogeneous on a small scale. However, the lots are uniform when the amount used in compounding rubber is considered.

Some impurities like palmitic acid in stearic acid do not affect vulcanization of rubber differently than pure material and can be present in substantial amounts. Other impurities in small amounts have a pronounced effect as previously noted. Since the nature of the impurities is generally not known, chemical tests cannot be used for assessing behavior in rubber. A new lot of material must be tested in rubber to determine its equivalency to previous lots. Even so, the rubber must be selected with care since some rubbers are more sensitive than others in detecting differences in lots of compounding materials.

Although successive lots of compounding materials are essentially equivalent in rubber, no attempt is made to reproduce lots of rubbers with identical properties. Since a compounding material cannot be evaluated independently of a rubber and other materials, certificates are issued only for the rubbers. Theoretically, the certificate applies to a composite of all materials in the compound. The values reported on a certificate are for technological characteristics influenced by the testing procedure and are not inherent properties. Environmental conditions affect the values, so the complete evaluation is made in a laboratory having controlled temperature and humidity. Temperature of mills, vulcanizing presses, etc., are also closely controlled. Statistical designs are used to eliminate as many systematic effects as possible. Because most laboratories are not able to adhere to strict conditions, new lots are evaluated only at NBS and the conditions used at NBS are given in the certificates. The uncertainty in the values given in the certificate reflects variations in the lot of rubber plus any testing error that remains because of the limited number of tests.

The five rubbers issued as SRM's are natural rubber, acrylonitrile-butadiene rubber (NBR), isobutene-isoprene rubber (butyl), and two types of styrene-butadiene rubber (SBR). If the rubbers are not properly stabilized with antioxidant, they change during storage; e.g., the Mooney viscosity of two lots of butyl rubber decreased in viscosity markedly on storage due to inadequate stabilization. Since the primary use of this rubber is for verification of Mooney viscometers, such a change is serious. The SBR reference materials increase in Mooney viscosity during storage. For this reason, they are not recommended for verification of the procedure for determining Mooney viscosity. It is planned to delete Mooney viscosity from future certificates for SBR. Now, NBR is recommended for this purpose. Since only one lot of NBR has been established, no prediction can be made concerning the stability of future lots. What is needed is an accelerated test to determine stability of rubbers during storage.

Chloroprene rubbers have been notorious for their instability at room temperature. Although requests have been made for an SRM of this type of rubber, none has been established since cold storage facilities are not available at NBS. A request for such storage was made when the Gaithersburg facilities were planned, but no cold storage room was included. Consideration has been given to establishing an SRM of EPDM rubber, but the rubbers produced by different companies have not been sufficiently alike to decide on one to use.

Large lots of the rubbers and compounding materials are established because of the manner in which they are used and of the economies involved. They are certified for use in specific tests relating to rheological or vulcanization characteristics of rubber. They are not suitable for reference in chemical and other tests using a small amount of material for the specimen, except for the few materials of relatively high purity and homogeneity.

The SRM's for rubber compounding are used primarily for evaluation of raw materials and are not suitable for evaluating vulcanized products. As mentioned by R. J. A. Neider in his symposium paper, there are reference materials used for evaluating the swelling and deterioration of vulcanizates by hydrocarbon oils. ASTM designates three reference oils and several other reference materials for this purpose. Since these oils are not definite hydrocarbons, there has been difficulty in reproducing lots by the companies supplying and distributing them. Currently, they are identified by aniline point, kinematic viscosity, and flash point. The aniline point is the one which correlates most closely with swelling, but it is not adequate to characterize the oil for purposes of a reference material. NBS is conducting a research investigation of other characteristics to define these oils for reference purposes. These ASTM oils are used worldwide and have been adopted by ISO. A. J. Streiff mentioned that there is an API project on the higher boiling fractions of oils at the Bureau of Mines Station in Laramie, Wyoming. This project may have useful information for characterizing these oils.

Other reference materials specified by various standardization organizations involving rubber are the following:

1. ASTM E249 prescribes a standard tire for measuring the coefficient of friction of roadways. A tire manufacturer distributes the standard tires.

2. The measurement of surface frictional properties with the portable tester requires a reference rubber vulcanizate for the slider (see ASTM E303). The distributor of this material is not known.

3. Federal Motor Vehicle Safety Standard 116 and Society of Automotive Engineers Standard J 1703b on brake fluids require standard SBR brake cups. NBS developed a standard formulation for EPDM brake cups used in testing, but these cups have not been included in standards to date. SAE is the distributor of the standard brake cups.

4. ASTM abrasion tests D1630 and C2228 prescribe standard vulcanizates for reference in determining the abrasion resistance index. The Rubber Manufacturers' Association distributes the material for D1630.

5. A reference material similar to NBS SRM 378, Oil Furnace Black, is used in the carbon black and rubber industries to evaluate carbon black production. Very large lots are produced because of the large amount of material used. No attempt is made to have successive lots equivalent. These blacks are designated IRB No. _3_ signifiying a particular lot of industry reference black.

A problem with the use of rubber vulcanizates for SRM's is the change in characteristics during storage. For some tests, the change is either slow or the effect of aging is small on the characteristic of interest. In general, it is not feasible to establish a large lot of vulcanized rubber and distribute the material over a long period of time. Therefore, NBS established in 1970 an interlaboratory program for tensile properties of rubber. Since then four other programs have been established covering tear resistance, hardness, compression set, Mooney viscosity, and vulcanization characteristics obtained with the cure meter. Participation in the programs is by subscription. In each program, two materials in duplicate are distributed to participants four times a year. The results are returned to NBS for analysis. As soon as a participant's results are received, NBS data on the same material are sent so that immediate corrective steps can be taken if necessary. After the deadline for returning data, the results from the particpants are analyzed by computer. Both a preliminary report giving only the participants and overall results of the analysis and a final report that gives results for all participants identified only by code are prepared. These programs have been helpful to participants obtaining widely discrepant results, but they have not reduced the variation in testing for other participants.

Participation in these programs is worldwide. However, the number of participants is a small percentage of the number of laboratories testing rubber. Besides the variations observed among laboratories, the variability in testing two different rubbers is not the same. For example, tensile tests of SBR vulcanizates are much more variable than those of butyl or NBR vulcanizates. Therefore, a single value cannot be given for the repeatability or reproducibility of a particular test. Also, some tests have excessive variability. The uncertainties in values of tear resistance and compression set are so large that these tests are virtually meaningless. The large variability among laboratories in compression set determinations is surprising. Thus far, the cause of this variability has not been found.

In summary, both SRM's and interlaboratory programs serve useful functions for standardization of test and quality control in the rubber industry. Much work needs to be done, and these activities need to be expanded to assure that test results obtained throughout the industry are meaningful and reliable.

METROLOGY

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I. Introduction

George T. Armstrong

I would like to make reference to the early lecture in this Symposium by Robert D. Huntoon, in which he discussed measurement systems, how one carries on a really systematic measurement system, and the kinds of implements available for putting it into effect. In this lecture, he referred to calibrated instruments and to standard reference materials. Of course, we in this Conference are particularly concerned with reference materials. These reference materials generally, although he did not discuss this point, fall into two categories.

First there are those that are used to characterize materials. If one examines the program as a whole, one will see that all of the panels, except this one, are about reference materials that are used to calibrate materials. By this I mean they are materials very like the materials with which they are expected to be compared.

When we come to the subject matter of the metrology panel, we find that we seem to have a different category of reference materials. Here we have reference materials that have a certain property and that may be used to calibrate instruments that have very little, if anything, to do with the properties of that material except for one very specific parameter of the material. In fact, what they do have to do with is some unit of the measurement system. That is, they have to do with an optical property, a thermal property, or a magnetic property. These properties are essentially independent of the kind of materials. That is, it is not important whether one is dealing with rubbers, polymers explosives, or refractory materials. The property extends over a wide range of classes of materials; and that is, in my view, the essential difference in the scope of the discussions of this panel as contrasted with the other panels.

To give some concept of the scope of the potential coverage of the panel, we list below the NBS-SRM's that comprise the metrology standards.

A. Density standards
B. Heat standards
    1. Superconductive thermometric fixed point devices
    2. Freezing point standards
        a. Defining fixed points*
        b. Determined reference points*
    3. Melting point standards*
    4. Calorimetric standards
        a. Combustion calorimetry*
        b. Solution calorimetry
        c. Heat source calorimetry
        d. Heat capacity*
    5. Differential thermal analysis
    6. Vapor pressure standards
    7. Thermal conductivity standards
    8. Thermal expansion standards
    9. Thermocouple materials*
C. Magnetic standards
    1. Magnetic susceptibility standard*
D. Permittivity standards
E. Optical standards
    1. Spectrophotometric standards*
        a. Color standards for spectrophotometric tristimulus integrator
        b. Glass and liquid filters for spectrophotometry
    2. Thermal emittance standards*
    3. Refractive index standards*
    4. Reflectance standards*

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* Discussion in this summary.

This is not really a complete list of SRM's that could be classed as metrology standards. The panel does not cover completely all of the materials listed above. We discussed calorimetric standards, including standards for reaction calorimetry and for non-reacting systems. Dr. Venable spoke on optical standards; Mr. Foster spoke on the temperature standards; Mr. Mundy spoke on the magnetic susceptibility standards; and Mr. Crovini spoke about a more general subject--Standard Reference Materials in the Dissemination of the Measurement Units.

One further remark, I went through the preparation of material for this panel with the idea of covering the SRM's that were available, the inaccuracies, and so on, without much thought to needs for additional standards for metrology. I had my eyes and ears opened when Robert Powell made a lecture on the same subject that we talk about here, though it did not have the same title. Powell spoke about SRM needs and for measurement of physical properties in science in a very broad way, and after listening to him I realized how narrowly I had looked at the subject. I left open for those attending the panel the possibility that the limited scope presented by the panel members could be expanded during the discussion period to comment on the points raised by Powell.

II. Calorimetric Reference Materials

George T. Armstrong

I should like to begin the discussion of calorimetric reference materials by referring to two modes of use, which, incidentally, are applicable to other kinds of reference materials, too. These two modes are really quite distinct in the actual way they are used in the laboratory.

First the materials are used for the calibration of apparatus. By this usage, they place measurements in the framework of the National Measurement System (SI). For calorimetric measurements this means referring heat measurements to the joule, which is realizable, by definition, in terms of the basic units mass, length, and time. The joule is also realizable rather easily in practice by the use of time with the electrical units, the volt, the ohm, and the ampere. It is not so easily realized in terms of some other performance properties of materials. In particular, the measurement of energy that appears as heat energy, and the measurement of energy that appears as chemical reaction energy is actually a rather difficult problem. Thus, one of the very important uses of calorimetric reference materials is to place our measurements of chemical reaction energies and of heat capacities and other thermal properties of materials in terms of the more precisely definable and more easily realizable mechanical units.

In distinction to this, a less widely used mode of usage of these reference materials is for the intercomparison of laboratories. This is essentially a method of refining and improving measurement techniques. By eliminating possible differences in the samples tested as a source of differences in measurements, the use of SRM's in various laboratories permits a comparison of measured values for what is sometimes a very complex process, and provides a resource for establishing the reasons for differences between laboratories.

In calibration, a calorimetric reference material has two advantages. For a large number of applications in calorimetric measurements, one does not need as complicated an apparatus if one uses an SRM. In fact, one can eliminate the need of a routine calorimetry laboratory for any kind of electrical measurement competence. For calibration, one can carry out calorimetric measurements of exactly the same kind as are going to be performed in the laboratory. One or two reference materials are widely used for this purpose.

The other advantage is the elimination of a wide range of potential systematic errors by eliminating the need for electrical measurements. In trying to intercompare two different kinds of processes--to measure an electrical energy and compare it with a chemical energy, systematic errors are possible because these are really quite different processes being carried out in the same instrument. If one has a reference material on which one can rely, one does not have to worry about the transfer from one process to another.

I should like to discuss the benzoic acid reference material that is used in bomb calorimetry as a means of establishing the chemical energy scale in terms of the joule. Benzoic acid has been universally adopted, and it is a very important reference material, having two very broad applications.

One application is its use in essentially every combustion calorimetry laboratory for determining the properties of fuel. This has meant for this nation, for Europe also, and so far as we are aware, wherever one is interested in the properties of such fuels as coal, petroleum, wood, anything that burns, that the heating values are determined by bomb calorimetry; and the calorimeter is calibrated with benzoic acid.

There is another rather important application of benzoic acid, and that is its use in scientific laboratories where people are interested in determining the fundamental properties of materials. The thermodynamic properties of pure substances can be established in terms of the International System of Units if one can devise a bomb calorimetric procedure for carrying out a chemical reaction involving that pure material, and if one can calibrate this calorimeter with benzoic acid. On that basis I should say that a very large fraction of all the chemical thermodynamic data published in tables of thermochemical values actually refer back to the energy value assigned to benzoic acid. So this is really quite an important substance.

We list below a few criteria that have been established as attributes important in the acceptance of a substance as a primary reference material for bomb calorimetry; and these criteria apply well to benzoic acid, (a) easily obtainable in a pure state, (b) stable, (c) non-hygroscopic, (d) not too volatile, (e) easily compressible into pellets, and (f) completely combustible in the bomb.

