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1981 Annual Report Office of Standard Reference Materials

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Washington, DC 20234

October 1981

Final

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U.S. DEPARTMENT OF COMMERCE
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1981 ANNUAL REPORT OFFICE OF STANDARD REFERENCE MATERIALS

G. A. Uriano and S. D. Rasberry, Editors

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1. INTRODUCTION

This report summarizes the major operational and technical activities of the Office of Standard Reference Materials (OSRM), National Bureau of Standards (NBS) for the fiscal year ending September 30, 1981 (FY81). The major technical and operational highlights which occurred during FY81 are described as well as OSRM personnel and budget resources, budget initiatives and a number of planning and budgetary issues facing the SRM program.

1.1 Program Description

Standard Reference Materials (SRM's) have been produced, certified, and issued by NBS since 1906. These materials, with specific chemical or physical properties certified by NBS, have found wide acceptance especially by industrial users needing to maintain or increase high levels of productivity. Today, 84 of the 100 largest manufacturers in the U.S. buy and use SRM's. Together with 10,000 other users, they buy over 40,000 SRM units per year at a total price of about $3,500,000. The SRM's have a vital role in promoting industrial productivity by helping companies maintain:

- -- Reliability and uniformity of materials in meeting specifications.
- -- Quality control in raw materials and produced goods or services.
- -- Interchangeability of materials and subcomponents.

In addition to the industrial customers, major SRM users also include federal and state governments, universities, and nonprofit research establishments, particularly for SRM's used in the areas of health, environmental protection, metrology, and forensic science. Approximately 1,000 different SRM's are currently available with a total inventory market value of over $18 million. Table 1.I summarizes the types produced.

Table 1.I

SRM Types Produced at NBS

Steels
Steelmaking alloys
Cast irons
Cast steels
Nonferrous alloys
Gases in metals
High purity metals
Electron probe microanalytical
Standard chemicals
Clinicals
Biologicals
Botanicals
Environmentals
Industrial hygiene
Metallo-organic compounds
Fertilizers
Ores
Minerals
Refractories
Carbides
Glasses
Cements
Trace elements
Nuclear materials
Radioactivity
X-ray diffraction
Isotopics
Ion activity
Mechanical and metrology
Superconductive thermometric
Freezing points
Melting points
Calorimetric
Vapor pressure
Thermal conductivity
Thermal expansion
Thermal resistance
Thermocouple materials
Magnetic
Optical
Gas transmission
Permittivity
Reference fuels
Resistivity
Rubber materials
Computer tapes
Sizing standards
Color
Photographic
Surface flammability
Smoke density
Water vapor permeance

The first four standard samples issued by NBS in 1906 helped cast iron manufacturers improve productivity by increasing their control over the manufacturing process. Well characterized, certified NBS standard samples of cast iron chips served as a check on the composition of the cast iron being produced. One of those original samples has been reissued thirteen additional times and is still in use today. This fact illustrates NBS's commitment to provide continuity of service. As long as a strong need exists for an SRM and it is not available from another source, the Bureau strives to continue to provide it.

By 1911, at the request of such organizations as the American Steel Manufacturers Association and the American Chemical Society, NBS had available about 25 different reference materials. These materials included SRM's for determining the composition of steels, brasses, ores, and sugars and a combustion SRM for calorimetry. Materials research conducted by the Bureau has always been the central resource for the Standard Reference Materials effort. SRM's are characterized and certified largely on the basis of analytical methods developed in the course of that research. For many years, the NBS analytical chemistry program served almost exclusively as the basis for SRM development. Today, however, virtually all major NBS technical areas participate directly, from radiation research to computer science.

Between the two World Wars, SRM activities grew slowly but steadily. Industrial needs for materials for chemical analysis were the major--almost exclusive--impetus. Starting in World War II, the needs for SRM's began to grow and change. As a primary national laboratory for materials research, NBS contributed to the Manhattan Project through pioneering work in the separation of uranium isotopes and developing SRM's for isotopic composition of materials containing uranium and plutonium.

After the war, breakthroughs in the fields of nuclear physics, electronics, and polymer research brought new demands for Standard Reference Materials. By 1951, there were samples for spectrographic as well as chemical analysis of raw and processed materials (primarily metals, ores, chemicals, and ceramics) and special hydrocarbon blends for calorimetry. SRM's had been developed for evaluation of color and fading characteristics of materials. Samples were being certified for important physical properties such as pH, melting point and radioactivity.

In the early 1960's, NBS realized that SRM's were becoming increasingly important to industry and that industrial demand would continue to grow. The Bureau also recognized the potential contribution SRM's would have in solving measurement problems in emerging areas of national need such as clinical and environmental analysis. Consequently, in 1964, the Office of Standard Reference Materials (OSRM) was established and given the responsibility of directing all SRM activities. Previously, the individual technical divisions had managed the SRM program through the

Analytical Chemistry Division. With the establishment of a new office, a number of new thrusts were developed. New program areas were identified and initiated, including the start of what was to become a major effort in developing SRM's for clinical chemistry.

1.2 Demand for SRM's and External Trends Affecting the Program

The last fourteen years has seen the NBS-SRM Program greatly expand the nature and scope of its activities. In 1966, NBS offered 559 different SRM's for sale, which were intended to serve the measurement needs of rather limited but important segments of the U.S. economy. At that time, the majority of SRM's consisted of compositional standards (primarily certified for bulk constituents or purtiy) designed for use in quality control systems during mining and manufacturing of raw and processed industrial materials. The SRM inventory primarily consisted of metal bearing ores, metals and alloys, cement, glass, and inorganic chemicals.

In 1969, SRM development and production activities were involved in only six NBS technical divisions with over 90 percent of the production occurring in what was then the Analytical Chemistry Division. At that time, NBS management recognized that SRM's could serve as an important mechanism for transferring the output of a broad spectrum of NBS measurement programs--including physical and engineering measurements as well as chemical measurements to the user community.

By 1981, the SRM Program was considerably strengthened through the participation of 23 technical divisions and eight program offices within NBS. This enabled NBS to increase the number of SRM's by over 500 (i.e., by nearly 100 percent in the last 14 years). Included were SRM's in many new areas such as computer technology, fire safety, forensic science, and radiopharmaceuticals, with particular recent emphasis on the two important areas of environmental and clinical measurements. The expansion of the SRM Program was accompanied by a corresponding expansion of the customer base as indicated by SRM sales. In the period 1969-1981, SRM sales more than doubled to $3.5 million for FY81, of which approximately $1,400,000 is recovered production capital. The number of units sold each year also increased steadily over this period. In 1971, NBS sold 29,600 units of SRM's; and in 1981, approximately 40,000 units were sold.

The considerable expansion in the scale and scope of the NBS-SRM Program as well as the increased participation of many different technical areas within NBS, has been in response to a number of trends, which have been and are continuing to occur in the world. The trends are summarized below:

.1 Increased Importance of Measurement Compatibility in a Technological World

The importance of compatible and accurate measurement systems to international and domestic commerce, to the development and enforcement of health and safety regulations, and to science and technology continue to grow.

As evidence of the importance of reference materials to assuring measurement compatibility on a worldwide basis, a number of important international standards organizations have initiated reference materials activities in recent years, including the International Standards Organization (ISO), the Organization for Legal Metrology (OIML), the International Union of Pure and Applied Chemistry (IUPAC), and the World Health Organization (WHO). In addition, programs aimed at the development and certification of Standard Reference Materials have been initiated (or expanded) in a number of countries including France, Brazil, Korea, Poland, USSR, and Japan. The nine countries of the European Economic Community (EEC) have initiated a multi-nation reference material program under EEC sponsorship. More recently, the People's Republic of China (PRC) has established an Institute for Reference Materials, which is associated with the Chinese National Institute of Metrology. The PRC sent three scientists to NBS for training on reference materials related projects during FY81.

During the next decade, international SRM activities are expected to increase dramatically, including the joint development of multi-national certified reference materials and increased requirements for the use of reference materials to meet international standards.

.2 Increased Cost of Raw/Processed Materials and Energy

Recent increases in the cost of raw and processed materials, as well as the cost of energy, have resulted in the development of more stringent procurement specifications for materials sold in national and international commerce. Standard Reference Materials are being increasingly used to provide a basis for the arbitration of disputes between producers and users of materials, as well as for traditional uses as part of production quality control systems.

.3 Increased Development of New Materials in High Performance Applications

The development and use of materials for high-performance applications has increased considerably in recent years. This trend is leading to the development of a wide variety of new high-performance materials serving many diverse uses. Examples range from high-temperature corrosion-resistant alloys used in aircraft turbine blades to plastic foams used in building construction. Many of these high-performance materials are used in critical applications where their failure in service could result in serious safety hazards. This has led to the development of rigidly enforced trade specifications and to the need for reliable production quality control, which in turn has resulted in increased demand for SRM's.

.4 Increased Development and Implementation of Government Imposed Health and Safety Regulation

The trend to greater federal, state and local government regulation of the environment, health care system, and transportation systems is also resulting in intense demand for new SRM's. Effective development and enforcement of regulations depends on the availability of accurate, reliable, and compatible measurement systems. The NBS response to this trend has been the establishment of a number of programs aimed in part at providing a reliable measurement base for regulatory agencies. These have included the Environmental Measurements Program, Nondestructive Evaluation Program, Resource Recovery Program, Recycled Oil Program, and the Nuclear Safeguards Program. All of these programs have required the development of new SRM's to serve as measurement technology transfer mechanisms. An increasing number of government regulations in the environmental, health, and nuclear areas are expected to mandate the use of NBS-SRM's directly or the use of commercial reference materials traceable to NBS-SRM's.

1.3 Current and Future Need for SRM's

The use of NBS-SRM's by the Nation's primary metals industry illustrates their importance to the United States economy. For example, NBS steel SRM's are relied upon to verify that the analytical instruments used to measure the constituents in steels are, in fact, measuring correctly and within the allowed limits of error. The quality of the steel is dependent on the quantities of the specific constituents; too little of these critical constituents results in poor quality steel, while too much results in waste of money and natural resources usually with no improvement in the quality of the steel. For instance, the presence of vanadium in iron produces a tough steel. Similarly, specific amounts of chromium and nickel make the steel stainless (corrosion resistant). Steel chemists must analyze each batch of steel for constituents and adjust the mixture when necessary. They periodically verify the measurements made by their equipment through the use of certified NBS-SRM's, which correspond to the particular alloy being produced.

In addition to the example cited above, many new demands for SRM's have occurred in nonindustrial areas, particularly with respect to improving the accuracy and reliability of clinical and environmental measurements. These demands include the following:

.1 Industrial Quality Control

Over 800 SRM's are currently used directly for establishing and maintaining measurement quality control in a variety of industries including metals, glass, ores, rubber, plastics, primary chemicals, energy generation, measurement instrumentaiton, and computers. Industrial SRM's are also used in a number of important engineering applications. For example, SRM's are used to (a) standardize materials; (b) standardize computer components such as magnetic tapes (GSA purchase specifications are based in part on these SRM's); and

(c) evaluate the quality of electronic components such as integrated circuits. OSRM projects that 220 new SRM's will be needed to serve industrial customers by FY86 (Table1.II). These include 80 new metal compositional SRM's (primarily high-performance alloys), 30 nonmetal SRM's (including both physical and compositional properties or ores, glass, and inorganic chemicals), 24 new chemical SRM's (including a series of new synthetic rubber standards), and 46 new engineering standards; e.g., for evaluation of dimensions of integrated circuits. Also needed are 40 isotopic, assay, radioactivity, and physical property SRM's for nuclear applications. During this time period, NBS is also expected to discontinue 246 industrial SRM's contained in the existing inventory, including 108 metal compositional SRM's and 58 engineering SRM's. Thus, the total number of industrial SRM's in inventory is expected to decrease slightly over the next five years, although the spectrum of SRM users will continue to broaden.

.2 Health

Over 40 SRM's are now being used to improve the accuracy of over four billion measurements made annually in hospital laboratories at an estimated cost of more than $8 billion. NBS SRM's and reference methods help provide the basis for: (1) the regulation of *in vitro* diagnostic products by the Food and Drug Administration (FDA); (2) the proficiency testing of 7,500 clinical laboratories by the College of American Pathologists (CAP); (3) the proficiency testing of 1,000 laboratories in the Medicare network by the Center for Disease Control (CDC); and (4) has begun to provide a critical component of the new National Reference System for Clinical Chemistry (NRSCC), recently established by the National Committee on Clinical Laboratory Standards.

The 1976 OSRM clinical impact assessment study, recent long-range planning studies, and other information indicate that 25 new clinical SRM's will be needed before 1986 (Table1.II). The most important needs are for human serum matrix standards characterized for clinically important constituents and also SRM's for enzyme and enzyme reagent materials, individual proteins, peptides, hormones, and vitamins.

.3 Environment

Over 80 SRM's are now being used to assure measurement compatibility in both air and water pollution analyses. A series of 64 gas SRM's provide the accuracy basis for motor vehicle pollution monitoring and mileage testing, as well as for stationary sources and ambient air monitoring. Use of many of the gas SRM's is mandated by EPA regulations. A limited number of trace element standards is also available for use in water pollution analysis and monitoring of industrial atmospheres.

The Environmental SRM category has been the fastest growing category during the past five years. However, the rapid growth of environmental SRM's is expected to slow considerably in the next five years as a result of expected reductions in resources to support projects in this area. OSRM estimates that 25 new gas SRM's and 30 new water pollution SRM's will be needed by FY86. Major emphasis must be placed on the development of SRM's for trace analysis of organics in air and water (e.g., PNA's, PCB's, and pesticide residues), for quantitative analysis of toxic chemical species (as opposed to elemental analysis). Also needed are SRM's for chemical and physical characterization of particulates (including asbestos-like materials), although it is unlikely that any such SRM's will reach production stage in this five-year period.

.4 Science and Metrology

Currently, over 100 SRM's help to maintain basic measurement quantities such as temperature. For example, SRM's are used in the establishment of fixed reference points for the International Practical Temperature Scale (IPTS), the scale to which all temperature measurements ultimately must be referred. Recently, SRM's have contributed to improving the compatibility of thermal conductivity with a worldwide network of laboratories working through the North Atlantic Treaty Organization and in cooperation with CODATA.

OSRM projects that 10 new metrology SRM's will be needed by 1986, including a series of new temperature SRM's (to extend the temperature range of the IPTS scale), and a number of electrical reference standards.

Summary

Based on well-characterized needs identified through SRM proposals, various surveys and discussion with key NBS, other agency, and private sector technical managers, OSRM projects that NBS will have to maintain an inventory of over 1,000 SRM's during the period FY82-86 to meet customer demands in an orderly fashion. Table 1.II summarizes the projected SRM production necessary to meet anticipated customer needs in each category. Over $18 million in production capital will be needed in the FY82-86 period to produce an expected 537 renewals and 310 needed new SRM's. OSRM also projects that 316 existing SRM's will be discontinued during this period.

Table 1.II

OSRM Projection of Demand for SRM's

FY82-86

SRM Category	Current Inventory[+]	SRM Renewals* FY82-86	New SRM's Needed FY82-86	Current SRM's To Be Discontinued FY82-86	Needed Inventory To Meet Demand FY86	Net Change To Meet Demand (%)
Metals	316	53	80	108	288	- 8.9
Nonmetals/Glass	74	15	30	10	94	+27.0
Chemicals/Rubber/Plastic	105	23	24	24	97	- 7.6
Nuclear	30	10	20	0	50	+66.7
Radioactivity	156	71	20	38	138	-11.5
Engineering	146	146	46	58	134	- 8.2
Environmental Gases	54	145	25	10	69	+27.8
Environmental Liquids/ Solids	35	21	30	6	59	+68.6
Health	42	33	25	6	61	+45.2
Science/Metrology	105	20	10	48	67	-36.2
Total	1,063	537	310	316	1,057	- 0.6

[+] As of July 31, 1981.

*Includes a number of multiple renewals in the Radioactivity, Engineering, Environmental Gases, and Health category.

2. TECHNICAL ACTIVITIES

2.1 Introduction

Section Two is a summary of the technical and related activities required to research, develop, produce, inventory and sell Standard Reference Materials. Parts 2.4 and 2.5 provide highlights of specific technical projects for FY81.

2.2 Summary of New and Renewal SRM's

Table 2.I summarizes the number of new and renewal SRM's produced in FY81 as distributed over major program categories. Fifty-nine new and 139 renewal SRM's were completed with the largest number being in the metals, radioactivity and environmental categories.

2.3 FY81 SRM Sales Report

Table 2.II summarizes SRM sales in terms of units, production income and total income for the year ending September 30, 1981. The $3,472,900 in total and $1,432,000 in production income were both records for the SRM program and represent one-year increases of 16 percent and 25 percent respectively. The 40,304 units sold is a decrease of one percent relative to last year.

During FY81, over 10,000 orders and 4,000 technical inquiries were processed. A comprehensive evaluation of all SRM's in inventory resulted in $177,176 worth of material being obsoleted, which is less than three percent of the value of the inventory plus work-in-process. At the end of FY81 approximately 250,000 sales units of SRM's were carried in inventory with an asset value of $6,113,000 (including other agency costs) and a market value of about $18,000,000.

2.4 Highlights of Research Projects

This section describes SRM research highlights during FY81. Forty SRM research projects were active during the year in seventeen different NBS divisions. Rather than provide a complete review, some major highlights are described.

Table 2.I

SRM's Produced in FY 1981

Category	New	Renewals	Total
INDUSTRIAL			
Metals	17	21	38
Nonmetals	1	3	4
Chemicals/Rubber/Plastic	3	4	7
Engineering	1	30	31
Radioactivity	4	27	31
Subtotal	26	85	111
ENVIRONMENTAL			
Gases	4	24	28
Liquids/Solids	2	7	9
Subtotal	6	31	37
HEALTH	4	4	8
SCIENCE/METROLOGY	23	19	42
TOTALS	59	139	198

Table 2.II
FY 1981 SRM Sales by Category

	Units	$ Production Income(NBS)	$ Total Income*
INDUSTRIAL			
Metals	14,394	$290,722	$979,490
Nonmetals	3,889	37,433	211,192
Chemicals/Rubber/Plastic	5,838	95,856	360,402
Engineering	5,749	207,603	412,056
Radioactivity/Nuclear	2,024	175,539	305,661
Subtotals	31,894	807,153	2,268,801
ENVIRONMENTAL	3,537	305,155	586,688
HEALTH	3,100	128,947	294,649
SCIENCE/METROLOGY	1,470	188,077	298,949
GM/RM	303	2,996	23,858
TOTALS	40,304	1,432,328	3,472,945

*Includes income collected for other agencies and other factors.

.1 Succinonitrile Triple Point Standard

B. W. Mangum

Temperature and Pressure Measurements
and Standards Division
Center for Absolute Physical Quantities

During FY81, one relatively large glass cell of succinonitrile (SCN) was obtained and some preliminary measurements were made of its melting behavior. The cell contained approximately 300 g of SCN. The melting behavior was observed by means of a standard platinum resistance thermometer (SPRT), used in conjunction with a Cutkosky ac resistance-ratio bridge.