The procedure that one uses in the establishment of the heating value of the benzoic acid is as follows. First, in the standardizing laboratory a procedure is devised for putting into the calorimeter a known amount of electrical energy and measuring the corrected temperature rise of the calorimeter, say in degrees Celsius. An energy equivalent of the calorimeter is established in terms of the electrical energy put in as the temperature rises, and that energy equivalent has the units of joules per degree Celsius. Then one causes the combustion of benzoic acid in the bomb calorimeter under certain well specified conditions and again measures the corrected temperature rise. Using the energy equivalent of the calorimeter, the weight of the sample, and the corrected temperature rise, one can calculate the energy of combustion, $-\Delta U_B^\circ$, in joules per gram. This is the process that is carried out in the standardization laboratories, and has been done in more than one place: at the National Bureau of Standards, the National Physical Laboratory, and in several other laboratories around the world.

One test of the accuracy with which we know the process going on in an electrical heat measurement or a chemical heat measurement is in our ability to estimate the errors of the experiment. In Table 1 are shown four principal factors that contribute to the errors: the corrected temperature rise that occurs in both experiments is estimated to contribute a few thousandths of a percent. Buoyancy corrections apply not to the weight of the sample that is burned, but to bringing the calorimeter to constant weight. Mass of benzoic acid, of course, appears only in the benzoic acid experiments, and the error in electrical energy occurs only in electrical calibrations. We find that we are able to estimate the standard deviation of an experiment at about two thousandths of a percent for both the electrical and chemical processes. The observed standard deviation of an experiment is about three thousandths of a percent in the case of the combustion measurements and about seven thousandths of a percent in the case of the electrical measurement. This is a surprise because actually one would expect that a chemical process as complicated as burning a material like benzoic acid would be much more random and lead to more scatter than a clean reproducible physical process such as measurement of an electrical energy in a heater. Nevertheless, this seems to be the situation, that one is actually able, in a calorimeter such as the one we use and in our present state of understanding of the calorimetric process, to measure chemical energy converted to heat more reproducibly than one can measure electrical energy converted to heat. This is the kind of information that allows us to search for possible errors in the calorimetric process.

Table 1. Estimated Random Errors in Bomb Calorimetry of Benzoic Acid

Source of Error	Benzoic Acid Combustions	Electrical Calibrations
Corrected Temperature Rise	0.0016%	0.0013%
Buoyancy Correction	0.0018	0.0018
Mass of Benzoic Acid	0.007	---
Evaluation of Q_E	---	0.004
Estimated s.d. of experiment	0.0024%	0.0023%
Observed s.d. of experiment	0.003	0.007

Another indication of the accuracy with which this chemical reference material is known is found in the measurements that have been made over a rather long period of time on highly purified material, listed in Table 2. These date from as early as 1934 and were done at the National Bureau of Standards, at the Free University in Amsterdam, and at the National Physical Laboratory. One observes that the measurements made in the more recent series, which date back to 1968, are in extremely good agreement; the range of values is less than one hundredth percent.

Table 2. Accuracy of the Primary Standard -- Benzoic Acid Comparison of Determinations on NBS-SRM No. 39

	ΔU_c (Standard Conditions) $J \cdot g^{-1}$
Jessup and Green (1934)	26432.0
Jessup (1942)	26433.8
Prosen and Rossini (1944)	26434.7
Coops, Adriaanse and Van Nes (1956)	26435.0
Churney and Armstrong (1968)	26434.4
Gundry, Harrop, Head, and Lewis (1969)	26434.4
Mosselman and Dekker (1969)	26432.7

A pictorial view of some information in table 2 is given in figure 1, which gives the average values from some of the measurements. In the figure THIS WORK refers to the work of Churney and Armstrong (1968). Some measurements, in particular the last two, from table 2 are not shown in figure 1. Also, the work of Challoner, et al, (1955) listed in figure 1, was done on a different benzoic acid sample and is not listed in table 2. The gray areas represent our estimates of the uncertainties in the experiments. There is some ambiguity about our understanding of the real accuracy because the measurements have been subjected to a rather large correction, for possible deviations of thermometer temperatures from average surface temperature. In the work of Challoner, et al, the correction was actually applied, while in our work it was not, but it was estimated. The direction of the arrow shows the direction of the correction. The dashed lines show the average values that were not used. We think there is a potentiality of an uncertainty in this reference material of as much as one hundredth of a percent.

Table 3 is a table of chemically determined energy equivalents for a calorimeter obtained from a typical short series of experiments with benzoic acid. Here one obtains a standard deviation of a few parts in a hundred thousand for the mean, typical for a precise thermochemistry laboratory.

Table 3. Data from Calibrating Experiments with Benzoic Acid

Expt. No.	Mass of benzoic acid, g	Δe_1, j/ohm	ΔRe ohms	qi, j	qn, j	Es, j/ohm	Deviation from mean j/ohm
1	1.51107	18.1	0.292263	36.7	8.8	136796.9	+ 2.5
2	1.51352	18.2	.292770	34.9	9.2	136776.2	-18.2
3	1.51149	18.1	.292366	35.0	8.3	136779.1	-15.3
4	1.51302	18.9	.292601	34.7	9.4	136809.4	+15.0
5	1.49983	18.9	.290099	35.6	9.7	136791.8	- 2.6
6	1.50962	18.8	.291939	34.9	8.1	136808.2	+13.8
7	1.51083	20.7	.292194	35.0	8.8	136799.0	+ 4.6
Mean						136794.4	
Standard deviation of the mean						±4.9	

Another kind of problem is encountered, not in the testing laboratory interested in the heating values of fuels, but in the laboratory that is trying to establish the fundamental thermochemical properties of matter. One encounters problems other than just those of measuring a heat quantity. One encounters a very difficult problem of establishing a chemical process that can be carried out in the calorimeter and that is thoroughly understood, so that the process can be established in terms of a standard thermodynamic state of the material.

Typical combustion problems that one must solve if one is to make thermochemical studies of materials other than carbon, hydrogen, oxygen compounds include difficult combustion, formation of acid products leading to corrosion, and possible inhomogeneity of products. These would be the problems of organic compounds containing fluorine (giving CF_4 or HF in the products), chlorine (leading to Cl_2 and HCl), nitrogen (leading to NO_x and NO_3^-), and phosphorus (leading to ion complexes of PO_3, PO_4, P_2O_7, and P_3O_{10}). Complex processes occur, and these may not occur to the same degree in all compounds.

The next series of reference materials in thermochemistry have been proposed to assist in solving these problems.

Table 4 lists substances that have been proposed over the years for bomb calorimetry many of which were intended to help solve these problems.

Table 4. Thermochemical Reference Materials Proposed for Bomb Calorimetry

2,2,4-trimethylpentane	$C_8H_{18}(\ell)$	volatile hydrocarbon
naphthalene	$C_{10}H_8(c)$	formerly available
benzoic acid	$C_7H_6O_2(c)$	transfer standard
sucrose	$C_{12}H_{22}O_{11}(c)$	formerly available
salicylic acid	$C_7H_6O_3(c)$	
succinic acid	$C_4H_6O_4(c)$	C, H, O-compound
acetanilide	$C_8H_9NO(c)$	
hippuric acid	$C_9H_9NO_3(c)$	
urea	$CH_4N_2O(c)$	N-compound
nicotinic acid	$C_6H_5NO_2(c)$	
THAM*	$C_4H_{11}NO_3(c)$	
thianthrene	$C_{12}H_8S_2(c)$	
thioglycolic acid	$C_2H_4O_2S(\ell)$	
sym-diphenylthiourea	$C_{13}H_{12}N_2S(c)$	S-compound
sulfanilamide	$C_6H_8N_2O_2S(c)$	
benzotrifluoride	$C_7H_5F_3(\ell)$	
p-fluorobenzoic acid	$C_7H_5O_2F(c)$	F-compound
pentafluorobenzoic acid	$C_7HO_2F_5(c)$	
m-trifluoromethylbenzoic acid	$C_8H_5O_2F_3(c)$	
trichlorophenol	$C_6H_3OCl_3(c)$	
m-chlorobenzoic acid	$C_7H_5O_2Cl(c)$	Cl-compound
p-chlorobenzoic acid	$C_7H_5O_2Cl(c)$	
o bromobenzoic acid	$C_7H_5O_2Br(c)$	Br-compound
m-iodobenzoic acid	$C_7H_5O_2I(c)$	I-compound
triphenylphosphine oxide	$C_{18}H_{15}OP(c)$	P-compound

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* tris(hydroxymethyl)aminomethane

The 2,2,4-trimethylpentane is intended to solve the problems of handling volatile hydrocarbons. This provides a way for an operator to test whether he knows how to carry out combustion of a volatile hydrocarbon. It is not perfect in this respect because there are many volatile hydrocarbons of interest to industry that are mixtures. Unfortunately, a pure compound does not test the operator's ability to handle hydrocarbon mixtures in which the composition may change if he happens to be losing some by volatilization.

Naphthalene has been discontinued as a reference material; as has sucrose, though sucrose is certified for other purposes. Beginning with salicylic acid, the rest of the compounds have not been certified for bomb calorimetry, but they have been proposed for the purposes listed.

I should like to mention where these proposals come from. The principal source of suggestions for reference materials has been from the International Union of Pure and Applied Chemistry. For many years the subcommission of Chemical Thermodynamics and Thermochemistry of the Physical Chemistry Division has suggested reference materials and nearly all the early reference materials received their support. In recent years the IUPAC Commission on Physical Chemical Measurements and Standards have had a working group on calibration; and this group has been gathering recommendations for reference materials for combustion calorimetry and other kinds of calorimetry.

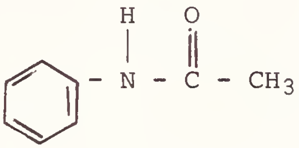
Other contributing groups have been the national calorimetry conferences. The U.S. has a Calorimetry Conference and there have been similar conferences in several other nations. Most of the suggestions aside from the work of the IUPAC however have come from the U.S. Calorimetry Conference.

Table 5 refers to two candidates for a nitrogen compound that we have been proposing to issue as a NBS-SRM. The data shows that urea gives a reproducibility equal to that of benzoic acid even though there is some difficulty in getting ignition because of the nitrogen. Acetanilide is another candidate; this is easily ignited. Apparently the problem of obtaining a nitrogen compound has been solved, and we expect that one will be issued rather soon.

Table 5. Candidates for an N-Containing Reference Material

Acetanilide (C_3H_9NO)

Run No.	$-\Delta H^\circ_c$ (28°C) J/g
437	31222.57
438	31224.99
439	31223.96
440	31225.78
441	31226.67
Mean	31224.79
Sdm	±0.71



Urea (CH_4N_2O)

Run No.	$-\Delta H^\circ_c$ (28°C) J/g
430	10536.44
431	10535.21
432	10535.52
433	10534.90
434	10535.93
435	10536.00
Mean	10535.66
Sdm	0.23

$NH_2 - C(=O) - NH_2$

One of the very important uses of the reference materials, to which we have referred, is to allow comparisons between laboratories. Table 6 illustrates the kind of differences between laboratories that are obtained with some of the reference materials that were listed in Table 4. The values of the enthalpy of combustion are given with the uncertainties of the reported values, and the differences of the values from a value that is not listed here, but which was determined in our laboratory. We observe differences between laboratories--the National Bureau of Standards, the Bureau of Mines Bartlesville Laboratory, the National Physical Laboratory, and others--differences that amount to a few, or sometimes less than one, kJ·mol^{-1} out of numbers that are typically three thousand kJ·mol^{-1}. This is the kind of agreement that can be expected for well characterized materials measured by laboratories in which highly qualified scientists are carrying out the measurements. Among the sulfur compounds there seems to be a significantly poorer internal precision of the measurements, though the differences between laboratories are no greater than for the other substances.

Table 6. Comparative Values[a]

Substance	Reference	$-\Delta H^\circ_c$ (at 25 °C)[b] and uncertainty kJ·mol^{-1}	Difference from this work kJ·mol^{-1}
o-fluorobenzoic acid	Good, Scott, Waddington (1956)	3080.68±1.50	-0.73
p-fluorobenzoic acid	Good, Scott, Waddington (1956)	3061.60±1.21	+1.41 and +2.17
p-fluorobenzoic acid	Cox, Gundry, Head (1964)	3063.23±0.88	-0.22 and +0.54
o-chlorobenzoic acid	Smith, Bjellerup, Krook, Westermark (1953)	3094.07±8.4	-6.27[c]
m-chlorobenzoic acid	Smith, Bjellerup, Krook, Westermark (1953)	3069.38±8.4	-1.09[c]
p-chlorobenzoic acid	Bjellerup, Smith (1954)	3065.62±1.67	-0.99[c]
	Hajiev, Agarunov (1968)	3064.78±3.14	-0.15
	Hu, Sinke, Mansson, Ringner (1972)	3062.98±0.75	1.65
		3062.77±1.05	1.86
		3062.94±0.84	1.69
acetanilide	Wadso (1962); Cox and Pilcher (1970)	209.53±1.38[d]	-0.01
	Wadso (1962); Domalski (1972)	210.45[e]	+0.93
urea	Huffman (1940)	631.78±0.17	-0.03
	Sunner (1946)	633.87±1.68	-2.12
	Mansson and Sunner (1963)	631.36±0.08	+0.39
nicotinic acid	-	-	-
creatinine	Huffman, Ellis, Fox (1936)	2335.97±0.42	-1.44
thianthrene	Hubbard, Katz, Waddington (1954)	7251.50±2.20	+0.41[f]
	Keith and Mackle (1958)	7250.31±2.88	+1.60[f]
thianthrene	Sunner and Lundin (1953); Sunner (1963)	7252.08±1.17	-0.17[f]
	Hu, Yen, Geng (1966)	7252.54±2.18	-0.63[f]

---

[a] Early values, prior to 1936 are of historical interest only.