Based on the preliminary testing of this one sample in this cell, two new cell designs have been made and samples in these new cell designs have been ordered. One of the new cells is to be similar in shape to a triple-point of water cell and is to contain approximately 750 g of succinonitrile. That sample, when delivered toward the end of 1981, will be very carefully investigated with an SPRT as to its melting/freezing behavior, the value of the triple-point temperature on the IPTS-68, and the reproducibility of the triple-point temperature, both with time and as a function of mantle preparation.

The second design will incorporate approximately 50 g of succinonitrile in a glass cell similar to and only slightly larger than SRM 1968 - the gallium melting-point standard. The thermometer-well of this cell is to be approximately 0.150 inch in diameter, so that it will accept thermistor thermometers, thermocouples and small industrial-type platinum resistance thermometers. It is anticipated that this relatively small sample will be a very useful temperature fixed point for the clinical laboratory, as well as for industrial and general laboratory use.

From the preliminary results of our investigation, it appears that the triple-point temperature of succinonitrile is stable, has a value near 58 °C, and is fairly easy to realize. The melting plateau appears to be fairly flat, perhaps a few mK melting range at most. This implies that the material can be highly purified by the zone-refining method used in the preparation of our sample. Since succinonitrile is an organic compound, it has two minor disadvantages, a low thermal conductivity and a small heat of fusion. These disadvantages, however, are not serious ones and certainly do not preclude in any way the use of this material as a temperature fixed point.

.2 Rubidium Melting Point Reference

B. W. Mangum

Temperature and Pressure Measurements
and Standards Division
Center for Absolute Physical Quantities

During FY81, we did extensive testing of rubidium in steel cells. Prior to the testing, however, we encountered several difficulties. A 1-kg sample, supposedly of highest purity, was shipped to us in what we later found out to be an industrial grade container, which caused contamination of the rubidium. This then required the procurement of another sample, of the highest purity material commercially available, from a different supplier. We had previously constructed an all-stainless steel handling and transfer system so that we could attempt additional purification of the rubidium by vacuum distillation. It was extremely difficult to monitor that system in such a way as to know just where the rubidium was in the system and how much was at any given place. An even bigger problem occurred after the transfer of the rubidium into steel cells - that was the clean-up process. The distillation and transfer system contained small quantities of rubidium throughout and because of its extreme reactivity, the rubidium was difficult to remove in a controlled manner. Consequently, we contracted with a producer to transfer under vacuum, a 1-kg sample of pure rubidium into seven stainless steel cells which we had constructed, cleaned, dried, and then evacuated under high vacuum at elevated temperatures.

The samples of rubidium, in the stainless steel cells, obtained from the contractor, were investigated with regard to their melting/freezing behavior, their melting-point temperatures, their freezing-point temperatures, and the reproducibility of the melting-/freezing-point temperatures.

The melting behavior and the melting-point temperature of a given cell was reproducible to within about ±0.01 °C. The maximum temperature attained after recalescence began during freezing experiments on any given cell was reproducible to $\leq$ ±0.01 °C. The freezing point or, more specifically, the maximum in the freezing curve may be somewhat easier to realize in the general laboratory situation than the melting point. The melting point, on the other hand, enables one to perform numerous calibrations using the same melting experiment. The melting-point temperature, as used here, refers to the value of the "plateau" of the melting curve. Thus, both melting-point and freezing-point determinations are practical.

Although the melting-point and the freezing-point temperatures for a given cell were reproducible to about ±0.01 °C, the spread among the cells was greater. The variation of the melting-point or the freezing-point temperature from cell to cell is thought to be due to different levels of impurities in the different cells. Since the samples were all taken from the same lot of rubidium, there must have been different amounts of contaminants in the different cells. This means that the SRM's cannot be assigned one melting-point and/or freezing-point temperature for all cells, but that any given SRM will have a melting-point and/or freezing-point temperature which may or may not be the same as that for another SRM. The SRM's will begin to be tested and stockpiled next year.

The triple-point temperature was determined to be 39.272 °C for pure rubidium.

.3 Investigation of Techniques for the Activity Calibration of ^{14}C and ^{99}Tc

B. M. Coursey and A. T. Hirshfeld

Nuclear Radiation Division
Center for Radiation Research

Two projects in the Radioactivity Group involved the measurement of long-lived radionuclides emitting only beta particles. The nature of beta spectra, with a finite number of particles with energies too low for detection, makes an accurate a priori estimate of the efficiency of most counting systems difficult.

In the case of ^{14}C, important for dating ancient objects, this efficiency had been maximized in past measurements by transforming the material into gaseous $^{14}CO_2$ and mixing it with the counting gas used in a group of well-characterized proportional counters. (See Method A, in table 2.III). However, a calibration performed in 1973 was disturbingly discrepant (about 1.4 percent) with a value obtained in 1958. Moreover, there were even larger discrepancies among the standardizing laboratories of nations with which we had compared values.

It was first considered that a direct counting of a gaseous ^{14}C compound which could also be dissolved directly in a liquid scintillator for comparison with past measurements should be attempted. This would eliminate any uncertainty in the transformation to a gas. However, available funds were not sufficient for this purpose, and two alternative approaches, both using liquid scintillators, were used. These same methods were also applied to the measurement of ^{99}Tc, a significant component of nuclear waste from power plants and a residue of the most commonly used radiopharmaceutical. Its very long half life ($2\text{x}10^5$ y) made the preparation of thin solid sources impossible.

The first technique uses theoretical calculations of beta spectra and liquid-scintillator response to deduce the ^{14}C and ^{99}Tc counting efficiencies from those determined with other (already calibrated) radionuclides. The results obtained using this technique are shown in method C of the table.

Data are being taken with the other, more complex, method (see Method D of the table). In this procedure, a known quantity of a radionuclide which

Table 2.III

Status Report of Intercomparison of Various Counting Methods for ^{14}C and ^{99}Tc

	CARBON - 14		TECHNETIUM - 99
HALF LIFE (Years)	5730		213,000
BETA-RAY ENERGY			
(MAX) (keV)	156.48		293.50
(AVE) (keV	49.35		84.60
A. GAS COUNTING	$4\pi\beta$(GC)		
1958 (NBS)	1.932 x 10^5 Bq g^{-1}	± 2.0%	Method not applicable for technetium
1973 (NBS)	1.906 x 10^5 Bq g^{-1}	± 2.0%	
1980 (NPL)*	1.932 x 10^5 Bq g^{-1}	± 2.0%	
B. EFFICIENCY TRACING	$4\pi\beta$-γ(LS)		
COBALT-60 (NBS)	1.962 x 10^5 Bq g^{-1}	± 2.0%	In progress
COBALT-60 (NPL)*	1.960 x 10^5 Bq g^{-1}	± 0.5%	
NIOBIUM-95 (NPL)*	1.964 x 10^5 Bq g^{-1}	± 0.5%	
C. COMPARATIVE METHOD USING LITERATURE DECAY SCHEME DATA (NBS)	$4\pi\beta$(LS)		
COBALT-60	In progress		4.409 x 10^4 Bq g^{-1} ± 1%
NICKEL-63	1.926 x 10^5	± 2.5%	
HYDROGEN-3	1.932 x 10^5	± 2.5%	4.419 x10^4 Bq g^{-1} ± 2%
SCANDIUM-46	1.939 x 10^5	± 2.5%	
D. EFFICIENCY TRACING MUTIPARAMETER FIT	$4\pi\beta$-γ		
Cesium-134	In preparation		
Europium-154			In progress

*NATIONAL PHYSICAL LABORATORY, Great Britain emits gamma rays in coincidence with beta particles is mixed with the ^{14}C or ^{99}Tc, and the counting officiency is varied by selecting, in turn, lower thresholds for the height of electronic pulses derived from the liquid scintillator. The counting rates for all selected gamma rays and for those that are in time coincidence with beta particles can be used to give a measure of the beta-particle-counting efficiency for that radionuclide. An extrapolation of the total beta-particle count rate as a function of efficiency to 100% efficiency is then used to measure the total activity in the sample. Such extrapolations have given somewhat inconsistent results in the past (see Method B of the table). The present experiments include an "efficiency-tracing" radionuclide with several beta groups for which the counting efficiency (for each) can be measured by selecting coincidences with corresponding gamma rays. A multiparameter extrapolation of the total beta count rate is then made to 100% efficiency for each. The results obtained with multiparameter fitting will then be checked against those of the first method.

.4 Measurement of Absolute Sputtering Yields

J. Fine

Surface Science Division
Center for Chemical Physics

The principal aim of this work is to obtain absolute sputtering yields of 1-5 keV ions on well-characterized elemental samples in order to improve the accuracy of depth profiling measurements by current surface analysis methods. The accuracy of depth profiling measurements is at present limited by the availability of accurate, reliable, sputtering yield data and by the lack of knowledge of the topographical and morphological effects produced by ion bombardment.

a. Sputtering yields: Quartz oscillator weight-loss method

A significant improvement has been made in the method by which in situ, dynamic sputtering yields are measured. The third harmonic in the signal from a gravity-crystal microbalance has been found to give greater accuracy and stability than the fundamental in measurements of mass loss due to sputtering. A smaller area of the crystal can be used than before and more uniform incident ion-current densities can be achieved. New electronics for third-harmonic detection from the oscillator have been designed and tested and calibration of the system is underway.

b. Sputter depth profiling: Use of combined Auger and x-ray analysis for determining elemental composition

Low-energy primary electrons (3-10 keV) are being used to excite x-ray emission in thin metallic films (< 70 nm). These low-energy x rays, primarily of less than 2 keV energy, have a depth sensitivity limited to about a single such thin film layer and give information of the type and amount of material contained in this thin surface layer. An ultra-thin windowed energy dispersive SI(Li) detector is used to monitor this x-ray emission simultaneously with the

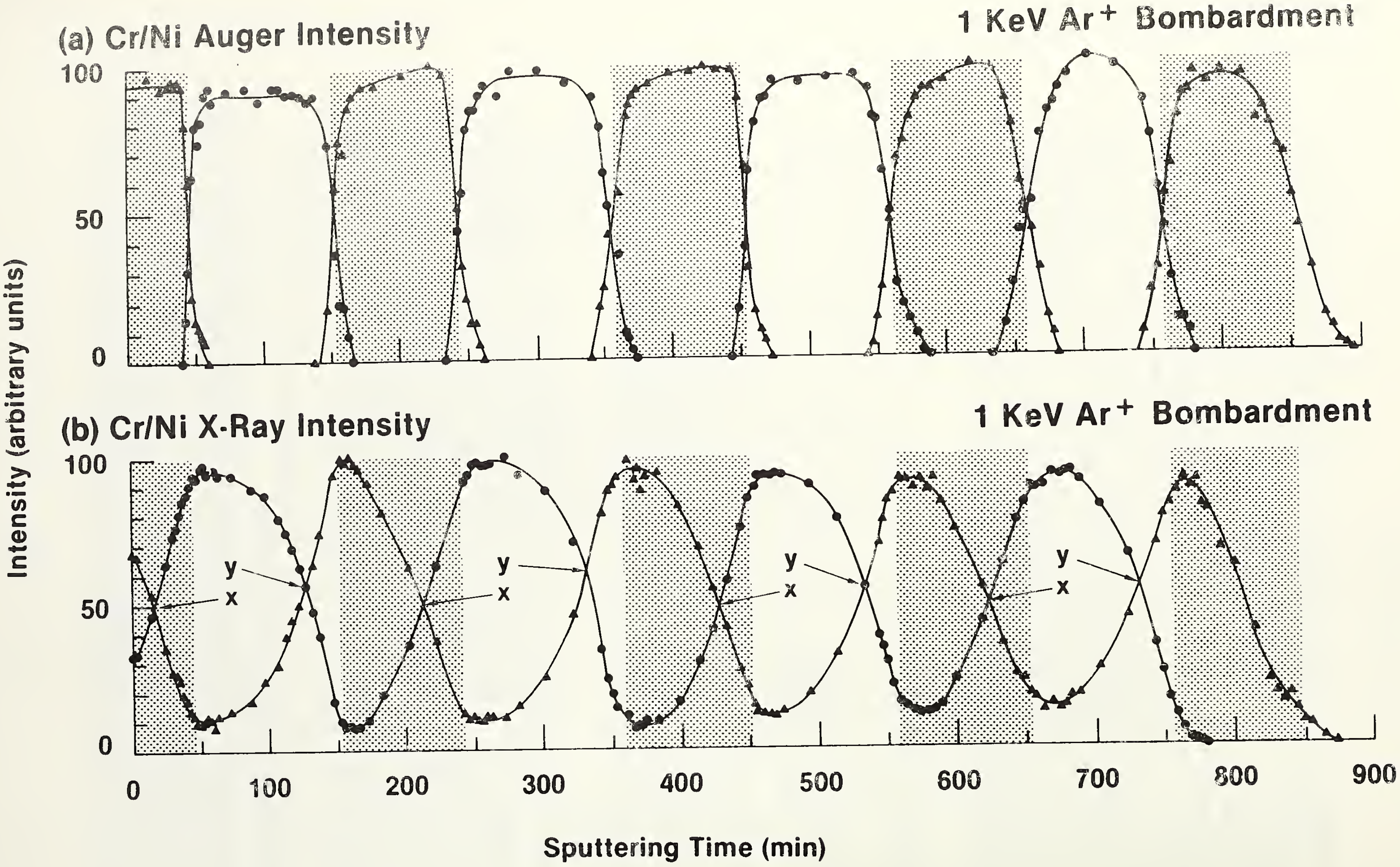

Figure 2.I Sputter depth profiles of a multilayered Ni/Cr thin film structure obtained from the emission of Auger electrons and x-rays. The intensity of emission, normalized so that the maximum of each constituent is 100, is plotted as a function of sputtering time for Cr (▲) and Ni (•). These profiles resulted from sputtering with keV argon ions. (a) Ni and Cr Auger measurements; (b) Ni and Cr x-ray measurements where X(Y) indicates the Cr/Ni (Ni/Cr) curve crossing points. The shaded areas correspond to the position of the unsputtered Cr films and are based on Auger intensities 50% points.

detection of Auger electrons so that at any point of a sputter depth analysis it is possible to obtain both the composition of the surface (Auger) as well as that of the underlying material near the surface. This new application of the combined technique to a metallic thin film system is providing new as well as more reliable depth data.

c. Development of SRM's for sputtering rate and depth profile analysis

The objective is to develop SRM's that would allow convenient determinations of ion-beam sputter-removal rates in commonly used surface-analysis instrumentation. Thin film reference materials of known thickness would be used to calibrate ion-gun current densities for particular operating conditions. This information together with sputtering-yield data for a range of materials would establish depth scales in the measurement of depth profiles.

As part of a joint U.S./Yugoslavia program between J. Fine and NBS and B. Navinsek at the J. Stefan Institute in Ljubjana, three types of thin-film structures have been fabricated by sputtering-deposition in Yugoslavia: 1) a thin film oxide of tantalum produced by reactive sputter deposition onto an in situ sputtered silicon substrate; 2) a multilayered Ni/Cr/Ni/Cr ... thin-film structure where the layers are about the same thickness (∿ 70 nm); and 3) a multilayered Ni/Ag/Ni/Ag ... structure where the Ag layer is considerably thinner than the 50 nm Ni layer. These structures were also deposited onto quartz oscillators so that sputtering yield measurements can be obtained by the mass-loss method. Sputter depth-profile analysis using Auger spectroscopy and x-ray fluorescence of the Ni/Cr and Ni/Ag structures indicate that each layer is completely resolved and that very little degradation in depth resolution is observed in sputtering through all nine layers of the structure. Results of such a depth profile analysis on the Ni/Cr system are shown in Figure 2.I; these well-defined repetitive profiles indicate the suitability of this multilayered material for sputter profile calibration.

.5 Variation with Time of the Heat of Combustion of Coal

D. R. Kirklin

Chemical Thermodynamics Division
Center for Chemical Physics

Commercial laboratories need a powdered coal sample with a certified heat of combustion to evaluate their calorimetric techniques and procedures. SRM 1632a (bituminous coal) and SRM 1635 (sub-bituminous coal) are presently being employed by commercial laboratories to calibrate their instruments and to check their analytical techniques and procedures employed in the determination of trace elements in fossil fuels. The heats of combustion of SRM's 1632a and 1635 are not certified because the long term stability (> 1 yr) of the heats of combustion have not been rigorously established. Therefore, the combustion calorimetry laboratory of the Chemical Thermodynamics Division has measured the heats of combustion of SRM's 1632a and 1635 to determine the variation of this important property with time.

The heat of combustion of SRM 1632a was measured in October 1979, April 1980, and June 1981. The mean heat of combustion was 26.388 $MJ \cdot kg^{-1}$ (11 345 $Btu \cdot lb^{-1}$) in October 1979 and when last measured in June 1981 was only 26.048 $MJ \cdot kg^{-1}$ (11 199 $Btu \cdot lb^{-1}$). This observed decrease of 146 Btu• exceeds the ASTM recommended intralaboratory repeatability of 50 $Btu \cdot lb^{-1}$. This observed decrease of approximately 1.30 percent is believed to be due to the slow oxidation of coal samples upon storage at laboratory conditions.

The SRM coal samples are being stored under laboratory conditions, oxidizing atmospheres, and inert atmospheres. The heats of combustion will be remeasured in fiscal year 1982 to determine further the variation of the heats of combustion of SRM coals with time.

.6 Modernization of Color Fading Standards

H. Okabe

Molecular Spectroscopy Division
Center for Chemical Physics

The NBS SRM's 702 and 703 are plastic chips containing quinoline derivative dye. They have been used in the color and fabric industry as simple and inexpensive standards for measuring the total output of carbon arc lamps. Calibration has been made, however, in terms of an increase in transmittance as a function of Standard Fading Hours, arbitrary units of exposure using the NBS master carbon arc lamp. This project aims at providing an absolute standard for lamp output in terms of $joules \cdot cm^{-2}$ absorbed by the plastic plates.

The results of this work are: (1) fading rate of the plates measured by the decrease of absorbance at 420 nm is independent of incident wavelengths, 366, 404.7, and 435.8 nm; (2) the quantum yield of fading is initially 2×10^{-5} and it decreases with exposure; (3) the fading rate increases at higher temperature; and (4) the correlation between the fading by lamp exposure and that by solar exposure is obtained using a filtered 1000 W Xe arc, a simulated solar radiation source. The fading plates provide simple and inexpensive means to measure the integrated lamp output and solar energy. More detailed information is contained in a manuscript submitted to Applied Optics. Typical relationship between the decrease in absorbance and energy absorbed is shown in the figure 2.II for (A) 0.06" plate and (B) 0.124" plate.