[b] Values and uncertainties are those given by Cox and Pilcher (1970).

[c] Values for chlorobenzoic acids were adjusted 0.35 kJ·mol^{-1} for the difference between [HCl + 200 H_2O] (ℓ) and [HCl + 600 H_2O] (ℓ).

[d] Enthalpy of formation computed by Cox and Pilcher from Wadsö reaction energy.

[e] Enthalpy of formation computed by Domalski from Wadsö reaction energy.

[f] Values for thianthrene were adjusted 0.18 kJ·mol^{-1} for the difference between [H_2SO_4 + 100 H_2O] (ℓ) [H_2SO_4 + 115 H_2O] (ℓ).

Rather than leave you with the impression that there is only one class of processes that is of interest in calorimetry, I shall mention that in the field of solution calorimetry a strong need exists for reference materials. In mineralogy and mineralogical chemistry where one has to dissolve minerals, usually in hydrofluoric acid, to determine their thermochemistry, there exists a problem of comparability of laboratories and also of establishing the accuracy of the calorimeter.

Crystalline alpha-quartz, which undergoes the reaction shown below, is available from NBS as an SRM.

$$SiO_2(c, \alpha\text{-quartz}) + 6\ HF(aq, 24.4\%) = H_2SiF_6(aq, 24.4\%\ HF)$$

$$+ 2\ H_2O(\ell)\ \Delta H^\circ(\text{at } 358.18\ K) = -2362.2\ J\cdot g^{-1}$$

Standard deviation of the mean, 0.2

Uncertainty (estimated), 1.1

Table 7 shows comparative values obtained in several different laboratories for the enthalpy of solution of α-quartz, referring to the above process. The values were not, however, determined on material from the same source. The differences listed in the right hand column are differences from work done by Kilday and Prosen--the last value listed. You will note that uncertainties in this process as indicated by the differences between laboratories are of the order of a few tenths percent--substantially larger than those for the bomb calorimetry. The measurements are done in a quite different kind of calorimeter.

Table 7. Comparison of Some Values Reported for the Enthalpy of Solution of α-quartz in HF (aq)

Investigator and Year	ΔH(80 °C) in 24.4% HF kJ mol^{-1}	Difference from this work kJ mol^{-1}
Roth and Troitzsch (1932)	140.66	-1.28
Troitzsch (1936)	142.80	+0.86
Torgeson and Sahama (1948) (Bur. Mines)	141.17	-0.77
King (1951) (Bur. Mines)	142.38 141.58	+0.44 -0.36
Kracek, et al (1951) (Geophys. Lab., Carnegie Inst.)	142.38 141.68	+0.44 -0.26
King (1952) (Bur. Mines)	142.16	+0.22
Jeffes, et al (1954)	142.79	+0.85
Stevens and Turkdogan (1955)	141.24	-0.70
Waldbaum and Hovis (1970) (Harvard Univ.)	142.23	+0.28
Kilday and Prosen (1973) (NBS)	141.94	---

Another NBS-SRM also used for solution calorimetry is tris(hydroxymethyl)aminomethane. It is used in the processes listed below.

	ΔH(at 298.15 K) $J \cdot g^{-1}$
$(CH_2OH)_3CNH_2(c)$ + 1.21 NaOH(aq, 0.05 N)	141.70 ± 0.19
$(CH_2OH)_3CNH_2(c)$ + 2.42 HCl(aq, 0.10N)	-245.76 ± 0.26

I shall give only a very brief mention of the fact that there are similar problems with non-reacting systems. Sapphire (α-Al_2O_3) is available as a heat capacity SRM, certified for temperatures up to 2250 K. Sapphire is well understood and provides a suitable reference material for refractory oxides up to this temperature. However, for refractory metals in the upper temperature range the situation is very poor. Figure 2 shows comparative measurements of the heat capacity of tungsten. We see here, in the determination of enthalpies or heat capacities in the range from 1000 to 3500 K, a rather strong need for an SRM. It is not clear to what extent the differences observed between laboratories are due to differences in the material that was studied and the measurement apparatus that was used. Molybdenum shows similar differences.

I am afraid this has not been a well-balanced presentation concerning reference materials for calorimetry. I am very much interested in the subject myself and this has undoubtedly biased my presentation, but possibly the subject may come up in the discussion and we may get a better balanced picture.

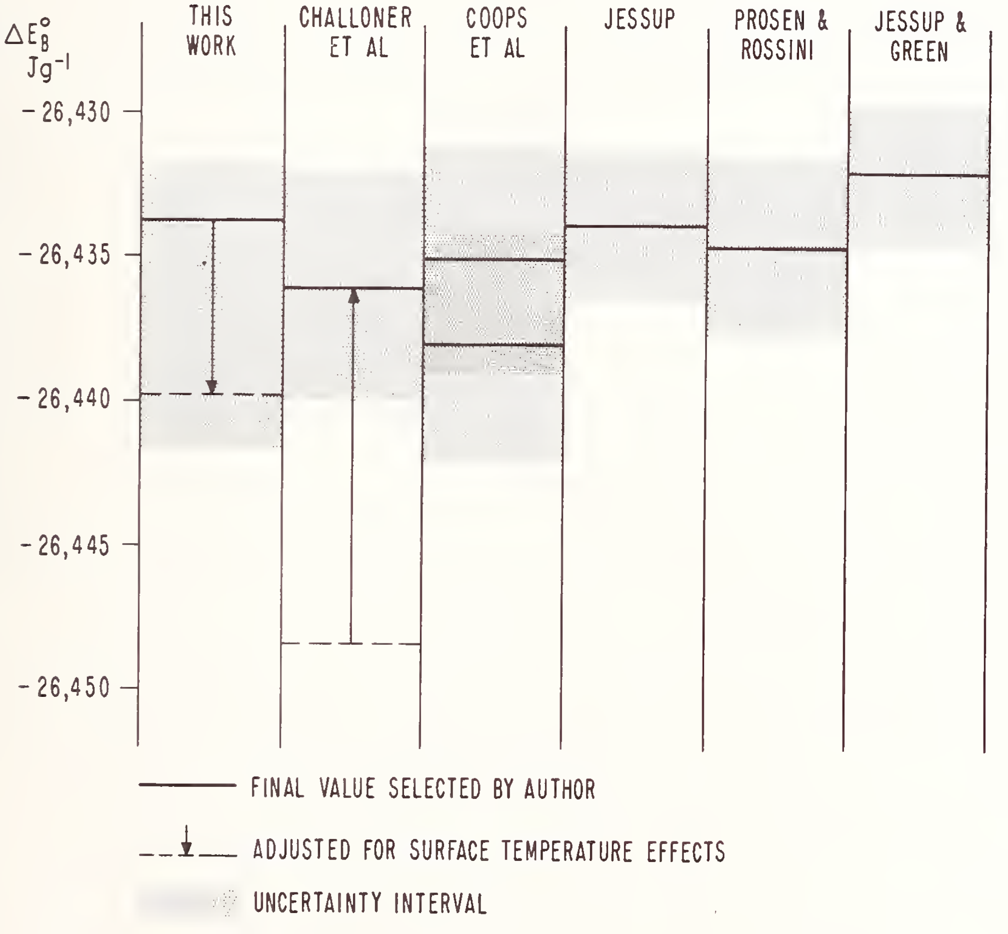


Figure 1. Mean values and uncertainty bands for several determinations of the energy of combustion of benzoic acid

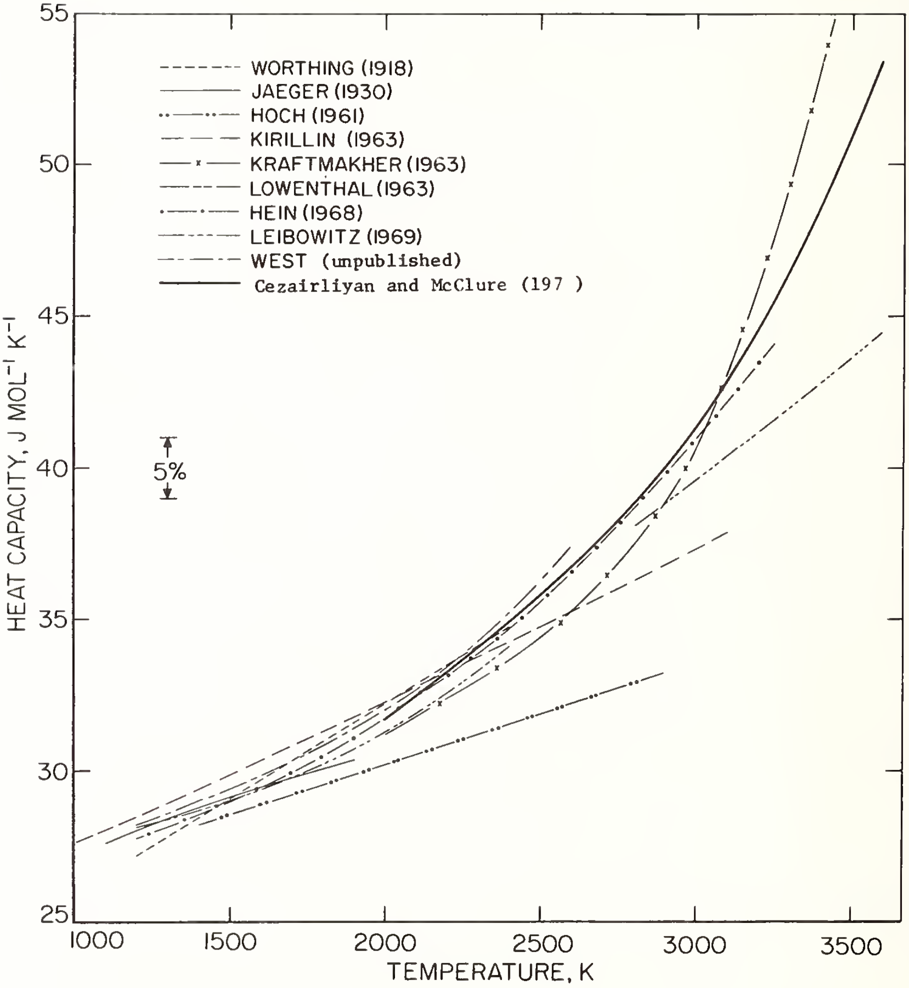


Figure 2. Molar heat capacity of tungsten, 1000 to 3500 K, comparative measurements

III. Temperature

R. B. Foster

The important aspects of precision temperature standards and of the International Practical Temperature Scale of 1968 (IPTS-68) were discussed by Robert Powell during the Thursday afternoon plenary session. It was pointed out that temperature was one of the fundamental measurement areas and that practical temperature measurements are dependent on SRM's. The following describes how a large industrial laboratory uses SRM's in temperature measurements.

The Primary Standards Laboratory (PSL) at Sandia Laboratories supplies standards for at least 14 integrated contractors of the Atomic Energy Commission. The standards laboratories at the various integrated contractors supply standards to their own plants and to the various suppliers and contractors who supply materials and services to the integrated contractor. Standards for PSL are calibrated by NBS. Thus there may be several steps or transfers between NBS and the ultimate user.

Consider how these transfers might take place with precision platinum resistance thermometers (PRT) if SRM's did not exist. NBS would probably have a bank of reference standard PRT's that would be laboriously compared to a gas thermometer once every five to ten years. Then a bank of working standard PRT's would be compared to the reference standard PRT's every year. A bank of PRT's from PSL would be periodically sent to NBS and PRT's from the integrated contractors would then be compared to the PSL standards. With the degradation of accuracy at each step the end point accuracy would be well below the capability of the PRT.

SRM's are available for the defining fixed points for the PRT region of IPTS-68; hence, with proper techniques, the maximum accuracies are available at any level. PSL uses the freezing points of zinc and tin to calibrate between 10 to 30 PRT's per year. Zinc and tin are SRM's. Figure 1 shows the actual freezing of a tin cell. Since high-purity tin super cools significantly, the cell is removed from the furnace to initiate the freeze. There is ample information in the literature for construction of freezing point cells and furnaces; however, cells and furnaces are commercially available for most of the metal freezing points.

NBS uses the freezing points of gold and silver and the temperature of the freezing point of antimony to calibrate platinum-10% rhodium vs platinum thermocouples. SRM's are not currently available for these points; but, the SRM's copper and aluminum are available and their freezing points can be used to calibrate platinum-10% rhodium vs platinum thermocouples. PSL calibrates platinum-10% rhodium vs platinum thermocouples by comparison with an NBS calibrated thermocouple. The thermocouples being compared are welded together at the working junction then cycled through temperatures up to 1100 °C. This method has been satisfactory for present accuracy requirements.