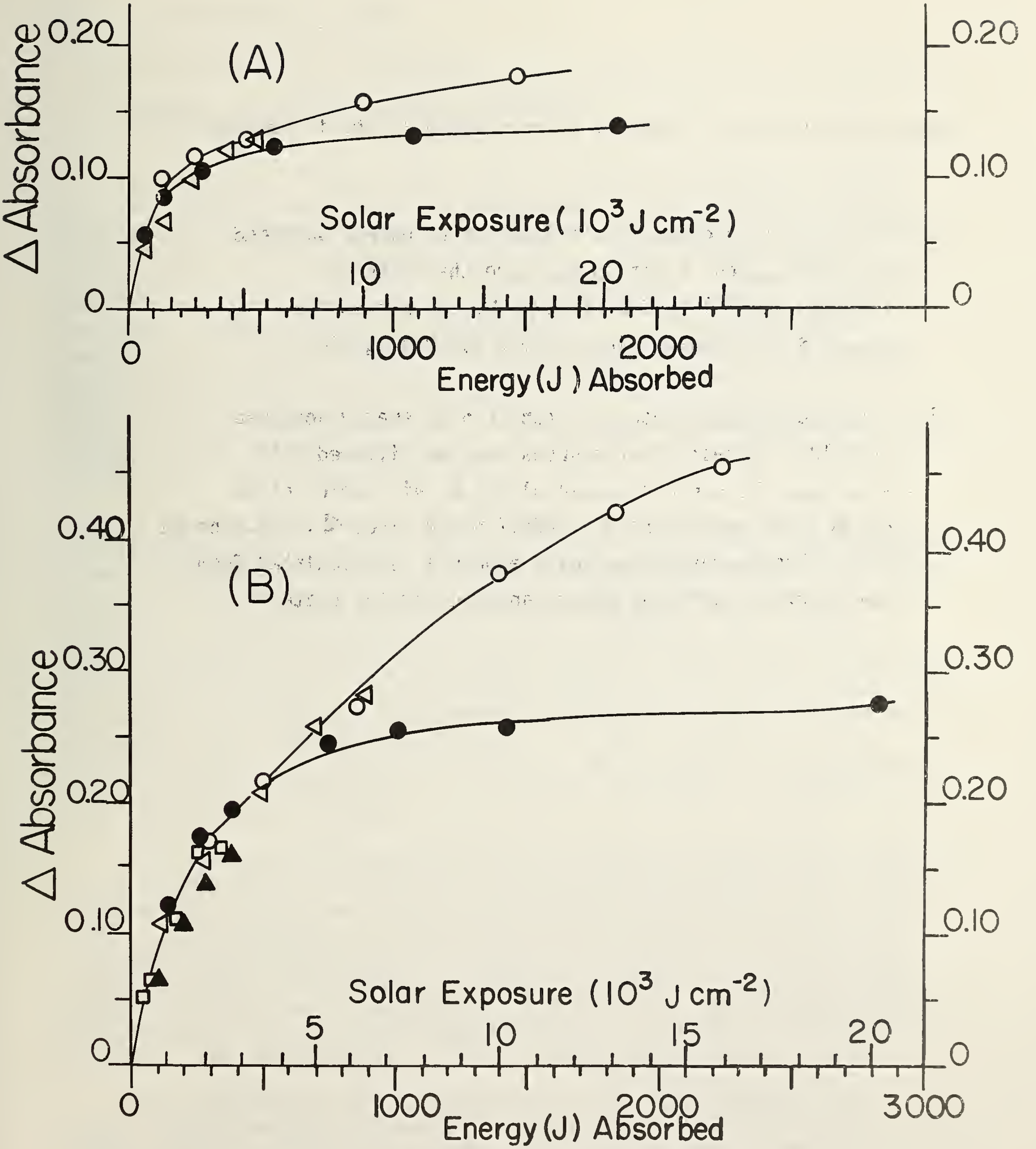
(A)
Δ Absorbance
0.20
0.10
0
Solar Exposure (10^3 J cm^{-2})
10
20
0
1000
2000
Energy (J) Absorbed
(B)
Δ Absorbance
0.40
0.30
0.20
0.10
0
Solar Exposure (10^3 J cm^{-2})
5
10
15
20
0
1000
2000
3000
Energy (J) Absorbed

Figure 2.II

Graphs (A) and (B) of Figure 2.II correspond to the following:

(A) Decrease in absorbance as a function of energy absorbed by 0.06" plates; light sources are the filtered (Corning CS1-75) 1000 W Xe lamp, ○, non air cooled plate, ●, air cooled plate, and ◁ 435.8nm Hg line.

(B) Decrease in absorbance as a function of energy absorbed by 0.124" plates; light sources are the filtered 1000 W Xe lamp, ○, non air cooled plate, ●, air cooled plate, and ▲, 366 nm Hg line, □, 404.7 nm Hg line, ◁, 435.8 nm Hg line. The corresponding solar exposure is calculated from the fractions of solar energy absorbed by the plates.

.7 Sulfur in Metals by IDMS

W. R. Kelly and P. J. Paulsen

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Center for Analytical Chemistry

The objective of this research was to develop an isotope dilution mass spectrometric method for the determination of sulfur that would be precise and accurate for copper and iron base materials containing less than 20 µg/g. Thermal ionization of As_2S_3 from silica gel was investigated and adopted because it promised to provide both a lower blank and improved precision compared with the SSMS-ID procedure developed last year. Classical chemical methods are not applicable at sulfur concentrations below 50 µg/g. The new instrumental techniques have the sensitivity to measure microgram amounts of sulfur; however, they rely on standards of high concentration to determine a calibration curve which is extrapolated to low sulfur values. In this calibration procedure, a small error in the slope or an offset in the curve becomes greatly magnified at low sulfur values.

In the development of this new technique, advantage was taken of the knowledge gained from the isotope dilution spark source determinations of Burke, Paulsen, Maienthal, and Lambert (1982). Techniques for spiking, sample dissolution, and reduction of sulfate to H_2S were essentially unchanged. The H_2S was converted to As_2S_3 instead of Ag_2S. The As_2S_3 was dissolved in NH_3 solution and loaded with silica gel onto single rhenium filaments. The altered $^{32}S/^{34}S$ ratio was determined by measuring the AsS^+ ion currents. The measurement precision by this technique is 0.2 percent or better which represents at least a ten-fold improvement compared to spark source determinations. Of equal importance is the five-fold reduction in blank to 0.1 µg S. The variability in the blank constitutes the largest source of uncertainty for samples containing less than 20 µg/g of sulfur.

For high accuracy determinations of sulfur by isotope dilution, the isotopic composition of sulfur must be determined in each sample. This is necessary because the isotopic composition is variable in nature as a result of mass dependent fractionation during biological and geological processes. The relative range in the $^{32}S/^{34}S$ ratio can be as large as 10 percent which could result in a bias of 2 percent in the calculated sulfur concentration. This potential source of bias was eliminated by measuring the isotopic composition of sulfur in each Standard Reference Material. The range for the $^{32}S/^{34}S$ in these materials was 2 percent.

As a demonstration of the potential of this new technique, the sulfur content has been determined in two copper base and two pure copper Standard Reference Materials. Individual values for one gram replicates as well as the values for chemical blanks are given in Table 2.IV. The average value of the blanks given in Table 2.IV is 0.14 µg and the range is 0.07 µg. If one were to assume that the range was an estimate of the blank variability, then the overall uncertainty would be about one percent for the SRM's containing 20 ppm sulfur and about

Table 2.IV. Sulfur Content in Copper Base SRM's as Determined by Thermal Ionization Mass Spectrometry

Sample	µg/g	Blank, µg
SRM 184		0.14, 0.18
2	17.3	
3	17.7	
4	17.4	
5	16.6	
Average =	17.3	
SRM 52c		
S-14	19.5	0.14
S-15	20.1	
S-16	19.7	
Average =	19.8	
SRM 1035 Composite		0.11
1	22.3	
2	22.2	
3	22.2	
Average =	22.2	
SRM 1035 Samples from individual cans of unpackaged material		0.12
Can 1 (top)	22.4	
Can 1 (bottom)	22.3	
Can 3 (top)	22.5	
Can 3 (bottom)	22.5	
Average =	22.4	
SRM 1034 Composite		0.13
1	2.7	
2	2.8	
3	2.8	
Average =	2.8	

two percent for SRM 1034. These uncertainties include, in addition to the blank variability, a 0.2 percent measurement and 0.25 percent spike calibration uncertainty. This technique in its present form could determine sulfur in metallic matrices at the 1 ppm level to better than five percent. At the present time, this new technique stands alone in its capability to determine accurately and precisely sulfur at the sub-20 ppm level. In addition, it also has the capability to determine sulfur at high concentrations ($\geq$0.1 percent sulfur) in biological and fuel samples to better than one percent.

This new technique is being used to certify the following copper and iron base Standard Reference Materials for sulfur: C1253, 394, High Purity Fe Sponge, 131b, and 891.

.8 D.C. Plasma Spectrometry

M. S. Epstein

Inorganic Analytical Research Division
Center for Analytical Chemistry

Research has been directed towards the development of the dc plasma/echelle spectrometer system as a tool for high accuracy analytical work. The areas investigated have been:

(a) Characterization of the resolution capabilities of the echelle spectrometer relative to the broadened analyte-element plasma linewidths--measured plasma linewidths were found to significantly limit the ultimate resolution capabilities of the echelle.

(b) Thermal equilibration of the echelle spectrometer to promote long-term stability--spectrometer thermal gradients were correlated with heat generated by the plasma, room temperature fluctuations, and exhaust system flow rates to develop procedures which will stabilize the spectrometer throughput to at least ± 10 percent for a typical analysis time of about four hours.

(c) Determination of low and high concentration noise sources--by determining the relative contributions of analyte and plasma flicker and white noise and dark-current shot-noise to the total noise which limits detection or precision, we have been able to optimize sampling times and spectrometer slit widths.

(d) Evaluation of an ultrasonic nebulizer for sample introduction--the unmodified nebulizer was found to provide detection capabilities equivalent to a pneumatic nebulizer with a slight degradation in precision. Addition of a desolvation chamber and/or modification of the plasma sample-introduction tube should produce a significant enhancement of detection capability.

(e) Development of methods to correct for interelement interferences using chemical buffers--a requirement for close matrix-matching of acid concentrations of standards and samples when lithium buffer solutions are used was found.

The result of this work has been an understanding of some of the parameters and mechanisms which influence accuracy using a dc plasma/echelle spectrometer system. Based on this, procedures have been developed which will provide better than ten percent accuracy without standard addition procedures and accuracy to within one to two percent when standard addition is employed. Results of this research were presented by M. S. Epstein in an invited talk at the Eighth Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, in September 1981.

.9 Quantitative Recovery of Iodine from Biological Matrices

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Center for Analytical Chemistry

The goal of this research has been the development of a quantitative method for the recovery of iodine from biological matrices. Quantitative separation is the key step in determining ultratrace levels of iodine in biological SRM's by isotope dilution mass spectrometry.

A literature search of trace iodine separations was completed and possible separation methods identified. Most of the effort has been directed to the separation of iodine by quantitative oxidation of iodide to iodate during the "wet-ashing" of botanical material. Various "wet-ashing" methods have been investigated including chloric acid, nitric-sulfuric acids, fuming nitric-sulfuric acids, and fuming nitric-sulfuric-perchloric acids. The latter two acid combinations proved to be the most effective.

After destruction of the organic matrix and oxidation of iodide to iodate, iodine can be separated by reduction to iodide and precipitation as silver iodide or by reduction to iodine followed by distillation.

Preliminary experiments showed reasonable recovery of 200 to 500 μg of iodide added to 1-g leaf samples, so attention was directed to recovery of trace quantities of iodide from strong acid solutions by coprecipitation of iodide with silver chloride. Experiments with ^{125}I as a radio-tracer showed that quantities of iodide as low as that contained in the tracer (<1 mg I^-) could be recovered with better than 95 percent efficiency when coprecipitated (from strongly acidic solutions) with ∿4 mg of silver chloride.

The recovery of trace iodide from botanical material was then investigated. One gram samples of SRM 1572, Citrus Leaves, which contained about 2 µg/g I^- were spiked with ^{125}I and "wet-ashed" with fuming nitric-sulfuric acids. The iodate resulting from this oxidation was reduced to iodide with hydrazine in sulfate, coprecipitated with silver chloride, and removed from solution by filtration. The results of these experiments showed that better than 90 percent of the iodide was recovered by the coprecipitation with silver chloride.

The results of this investigation will be applied to the determination of iodide in SRM 1572 and other botanical SRM's by isotopic dilution mass spectrometry.

.10 Development of a Radiochemical Separation Procedure for Tin in Biological SRM's

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Center for Analytical Chemistry

Although tin has been shown to be essential for mammalian nutrition [1], it can be highly toxic in some forms [2]. Unfortunately, tin cannot be readily determined in biological materials because of the naturally occurring low levels. Relatively little reliable data concerning the tin concentrations in human and animal tissues and fluids exists, and very few biological reference materials with known tin concentrations are available. None of the eight NBS biological SRM's issued have certified or "information only" values for tin. Biological SRM's with certified tin concentrations would be of great value to analysts wishing to determine tin.

Neutron activation analysis can be used to determine tin in most biological materials, at the naturally occurring levels, if a radiochemical procedure is used to separate tin from interfering elements and the background level of radiation (noise) is reduced. Both the ^{113}Sn and ^{117m}Sn isotopes can be used to quantify tin if the interfering ^{160}Tb (for ^{113}Sn) and ^{47}Sc (for ^{117m}Sn) isotopes are removed. This has been accomplished with a separation procedure based on the extraction of SnI_4 into toluene. The sample is initially dissolved with nitric, sulfuric, and hydrofluoric acids along with hydrogen peroxide, followed by a filtration step to remove precipitated oxides and sulfates from the final sulfuric acid solution before extraction into toluene. Carriers are used to assure a quantitative recovery (>99.8 percent) and maximize the decontamination.

Five samples of SRM 1571 (Orchard Leaves) have been analyzed by the above procedure. The preliminary concentration value of 290 ± 17 (1s) ng/g agrees favorably with two of the literature values (294 ± 16, and 290 ± 20, compiled by Gladney [3]. The reduction in background radiation was better than a factor of 1000, and no Sc or Tb could be detected using other, more intense, γ-rays, indicating decontamination factors of >20,000 for Sc and >1,000 for Tb.

Research is continuing to further improve this method. A small fraction of the selenium, ∿1 percent, accompanies the tin through the separation and can elevate the background around the tin peaks in some matrices. Therefore, efforts will be directed at selenium reduction. Other SRM's with lower tin concentrations, such as Bovine Liver (SRM 1577), will be analyzed to evaluate the suitability of this procedure to provide certification quality data for new SRM's.

References:

[1] Schwarz, K., Milne, D. B., and Vinyard, E., Biochem. Biophys. Res. Commun., 40, 22 (1970).

[2] Schroeder, H. A., Environment, 13, 18 (1971).

[3] Gladney, E. S., "Compilation of Elemental Concentration Data for NBS Biological and Environmental Standard Reference Materials," Los Alamos Informal Report LA-8438-MS (1980).

.11 Development of ID/MS for Trace Concentrations of Vanadium

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Center for Analytical Chemistry

There have been few SRM's certified for vanadium due to the extremely low levels of this element in most natural, biological, and environmental materials (excluding fossil fuels). Many cases of vanadium toxicity have been reported in connection with the use of fossil fuels. It is significant that the most concentrated natural sources of vanadium are fossil fuels such as oil and coal; in oil, it is often the major inorganic component. Vanadium is also ubiquitous in industry in the form of ferro-vanadium alloys or other species used in dozens of processes as the major catalyst. The development of an isotope dilution mass spectrometric (ID/MS) procedure to analyze vanadium will enable NBS to certify this important element in a large variety of requested materials.

The first high accuracy measurement of vanadium by ID/MS was completed during the year on proposed SRM 1634a, Trace Elements in Fuel Oil. The newly developed chemical and mass spectrometric methods were applied initially to this SRM because of its relatively high vanadium concentration (∿ 50 ppm). One-half gram samples were analyzed from each of six different bottles of SRM 1634a. The results, reported below, show a high degree of precision. Future efforts will be directed at the high accuracy analysis of vanadium at concentrations below 1 ppm.

Vanadium Concentration in SRM 1634a, Trace Elements in Fuel Oil

Sample No.	µg V/g
1	55.72
2	55.82
3	55.78
4	55.69
5	55.76
6	55.70
Average =	55.75
Range =	0.13

In developing the chemical procedure for determining vanadium by isotope dilution, extensive research to decontaminate the spike material (^{50}V) was necessary. The isotope obtained for the spiking was found to be unsuitable in its initial condition due to contamination by potassium and other elements. A separation technique was developed to purify the ^{50}V isotope which also was tested for the removal of isobaric interferences; specifically, the mass 50 isotopes of titanium and chromium.

Before precise isotope ratio measurements were made, a thorough investigation of the various modes of thermal ionization was completed. Studies of the ionization patterns and efficiencies of vanadium revealed distinct differences between several pretreatment methods and between different molecular forms. The final form chosen for loading the sample onto the mass spectrometer filaments was vanadium oxychloride; $VOCl_3$ is believed to be its major constituent. This is produced by final treatment with $HClO_4$ and HCl and filament drying with heat, in air.

The chemical separation of vanadium from other metals was based on the formation of the peroxide complex and the use of cation exchange chromatography. The peroxide complex prevented the ion exchanging of vanadium while reducing chromium to its trivalent state. The reduced chromium, along with the other metals, remained bound by the ion exchange column. The chemical separation, as well as sample preparation and final vanadium specie adjustment, were done under Class 100 clean room conditions. This procedure was found to produce blanks below 1 ng while eliminating the chromium and titanium present at comparable concentrations. During this separation, approximately 20 specific elemental components, present at lower concentrations in the fuel oil matrix were also removed. A series of oxidative steps, employed as a pretreatment, resulted in a sample having uniform characteristics for mass spectrometric analysis.

.12 Metal-on-Quartz Filters

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This research was initiated as a result of inconsistency observed in the transmittance of commercially-produced chromium-on-quartz filters (SRM 2031) intended for use in the verification of the transmittance and absorbance scales of ultraviolet and visible spectrophotometers. A potential problem with this SRM was first noted when it was observed that there was a correlation between the measured transmittance and the particular filter holder position utilized in the high accuracy spectrophotometer for measurement. This correlation initially suggested that the chromium film might not be sufficiently uniform since it was known that the different holder positions did not present exactly the same portion of the filter to the incident radiation in every case. A more significant clue, however, turned out to be the observation that the filters which exhibited the largest positional transmittance dependence also exhibited the largest differences when the transmittances obtained with a tungsten source were intercompared with the transmittance values obtained with a deuterium source. This information clearly was not consistent with an inhomogeneity problem and consequently another explanation was necessary. Since, at a fixed wavelength and spectral bandpass, these two radiation sources can differ most notably only in their degree of polarization, it was surmised that the observed problem could be due to a polarization effect in the filters. A sheet polarizer was subsequently installed in the high accuracy spectrophotometer and the existence of a definite polarization effect was quickly verified. Intercomparison of transmittance values obtained with 0 and 90° polarized radiation showed differences as large as 12 percent in the worst instances. Systematic studies have since confirmed that this polarization effect, when present, is a characteristic of the chromium film itself rather than the result of any strains introduced by the optical contact and related operations used in the assembly of these "sandwich-type" filters. An alternate commercial laboratory is now being used to perform the metal coating. By spinning the quartz plate and controlling more carefully the deposition parameters, the percentage of filters that exhibit a polarization effect has been reduced from about 50 percent to less than 10 percent.

.13 Light Elements in Complex Matrices

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Center for Analytical Chemistry

The intent of this project was to establish the validity of nuclear methods of analysis for light elements (H, B, C, N, Al, Si, and S) in

SRM's from natural sources. To accomplish this, it is necessary to show reproducibility in the analysis of simple substances, detection and elimination of interelement interferences, and accuracy in the analysis of known materials of complex composition.