A primary calibration of an optical pyrometer is based on the freezing point of gold. Gold is not available as an SRM, but copper with a freezing temperature only 20 °C above the gold point is available as an SRM. In 1969, R. D. Lee at NBS designed a simple copper freezing point blackbody for checking optical pyrometers. The accuracy of the copper point is satisfactory for the calibration of most optical pyrometers. PSL used a bank of NBS-calibrated vacuum ribbon filament lamps for reference standards. Copper freezing point is used to check the bank of lamps for drift. Originally a commercial version of the Lee copper point blackbody was used, but it failed after a few freezes.

A copper freezing point blackbody was developed at PSL for use in the graphite tube furnace shown in figure 2. The furnace tube has a 20 mm inside diameter and is wrapped with graphite wool and enclosed in an argon purged quartz tube. A boron nitride sleeve with a graphite crucible for the copper is placed inside the furnace tube. In figure 2, the furnace is operating at about 2000 °C and is being used in an interferometry experiment.

It is often desirable to use SRM's at the working level as well as in the standards laboratory. SRM's can frequently be used to make an in-place check of a temperature calibration. For example, a sample of tin, zinc, or lead may be placed in thermal contact with a thermocouple that is measuring the temperature of a furnace. As the temperature of the furnace passes a freezing or melting point a short plateau can be observed on a recording instrument. A similar procedure, which is frequently used, is to wrap a wire or foil made from an SRM around a thermocouple junction. When the melting temperature of the SRM is reached, a plateau occurs in the temperature as the material melts and falls off. This is obviously a one shot check. In some cases, the thermocouple leads are jointed with a short SRM wire. The thermocouple then opens when the wire melts.

At much higher temperatures, SRM's are used to make in-place calibrations of films and various types of radiation pyrometers. In events such as explosive testing, pulse heating, or reentry burning, SRM samples can be included. On film the track of a moving object will get dim then suddenly brighten as the SRM super-cools then returns to its melting temperature. Likewise, the indication of a radiation pyrometer would decrease then suddenly rise while viewing such an event. The peak after the sudden rise would be the calibration point.

This has been a very brief review of the use of SRM's in temperature measurements in one laboratory. SRM's are used in the primary calibration of the most precise standards, and SRM's are used at the working level in testing, research, and development.

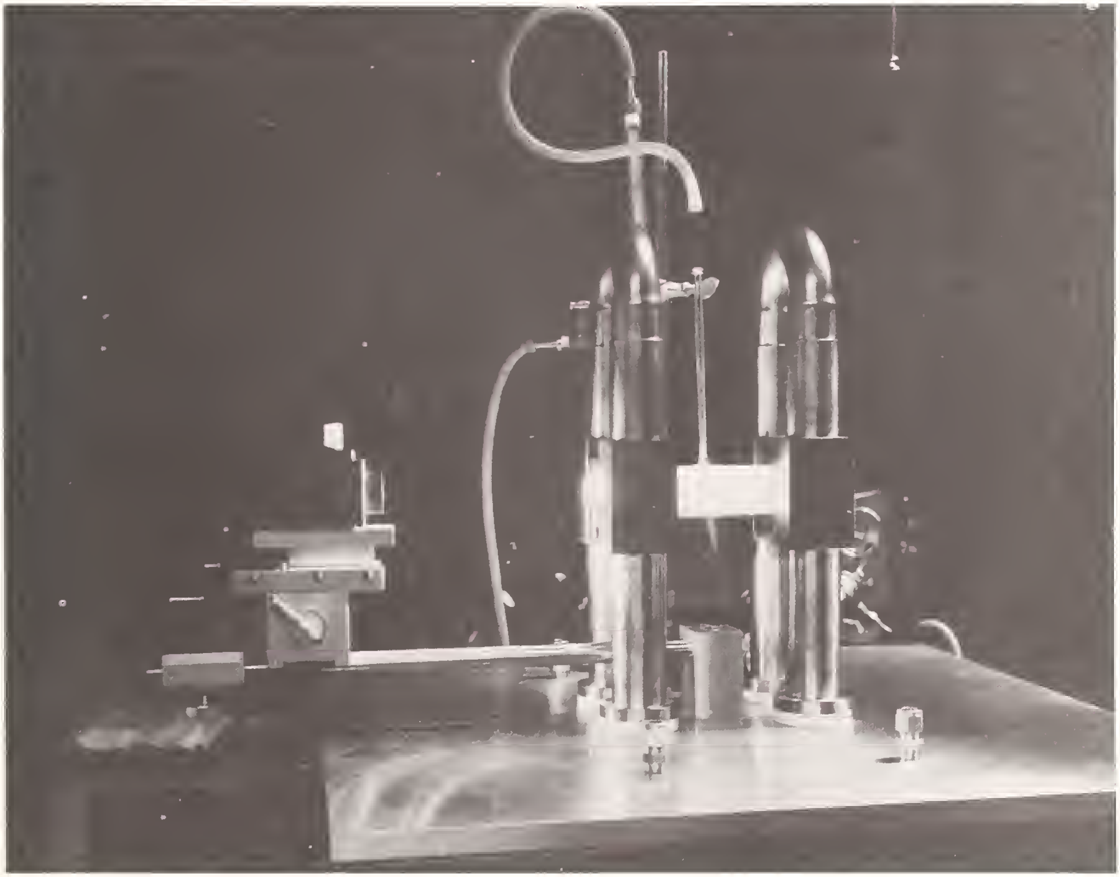


Figure 1. Tin and zinc freezing point SRM's are used in the calibration of PRT's, shown here is the actual freezing of a tin cell

Figure 2. An argon purged quartz tube holds a graphite tube furnace being used in an interferometry experiment

IV. Optical Standards

W. H. Venable

The remarks presented here represent an informal introduction to the optical standard reference materials and it should be understood that it is not intended to be technically explicit in many respects.

First let us list the optical SRM's arranged in order. These SRM's are listed in the Standard Reference Materials 1973 Catalog (NBS Special Publication 260), pages 65-67.

SRM	Type (Name)	Optical Property Certified
217b	2,2,4-trimethylpentane (4 samples of varying volumes)	Index of Refraction
930a 931	Glass and liquid filters for UV and visible spectrophotometry	Absorbance and transmittance over a range from 440 to 635 mm
1402-9	Emittance standard (22 standards of varying materials, shapes, and sizes)	Normal spectral emittance at 136 wavelengths in the 1 to 15 micrometer region
1420-8		
1440-5		
2001-8	Aluminum on glass and gold and gold on glass	Specular spectral reflectance
2101-5	Color standards for spectrophotometer-tristimulus integrator systems	A chart of tristimulus values

The first SRM, 2,2,4-trimethylpentane, is certified not only for refractive index, but also for density and heat of combustion. This SRM comes in a breakable ampoule. It allows the user to empty the material into an instrument, presumably refractometer, with which index of refraction is a sensitive parameter, and establish whether the index of refraction indicated by the instrument is correct.

The measurement and certification of optical reference materials is carried out in the Optical Radiation Section in the NBS Heat Division. The work of this section includes spectrophotometry, which is the measurement of transmittance of light flux passing through a medium by taking account of absorption, reflection, or refraction. The Optical Radiation Section deals with the measurement of optical radiation quantitatively by radiometry and photometry.

One of the chief interests of the radiometric work is its application to determination of temperature, at very high temperatures, through radiation. To do this, of course, one needs to know thermal emittance of surfaces. The thermal emittance SRM's thus have a natural connection here.

The thermal emittance SRM's have three different surfaces which are calibrated, that is measured for their thermal emittances at various temperatures. These can be used in a number of ways. If one is interested in calibrating an instrument that measures thermal emittance, this SRM can be placed in the instrument to see if the measurement is indeed what would be expected, based on the known behavior of the instrument. Except for very narrow bands of thermal emittance, one needs to know a great deal more about the instrument to make use of such an SRM, but at least it is available and is characterized as a function of wavelength.

Closely related to emittance is specular reflectance. These SRM's are numbered from 2001 to 2008. There are two different surfaces of these, gold and aluminum. They are mounted on various sizes and shapes of backings to give the larger number of SRM's. These are valuable in calibrating certain types of instruments for measuring reflectance. These SRM's have smooth surfaces.

They are to calibrate instruments that are being used to measure the reflectance of smooth surfaces. Using mirror-like surfaces one avoids problems of uncertainty in the solid angle that is intercepted by using a very narrow beam of very small solid angle and a large opening, large enough to include the whole beam.

So there is a distinction in the use of the emittance and the reflectance SRM's although they are closely related. The emittance SRM deals with penetration of radiation through the surface; the reflectance SRM, with reflection from the surface. Since they are related, one can cover the same types of measurements with both types of SRM's; but there are advantages in given cases of one over the other.

Finally we have the spectrophotometric SRM's. There is a set of three neutral glass filters (930a); a set of liquid, absorbance standards (931a); a set of five colored-glass filters (2101-2105).

This completes the list of SRM's in the catalog. In addition, there are a number of others under consideration. These include: fluorescent standards of some sort, perhaps; diffuse reflectance standards, almost certainly; and others in different wavelength frames, infra red, near infra red, visible, and ultraviolet. We could go on speculating about others. There are also possibilities for SRM's for calibrating appearance factors such as gloss, haze, and other similar physical properties.

This brings us to the main point I want to bring up. There are strong points and weak points to the certification of SRM's. A strong point is the measurement and documentation of the values assigned to the properties certified. But the thing that is not very well documented is "What is it good for?" "What do you do with it?" There is a very great difficulty here.

Consider the spectrophotometric standards. These were calibrated, according to the document, for spectrophotometric tristimulus integrator systems, devices for measuring color. When these were devised in the 1960's analog computation was in its "heyday." The colorimeters that were used then, the most advanced models, used a spectrophotometer with an analog calculator to integrate the spectrophotometer output. One would, for example, measure reflectance as a function of the wavelength; in the electrical analog calculator this would be folded into an imaginary function for a light source in the calorimeter; and out would come a value for the color. The SRM's 2101-2105 were designed to check the performance of these rather complicated devices. But the point is that these were designed for instruments that have gone out of style long ago. There is still a need for something like this to be used for current instruments that use digital techniques or spectrally selective detectors in their calculations, but these standards are not being used to their full potential value today.

The information that is given for SRM's 2101-2105 is simply the color; no information about transmittance at any given wavelength. As a result they can provide only a check and one must go back to other transmittance standards, such as the neutral filters or a color filter, for which spectral transmittance is supplied. Thus, one aspect of the documentation is that, if it is prepared with specific information for use with certain technology, it may be limited to just one technology. And when that technology changes, unless the documentation is correspondingly changed, the SRM's lose utility.

Another difficult aspect of the SRM's is the limited amount of information about the instrument performance that one gets by relying an a single device to calibrate an instrument that has a large number of possible sources of error. The chances are very small that this procedure will calibrate the instrument very well.

As an example of the latter problem, we may refer to SRM 930a. These are three filters of transmittance at intervals of 10 percent, with nominal values of 0.1, 0.2, and 0.3. In the initial concept of this measurement these were measured to four places. That is, precise values like 0.1987 were given, with the last figure indicating the significance. This has been relaxed to some extent. The original figure was one part in 10,000 but this has been reduced to 5 parts in 10,000; but this is somewhat immaterial compared to the intended use of the filters. They are "to check the accuracy of the photometric scale of spectrophotometers and to provide a means of interlaboratory comparison of spectrophotometric data."

In a typical spectrophotometer one has two beams of light striking a single detector. Now having adjusted the instrument to give equal responses to the two "open" beams, one inserts the standard and one beam is attenuated. Less light gets through. One compares the two beams by alternatively, using a chopping system, allowing light to come from one beam and the other. Voila, the instrument is adjusted to read exactly 0.1987, and is calibrated. Now take the standard reference material out and insert two cuvettes, one in each beam, and the instrument works again, but is it free of error?

What may be happening is that during the calibration radiation reflected from the standard filter strikes the detector by another path. Then in the actual measurement in which cuvettes are used, different samples are there and no way exists to put the original reflections back in. In addition, the cuvettes introduce other surface reflections, so that the transmittance of the cuvettes is an unknown quantity, depending for example on the exact refractivity of the material the walls are made of, and the materials within it. Thus, one has not learned a lot by using this SRM.

SRM 930 is stable, one can put it in an instrument daily. If one observes a departure from the value one has been observing day after day, one can call for a repairman. For that, however, one does not need four figures. It is simply necessary to say that it transmits nominally 20%, and that it is stable. The point is that the SRM alone will not carry the entire burden of eliminating systematic errors.

There are at NBS two spectrophotometric groups. One of them is connected very closely with SRM's, and produces the neutral filters and solutions. These are necessary, but not sufficient for accurate measurement. There is another spectrophotometry group that seeks to prevent instrument problems. Working with the instrument designers, this group provides much more specialized reference materials to help see that instruments are designed and built without inherent sources of error. This approach is called Measurements Assurance Program, which has an acronym MAP. MAP must work hand in hand with SRM's if the measurement system is to be made stable.