The primary analytical method used is neutron-capture prompt gamma-ray activation analysis (PGAA), building upon the procedures developed at the NBS reactor by workers at the University of Maryland and NBS. Measurements of carbon were also performed by instrumental photon activation analysis (IPAA) at the NBS Linear Accelerator.

High purity urea (SRM 912 and Ultrex), tris buffer (SRM 922 and Baker), SRM 17 sucrose, ammonium sulfate (Spex and Johnson Matthey), graphite, and elemental sulfur were used as standards for C, H, N, and S. Samples of SRM 1632a and 1635 coal, 1634 fuel oil, n-octyl sulfide, and a suite of Nigerian coals were analyzed by PGAA. The SRM coals also were analyzed by IPAA, using two different high purity graphites as standards.

The usefulness of the technique is determined by the sensitivity (in units of counts/second per gram of element) and by the background. These parameters were evaluated as follows:

Element	Best Energy keV	Sensitivity counts/sec·g	Background counts/sec	Determination limit for 10 hr. Irrad.
H	2223.3	688 ± 30	2.578 ± .005	35 μg
B	477.6	418000	0.986 ± .007	0.03 μg
C	1261.9	0.326 ± .008	0.0054 ± .0016	2.8 mg
N	1884.8	2.38 ± .02	0.078 ± .002	1.4 mg
S	840.4	40.45 ± .07	0.12	0.1 mg

Irradiations for these elements in SRM's and other samples have been completed. Each analytical line in the gamma-ray spectrum may be subject to interferences from nearly-coincident lines due to another element. A correction for these interferences can in general be made by observing a clean line of the interfering element. Assessment of the magnitudes and uncertainties of these corrections are the major task to be concluded in the final phase of data analysis. Counting of coals for the IPAA determination of carbon is in progress.

.14 Two-Dimensional Proton NMR Spectroscopy of Hydroxyl Proton Coupled α- and β-D-Glucopyranose

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Center for Analytical Chemistry

Solutions of α- and β-D-glucose in dimethylsulfoxide-d_6 (DMSO-d_6) are of interest as stable systems for the quantitative analysis of D-glucose (dextrose) SRM's by proton and carbon-13 NMR. However, inhibition of hydroxyl proton exchange in these solutions results in complex 12-proton spin systems that are difficult to interpret by conventional techniques. The proton NMR spectra of the major and minor components of SRM D-glucose (α-D-glucopyranose and β-D-glucopyranose, respectively) in DMSO-d_6 solutions have now been analyzed completely by application of the two-dimensional, 'J'-resolved technique at 400 MHz. One great advantage of this technique is the separation of chemical shift and coupling constant information into different dimensions, which allows complex, overlapping proton signals to be disentangled by cross-section-shift between these signals.

The complete, two-dimensional proton NMR spectrum of β-D-glucose in DMSO-d_6 solution is shown in Figure 2.III. Display of the 'J'-spectra cross-sections of the β anomer (see Figure 2.IV) permits the separation of all spin multiplets except the doublets due to HO-2 and HO-3, the chemical shifts of which are accidentally coincident under these conditions. Complete coupling constant data obtained by measurement of the 'J'-spectra cross-sections for both α and β anomers are shown in Table 2.V.

Table 2.V. Proton Coupling Constants (Hz) of α- and β-D-Glucopyranoses in DMSO-d_6 Solutions, Measured by 2-D NMR[a] at 400 MHz.

Anomer	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
α	3.6	9.7	8.7	9.7	2.3	5.0	11.2
β	7.7	8.9	8.5	9.4	2.2	5.9	11.8

Anomer	$J_{1,HO-1}$	$^4J_{2,HO-1}$	$J_{2,HO-2}$	$J_{3,HO-3}$	$J_{4,HO-4}$	$J_{6,HO-4}$	$J_{6',HO-6}$
α	4.8	1.2	6.6	4.8	5.4	5.2	6.4
β	6.6	0	4.7	4.8	4.9	5.5	6.3

---

[a] Data size: 8K x 128; Digital resolution in 'J' domain: 0.24 Hz/point.

These spectral analyses have been confirmed by other experiments in which simplified spectra were obtained for α- and β-D-glucopyranose by addition of one drop of trifluoroacetic acid to the DMSO-d_6 solutions. This procedure greatly increased the rate of hydroxyl proton exchange, and thereby removed

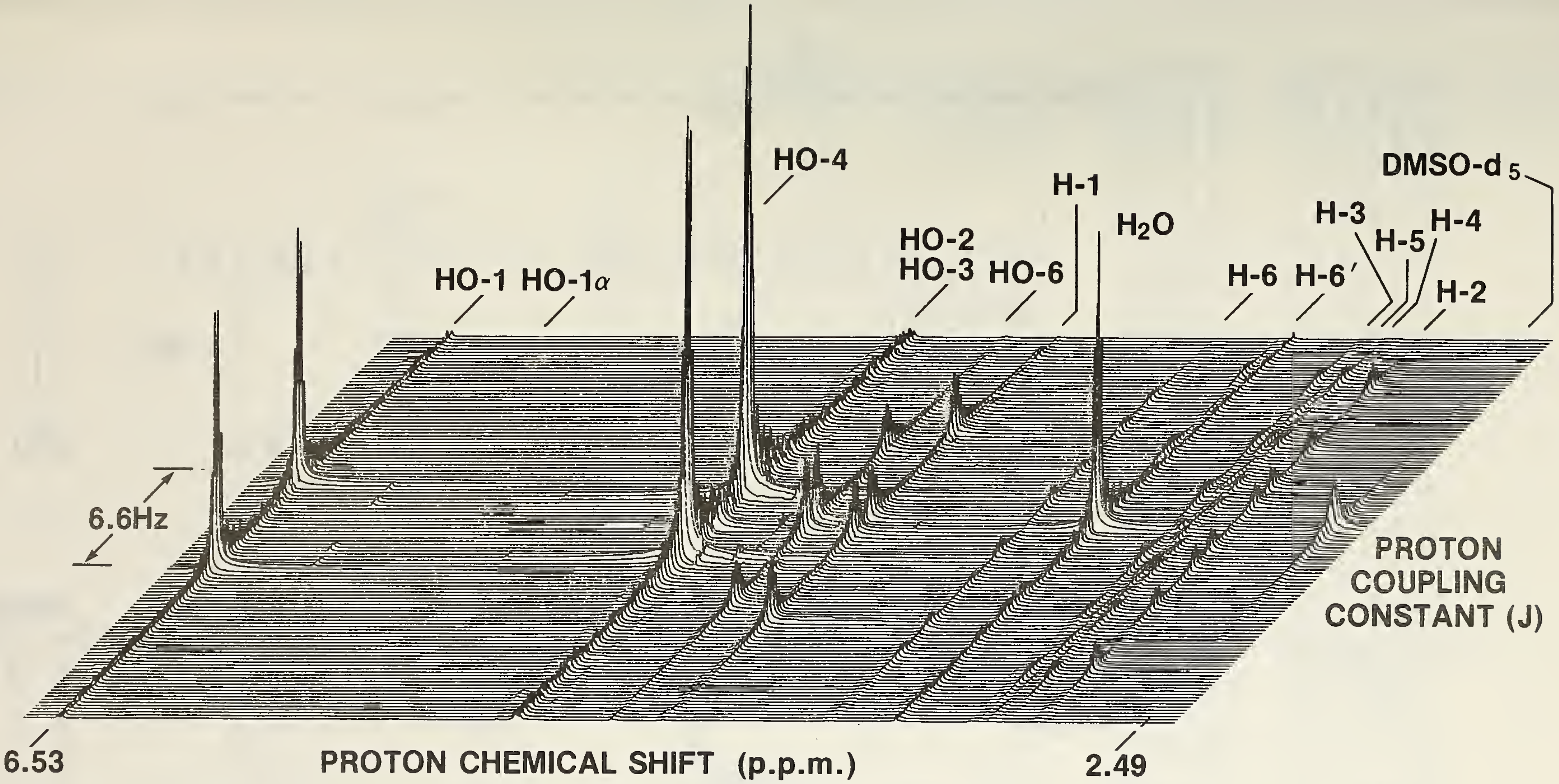


Figure 2.III 2D J-resolved proton NMR spectrum of β-D-glucose in DMSO-d_6 at 400 MHz.

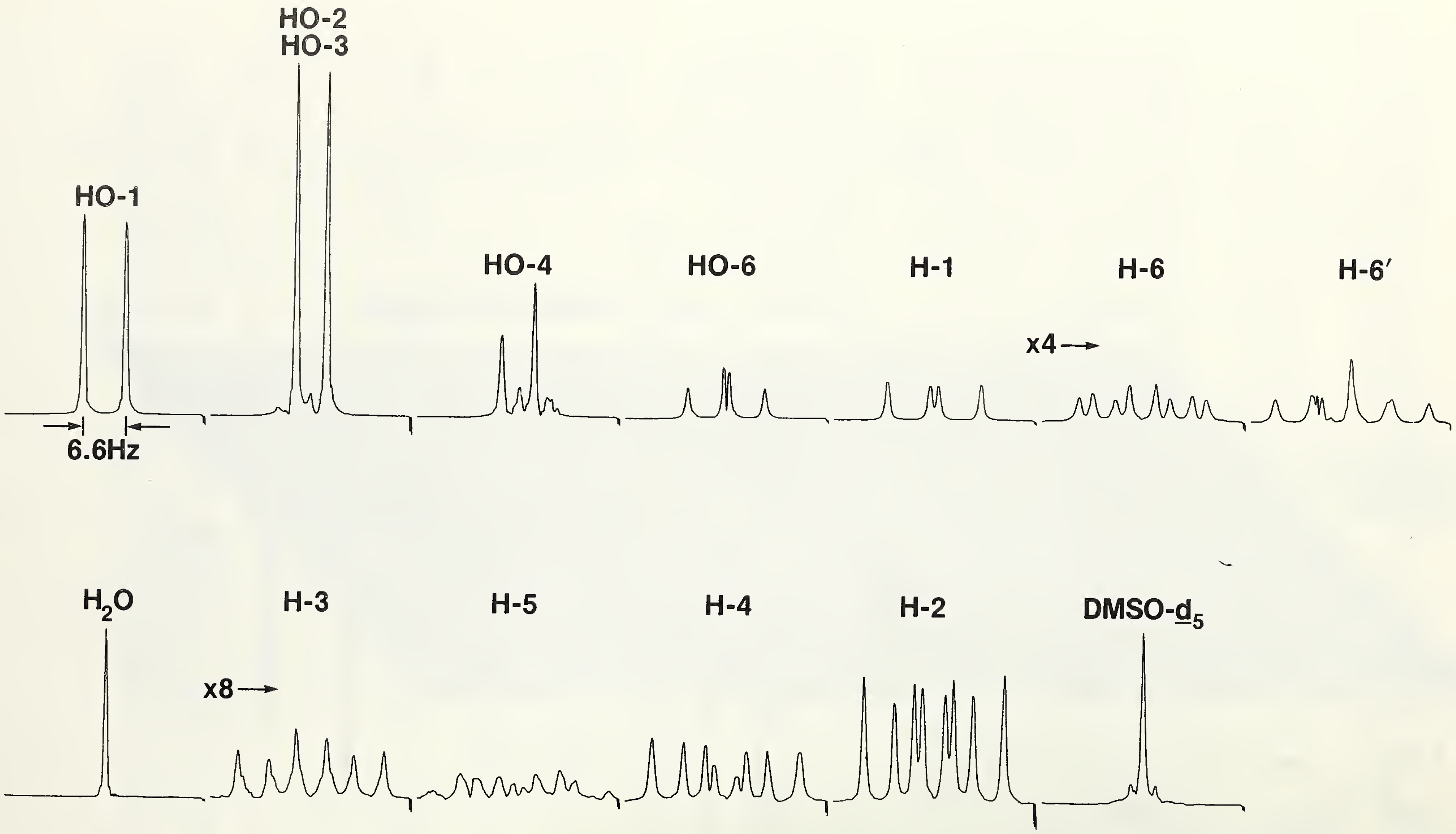
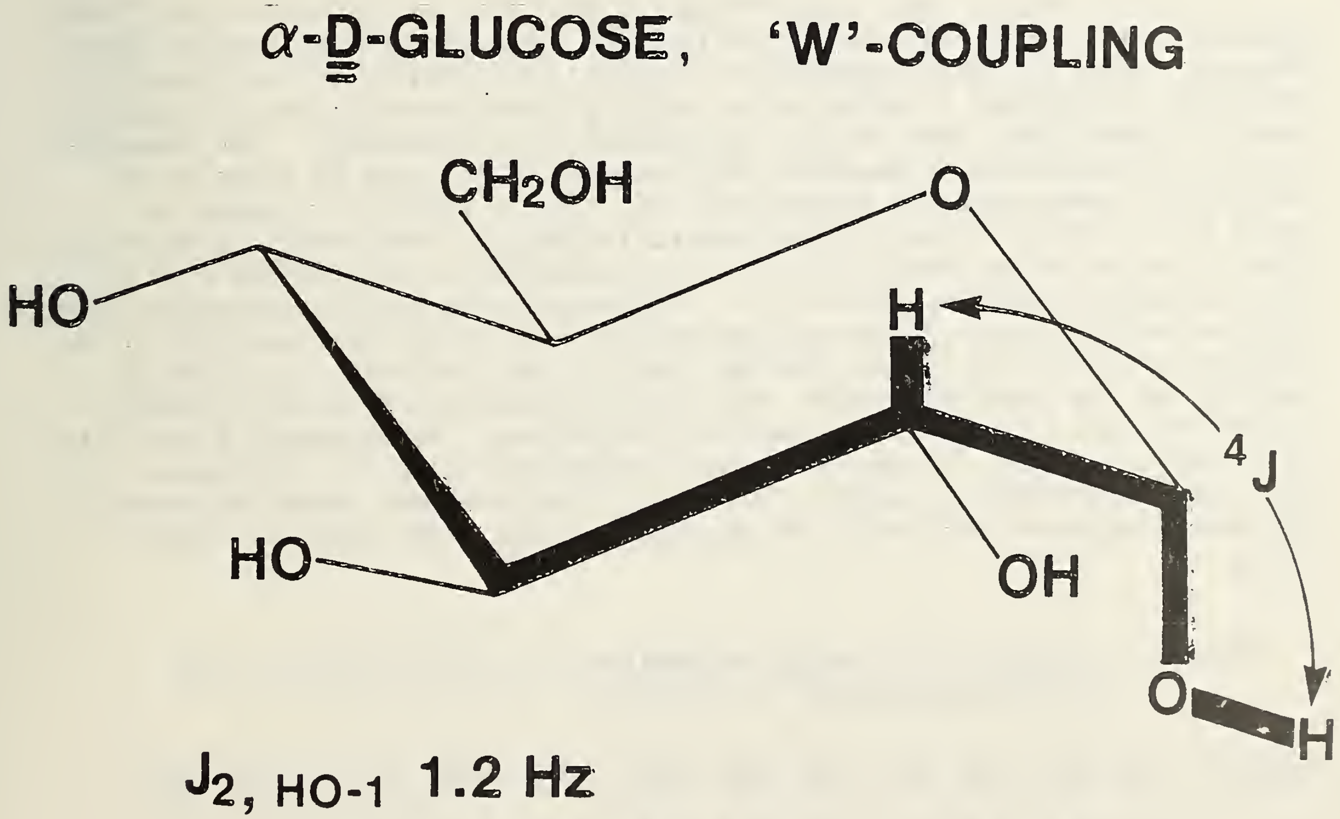


Figure 2.IV 2D NMR J-spectra at 400 MHz, β-D-glucose in DMSO-d_6, hydroxyl protons coupled.

the hydroxyl proton coupling constants from the CH proton spin multiplets. The addition of a catalytic quantity of trifluoroacetic acid also speeded anomerization, so that for additional confirmation of the spectral assignments of individual anomers by homonuclear spin decoupling, automated sequences of seven double-resonance experiments were performed, within 7-9 min after the addition of the acid, before significant anomerization had occurred.

The vicinal CH proton coupling constants indicate that α- and β-D-glucopyranose both adopt the $^4C_1$ chair conformation in DMSO-d_6 solution. Specific evidence for existence of the α-anomer in conformation (A), shown below, in which H-2, C-2, C-1, O-1, and HO-1 adopt a planar 'W'-arrangement, is afforded by observation of the unusual long-range coupling constant, $J_{2,\ HO-1}$ 1.2 Hz.



(A)

This coupling constant is not observed for the β-anomer, and, in fact, the planar 'W'-arrangement is sterically impossible in this anomer. The favored orientation of HO-1 in the α-anomer may be attributed to steric crowding of HO-1 by DMSO-$\underline{d}_6$ molecules hydrogen bonded to HO-2 and HO-3.

The efficiency of data acquisition for both one- and two-dimensional NMR depends on the proton spin-lattice relaxation times (T_1) of the sample, since the pulse sequence cannot normally be repeated at intervals of less than $5T_1$. Therefore, the proton T_1 values of α- and β-D-glucopyranose have been measured under the conditions used for the two-dimensional spectroscopy. The inversion-recovery method was used together with analysis of the data by means of an iterative, three-parameter exponential fit. The T_1 results are shown in Table 2.VI. For solutions of the anomers in DMSO-$\underline{d}_6$, the pyranoid ring protons show T_1 values in the range 0.5-0.7 s, the methylene protons values of 0.3 s, and the hydroxyl protons, 0.9-1.1 s. This interesting difference between ring (CH) protons and hydroxyl protons may be due to either greater mobility of the hydroxyl protons (shorter correlation time), or to association (by hydrogen bonding) of the hydroxyl protons with solvent molecules containing deuterium nuclei that are relatively poor relaxers of protons. Measurements of solutions of α- and β-D-glucose in non-deuterated dimethylsulfoxide are in progress, to test these hypotheses. However, the results indicate that the pulse sequence for two-dimensional NMR should not be repeated more often than once every 5.5 s.

Table 2.VI Proton Spin Lattice Relaxation Times (T_1, Sec) of α- and β-D-Glucopyranoses[a] at 400 MHz.