Finally, a real problem that has to be dealt with is the much more elusive explanation of what the various materials should be used for and how to use them. There the present instructions are very weak. The strong point in the NBS programs has been providing good materials, well characterized and accurately measured. We are very much interested in seeing instructions on how to use these materials accompany them. This idea may be a starting point for some discussion.

V. Magnetic Susceptibility Standards

R. E. Mundy and G. A. Candela

Most methods used for determining magnetic susceptibility are relative measurements; therefore, the calibration of the apparatus depends upon a sample of known susceptibility. Laboratories that measure magnetic susceptibilities have a definite need for reliable and accurate standards. However, until recently there has been no adequate standard calibrant for magnetic susceptibility measurements. The NBS Office of Standard Reference Materials recently made available four SRM's to calibrate instruments used to measure magnetic susceptibility. These SRM's are aluminum, platinum, palladium, and manganese fluoride. The magnetic gram susceptibility of these materials has been determined at room temperatures (295-299 K), and aluminum has also been measured at liquid nitrogen temperature (77.7 K).

An apparatus was constructed at NBS to measure the absolute susceptibility by the Gouy method. [1] The expression, $f = (k/2\mu_\circ) \text{ grad } B^2$, relates the quantities force-per-unit volume (f) and the field (B) to the field independent isotropic magnetic susceptibility (k). The component of force in a given x direction on a piece of homogeneous matter of volume V is then given by:

$$F_x = \frac{(k - k_M)}{2\ \mu_\circ} \int_V \frac{\partial B^2}{\partial x}\, dV,$$

where k_M is the susceptibility of the surrounding medium, and $\mu_\circ$ is the permeability of free space.

In the Gouy method, a cylinder of matter with constant cross sectional area (a) and uniform density is oriented with its axis in the x direction. The force in the x direction is given by:

$$F_x = \frac{a(k - k_M)}{2\mu_\circ} \int_{x_0}^{x_1} \frac{\partial B^2}{\partial x}\, dx = \frac{a(k - k_M)}{2\mu_\circ} (B_1^2 - B_0^2),$$

where B_1 and B_0 are the fields at x_1 and x_0, respectively. When $k >> k_M$, the gram susceptibility is then equal to:

$$\chi_g = \frac{2\ F_x\ \mu_\circ}{(M_s/\ell)\ (B_1^2 - B_0^2)},$$

where ℓ is the length of the cylindrical sample and M_s is the mass of the sample.

Figure 1 shows a photograph of the apparatus used to make the measurements. The balance and sample are enclosed so the atmosphere may be controlled. Dry nitrogen gas at atmospheric pressure was used for these measurements. The balance used to weigh the samples and to determine the force is a semimicro balance with a sensitivity of ± 0.02 mg. B_1 was measured by a proton resonance magnetometer and B_0 was measured by a calibrated Hall effect flux density meter. The magnetic fields used were $1000 \leq B_1 \leq 7500$ gauss and in all experiments $B_0^2 < 0.005\ B_1^2$. The sample lengths were measured by direct comparison to gage blocks. The temperature was measured by a calibrated copper constantan thermocouple.

The materials for these SRM's were of the highest purity obtainable. Each SRM was thoroughly cleaned and etched. The etchants used were the following:

SRM	Etchant	
Al	HF/H_2O	1:1
MnF_2	HF/H_2O	1:10
Pd and Pt	HCl/HNO_3	3:1, hot

Finally, the materials were thoroughly rinsed with distilled H_2O.

The following gram susceptibilities were obtained as a function of temperature.

Temperature K	Al	Pt $10^6\ \chi_g$, $cm^3\ g^{-1}$	Pd	MnF_2
77.7	.696	--	--	--
295	.605	.993	5.28	124.0
296	--	.992	5.27	123.7
297	.604	.991	5.26	123.3
298	--	.991	5.25	123.0
299	.603	.990	5.24	122.6

The magnetic susceptibility values are estimated to have an uncertainty less than ± 0.5 percent.

Although only the gram susceptibilities are certified, the volume susceptibilities at 297 k are given below as an aid in the selection of the appropriate SRM.

SRM	Type	Volume Susceptibility 10^6 k
763	Aluminum	1.63[a]
764	Platinum	21.2
765	Palladium	63.1
766	Manganese Fluoride	484

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[a] 1.87 at 77.7 K

The following SRM forms are available.

SRM No.	Type	Form	Size
763-1	Aluminum	Cylinder	3 mm dia. x 3 mm long
763-2		Wire	0.5 mm dia. x 250 mm long
763-3		Rod	6 mm dia. x 175 mm long
764-1	Platinum	Cylinder	3 mm dia. x 3 mm long
764-2		Wire	0.5 mm dia. x 50 mm long
765-1	Palladium	Cylinder	3 mm dia. x 3 mm long
765-2		Wire	0.5 mm dia. x 50 mm long
765-3		Sponge	one gram
766-1	Manganese Fluoride	Cube	3 mm sides

It is encouraging to note for an international conference that approximately one-half of the samples sold to date have been to foreign countries.

We wish to thank Mr. W. J. McKean of the Solid State Materials Section for the length measurements and the formation of several samples.

Reference

[1] Candela, G. A. and Mundy, R. E., IRE Transactions on Instrumentation, Vol. I-11, Nos. 3 and 4, December 1962.

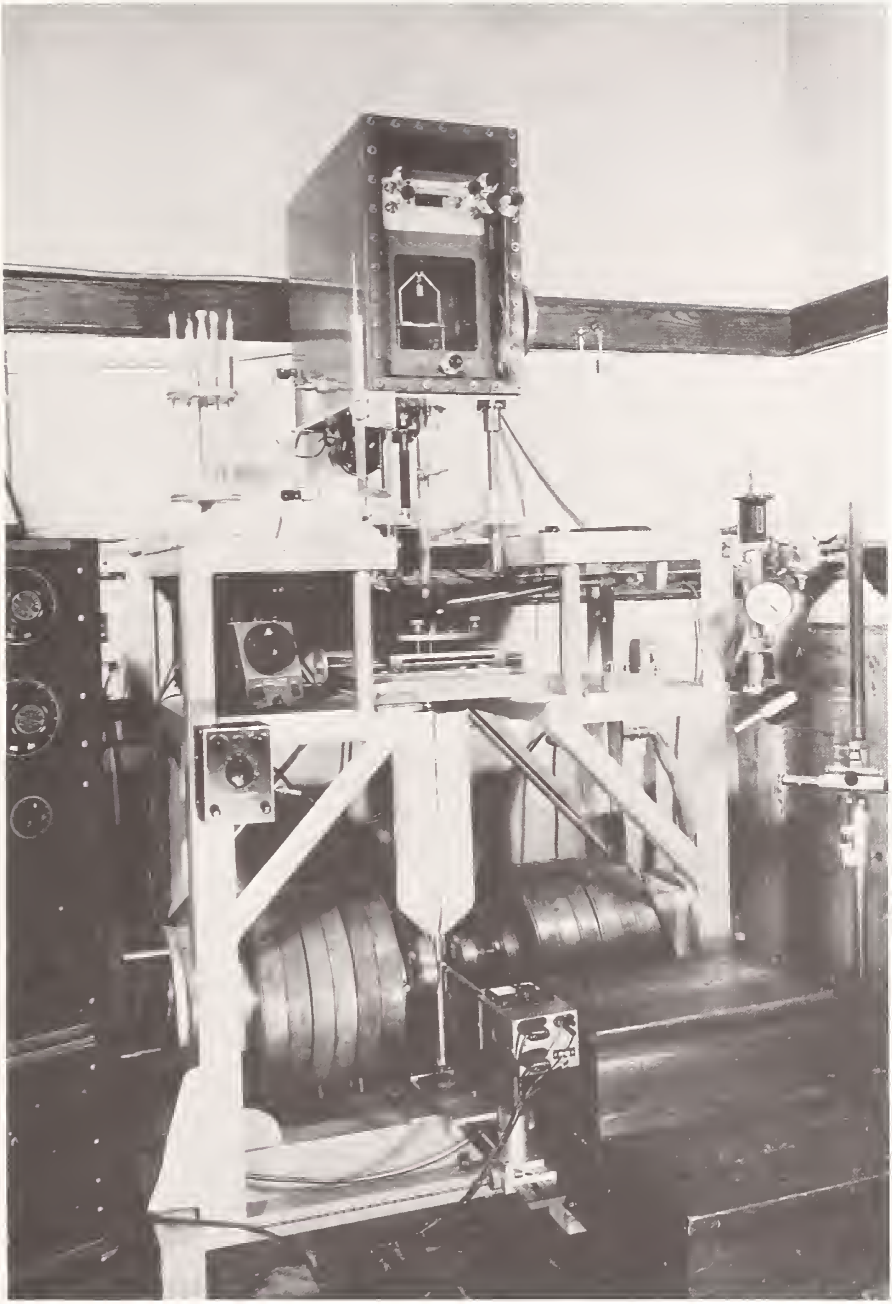

Figure 1. Apparatus constructed at NBS to measure absolute susceptibility by the Gouy method

VI. Standard Reference Materials in the Dissemination of The Measurement Units

L. Crovini

I should like to get this symposium away from the idea accepted in some places that SRM's are independent of the system of units. I should like to focus attention on the problem of the dissemination of units, and I shall make direct reference to those familiar to me, that refer to the temperature scale.

Let me refer first to the general case of a hierarchy of calibration chains. Refer to figure 1 please. In the first step we have a primary laboratory, which is generally unique in a country, which realizes the units making the primary standards, and which communicates with a system of secondary laboratories through some sort of parastructure. These secondary laboratories are maintained at an industrial level. They keep substandards, which they compare with the primary standard, a transfer standard. By referring to it, they make calibrations for a number of field laboratories that deal with the quantity in some process, in production, or some other application.

This chain may be split into more levels. In general, the accuracy that one achieves for the primary standards, as well as for those needed at the field level, is a function of the time available for the calibration at each step. As the needs for calibrations increase in number, this kind of chain tends to split into more levels just to take care of them. Increasing accuracy at the field level demands increased accuracy at the first level, and this, of course, results in an increased cost of the realization of standards, and increasing complexity of calibration procedure.

Let me refer specifically to the case of the high temperature scale. In an earlier talk we heard about the realization of this scale, which is generally made through some kind of optical pyrometer. In the best formulations, this is quite a complicated instrument, which can define the temperature of a black body and can disseminate this scale through the calibration of a reference lamp. Pyrometric lamps are then used to calibrate the whole series of optical pyrometers and this process involves a well known propagation of errors due to lamp instability, incorrect alignments, and colorimetry. High temperature thermocouples are required for precise measurements in places that cannot be reached through an optical path. In this case, a fourth calibration step is generally introduced. That is, a calibrated optical pyrometer will calibrate a thermocouple.

In figure 2 we see the range of the optical pyrometer that is used to measure temperature at the gold point and above. Also shown is the usual range in which high temperature thermocouples are used. The figure illustrates that over this entire range there is a fairly wide spectrum of fixed points available. Pure stable compounds when used as SRM's can help greatly in this situation. SRM's could be obtained for each fixed point by extracting samples from a homogeneous lot of a high-purity substance and certifying them through a round robin among several primary laboratories, possibly using different methods.

By using this kind of SRM's the dissemination of the temperature scale would be improved in several ways. There is a sufficiently broad spectrum of fixed points to calibrate practical optical pyrometers of any range. There would be more laboratory independence of the effective wavelength of the pyrometer than there is when one is using the lamp. This is because in some instances we are using optical pyrometers in the visible, in some other instances we are using optical pyrometers in the infrared. SRM's can help by providing effective independence of wavelength, rather than calibrating the wavelength dependence.

Interlaboratory cooperation should give a better accuracy at the reference temperatures and fewer instability problems with respect to the lamps. Also, usual pyrometers, like those used in most techniques of experiments, could be conveniently calibrated by replacing the ordinary specimen with an SRM of convenient shape. Some pyrometers, which are used directly in some special environment, or have some special requirement as to test procedure, or data acquisition, or other feature, are not easily transferred from the experiment location to the bench where they are to be used against the calibrator. In that case, by substituting the target with a specimen that is used as an SRM we have a direct calibration of this instrument; and we correct for many systematic errors that stem from the transfer of the apparatus from the place where it is employed to the calibration bench.

Thermocouples may also be calibrated against SRM's. Either by use of the crucible method or by calibration against an optical pyrometer, they have several advantages in some instances. Let me refer to thermocouples that are used in special environments like vacuum furnaces or argon furnaces. The coupling of the optical pyrometer to the thermocouple is sometimes very difficult. There is always a window in between, and the transmittance of the window can cause a systematic error. In this case, it is possible to place, from time to time, the thermocouple under measurement in an SRM that melts, and produces a reference temperature. All the systematic errors would be eliminated at once.

While it is clear that SRM's provide in general an alternate solution to the unit dissemination problem, there will be some definite advantages--a somewhat improved accuracy and a reduction of time spent on calibration in the primary laboratory. This is now quite an important point because a calibration burden sometimes prevents a primary laboratory from reaching better accuracy in this work. I believe that the use of SRM's would reduce the burden in the primary laboratory, and give more freedom for improving the accuracy of the primary standard. This pays for the drawback of the slightly increased complexity of equipment and methods in the secondary laboratories.