Anomer	H-1	H-2	H-3	H-4	H-5	H-6	H-6'	HO-1	HO-2	HO-3	HO-4	HO-6
α	0.7	0.6	0.6	0.6	0.5	0.3	0.3	0.9	1.1	1.0	0.9	1.0
β	0.6	0.7	0.6	0.6	0.6	0.3	0.3	1.1	1.0	1.0	0.9	1.1

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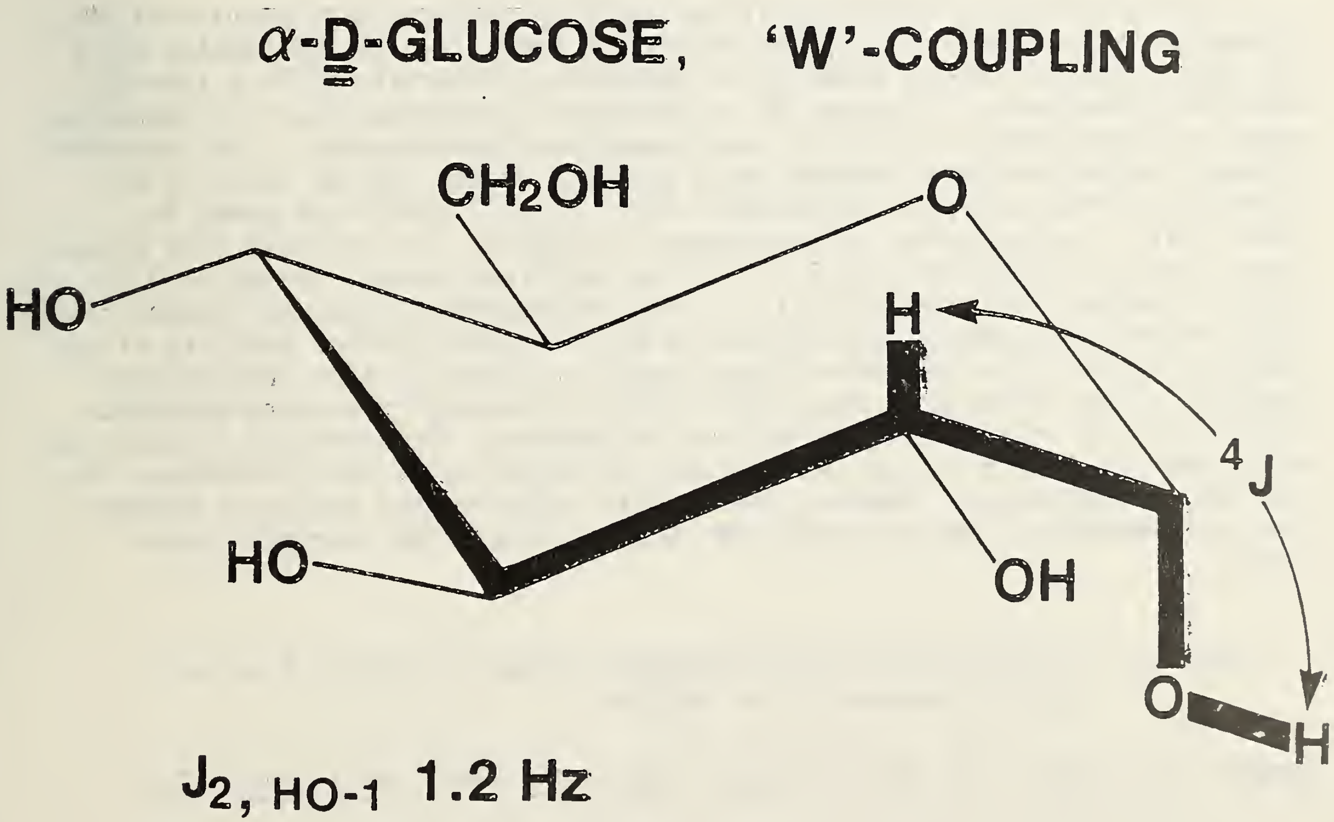
[a] Concentration: 100 mg of α- or β-D-glucose in DMSO-$\underline{d}_6$ (1.0 mL).

the hydroxyl proton coupling constants from the CH proton spin multiplets. The addition of a catalytic quantity of trifluoroacetic acid also speeded anomerization, so that for additional confirmation of the spectral assignments of individual anomers by homonuclear spin decoupling, automated sequences of seven double-resonance experiments were performed, within 7-9 min after the addition of the acid, before significant anomerization had occurred.

The vicinal CH proton coupling constants indicate that α- and β-D-glucopyranose both adopt the $^4C_1$ chair conformation in DMSO-d_6 solution. Specific evidence for existence of the α-anomer in conformation (A), shown below, in which H-2, C-2, C-1, O-1, and HO-1 adopt a planar 'W'-arrangement, is afforded by observation of the unusual long-range coupling constant, $J_{2,\ HO\text{-}1}$ 1.2 Hz.



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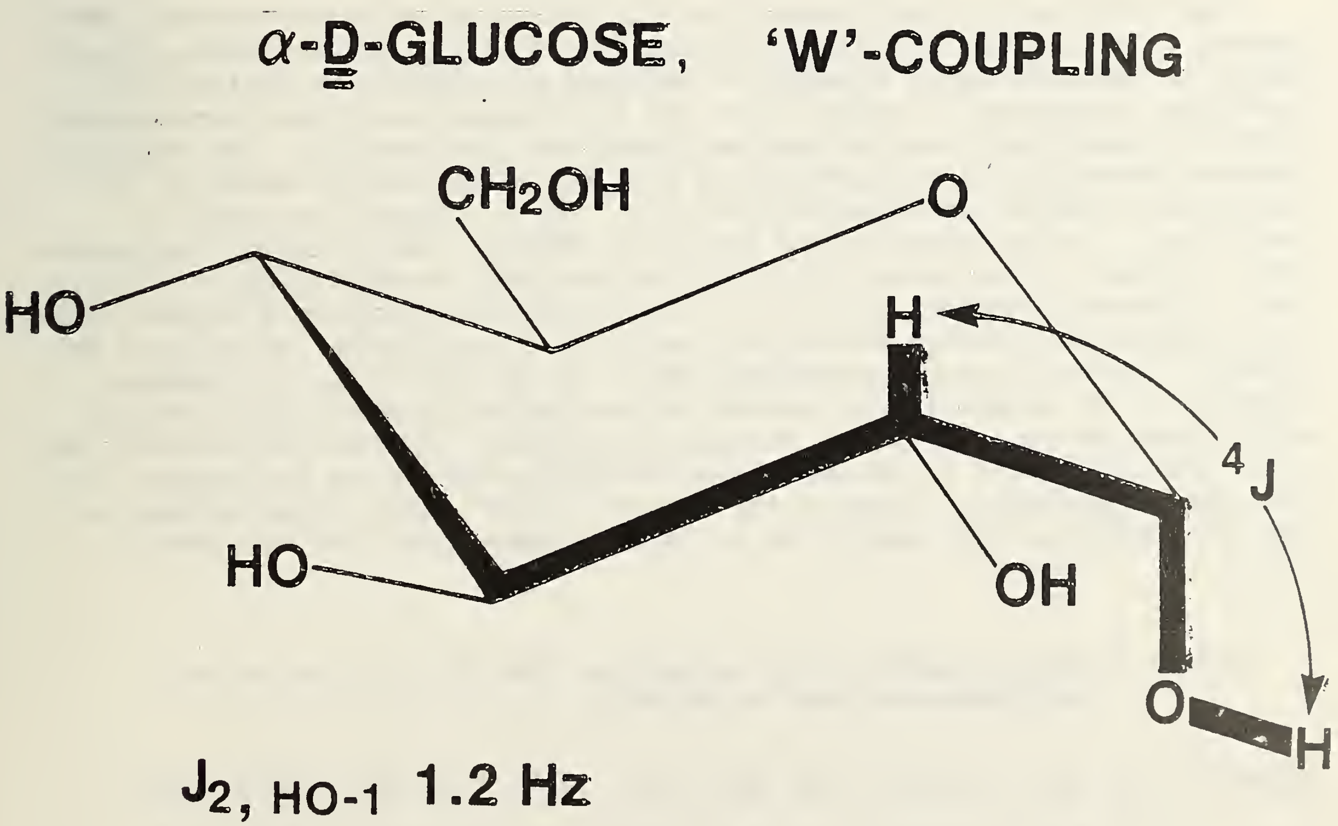

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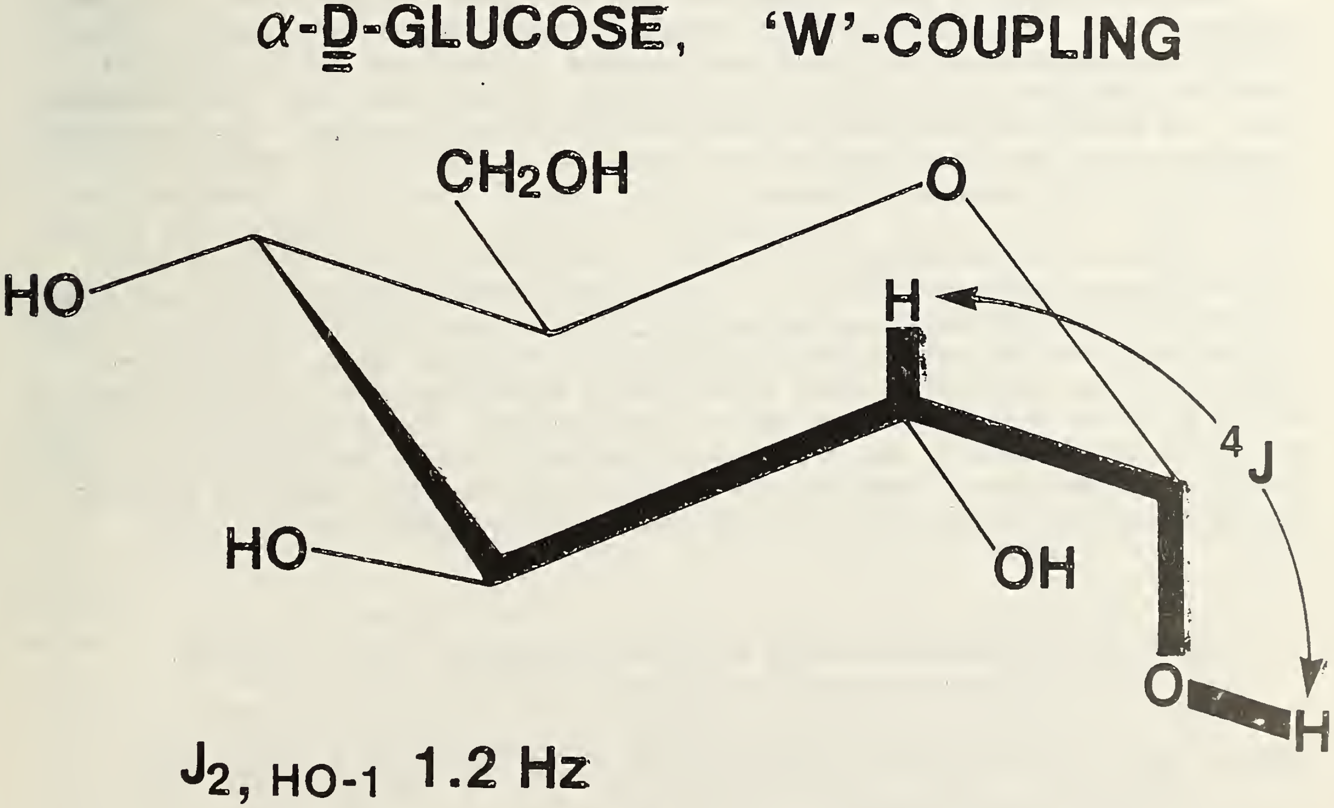

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[a] Concentration: 100 mg of α- or β-$\underline{D}$-glucose in DMSO-$\underline{d}_6$ (1.0 mL).

.15 Comparison of Two Isotope Dilution Definitive Methods for the Determination of Glucose in Serum and Evaluation of the AACC Reference Method for Glucose

A. Cohen, H. S. Hertz, J. Mandel, R. Schaffer, L. T. Sniegoski, T. Sun,
M. J. Welch, E. White, V

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Center for Analytical Chemistry

The measurement of serum glucose levels is one of the most important and most commonly performed analyses in the clinical laboratory. Clinical chemists employ many different methods to determine serum glucose levels. When these methods are compared on serum pools, serious discrepancies are found in the results. Methods of demonstrated high accuracy and precision are needed to provide an accuracy base to which the clinical methods can be compared. The Center for Disease Control undertook the development of a reference method with which clinical laboratories could evaluate their procedures. To establish the accuracy of the proposed reference method [a modified hexokinase/glucose-6-phosphate dehydrogenase (HK/G6PDH) procedure], the Standards Committee of the American Association for Clinical Chemistry asked NBS to develop an isotope dilution mass spectrometric (ID/MS) definitive method for serum glucose.

A brief description of the first ID/MS method for serum glucose developed at NBS is as follows: A known weight of uniformly labeled ^{13}C-glucose is added to a known weight of serum. After the serum is allowed to equilibrate, it is freeze-dried. The serum is then treated with acetone under anhydrous conditions to convert glucose into 1,2:5,6-di-O-isopropylidine-α-D-glucofuranose (DAG). Three thin-layer chromatography steps are employed to separate DAG from other reaction products including the acetone-condensation products with other hexoses. For the initial comparison of this method with the reference method, samples were introduced to the mass spectrometer via the direct insertion probe. All later work involved sample introduction via packed column gas chromatography. Measurements are made on a low resolution magnetic sector instrument operated in the electron impact (EI) mode. Magnetic switching is employed in the sequential monitoring of the $(M-15)^+$ ions for the labeled and unlabeled DAG. The measured unlabeled/labeled ratio from serum samples is compared with the measured ratios of calibration standards, which consist of known weights of SRM glucose and uniformly labeled ^{13}C-glucose, converted to DAG. For quantitation, each sample measurement is bracketed by measurements of the two calibration standards whose ratios most closely bracket that of the sample. Linear interpolation is then used to calculate the amount of glucose in the sample.

The results of the initial comparison of our ID/MS method with the HK/G6PDH reference method is summarized in Table 2.VII. The reference method results are a composite of the results obtained from twelve laboratories, including NBS, on five serum pools analyzed in quadruplicate over a five-day period. The results demonstrate that the methods agree well for all pools tested. A full report of this study is undergoing review for publication as an NBS 260 report.

Table 2.VII Comparison of Candidate Reference Method Results with ID/MS Target Values. Differences and Standard Deviations in mg/L.

	Manual[a] - ID/MS		Semi-Automated[b] - ID/MS	
Pool Mean	Difference	S.E.D.[c]	Difference	S.E.D.[c]
409.0	4.4	4.5	8.9	2.9
785.8	7.6	5.5	4.1	4.0
1344.4	- 1.1	7.3	- 3.0	6.3
1969.7	-19.2	9.8	-32.2	9.0
2978.7	-36.9	13.9	-48.6	13.6

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[a] Candidate reference method with manual pipetting.

[b] Candidate reference method with semi-automated pipetting.

[c] Standard error of the difference.

A second ID/MS method was devised to provide a much simpler wet chemical procedure as well as to verify the accuracy of the DAG method. This approach utilizes the same labeled glucose, but differs markedly otherwise. After equilibration, the serum is treated with ethanol to precipitate protein and the deproteinized serum is freeze-dried, treated with 1-butylboronic acid in anhydrous pyridine followed by acetic anhydride to form the derivative, α-D-glucofuranose cyclic 1,2:3,5-bis-(butylboronate)-6-acetate (glucose BBA). Separation of glucose BBA from the BBA derivatives of other monosaccharides is accomplished by gas chromatography using a 100 m SCOT capillary column. Measurements are made in the electron impact mode, using the $(M-57)^+$ ion, which is a prominent fragment ion for glucose BBA but only a minor fragment ion in the mass spectra of other hexose BBA's. Bracketing of the samples with similarly derivatized calibration standards is again used for quantitation. Table 2.VIII shows the results for the comparison of the two ID/MS methods, methods, at NBS, with the reference method, performed simultaneously at CDC, on three human serum pools.

Table 2.VIII Comparison of the Two ID/MS Derivative Methods and the CDC Reference Method on Three Human Serum Pools Sampled Simultaneously. Mean Results are in mg Glucose/g Serum.

	DAG		Glucose BBA		HK/G6DH	
Pool	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)
A	0.6843	0.29	0.6779	0.19	0.6845	0.51
B	1.803	0.15	1.790	0.17	1.794	0.29
C	2.919	0.24	2.901	0.18	2.912	0.22

The agreement of all three methods is excellent (<1 percent range for each pool). To check for interferences, samples from each pool were remeasured under isobutane chemical ionization (CI) conditions, with monitoring of the $(M+1)^+$ ions for both DAG and glucose BBA samples. The CI results agreed with the EI results within the uncertainties of the measurements.

Our results have shown that both ID/MS methods are very precise, and after exhaustive testing, we have found no bias sufficient to interfere with the intended uses of either method. Therefore, each method satisfies the requirements for a definitive method. However, when the two are compared on identical serum samples, the DAG results are consistently higher than the glucose BBA results by a small but statistically significant amount (<1 percent for all pools tested). When compared on an aqueous glucose solution, the two methods agree within the uncertainties of the measurements. Therefore, the small systematic difference observed is related to the presence of the serum matrix. The two ID/MS methods have been described in a manuscript to be submitted to Biomedical Mass Spectrometry. The excellent agreement of the KH/G6PDH results with the ID/MS definitive method values proves that the CDC method fulfills the requirements of a reference method.

.16 Comparison of Two (IDMS) Methods for Determination of Total Serum Cholesterol

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Both U.S. and international societies for clinical chemistry recognize the need for definitive (i.e., essentially bias-free and highly precise) methods that can serve, along with high-purity SRM's, as the accuracy base for clinical chemistry. NBS has developed a candidate definitive method for total serum cholesterol involving ID/MS. Our publication [Clin. Chem. 26, 854-860 (1980)] provides data that show the absence of interferences in the ID/MS measurements involved in the method and the high reproducibility of the results, thus demonstrating the method's accuracy and precision. To ensure scientific validity, we sought external confirmation by comparison with another laboratory.

Researchers at the Karolinska Institute (KI), Stockholm, Sweden, who were the first to report an ID/MS method for total cholesterol [1], used their method to analyze samples of the same serum pools as were run at NBS. Their analyses gave results with mean values consistently lower than the NBS values for those pools. NBS study of the cholesterol used at the KI as primary standard revealed that it contained lathosterol, an isomer of cholesterol that interfered with the KI measurement method. When the KI reanalyzed the serum pools with SRM cholesterol used as the primary standard, the bias was no longer evident, with mean values for the pools ranging from 1.5 percent below to 1.5 percent above the NBS mean values (Table 2.IX). The imprecision of the results obtained at the KI was about the same for the two series of analyses and were from three to ten times larger than the NBS values. Several aspects of the KI method have been identified as contributing to the imprecision.

Although no systematic bias is now apparent between the two methods, the imprecision of the KI method limits its usefulness for confirming the accuracy

Table 2.IX Total Cholesterol Concentrations as the Mean ± One Standard Deviation of the Mean in mmol/L, for Five Serum Pools, as Determined by ID/MS in Two Series of Analyses at the Karolinska Institute (KI) and One at the National Bureau of Standards (NBS).

Laboratory		Pool				
	N[a]	A	B	C	D	E
KI/first[c] series	8	3.39 ± .058[b]	4.68 ± .036	6.11 ± .046	7.35 ± .054	8.59 ± .088
KI/second[d] series	8	3.39 ± .019	4.73 ± .059	6.15 ± .046	7.57 ± .112	8.85 ± .064
NBS	16	3.43 ± .006	4.72 ± .008	6.15 ± .011	7.47 ± .011	8.79 ± .015

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[a] N is the number of measurements per pool.

[b] Calculated from an analysis of variances [2].

[c] Analyses performed without SRM Cholesterol as the primary standard.

[d] Analyses performed with SRM Cholesterol as the primary standard.

of the NBS method as a definitive method. (The KI method was not designed to serve as a definitive method.) Conversely, the NBS method, which has been rigorously tested for accuracy in-house, does prove that the KI method fulfills the accuracy requirements of a reference method. The comparison of these ID/MS methods has been described in a manuscript submitted to Clinical Chemistry.

References

[1] I. Bjorkhem, R. Blomstrand, and L. Svensson, Clin. Chim. Acta 54, 185 (1974).

[2] J. Mandel and R. Paule, Anal. Chem. 42, 1194 (1970).

.17 Methods Development for the Analysis of Organic Nutrients in Food

J. M. Brown-Thomas and S. A. Margolis

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Center for Analytical Chemistry

The primary objective of this program was to develop and evaluate analytical methods for the analysis of fat and water soluble vitamins in a food matrix which might in the future be used as a Standard Reference Material. Our initial investigations have involved the determination of vitamin D, nicotinic acid, nicotinamide, and thiamin in a nonfat dried milk sample. The methods developed involved initial isolation of vitamins from the matrix by solvent extraction, followed by high performance liquid chromatographic analysis.

a. Vitamin D_2 (Fat-Soluble Vitamin) The method of sample preparation for the analysis of vitamin D_2 utilized an enzymatic hydrolysis of the lipid component of the sample at neutral pH. After pH adjustment of the hydrolysate to 7.7, fatty acids were freed from the matrix by solvent extraction.

High performance liquid chromatography (HPLC) was used for separation of the D_2 and D_3 forms of the vitamin. Figure 2.V shows this separation from a synthetic mixture and Figure 2.VI gives the chromatographic analysis of vitamin D_2 in a milk extract using the method described above.

Final quantitation analysis of vitamin D_2 has not yet been achieved. However, the level of concentration of the vitamin has been determined to be at the low (<50) parts-per-billion level. Further application of the technique will be the analysis of other selected fat-soluble vitamins in this matrix.

b. Nicotinic Acid, Nicotinamide, and Thiamin (Water-Soluble Vitamins) Sample preparation consisted of a 30 min. heat treatment in the presence of 0.5 mol/L H_3PO_4 or CaOH (sat). The resulting solution was adjusted to pH 3-4, passed through a small octadecylsilane (C-18) column and analyzed by HPLC.

Two HPLC systems have been developed for analysis of these extracts. One system involves the use of a cyano (CN) column and a phosphate/acetonitrile mobile phase; the other system uses a C18 column in conjunction with a tetrabutylammonium acetate/acetonitrile mobile phase. Figures 2.VII and 2.VIII are chromatograms of the nicotinic acid extracts. Figure 2.VII is a chromatogram from unspiked milk and 2.VIII is a chromatogram from milk spiked with 50 μg/g of nicotinic acid. These data suggest that the milk sample did not contain detectable levels of nicotinic acid although microbiological assay showed 10 μg/g nicotinic acid. We are now working to resolve this discrepancy.

Both chromatographic systems resolve nicotinamide, nicotinic acid, and thiamin. Future work will be focused on quantitative analysis of these compounds.

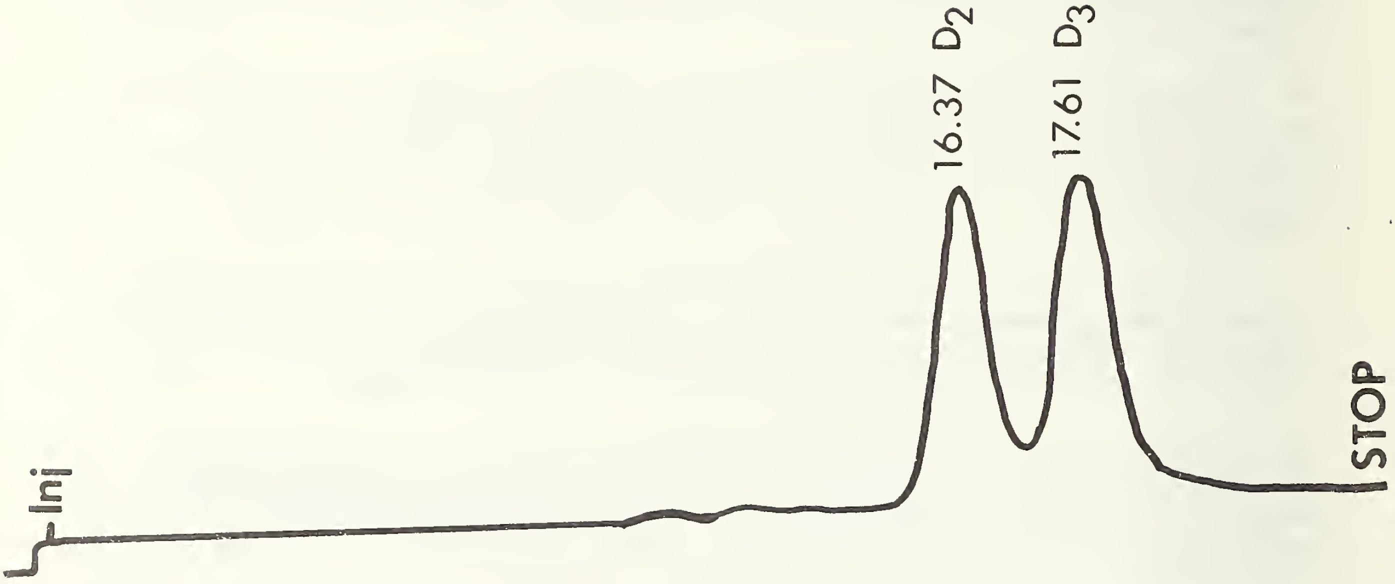

Figure 2.V Separation of Vitamins D_2 and D_3 using a Varian MCH-10 column.
Mobile Phase - 10% methanol in acetonitrile
Detection - UV (267 nm)

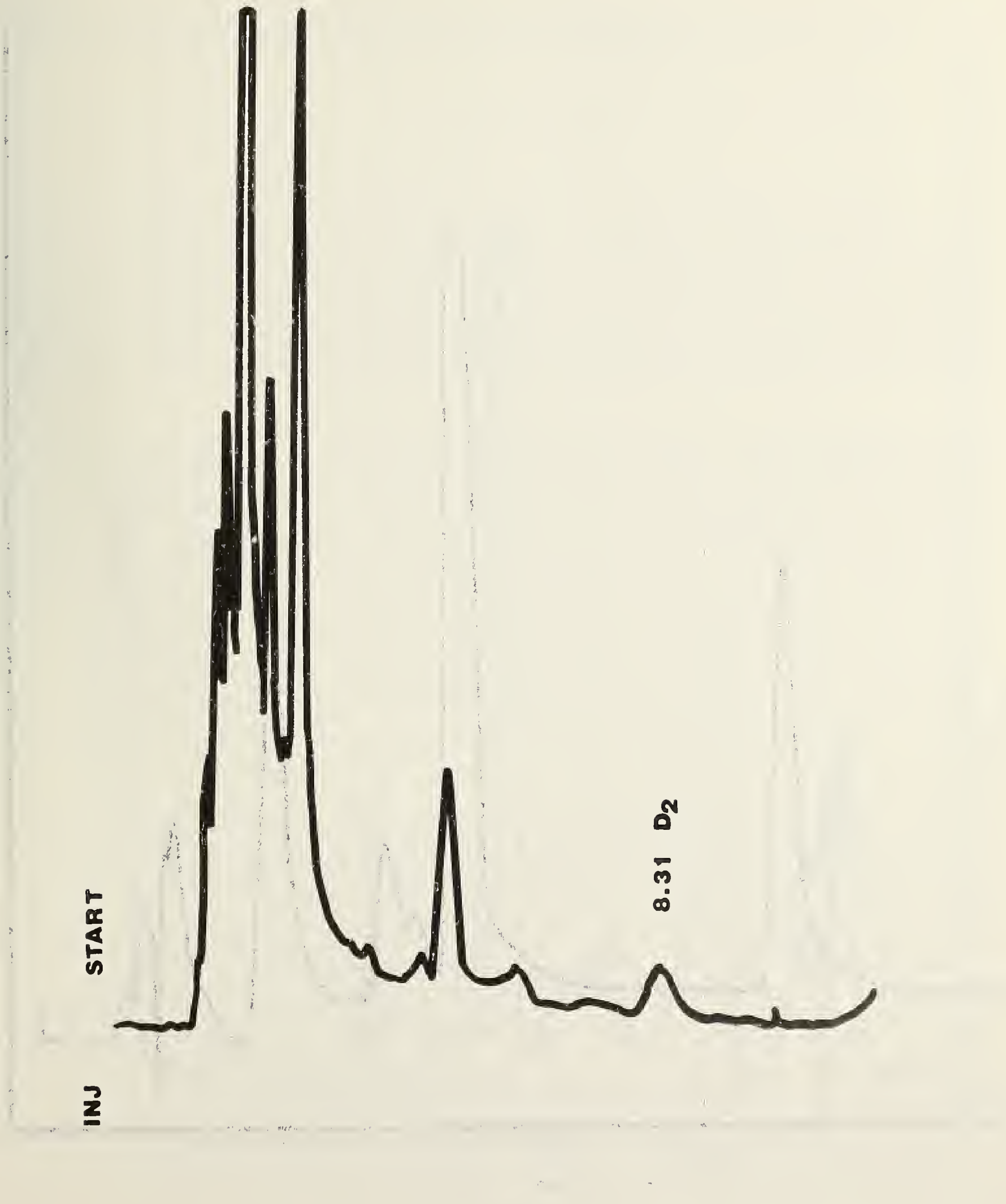

Figure 2.VI Analysis of Vitamin D_2 in a milk extract using a Varian MCH-10 column
Mobile Phase - 10% methanol in acetonitrile
Detection - UC (267)

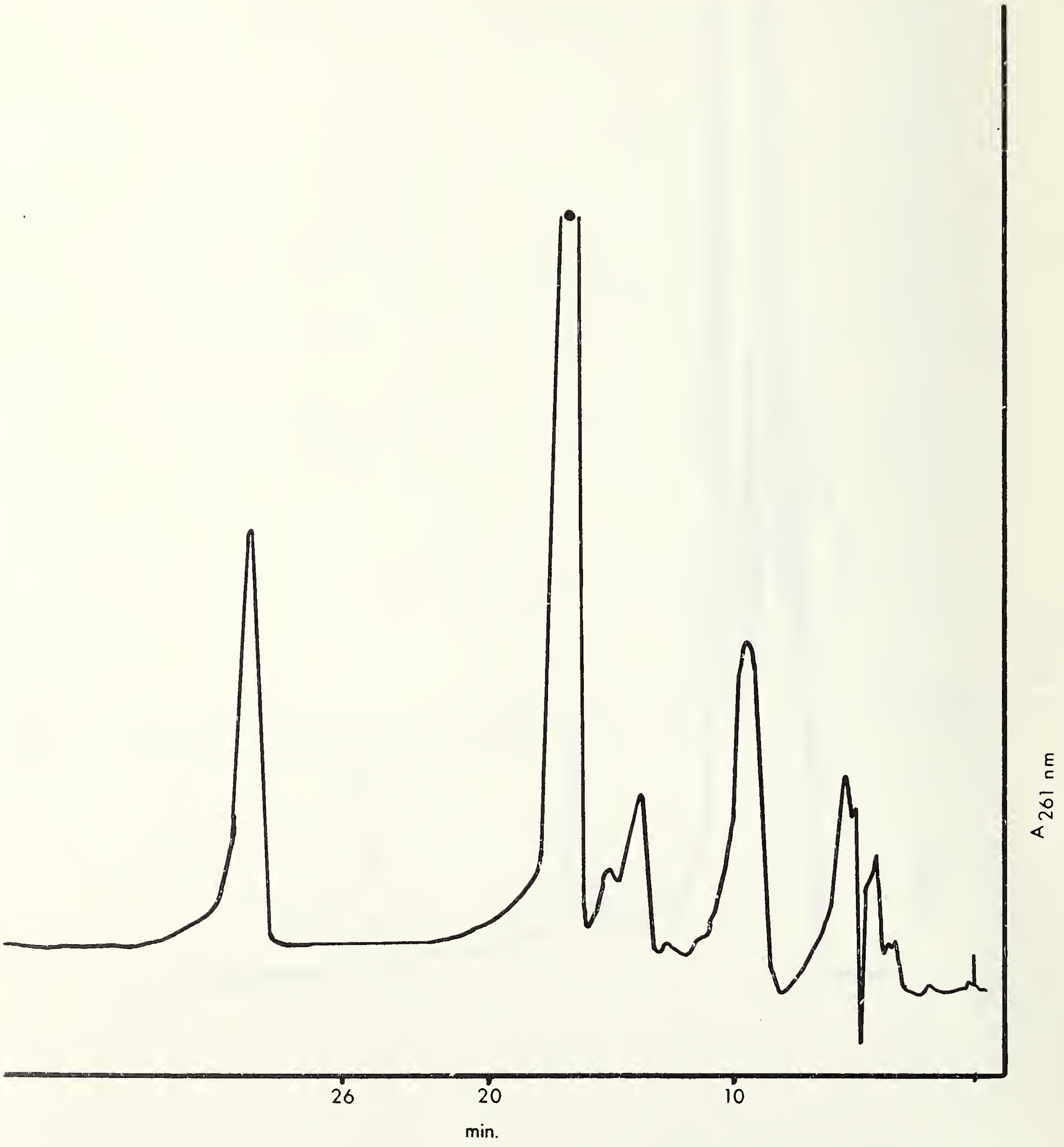

Figure 2.VII Acid extracted sample of dried milk powder.

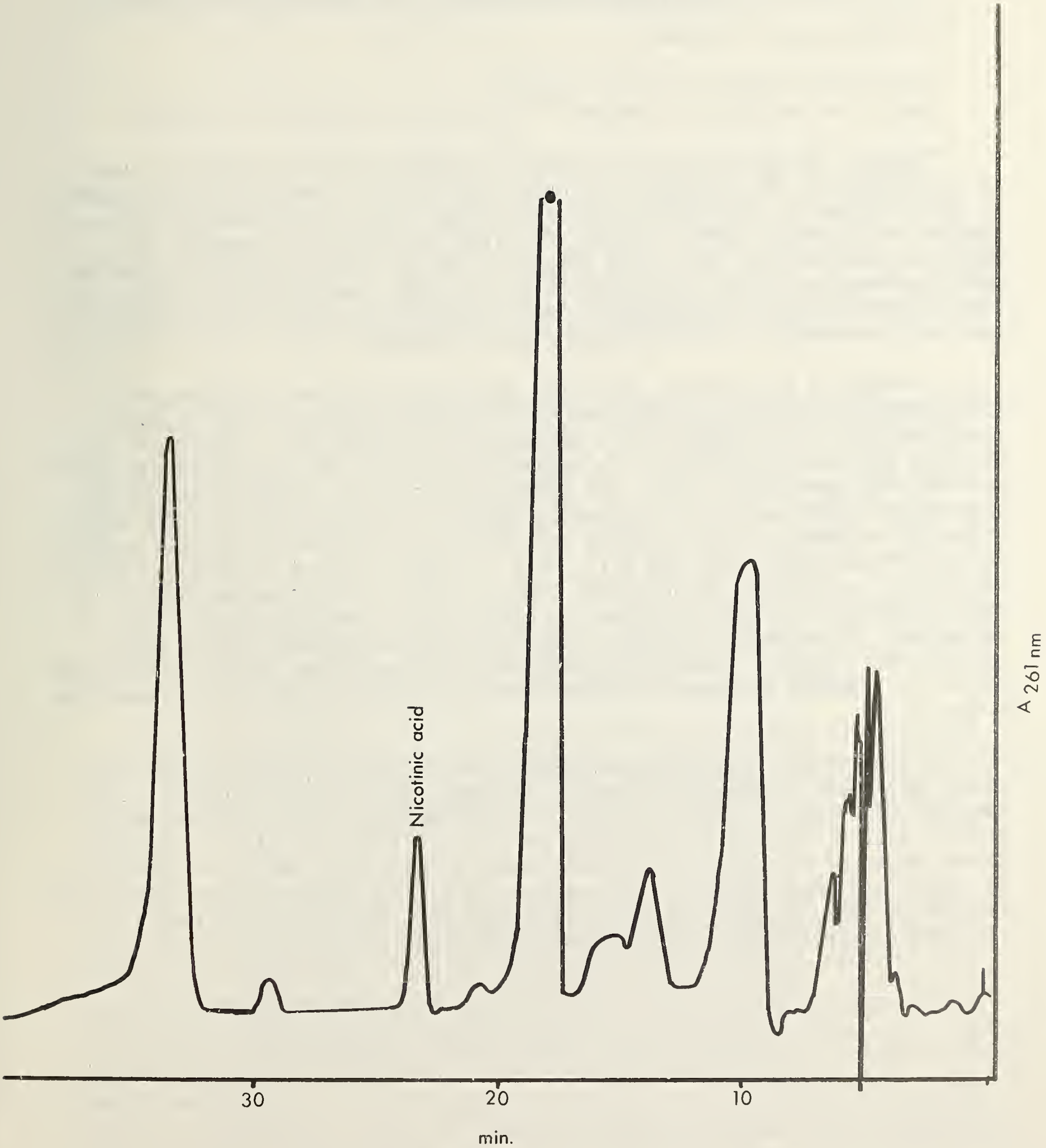

Figure 2.VIII Acid extracted sample of dried milk powder + 50 μg of nicotinic acid.

.18 Surface Reactions Related to Instability of Compressed Gas Mixtures

R. Miller and E. Hughes

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The work during the past six months has been directed primarily toward an evaluation of the desorption of organic molecules from the inner surfaces of gas containers. This work is considered of high priority because of a problem with certain SRM's in which the slow desorption of organics has become evident as the age of the samples increase. These organics probably were absorbed on valves on cylinder walls at some time prior to filling with the SRM mixture and become evident only after a long period of time when the concentration became great enough to measure.

A number of experiments have been performed to isolate the source of the contaminant organics. The preponderance of evidence is that a significant portion of the organics are halogenated hydrocarbons. Trichloroethylene has been identified as a surface contaminant of several valves which had not been previously used. The tentative conclusion was that trichloroethylene had been used as a degreasing agent at some time during fabrication. Attempts to remove all traces from contaminated valves were partially successful and it was found that the valve seat - a small disk of polymeric material -- was a major source of the desorbing organic. When the contaminated seat is replaced with a seat never exposed to organics the concentration of the contaminant is markedly reduced. However, contaminated seats which were washed with alcohol, rinsed with distilled water and baked at 100 °C for eight hours still showed evidence of contamination although a significant reduction occurred.

We plan to continue the experiments with valves in order to prepare a remedy which can be implemented easily by the specialty gas industry. In addition we expect to begin a series of experiments to define the effect on stability of the container condition prior to filling. We will screen a large number of mixtures - both those known to be stable and those known to be stable and those known to be unstable - for water content on the preliminary assumption that the level of water vapor reflects the effort involved in cleaning and drying the cylinder prior to filling.

.19 Thin Film Calibration Standards for Microanalysis

E. B. Steel, E. E. Newbury and P. A. Pella

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Analytical electron microscopy is a rapidly emerging and highly important microanalysis technique. Combining aspects of high resolution microscopy, diffraction, and chemical characterization on a scale of 10 nm or less analytical electron microscopy impacts a vast spectrum of scientific and technological disciplines, including materials science, biology, medical studies, semiconductor technology, solid state physics, catalyst analysis, and chemistry. The AEM chemical analysis methods are, however, limited by an almost total lack of appropriate standards.