Let us return to the calibration chain; it changes a little bit. Starting with the primary laboratory, we find now an acute need for a supplier who will supply the laboratory with the substances. Once the substance has been characterized and certified by the primary laboratory, there must be some distribution body, which will distribute the SRM's to the secondary laboratories and maybe also to field laboratories.

A number of national laboratories actually operate as the secondary laboratories for some primary standards whose absolute realization requires a large and very expensive installation. In most countries (and I do not mean to imply these are necessarily the less developed), the total amount of calibration and its relevance to the national economy sometimes does not pay for the cost of their primary standards. Hence they prefer to maintain adequate substandards and rely on other national laboratories for their primary calibration.

In the field of temperature measurement, the extension of the International Practical Temperature Scale below 13.81 K or its improvement at high temperatures will require considerable time for the realization and the adoption of the expensive equipment. During the last meeting of the Comite Consultative de Thermometrie, July 1971, it was considered that it might be convenient to have a secondary-level standard of calibration. Consequently, a working group was entrusted with the task of evaluating the possibility of intermeasurement.

SRM's should have a vital role in this case. For instance, in the event of a replacement in the IPTS of the standard thermocouple by the platinum resistance scale and the radiation scale, it could be practical to maintain a secondary level standard of calibration based on selected platinum--platinim-rhodium wires. This standard should range approximately from 600 to 1500 °C. The wires could be distributed to secondary laboratories and eventually to field laboratories directly. And for the best accuracy, the differences between the individual thermocouples and the reference table could be detected and accounted for by calibration at fixed points using reference materials.

So we see, in the temperature case, we have three alternate ways. The first is the conventional one using a strip lamp. SRM fixed points can provide another path that could be very close in accuracy to the first one, and sometimes even better. And we might also have another way, which would be at the secondary standards laboratory. These laboratories would supply standard thermocouple wires as SRM's, some reference tables, and some fixed points to characterize each individual wire especially where more accuracy is required. One thing should be clear. A secondary level of standards calibration never results in a duplication of effort if accuracy is to be evaluated in a specified hierarchy in such a way as to include any possible differences between the primary standards and the secondary standards.

This idea and this philosophy that I have expounded is extendable to all the units, other than temperatures. For instance pressure may be one of them. High pressure has very similar problems to high temperature and may find very similar solutions through the use of SRM's.

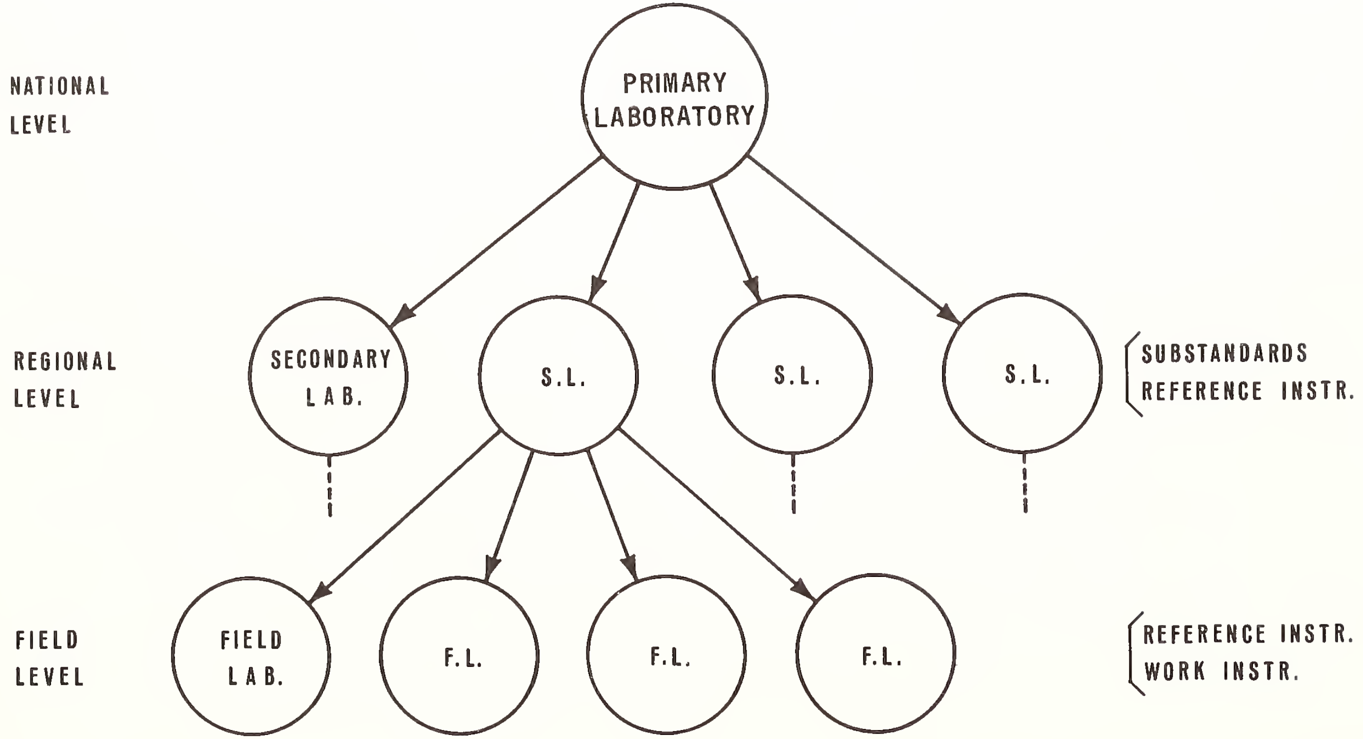

Figure 1. Calibration Chain

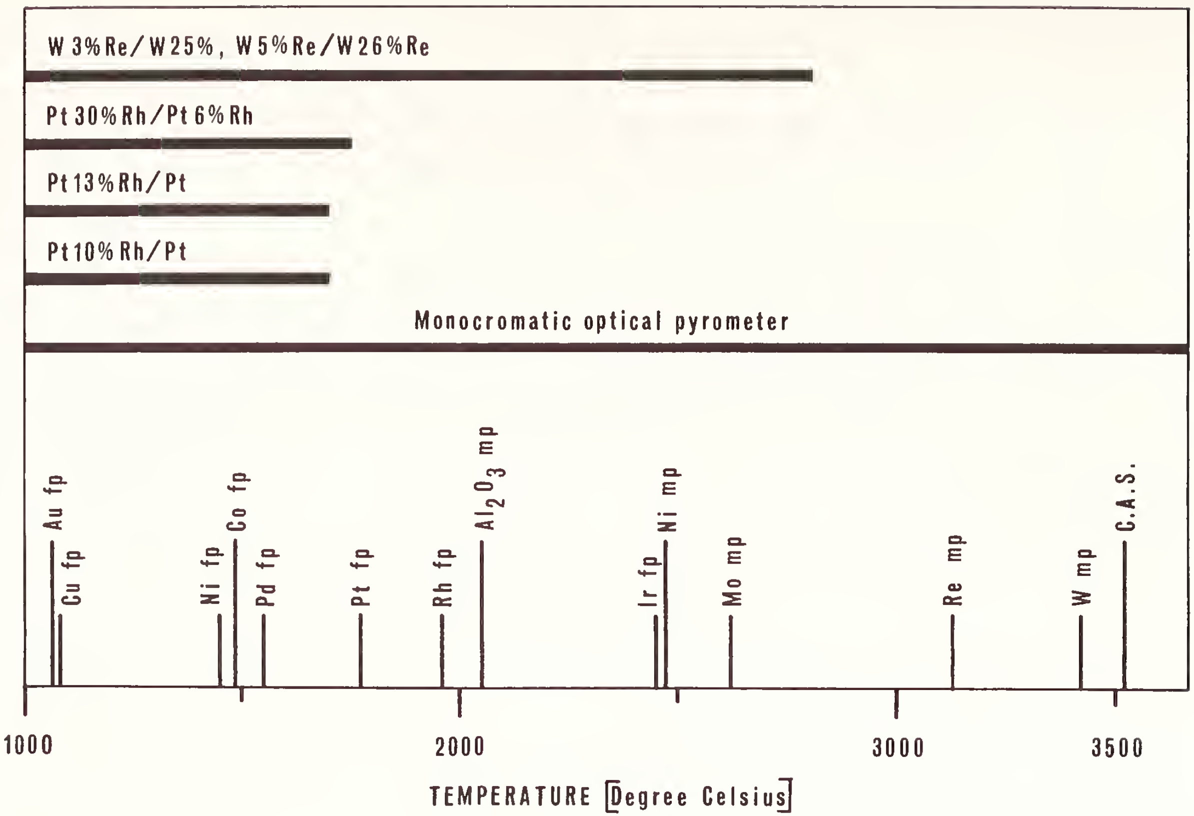

Figure 2. Available Fixed Points at High Temperature

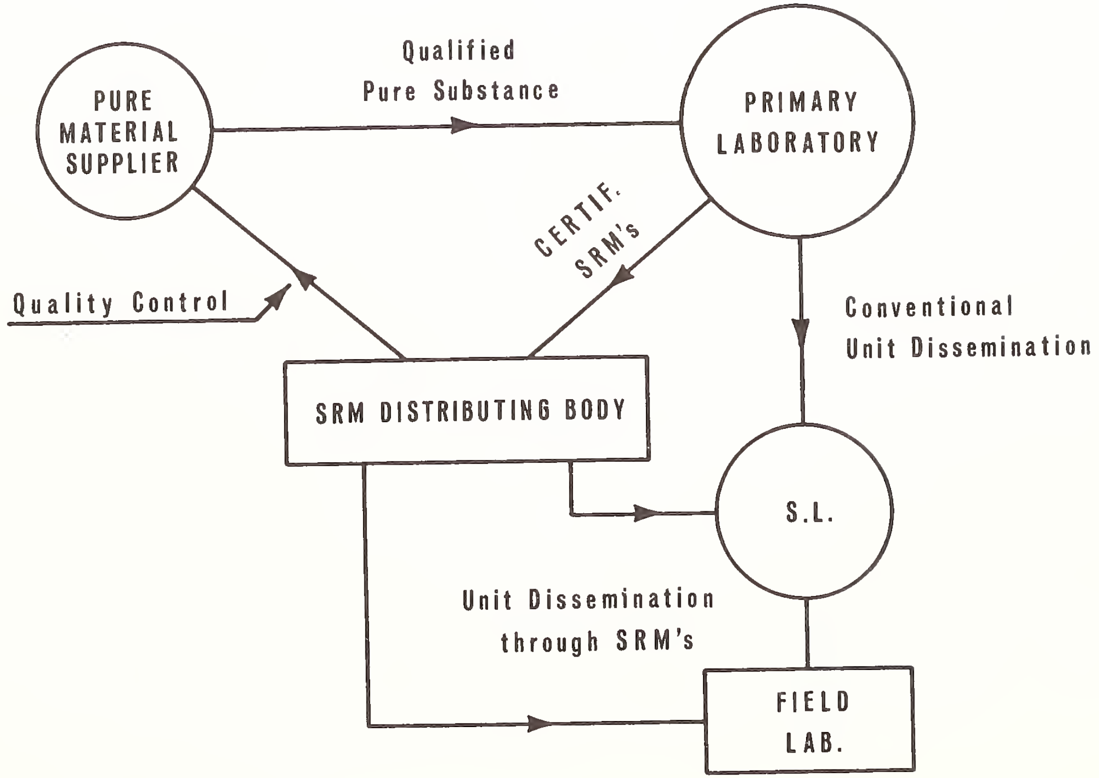

Figure 3. Calibration Chain with SRM's

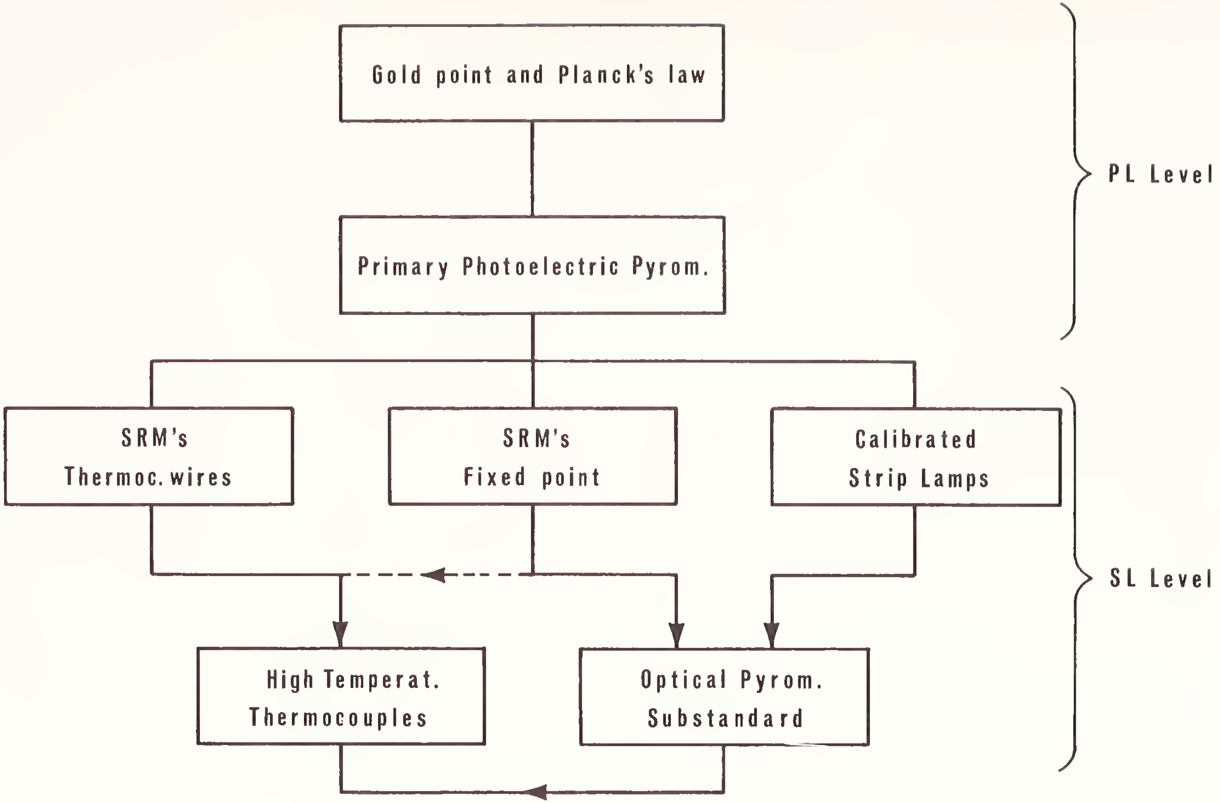

Figure 4. Dissemination Scheme of IPTS above the Gold Point

VII. Resume of Informal General Discussion

The early discussion centered around the need for reference materials at high temperatures.