The purpose of this research program is to develop appropriate standards for the microanalysis techniques of analytical electron microscopy (AEM). These techniques include energy dispersive x-ray spectrometry (EDS) (for determining elemental constituents with $Z \geq 11$) and electron energy loss spectrometry (EELS for $Z \geq 3$). Standards for analytical electron microscopy must be films with a thickness of the order of 100 nm and lateral dimensions to fit a 3-mm diameter circle. The desired elemental constituents differ depending on the analytical technique in question. For EDS work, it is desirable to have a standard with six or more elements selected such that their characteristic x-ray lines span the range of analytical interest, 1-10 keV. For EELS work, it would be useful to have standards containing lithium, beryllium, boron, carbon, nitrogen, oxygen, and fluorine.

Research activity in FY81 was directed toward producing compositions with low self-absorption of x rays which are appropriate for energy dispersive x-ray spectrometry and electron energy loss spectrometry. Three glass sputtering targets, with the bulk compositions listed in Table 2.X have been prepared. Glass K-411 in Table 2.X is a bulk Standard Reference Material (SRM 470).

The K-411 glass target has been sputtered to prepare 60 transmission electron microscope grids as a candidate thin film standard for a round robin analysis. The glass was sputtered onto a thin (20 nm) carbon film carried on a copper grid. A layer approximately 80 nm thick, as determined by double beam interferometry, was deposited. The thickness appears to be uniform from grid to grid. The thickness was chosen to eliminate the problems of absorption and fluorescence which were encountered with lead glass samples prepared in conjunction with P. Pella in FY80. This thickness gives a good peak-to-background in the EDS spectrum (Figure 2.IX). Aluminum and chlorine were also incorporated into the film due to contamination of the sputtering system. In the preparation of actual SRM materials, these would be eliminated by more careful decontamination.

Trial grids are now being distributed to four cooperating laboratories for evaluation. In addition to AEM analysis, the films will be analyzed by laser microprobe mass analyzer and by secondary ion mass spectrometry at NBS.

If the material passes the tests for homogeneity and stability, a large scale sputtering run of 250 grids will be made for preparation of an SRM candidate in FY82.

Table 2.X Compositions of Bulk Glass Sputtering Targets in Percent Weight

K-line Standards

Glass	Li_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	MnO_2	FeO
K411	---	15.00	---	55.00	---	15.00	---	15.00
K1732	5.00	---	10.00	65.00	12.00	---	8.00	---

L-line Standard

Glass	SiO_2	GeO_2	In_2O_3	BaO	ZnO
K1807	30.00	15.00	5.00	35.00	15.00

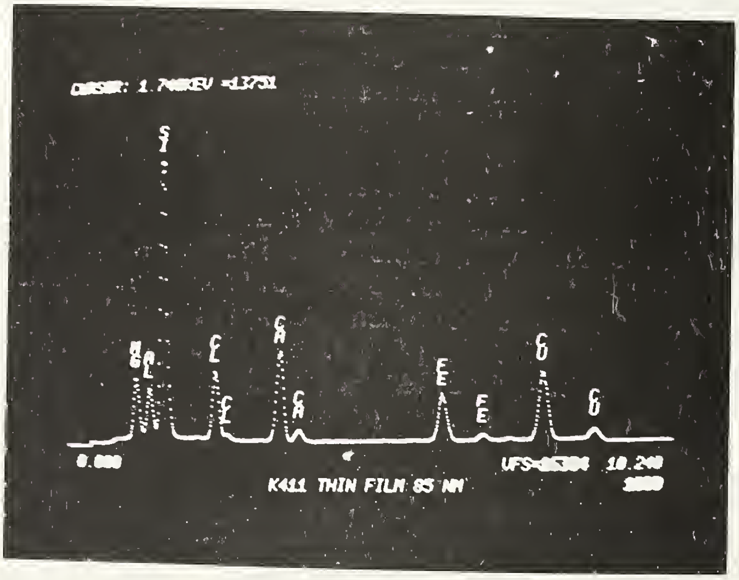

Figure 2.IX Spectrum of glass K-411

.20 Stability Testing of SRM's

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Center for Materials Science

This project was undertaken to determine the conditions under which biodeterioration, either by alteration of the matrix or certified concentration of elements, of biologically-fragile SRM's may occur and to make recommendations for certificate revisions necessary to prevent deterioration of current and projected SRM's by improper storage or handling. Of the SRM's examined, oyster tissue (1566), brewers yeast (1569), orchard leaves (1571), river sediment (1645), wheat flour (1567), and freeze-dried urine (2671, 2672), were sterile. Urban particulate (1648) contained over 20,000 viable microorganisms per gram.

When SRM freeze-dried urine was rehydrated with laboratory distilled water it became contaminated by the resident microbial flora commonly present in distilled water systems. Little or no microbial growth occurred in the contaminated urine when stored at 1 °C; however, at room temperature considerable growth and binding and in some cases volatilization of Hg (the only certified element in 2671) by the contaminants occurred within three days.

Other sterile SRM's can easily become contaminated by bacteria or fungal spores present in the air or on utensils used for sample removal. This will not pose a problem as long as the SRM's remain dry. The a_w (water activity) of the SRM's, defined as the ratio of the equilibrium pressure of water in the SRM to that of pure water at the same temperature (numerically identical to relative humidity), is the best measurement of availability of water to microorganisms [cf. Table 2.XI]. Microbes will not grow at $a_w < 0.60$, and all the SRM's examined had a_w values less than this value. Therefore, as long as these

Table 2.XI Incubation time (hours) required for 2 g quantities of wheat flour SRM to attain different a_w values when stored at various relative humidities (30 °C).

	Incubation Humidity				
a_w attained	60%	72%	86%	93%	100%
0.60	46	3/4	1/2	1/4	1/4
0.72	-	7 1/2	1	3/4	1/2
0.86	-	-	7 1/2	2	1
0.93	-	-	-	31 1/2	14
1.00	-	-	-	-	46

SRM's are opened only at relative humidities <60% they should not undergo biodeterioration, even if they are, or become, contaminated with microorganisms. However, at higher humidities, the biological SRM's rapidly take up water from the atmosphere and attain a_w values permitting microbial growth within hours or even minutes depending on the relative humidity they are exposed to. For example, 2-g quantities of brewers yeast or oyster tissue, which both support heavy fungal growth at $a_w = 0.70$, will reach this water potential after 1/2 and 1 3/4 hours, respectively, at 93% relative humidity. The table shows incubation times required for wheat flour SRM to reach different a_w values when incubated at various relative humidities.

Once microbial growth occurs, certified elements may be accumulated or volatilized by the contaminants. Both events occur with mercury in the urine SRM. Experiments to detect microbial volatilization of certified elements in other SRM's have not indicated this occurs. Current experimentation using a coupled gas chromatograph-atomic absorption system should improve our sensitivity and may reveal certified element volatilizations by contaminating fungi and bacteria growing in certain SRM's.

.21 Eddy Current Standards

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Center for Materials Science

The eddy current method is widely used in both the ferrous and non-ferrous metals industries for nondestructive detection of flaws such as cracks, inclusions, and variations in composition and microstructure in metals and metal parts via local changes in electrical conductivity. Primary conductivity standards are needed for reliable execution of this work, but to date, this need has been supplied by industry itself. The necessary range of conductivity for industrial testing is from 5.85 to 58.5 MSm^{-1} (1 to 100% IACS). NBS is currently acting on the provision of Al alloy standards in the mid-range of 17 to 35 MSm^{-1} (29 to 60% IACS). One hundred sets of four aluminum samples covering this conductivity range have been supplied to the Electrical Measurement and Standards Division for final calibration.

The properties desired in a primary conductivity standard are long term stability, durability, and low magnetic susceptibility. (In testing of high susceptibility steels, normal practice has been to apply a saturating magnetic field to reduce the differential permeability to a value near that of vacuum.) Hence, elemental metals and alloys of equilibrium phase composition, upon which stable nonconducting surface layers can be formed, are desirable. The surface properties are important not only for durability, but for reproducible lift-off behavior as well.

The overall aim is the selection of metals and alloys suitable for primary conductivity reference standards in the 5.85 to 14.6 and 35 to 58.5 MSm^{-1} conductivity ranges, and the preparation of specifications for their preparation and fabrication. Nine candidate materials which appear suitable on the basis of their reported physical properties and probable homogeneity and phase and surface stabilities have been identified.

The following metals and alloys will display conductivities within 1% IACS of the stated values:

Material (w/o)	Conductivity (% IACS)
OFHC Cu	100%
1.3 Zn + Cu	85%
2.4 Zn + Cu	72%
21.5 Zn, 2.5 Al + Cu	23%
7 Al + Cu	17%
1.5 Si + Cu	12%
3.0 Si + Cu	7%
Commercially pure Ti	3.5%
8 Al, 1 Mo, 1 V + Ti	1%

For these materials we are investigating the likelihood of attaining the desired metallurgical and surface properties. Questions concerning these materials and their preparation -- quality of starting materials, conditions of melting and solidification, heat and mechanical treatment, possible adverse affects in cutting, machining, and surface preparation -- are being addressed by search of the literature and inquiry of industrial practitioners about their experience and methods and by specific research as necessary.

This project is jointly funded by the Metallurgy Division, Office of Nondestructive Evaluation and OSRM.

.22 Abrasive Wear Standard

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Metallurgy Division
Center for Materials Science

This project is concerned with improving an abrasive wear test that is widely used in industry. It has been estimated that perhaps 50% of all wear can be traced to abrasion. Excavating, mining and agricultural machinery as well as a variety of equipment used in processing and handling abrasive material must be designed to minimize abrasive wear damage. Accurate data and appropriate test procedures are necessary both for equipment design purposes and to assist in the development of more economical and improved materials. The new ASTM standard dry sand/rubber wheel abrasive wear test (G65-80) is found to yield results that correlate well with service behavior when the stresses imposed on abrasive particles are relatively small. Project staff members have made significant contributions to the development of this standard test and participated in several interlaboratory test series.

The value of the standard dry sand/rubber wheel abrasive wear test method depends critically on an appropriate calibration procedure. Calibration is best accomplished through the use of reference specimens having consistent and well established wear behavior. Reference specimens of D-2 tool steel have been developed and are ready for issue. The specimen material was selected on the basis of our own studies and recommendations of ASTM G-2 committee members employing the dry sand/rubber wheel test. The reference specimens will be sold by NBS this fall in sets of 3 for use in standardizing this test. The possibility of developing additional reference wear test materials having higher and lower wear resistance than D-2 tool steel is currently under study.

The project to develop Standard Reference Materials for the dry sand/rubber wheel test has also included an extensive investigation of the effects of various machine test parameters and conditions. Abrasive wear data gathered during the past year concerning test variable effects have been analyzed and tentative conclusions have been reported in a draft report. Gaps in the information and questionable data will be the subject of future tests, including the effect of the lapse time or test order, moisture content of the sand, and sand flow rate. The machine is now operating with an arm that incorporates a load cell to measure the friction force. An infrared sensor is also in use to measure the surface temperature of the rubber rim. Both of these measured test parameters are being recorded on a dual channel recorder. To increase data recording and analysis capabilities an eight channel digital recorder is being made ready for operation.

.23 Particle Shape Characterization

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Center for Materials Science

Quantitative image analysis is being employed in another project to develop meaningful sand particle shape parameters which relate to their abrasiveness in wear tests. This project, is focused on characterizing the abrasive specified for the ASTM Dry Sand/Rubber Wheel Abrasion test. Abrasive shape has been shown to greatly affect abrasive wear and a more quantitative measure for particle shape could result in improved reproducibility. The goal of this study is to produce a standard method to conventional image analyzing equipment. During the past year a perimeter ratio method was seen to discriminate between sands with three different origins: foundry sand, beach sand, and crushed quartz. Future work involves exploring the variability of the perimeter ratio among batches of foundry sand, studying instrumental limitations for measuring perimeter ratios, and generating sampling requirements to obtain statistically significant values of the shape parameters.

.24 Pitting and Crevice Corrosion Standards

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Center for Materials Science

This project has dealt with the production of a standard test method for pitting and crevice corrosion of surgical implant metals. This ASTM test method is now at the Society Ballot level. Emphasis of the research this year has been on specimen design and test configuration and procedures. The test materials have been 316L stainless steel. The NBS laboratory acquired 316L stainless steel material from the same supplier as the one for the round robin test material. Eight specimens were made and additional tests were conducted to check various steps in the procedure. Contribution to the ASTM F-4 Committee on Medical Material and Devices was made including participation in two separate rounds of round robin testing. As a result of the first round robin, the specimen design and test configuration were changed to permit more accurate and valid testing. Preceding the second round robin tests, the passivation treatment used for implant metals was inserted in the procedure. It is probable that after some minor revision, this ASTM Standard of Test for Pitting or Crevice Corrosion of Metallic Surgical Implant Materials will be established. It will be the first corrosion standard test for surgical implant metals. Work is being done to refine the test method and also to produce a Standard Reference Material for 316L stainless steel and plans are being made to provide Standard Reference Materials for other surgical implant metals.

.25 Crystallite Microsize

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Center for Materials Science

The measurement of mean crystallite size by x-ray powder diffraction techniques is rapid and nondestructive. Crystallite size measurements are often used to characterize catalysts. However, techniques and analysis methods vary widely from laboratory to laboratory. The goal of this project is to provide a set of reference materials of well characterized mean crystallite size between 100 and 1000 Angstroms.

Cubic MgO was chosen as a candidate material because two sets of diffraction planes can be analyzed by the Warren-Averback method of analysis of diffraction line profiles to provide mean crystallite size values for two different crystallographic directions. MgO can be prepared either by precipitation followed by calcination or by collection of the smoke due to controlled burning of magnesium metal. The latter method is being developed to provide a calibration sample where the crystallites are not agglomerated and simultaneously have well developed crystallographic habit.

Initial SEM results have shown some, but not all, of the sufficient smoke particles for parallel diffraction and SEM calibration is being attempted. Preparation of the large quantities needed for a SRM of MgO will be by precipitation/Calcination methods. The precursor used to date is magnesium oxalate. Calcination at 600°C for one hour has yielded a sample with mean crystallite size of about 150 Angstroms. As expected the crystallites are extensively agglomerated. The crystallites have poorly developed habit; some even appear as doughnuts. Other precursors are being tested which hopefully will lead to crystallites with improved habit.

.26 Glass SRM Research

M. J. Cellarosi

Ceramics, Glass and Solid State
Science Division
Center for Materials Science

a. Glass Dielectric Constant SRM

This task was undertaken by NBS after the recommendations of ASTM Committee C14.04 on Physical and Mechanical Properties of Glass. Glass is used extensively in electrical/electronic applications, and an SRM for this property is designed to support the expanding role and sophistication of glass in this area.

During the year, interlab measurement activities were continued, several discrepancies in procedures and calibrations were resolved. This work is almost completed.

Viscosity SRM 711 samples were used over the frequency range 400 Hz to 10 kH_z. Statistical analysis of the data indicate that SRM 711 will qualify for Dielectric Constant SRM status. A new 3-electrode test cell fixture developed by NBS to minimize errors due to inductance/capacitance and stray factors was evaluated and accepted by ASTM for inclusion in standard procedures.

b. Glass Viscosity SRM

In anticipation for renewal of SRM 710 (Soda-lime glass), work to build a new precision viscometer was continued. NBS glass viscosity standards are very important in glass manufacture and research. Initial calibrations of the torque sensor assembly and rotational mechanism were carried out. Data indicate the need for modifications to insure better precision/reliability.

c. Glass High Temperature Resistivity SRM

Glass resistivities as a function of temperature in the molten range are important parameters for effective utilization of electric power and for productivity. NBS leads an ASTM task group on interlab testing, and to develop standard methods. A second round robin is in progress with SRM 711, which is already certified for electrical resistivity in the lower temperature ranges.

SRM 711 will also be certified for dielectric constant and loss characteristics, so this glass will cover a broad range of electrical properties. NBS statistical analysis of the first round robin indicated serious measurement discrepancies in the very high temperature range. NBS research is planned for FY82 to help resolve these problems.

.27 Computer SRM Research

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Center for Computer Systems Engineering

The SRM 3210 calibration system was completed and the production and issuance of the flexible disk cartridge SRM 3210 was successfully initiated. This effort included the development of the required documentation for the associated NBS SRM 3210 certificate.

Two members of the Computer Storage Media Group visited the R and D facility of the Storage Technology Corporation, Louisville, CO. They were given specialized information relative to the STC Very High Density (VHD) magnetic streaming media development program. It is anticipated that the Media Group will be requested by the industry to produce a Very High Density (VHD) magnetic streaming media SRM as soon as they finalize their approach. These VHD streaming media will perform as important backups to the state-of-the-art Winchester technology disk systems.

The minicassette SRM program which has been requested by the U.S. magnetic media industry (see ANSI draft standard X3B5/81-14 or later edition) was initiated by the Computer Storage Media Group as a secondary effort while awaiting VHD media decisions. Four reference minicassett transports and an initial lot of 100 potential minicassette SRM candidates were purchased. A Field Control Unit was designed in the media laboratory which controls the minicassette tape motion in both directions at high or low speeds. Read/write control circuits and a continuously varying write current control system were also designed.

.28 Thermal Insulation SRM Research

J. G. Hust

Thermophysical Properties Division
Center for Chemical Engineering

a. Fiberboard.

Measurements have been completed and an equation has been developed describing the experimental data to within the uncertainty of the measurements. The measurements and equation include a temperature range from 100 K to 350 K, gas pressures from high vacuum to atmospheric pressure, various specimen densities, and fill-gas species. The results of this work are now being correlated with Center for Building Technology results (at ambient conditions) and a special publication and certificate are in process.

b. High Temperature Insulation.

Various insulations for high temperature use have been considered during FY-81. A tentative selection of a commercial supplier has been made. The insulation selected has promising handling characteristics (similar to fiberboard) and, based on preliminary screening tests, appears to be adequately homogeneous. Homogeneity is a more serious problem with most of the high temperature insulations which have been considered.

2.5 SRM Production

This section contains selected highlights for SRM production projects in FY81.

.1 Benchmark Low Alloy Steels--SRM 1261a-1265a

Renewals of the "1200 Series," 1261a-1265a have been prepared from the same ingots used for the original series, but from adjacent positions within the ingots. With the exception of sulfur, little or no change in elemental composition was observed by comparison analysis utilizing several analytical techniques. For sulfur, analysis was made by the "definitive" method of spark-source, mass spectrometry-isotope dilution, by using the chip forms (SRM's 361-365) and comparing these values to values measured in chips taken from the disk form (SRM's 1261a-1265a) by combustion-infrared. The sulfur values that should be used, whether for the original series or the renewals are: 1261, 1261a, -0.015%; 1262, 1262a-0.037%; 1263, 1263a-0.005_7%; 1264, 1264a-0.025%; 1265, 1265a-0.0055±0.0003%. This certification was a cooperative project undertaken as part of the ASTM-NBS Research Associate Program.

.2 Line Pipe Steel--SRM 1269

SRM 1269, Low Alloy Steel (AISI 1526, Mod.) has a composition chosen for the "line pipe" steel industry. In addition, this SRM is expected to serve as Supplement No. 2 to the "1200 Series" of Irons and Steels. Twelve elements are certified, with chemical information given for 25 additional elements. This certification was a cooperative project undertaken as part of the ASTM-NBS Research Associate Program.