A discussant (Dr. White) made the point that, whereas we have well developed SRM's at low temperatures, the real need in several fields--heat conduction, thermometry, pyrometry, electrical conductivity, specific heat--is at high temperatures. Fundamentally we do not know very well what is happening in the materials at high temperatures; and unfortunately pronounced variations in data (see, Calorimetric Reference Materials, figure 5) make theoretical analysis very difficult. Experimental problems are very severe in thermometry. It was stated to be the solid state physicist's point of view that more effort should go into high temperature materials.

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Dr. Kientz discussed the needs of industry for test materials to which the IUPAC Commission on Physical Chemical Measurements and Standards is trying to respond.

There are many industrial problems of measurement, as for instance in the analytical chemistry or metallurgical laboratory. The problems often require measurements of mechanical and thermal constants and arise from the chemical engineering. The laboratories have good apparatus for measuring these, but lack sufficient SRM's to calibrate the apparatus in order to measure the constants or functions without appreciable systematic errors. The Commission on Physical Chemical Measurements and Standards has first tried to identify their needs, and to examine the availability of materials. Gaps in the availability of appropriate materials will then be noted, which will substantiate the need for additional materials, and possibly lead to making additional materials available.

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The question was raised by the Chairman, with respect to lists of reference materials such as are prepared by the IUPAC Commission or recommended in Ing. Crovini's paper, as to criteria for deciding how many reference materials are needed.

Dr. Kientiz pointed out that, as a result of the IUPAC study there are 40 to 50 substances for calorimetry, covering all fields. Dr. Cox responded that in principle such lists of reference materials are open-ended. In practice, however, practical limitations are imposed by the small numbers of well studied, well described systems.

After a system or substance has been recommended for a certain property, it does not necessarily follow that there is any institution actually offering that material as a certified reference material for the property. The IUPAC Commission does list sources where they are known.

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The question of justifying the cost of preparing and characterizing the material was raised by the Chairman and was not fully answered.

When one has a large number of reference materials, then one must face a substantial cost associated with choosing, preparing, characterizing, and issuing the material. For instance, benzoic acid used in bomb calorimetry is widely used in coal and other fuel testing laboratories, nutrition laboratories, and so on. It is widely distributed and pays its own way, even though sold rather inexpensively. There is also a need for the special thermochemical reference materials containing selected elements. In contrast to the benzoic acids there are not nearly as many buyers. The value of these may be extremely high from the point of view of scientific research and the reliability of the data obtained as a result of using them. These materials may be very important to a few people, but there will be only a few people who will really need them.

This question was not answered, except partially by Dr. Cox, who suggested that the standards institutions themselves largely decide this in terms of the organization of their work, their procedures for preparing, purifying, and characterizing the materials, and who does the work.

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Dr. Milazzo provided additional information about the work of the IUPAC Commission.

Many of the recommendations of the Commission come from studies of the literature because the Commission has neither facilities nor laboratories. But the members have some personal experience, and they give the Commission information about what they have tried in their own laboratories. An illustration is the calibration of spectrophotometers for the wavelength scale and the photometric scale.

For the calibration of the wavelength, the mercury lamp wavelength is well known. In this case the Commission need only recommend some special form of lamp containing, perhaps, some element other than mercury to extend the wavelength range of calibration below the mercury resonance line at 257 nm. Then with this special lamp, say containing zinc also, one can calibrate the wavelength scale down to the resonance line of zinc at 135 nm, nearly the practical limit of the working spectrophotometer. The commission does not need any particular working experience for this.

On the other hand, when one calibrates the photometric scale of the same instrument, a reference point is needed, a reference material with well known values of absorbance. This has until recently been essentially non-existent. Because Dr. Milazzo had need for capability in this area, the material is evaluated there. Thus, as a result of the experimental work done by one member a potassium dichromate solution of specified concentration and specified value of pH, has been recommended by the Commission.

In any case, values taken from the literature are only those which are really well ascertained and where the data are very good. Otherwise, values obtained by personal experience are used. This is the policy of the IUPAC Commission on Physical Chemical Standards. For the very best evaluations, highly-qualified laboratories must take over the work. The Commission members are not necessarily the people for such specialized work.

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High temperature materials needs.

Ing. Crovini suggested that we need to focus attention on some problems and to make a choice. For the spectrum of fixed points he presented, there are some quite old measurements but a good many recent measurements. It should be possible to provide samples that are well characterized (by data in the open literature). The question raised by Dr. Armstrong was whether there would be any users, or whether an alternate solution like a thermocouple of wider range than now available would find wide acceptance as a secondary standard.

In answer to this, with respect to optical pyrometry, the primary laboratories try to transfer the base units they maintain to as wide as possible a selection of instruments that refer to it. National secondary standards like tungsten strip lamps are widely used. But there are many places (not isolated cases) where the full accuracy obtainable with a tungsten strip lamp cannot be achieved. For instance, there has been quite a large demand for one or more secondary reference points to calibrate optical pyrometers to supplement or substitute for the tungsten strip lamp. A program was developed in IUPAC to characterize the aluminum oxide melting point or eutectic point. Persons working in high temperature environments need an instrument exactly calibrated at a reference temperature instead of referring to some transfer standard that may be useful for many purposes, but not for theirs. To select a preferred fixed point, information was needed from the persons working in the field as to the temperature range they are working on, and then a decision was made on one material out of that spectrum of needs. Some of them are really needed.

This comment was strongly seconded by Mr. Foster who stated that fixed point reference materials for higher temperatures are really needed. Apparently he would use them to check pyrometers, or his customers would reduce their demands on him if they could use them.

Dr. White stated that it should be clearly understood that one does not need just certified reference materials. Very good materials are often available commercially, say gold, silver, or zinc that have freezing temperatures far better than the ordinary user can measure. There is no need for a body like the Office of Standard Reference Materials to spend a lot of effort preparing many briquettes of a special material for distribution, when materials bought off the line have a purity of four or five nines.

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Dr. Milazzo made a comment that was particularly directed to Dr. Venable, and this concerned the elimination of systematic errors by simplicity of use. This led to an extended discussion of systematic errors.

It is not necessarily true that use of reference materials will eliminate systematic errors. One can eliminate a large part of the systematic errors as long as one makes comparative measurements of similar substances under the same conditions, in the same apparatus, and so on. But when one uses substances of different characteristics, it is not clear just what measures must be taken. So that when using the reference material systematic errors may be introduced on going to the measurement. Accepting such systematic errors introduced by transfer, one still has an advantage because the reference material and its documentation make good chemistry much easier. The measurements are therefore more free of random errors. The systematic errors are those introduced during transfer, and those occurring in the preparation of the reference material itself. The latter should be included in simplicity of use. Those who make the reference material must keep in mind the way in which it will be used and evaluated.

The discussion of systematic errors centered around the degree to which they can be eliminated from measurements by use of SRM's.

Dr. Armstrong described the nature of some of the systematic errors in the certification of benzoic acid. In the comparison of electrical and chemical heat measurements, systematic errors may be introduced because of the differences in the procedures. If every person who is going to do bomb calorimetric measurements is going to calibrate his calorimeter electrically, every person may introduce his own systematic errors into the comparison because of the use of different designs of calorimeters, different modes of heat transfer, and so on. This is because of limitations on our knowledge of the magnitudes of some of the parameters that may cause differences between the two processes. By using an SRM at least that variability is eliminated.

Dr. Milazzo suggested humorously that this replaces random systematic errors by systematic errors, but then went on to point out that the numerical value of the property accepted for the material is as free as possible of systematic error because all sources of systematic error are individually investigated and eliminated.

Armstrong contended that this is a hypothetically correct procedure, which is difficult to put into practice because of the lack of certainty whether the sources of systematic errors have been identified (as well as the great practical difficulty of actually determining contributions of some parameters experimentally).

The discussion of systematic errors was concluded by Dr. Milazzo referring to his original comment. In planning an experimental process to get a numerical value for any given property, one can investigate what kind of errors are common. One plans his experimental equipment with some logic and then one can see where some systematic error can come from its use, though we most certainly are not led to a complete answer.

Dr. Venable accepted the comment as a reasonable suggestion. A great deal of extra equipment is needed to investigate the systematic errors; and it would be wasteful for every laboratory to have all these pieces of equipment. That is where SRM's can be of great value, in that the standardizing laboratory can do all these extra experiments with the special equipment in the evaluation of the SRM. Those systematic errors that are eliminated for the user will allow him to obtain a better fixed point and at a lower cost in terms of effort than he would have if he had to do all these extra measurements himself.

The SRM should be rather completely documented. An outline or prospectus of a proper certificate was proposed by Dr. Venable. First, there would be a measured value and an illustrated measurement, i.e., an illustration, following instructions given in the certificate, of what the material is used for. Then a statement would be made concerning whether conclusions from the literature on the SRM are warranted. The mode of use should be given. For instance a combination of two SRM's might be better than one. This is a matter of experiment. Then a discussion of the precautions needed, extraneous processes that might occur, and other discussion of the relation between the SRM and its properties and the actual measurement. This would mean possibly a more extended document than now goes with SRM's. The document is probably more important than the material.

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Mr. Mundy made a few further comments on the potential users of the magnetic susceptibility SRM's. These were identified as university chemistry departments, chemical companies, and petroleum companies.

This led to a brief discussion of market analysis and the relationship of demand to the value of the SRM's. The relationship between impact of the SRM and the number that are used is not direct. In the computer field there are magnetic tape SRM's. There are few in existence--perhaps twenty or thirty, but these are sufficient to take care of an industry that is rather massive. Each material must be looked at separately to evaluate the impact it has, rather than looking at the number that are sold.

The time of introduction of new SRM's for new measurement techniques may be decisive in determining just what measurement techniques are adopted. A measurement technique that requires an SRM to calibrate the instrument might be rejected in favor of a more versatile technique if suitable SRM's are not available. This makes the value of market analysis somewhat questionable.

We do not have very good estimates of the time elapsed from conception to availability of an SRM. This is an important parameter, particularly for measurement techniques developed as basic research and later finding important technological application. For instance electron paramagnetic resonance, originally a scientific study only, now appears to have wider applications in the field of medicine. Similarly there will probably be Raman spectroscopy for possible quality control in the glass industry. In both instances, SRM's would be needed because neither instrument gives absolute measurements. So here are two methods of exploring the physical world that came out of basic science laboratories and are now starting to find wider applications in the economy--in industry.

A market survey for the above two examples is under way, and SRM's will be produced only on a favorable response. Even so markets are changeable. Many samples of a particular kind may be sold, and then the technology may be superseded by something else which suddenly terminates the demand. A market survey has to be interpreted, and a negative response may not be decisive in the determination whether to proceed with the production of an SRM.

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VIII. Principal Points Made at the Panel on SRM's for Metrology

G. T. Armstrong

A. A broad view of the scope and nature of SRM's for metrology was implicit in the remarks of Dr. Robert Powell at a plenary session (q.v.). The validity of his ideas should be examined, as well as its implications, with respect to the nature of SRM's available, the kind of documentation needed, the price and users of such materials, and its relation to the existing series of SRM's for metrology. Time was not available in the panel or in the period of the symposium to make this evaluation.

B. A strong plea was made for improved documentation of SRM's, expanding the information given in the certificates to include commentary on methods of use and other types of instruction and evaluation for the user. The OSRM should examine the level of documentation available and make an assessment of means for publishing additional information. It may be that in some instances documentation is available in supplementary publications which would meet this need, but which should be referenced in the certificate. This method should be explored as a general procedure.

C. There are several images of the availability of reference materials and the nature of certifications or evaluations that are necessary. These images should be more clearly defined and differentiated, as considerable confusion arises from unintentional confusing of the various images. The attributes of SRM's for metrology (possibly in part applicable to other classes also) as seen by the chairman are as follows.

1 The material conceived:

A material or substance selected because it has a property that is of interest and can be obtained in suitable form and purity for use.

2 The material realized:

Material is available from a supplier in known or stated purity adequate for the purpose. The supplier may be a national standardizing laboratory, but not necessarily.

3 The value assigned (alternatives):

a No value need be assigned, but the material is available for general use, and values from the literature are summarized.

b The standardizing laboratory has assigned a value to the particular material, which may deviate from pure material by a significant or unknown amount.

c The value is assigned by a standardizing laboratory to the pure material; real material is available for which impurities contribute negligible or precisely calculable amounts to the value.

For materials of which the purity available is adequate to make it acceptable as a standard, documentation of how the material purity was determined is of course essential.

Discussion at the Metrology Panel indicated that there seems to be no real uncertainty about the conception of the material (1). The realization of the material (2), however, allows two options. The necessity of assignment of a value to a realized material, however, seems to be interpreted in at least three ways as listed, but distinctions are not clearly drawn by any terminology or classification. In general I believe a material meeting attributes listed as 3b is the NBS concept of an SRM. However some members of the panel and audience seemed to believe materials having attributes (3a) and (3c) should also play a useful role. A classification such as the following might be considered:

(3a) Recommended research material

(3b) Certified Standard Reference Material

(3c) Recommended calibration material

D. There seemed to be general agreement among those present that processes in difficult measurement ranges such as high temperatures stand to gain much from use of reference materials having recommended or certified values of properties above 1000 K.

E. The implementation of a hierarchical scheme such as that of Ing. Crovini is actually realized in the United States quite well in some areas.

INTERCOMPARISON, QUALITY CONTROL AND STATISTICS

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The purpose of this panel was to discuss those aspects of interlaboratory comparisons exercises, questions of quality control, and the role of statistics as these affect the measurement process, and to recommend steps and procedures to make that process more meaningful.

Dr. Merten opened the discussion with an exposition of a meaningful measurement system in terms of six parameters. When sufficient care is expended to fix or determine or know the values and boundary conditions (if applicable) of these six parameters, then the result of the measurement process will be numerical results that have sufficient information value suitable for the end-purpose for which the measurement(s) were applied.

The six parameters are: (1) purpose of the measurement; (2) condition and characteristics of the matrix material; (3) sampling problems; (4) the analytical process per se; (5) the analytical quality control required; (6) the expression of the results, including the uncertainty inherent in the process. Dr. Merten discussed each of these in some detail and gave figures showing schematically the interdependence of the various parts. Finally, he concluded: (1) the quality or degree of information obtained from any measurement system is limited by factors that are inherent within the system itself; (2) that major efforts to improve one (isolated) part of the system to obtain a greater information value are not warranted, unless the other parts of the system are able to produce information at the desired level; (3) that the uncertainty of the final result must be based on considerations of all parts of the measurement system and not on only one or two aspects; (4) time and costs are often pragmatic considerations that should be considered. References 1 and 2 pertain to this part of the discussion.

Dr. Currie then proceeded to examine critically some of the assumptions surrounding the measurement process. Every measurement process must be defined and, indeed, known to exist. Definition is in terms of sampling, separation procedures (if required), the detection of appropriate signals that are related to the property under test, the evaluation of numerical data, and, finally the statement of the result in terms adequate to the end-use and with meaningful errors bounds given. At the outset it must be clearly understood that the entire process must be under control (in a state of quality control); otherwise, meaningful measurement cannot in principle take place.

Following definition and control, one must concern himself with sampling. At this stage the most common sources of error arise from sample heterogeneity and contamination. Once a sample has been taken, it may be subjected to chemical or physical separation followed by measurement of a response from an appropriate measuring device. Assumptions regarding the chemical yield or recovery and contamination introduced may be violated in the separation step, whereas the measured response may be in error due to faulty instrument calibration or inadequate signal resolution.

Numerical evaluation of measurement results usually involves assumptions about the random and systematic error components (distributions, magnitudes) as well as about the underlying mathematical (physical) model which relates the instrument reading to the basic physical or chemical response of the instrument to the sample. Finally, in order to make the results at all meaningful and useful, it is essential that they be reported adequately -- i.e., such that the estimated quantity as well as its uncertainty is communicated in a completely unambiguous manner. It should be noted also that the number of replications (n) ought always to be specified, as should the specific portion of the measurement process to which they apply.

Dr. Currie illustrated these points by work involving the production, both natural and man-made, of Argon-37.

In order to overcome the foregoing difficulties one must recognize the need for an explicitly-defined measurement process and pay heed to possible violations of the assumptions underlying its constituent steps. No better means exist for bringing the entire system into control than through the use of Standard Reference Materials and laboratory intercomparisons carried out in accordance with a well-defined protocol.

The appropriate references are (3-5).

Dr. Suschny next examined the question of how can one be assured of adequate or reliable results in the course of interlaboratory comparison exercises. One of the principal means of assuring good results is the use and inclusion of control samples during the actual work, together with well-written protocols that are used to define each step of the exercise. When possible, the control material should be an authoritative well-characterized material such as a SRM. Some of the questions addressed were: (1) the required frequency with which the control material should be used in the process in order to achieve a desired degree of reliability; and, (2) the total number of samples (replicates) required to be analyzed. References cited by Dr. Suschny are (6-8).

Dr. Mandel's discussion dealt with the use of control charts for the evaluation of measurements. The famous experiment of sampling from a bowl of numbered chips designed by Dr. W. Shewhart,originator of the control chart, was described. This experiment illustrates the variability inherent in small samples. By means of control charts the nature of this variability can be measured and monitored. When applied to the process of measuring, which may be viewed as sampling at random from a hypothetical, infinite population, the control chart similarly reveals the inherent variability of experimental results, as well as possible systematic shifts, trends, or cycles. An illustration is provided by a set of measurements of the counting rate of the gamma-ray intensity of cesium-137. The measurements, consisting of ten sets of four values each, are shown in table 1. The ten "subgroups" correspond to ten different days.

The average, $\bar{x}$, and the standard deviation, s, are given for each subgroup. These parameters are plotted in control chart fashion in figure 1. The central line, for each of the two parameters, is the average of the ten values obtained for it. The "control limits," indicated by dashed lines, represent the so-called "three-sigma" limits. If this particular measuring process were free of systematic changes, such as drifts, trends, or cycles, the probability for each point to fall within the band formed by the three-sigma control lines would be about 99 percent. It is apparent from the figure that the process is not "in statistical control," i.e., it does not conform to the requirements that must be satisfied by drawing random samples from a single statistical population. In fact, the figure suggests a downward trend for the last five days of counting. One must therefore include that systematic changes occur from day to day in the measuring procedure under discussion. It is not advisable, under such circumstances, to consider the average of the 40 measurements as a "best value" for the counting rate of the cesium sample.

This example shows that the control chart techniques is a powerful tool for the study of the stability of a measuring process. Dr. Mandel cited references (9-13).

Finally, Dr. Wernimont discussed a statistical test not very well-known to many measurement scientists - the Ruggedness Test of Dr. W. Youden. As the name implies, this statistically designed set of experiments allows a scientist to test how rugged his experimental procedure is; i.e., will a slight variation in temperature, or pH, or other important parameters affect the end results and if so by how much. Ordinarily, the scientist in designing his operating procedure will vary one such parameter at a time to arrive at optimum operating conditions. Through the use of the factorial ruggedness test many parameters are varied simultaneously. Thus, three paramters can be tested for ruggedness using only four analyses. Dr. Wernimont illustrated from real examples several uses of the ruggedness test. His references are (14-20).

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Table 1. Counting Rate* of a Standard Sample of Cesium 137 (Counts per Minute)

	Subgroup of Measurements									
	8581	8467	8551	8824	8752	8691	8736	8228	8414	8032
	8651	8462	8498	8801	8723	8655	8580	8407	8492	8223
	8589	8625	8298	8732	8685	8807	8196	8389	8579	8333
	8487	8609	8439	8771	8796	8798	8247	8379	8633	8421
$\bar{x}$	8577	8541	8446	8782	8739	8738	8440	8351	8530	8252
s	68	88	109	40	47	76	261	83	96	168

*Based on counting intervals of 4 minutes each.

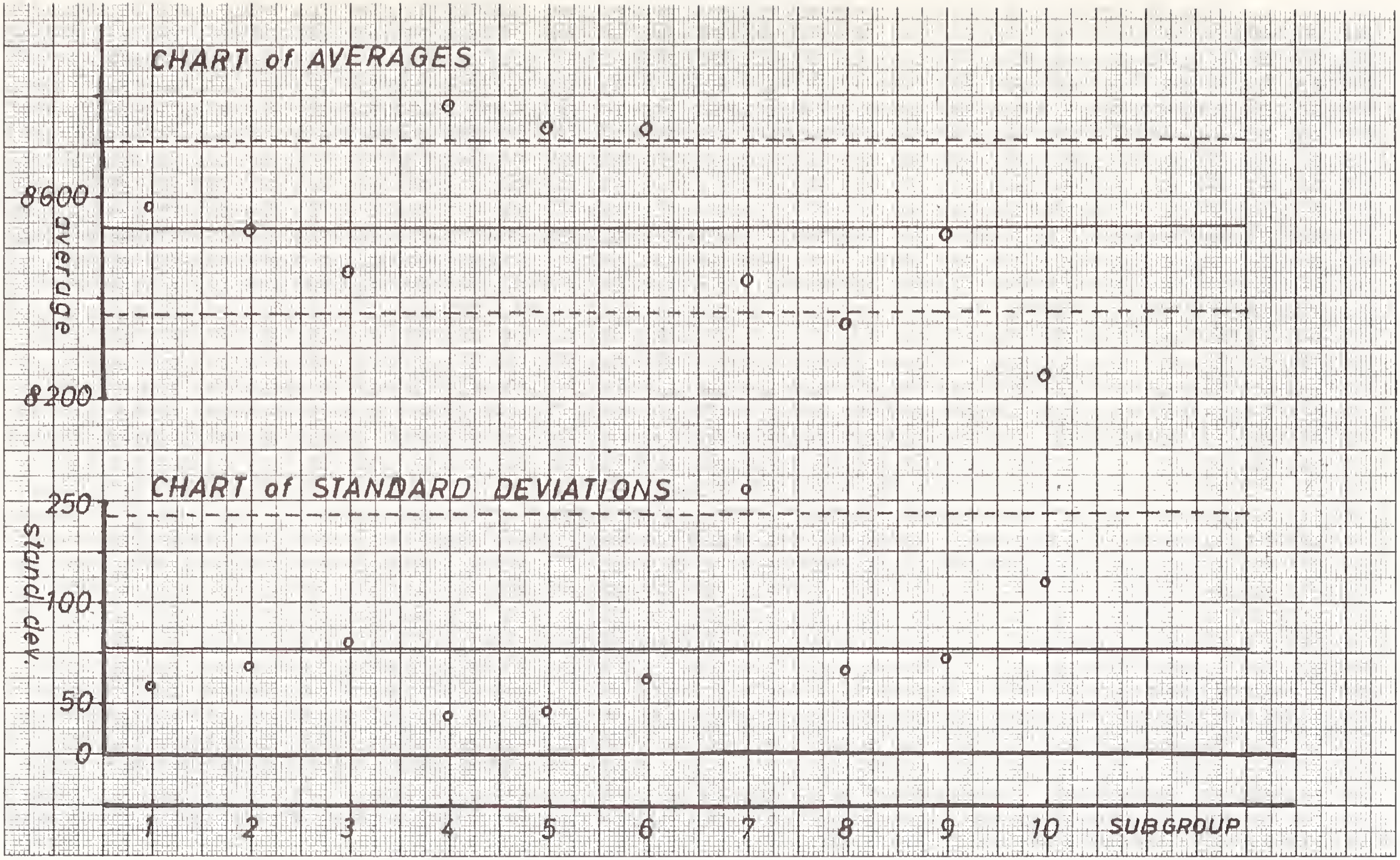

Figure 1. Control Chart: Counting Rate Cs-137

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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

This book presents the proceedings of the 6th Materials Research Symposium on "Standard Reference Materials and Meaningful Measurement" held at the National Bureau of Standards, Gaithersburg, Maryland, on October 29 through November 2, 1973. The symposium was sponsored by the NBS Institute for Materials Research. The purpose of the symposium was to explore ways that Standard Reference Materials (SRM's) could be used more effectively to bring about meaningful measurements both on a national and international scale, to explore the meaning of meaningful measurements, and to review the major paths now used to reach these measurements.

Starting with the relationship of SRM's to a national measurement system, the symposium reviewed SRM activities at the international level, various national programs, and industrial needs. The use of statistics, selection criteria, and steps for certifying SRM's were reviewed. Fifteen panel sessions reviewed the current status of SRM's and outlined future needs.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

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