.3 2 1/4 Cr--1 Mo Low Alloy Steel--SRM 1270

SRM 1270, 2 1/4 Cr-1 Mo Low Alloy Steel (A366 F22) - Planning for this SRM was coordinated through the Task Group on Temper Embrittlement, American Petroleum Institute. In addition, this SRM is expected to serve as Supplement No. 1 to the "1200 Series" of Irons and Steels. Eleven elements are certified, with chemical information given for 18 additional elements. This certification was a cooperative project undertaken as part of the ASTM-NBS Research Associate Program.

.4 Cast Steel--SRM C1173

The Composition of SRM C1173 was tailored to extend and complement existing SRM's 1138a, Cast Steel 1, and 1139a, Cast Steel 2. In so doing, a steel was obtained that exhibited unusual hardness properties.

For example, the directionally solidified "as cast" material exhibited a high hardness for the chill-cast surface (HRC 58 to 60). This is essentially the same as the water quench hardness *HRC 60); however, the surface opposite the chill-cast surface was relatively soft and permitted machining and stamping operations. With proper heat treatment, a very workable material was obtained (HRC 28). The concentration of twelve elements are certified in SRM C1173 (C-0.453, Mn-0.174, P-0.031, S-0.092, Si-1.38, Cu-0.204, Ni-4.04, Cr-2.63, V-0.42, Mo-1.46, Co-0.064, and Ti-0.037; all in % by weight). In addition, information values are given for six elements (Al, As, B, Pb, Nb, Zr). This certification was a cooperative project undertaken as part of the ASTM-NBS Research Associate Program.

.5 High Alloy Steels--SRM's C1287-C1289

SRM's C1287-C1289, High Alloy Steels, supplement the SRM's C1152-C1154, Stainless Steels, the "C" preceeding a SRM number denotes that the specimens were chill cast by a rapid unidirectional solidification technique. SRM C1287, ACI HK (AISI 310 Mod.), is certified for NI 21.16%, Cr 23.98%, and 13 other elements, with chemical information on 5 additional elements. SRM C1288, ACI CN-7M (A-743), is certified for Ni 29.3%, Cr 19.55%, Cu 3.72%, and Mo 2.83%, and 9 other elements with chemical information on 5 additional elements. SRM C1289, ACI CA-6NM (AISI 414 Mod.), is certified for Ni 4.13%, Cr 12.12%, Mo 0.82%, and 10 other elements, with chemical information on 5 additional elements. This certification was a cooperative project undertaken as part of the ASTM-NBS Research Associate Program.

.6 Hafnium Certified in Zirconium and Zircaloy-4--SRM's 1234-1239

Three zirconium metal and three Zircaloy-4 metal SRM's have been certified for their hafnium contents. Hafnium was determined by two independent analytical methods: isotope dilution-spark source mass spectrometry, and neutron activation. The concentrations range from 46 to 198 µg/g in SRM's 1234-1236, and from 31 to 178 µg/g in SRM's 1237-1239. The concentrations of 22 additional elements present in each SRM are listed for information only. A number of these may be certified at a later date as a result of collaborative testing.

The SRM's are in the form of solids 32 mm square and 19 mm thick. They are intended for use primarily in validating experimental data and in calibrating optical emission and other instrumental methods of analysis.

Because of its high capture cross section for neutrons, hafnium adversely effects the cost of producing nuclear power. Therefore, hafnium in reactor-grade, zirconium and Zircaloy must be removed down to parts-per-million levels. However, the difficulty of determining ppm concentrations of hafnium has led to disagreements between buyer and seller of reactor-grade zirconium materials. The reliability of hafnium determinations can be improved by analyzing unknowns relative to these new SRM's.

.7 15% Austenite in Ferrite--SRM 486

SRM 486 is intended for use in the calibration of x-ray diffraction equipment which is used in determining the amount of retained austenite in ferrous materials over the range of 10 to 20 percent. X-ray diffraction procedures recommended for these determinations require accurate measurements of the integrated intensity for a number of selected peaks.

Each specimen was individually certified by determining the nickel content by x-ray fluorescence. The calibration of the XRF measurements was based on the austenite content in 12 specially prepared specimens as measured with a quantitative microscope (QM). The certified value is believed accurate to within ±0.5 percent austenite. In special cases SRM 486 may be used as an x-ray fluorescence standard for determining the nickel content in nickel-iron or nickel-chromium-iron alloys.

.8 Dye Penetrant Test Block--SRM 1850

NBS recently began issuing this novel SRM, which contains accurately measured surface "cracks." It is intended for use in checking the sensitivity and performance of liquid dye penetrants and dye penetrant crack detection systems, as well as other systems and devices for surface defect detection.

The SRM test block (a cross section of a laminate of electrodeposited nickel and copper--the copper being electroetched to form the "cracks") is about 1/2 cm wide and 2-cm long and is mounted in an epoxy-resin disk about 5-cm in diameter and 1-cm thick. Each block contains four cracks approximately 0.2, 0.5, 1, and 2 μm wide with a separation distance of about 1.5 mm. Crack depth is several times the width--beyond the critical depth for showing dye penetrants.

The widths of the cracks at the middle of the block were determined from measurements made on a metallographic microscope using a filar micrometer eyepiece at a magnification of 1200. The accuracy of these measurements was checked by measuring the cracks in several test blocks with a scanning electron microscope (SEM) that had been calibrated for magnification accuracy by SRM 484a. Agreement was within 0.1 μm for the widest cracks to 0.06 μm for the narrowest.

9. Obsidian Rock and Basalt Rock--SRM's 278 and 688

NBS has issued two new geological reference materials, SRM 278, Obsidian Rock, and SRM 688, Basalt Rock. The two SRM's are intended for use in evaluating the accuracy of analytical methods and instruments used to analyze geological materials. Both SRM's are extremely homogeneous and offer the advantage of representing an actual geological material of the type frequently encountered by the mining and metals industry in geological research.

SRM 278 and SRM 688 are in the form of a fine powder which was crushed and ground to pass a 200 mesh sieve. SRM 278, Obsidian Rock, is certified for 18 major and trace constituents, with information given for another 16 trace constituents. SRM 688, Basalt Rock, is certified for 14 major and trace constituents, with information values given for another 17 trace constituents.

.10 Soda-lime-silica Glass for Gradient-furnace Liquidus Temperature--SRM 773

Standard reference material 773 is a soda-lime-silica glass that is certified for its liquidus temperature and is for use in checking test methods and in calibrating equipment specified in the ASTM C829-76 standard practices. Two methods are included in this ASTM standard, differing in the form of sample, apparatus, procedure for positioning the sample, and measurement of temperature gradient in the furnace. Certification of the materials was carried out at NBS by Mr. Mario Cellarosi.

Method A employs a trough-type platinum container (boat) in which small glass particles are fused together. Method B employs a perforated platinum plate on which larger glass particles are individually positioned one per hole, and are therefore melted separately from each other.

Certified values for the gradient-furnace liquidus temperature (allowing 24 hr. to reach equilibrium) are:

Method	Liquidus Temperature
A	988 ± 3 °C
B	991 ± 5 °C

SRM 773 is issued as a set of seven pieces, each one about 2.5-cm square by 0.6-cm thick. Prior to using the material it must be crushed by the user in accordance with the ASTM recommended procedure.

.11 Optical Microscope Linewidth Measurement Standard--SRM 475

SRM 475 is a reduced version of an earlier linewidth measurement standard--SRM 474. The new item is the same type photomask except rows C and D (which are repetitions of rows A and B) have been omitted to reduce the cost of calibration and certification at NBS.

This reduction benefits the customer in that the price for the new unit is about one-third lower than the earlier configuration.

SRM 475 is certified for measurement of linewidths from 0.5 to 10 μ. It continues to be of special interest to producers of integrated circuits because it is designed to assist measurement of opaque lines and clear spaces on integrated circuit photomasks in transmitted illumination. The accuracy of measured linewidths is the same as the earlier SRM which is equal to ±0.05 μm or better.

.12 Silicon Resistivity Standard for Eddy Current Testers--SRM 1523

SRM 1523 is a resistivity scale reference for the semiconductor industry. It can be used as a reference for semiconductor resistivity measurements based on the four-probe method (ASTM Method F-84-73) as well as those made by the eddy current method (ASTM Method F-673-80). The SRM consists of two slices of boron-doped silicon. One slice of (100) orientation, Czochralski grown with a nominal resistivity of 0.01 Ω/cm and the other slice of (111) orientation, float-zone grown with a nominal resistivity of 1 Ω/cm. Each slice has been individually measured and certified for resistivity by NBS.

.13 Polystyrene (narrow molecular weight distribution)--SRM 1479

SRM 1479 has been certified to have an average molecular weight of 1,050,000 g/mol, with a systematic error not expected to exceed 7%. The material is intended for the calibration and checking of instruments used in polymer technology for the determination of molecular weight and as a characterized sample for measuring other physical properties of polystyrene.

The new material is the third polystyrene to be certified for molecular weight. The two earlier offerings are SRM 705 (narrow molecular weight distribution) with an average molecular weight of 179,000 g/mol and SRM 706 (broad molecular weight distribution) having an average molecular weight of 258,000 g/mol.

.14 Butyl Rubber--SRM 1495

SRM 1495, isobutylene-isoprene (butyl) rubber has been certified for Mooney Viscosity Number according to the procedures described in ASTM Method D1646-74. The material is issued in bales of approximately 34 kg and is intended for checking the performance of Mooney viscometers when applied to rubber and rubber-like materials. The (ML 1+8) value for the SRM is 37.3 at 125 °C and 53.0 at 100 °C, while the (ML 1+4) value is 40.4 at 125 °C and 56.3 at 100 °C.

.15 Potassium Chloride for Solution Calorimetry--SRM 1655

SRM 1655 is for use in verifying or comparing results obtained by calorimeters measuring enthalpies of endothermic solution processes.

Normally, electrical energy calibrations are performed, and deviation of measured values from the certified value for the enthalpy of solution may serve as an indication of systematic errors in the calorimetry. If proper measuring instruments for electrical energy calibration are not available, the material may be used as a standard for calibrating a calorimeter. The material is certified with respect to the enthalpy of the endothermic process of solution in water when carried out under specified conditions. The energy absorbed during the solution of SRM 1655 in distilled water at 298.15K to form a solution with molality $m = 0.111$ $\mathrm{mol \cdot kg^{-1}}$ is (235.86±0.23) $\mathrm{J \cdot g^{-1}}$.

.16 Benzoic Acid, Acidimetric Standard--SRM 350a

This Standard Reference Material consists of highly purified benzoic acid and is intended for use in acidimetric standardization. It has a certified acidimetric assay of 99.9958±0.0027 weight percent and is homogeneous within the bounds of the random error uncertainty of the measurement process. Stereo and polarized light microscopic examination of the material, revealed no fluid inclusions or particulate contamination.

.17 TRIS, Basimetric Standard--SRM 723a

This Standard Reference Material consists of highly purified 2-amino-2-(hydroxymethyl)-1,3-propanediol [tris-(hydroxymethyl) aminomethane] (referred to as "TRIS"). It is intended for use in basimetric standardization, with a basimetric assay of 99.9703±0.0028 weight percent. No evidence was found for variability between samples from different segments of the lot beyond that accounted for by the random error of measurement. Thus, the material is considered to be homogeneous within the indicated uncertainty limits. Stereo and polarized light microscopic examination of SRM 723a show no significant particulate contamination.

.18 Human Serum--SRM 909

This SRM, the first certified by NBS for constituents normally found in human serum, was issued about one year ago. At that time it was certified for calcium, chloride, glucose, lithium, potassium, and uric acid. Subsequently, additional certification has been provided for cholesterol and magnesium. In addition, the concentrations of the seven enzymes have been determined in this SRM by a collaborative study using "best available" methods. The enzymes are: acid phosphatase (low level), alkaline phosphatase, alanine aminotransferase, creatine kinase, lactic dehydrogenase, and gamma glutamyltransferase.

.19 4-Nitrophenol--SRM 938

SRM 938, 4-Nitrophenol has been certified for use in calibrating spectrophotometers for clinical analyses in which 4-nitrophenol is the chromogenic compound that is formed. The certified apparent specific absorbance of the material at 401 nm and 23.5 °C is 131.48 ± 0.33 $L \cdot g^{-1} \cdot cm^{-}$ for solutions containing between 4 and 5 $mg \cdot L^{-1}$ in aqueous 0.010 $mol \cdot L^{-1}$ sodium hydroxide. Analysis of the material indicates 99.75% purity and no 2- or 3-nitrophenol at a detection limit of 1 part per 1000.

.20 Sodium Pyruvate--SRM 910

This Standard Reference Material (SRM) is certified as a chemical of known purity, especially for use in clinical chemistry. It is intended primarily for use in the calibration and standardization of procedures for pyruvate, lactic dehydrogenase, and glutamic-pyruvic transaminase determinations in clinical analyses, and for critical evaluation of the routine working or secondary reference materials used in these procedures. The material is certified as being sodium pyruvate, 98.7%, and parapyruvate, 0.9%.

.21 Oxygen in Nitrogen, 21 Mole Percent--SRM 2659

SRM 2659 supplements the two SRM's previously issued for 2 and 10 mole percent oxygen in nitrogen. They are intended for use in the calibration of instruments used for combustion control and respiratory gas analysis.

The nominal concentrations of oxygen in the three SRM's are:

SRM 2657	2 mole % Oxygen
SRM 2658	10 mole % Oxygen
SRM 2659	21 mole % Oxygen

Each cylinder is individually analyzed. The uncertainty in the certified oxygen concentration at the 95% confidence level does not exceed 1.0% relative. These SRM's were developed primarily for use in U.S. Environmental Protection Agency Method 20 which requires continuous source emission monitors for measurements of O_2 and NO_x. One of the procedures for determining the concentrations of O_2 and NO_x in the calibration gases uses SRM's as specified in EPA Protocol No. 1 (Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors).

.22 Sulfur Dioxide in Nitrogen for Stack Gas Analysis

In March 1981, several additional concentrations were made available in series of SRM's used in calibrating stack gas analysis. The complete range now is as follows:

SRM	Nominal Concentration ppm
1693	50
1694	100
1661a	500
1662a	1000
1663a	1500
1664	2500
1696	3500

.23 Methane and Propane in Air--SRM 1660a

This new standard reference material is intended for use in calibrating instruments used to differentiate the methane and nonmethane fractions of hydrocarbons in the atmosphere. Its nominal composition is 4 ppm methane and 1 ppm propane, in air, where each cylinder is analyzed and an individual certificate is issued. The SRM is intended as a primary standard of ambient air quality to which the concentrations of daily working standards may be related.

.24 Generator Columns for Polynuclear Aromatic Hydrocarbons--SRM 1644

This SRM was developed to generate known, accurate concentrations of anthracene, benzo(a)anthracene, and benzo(a)pyrene in water. Accurate concentrations of these low-solubility compounds, which range from 1 to 50 μg/kg (ppb) are difficult to achieve by other techniques. The certificate for this SRM lists the certified concentrations that are obtained when the generator columns are used as directed. The SRM consists of three stainless steel tubes, each packed with sea sand that is coated with one of the three compounds. In operation, a saturated solution results when water is flowed through the tube at a flow rate between 0.1 and 5 mL/min. The aqueous concentrations were determined by methods using high performance liquid chromatography and fluorescence. These two independent analytical methods gave concordant results.

Many compounds classified as polynuclear aromatic hydrocarbons (PAHs) are known to be carcinogenic or cocarcinogenic. Their determination in water samples is necessary to assess the environmental hazards associated with increased use of coal and the development of synthetic fuels. Anthracene, benzo(a)anthracene, and benzo(a)pyrene were selected to represent PAHs, because they have a three, four, and five-condensed ring structure, respectively, and are EPA Priority Pollutants.

.25 Stabilized Wine--SRM 1590

SRM 1590 is intended primarily for evaluating the accuracy of ethanol determinations in wine and calibrating the instruments used in these determinations. Disputes over the ethanol content of wines may be attributable to discrepant analytical results among laboratories. Because of the difficulty of validating these results, the American Society of Enologists suggested the development of this wine SRM to validate analytical data.

In addition to the certified concentration of ethanol, the certificate of analysis provides information on the concentrations of copper, iron, potassium, sodium, volatile acidity, and total acidity. These values, which are not certified, were obtained as a result of a collaborative study conducted by the American Society of Enologists. Samples were analyzed at NBS by two independent analytical methods: gas chromatography and titration of the ethanol after separation.

.26 Reflection Step Tablet--SRM 2061

Standard reference material 2061 is a calibrated reflection step tablet having 12 steps that cover the optical density range from 0 to 2 on gray scale paper from white to black. It is intended primarily for use in photographic applications requiring color balance or separation. The new SRM 2061 tablet is calibrated by the NBS Radiometric Physics Division using methods that conform to conditions specified for American National Standard Annular 45°; 0° Absolute Visual Reflection Density, Type 3000K, in ANSI PH2.17-1977.

The step tablet is 35 by 254 mm in dimension and each step is 20 by 35 mm. Measurements were made within a circle 4.76 mm in diameter at the center of each step. The certified values apply only to these areas. The densities listed for these areas are the averages of three independent measurements. The total uncertainty is 0.02 or 2%, whichever is greater.

.27 Computer Amplitude Reference, Disk Cartridge--SRM 3210

SRM 3210 is a reference magnetic flexible disk cartridge recording and reproducing systems.

At the request of Government procurement agencies, media testing laboratories, producers of computer magnetic media and producers of media handling and associated equipment, the National Bureau of Standards has developed and will supply unrecorded Secondary Standard Flexible Disk Cartridges (Computer Amplitude Reference) through the NBS Office of Standard Reference Materials.

The new material consists of a 200 mm(8 inch) unrecorded magnetic flexible disk cartridge whose dimensions conform to the American National Standards Institute (ANSI) Standards, the International Organization for Standardization (ISO) Standards, and the European Computer Manufacturers Association (ECMA) Standards.

Each flexible disk cartridge is calibrated in terms of the 100 percent signal levels established by the NBS Master Standard Flexible Disk Cartridge (Computer Amplitude Reference). These signal level calibrations are made at the test recording frequencies of 250,000 flux transitions per second on track 00 and at 500,000 flux transitions per second on track 76.

.28 Second Surface Aluminum Mirrors for Specular Reflectance--SRM's 2023-2024

SRM's 2023 and 2024 are intended for use in calibrating the photometric scale of specular reflectometers. SRM 2023 is 5.1 x 5.1 cm in size and SRM 2024 is 2.5 x 10.1 cm in size. The aluminum mirror is vacuum deposited on the surface of a 2-mm thick fused-quartz plate. This mirror is protected by a second fused-quartz plate attached to the first plate with epoxy cement.

The specular reflectance of the mirror was measured at 50-nm intervals from 250 nm to 900 nm, at 100-nm intervals from 900 nm to 1300 nm; and at 250-nm intervals from 1500 nm to 2500 nm. In addition to these wavelengths, the reflectance was also measured at the laser wavelengths 632.8 nm and 1060 nm. The research and development of the SRM was supported by the DoE Solar Thermal Program through the Solar Energy Research Institute.

.29 Plutonium-244 Spike Assay and Isotopic Standard--SRM 996

This SRM is certified for concentration and isotopic composition for use as a spike for plutonium determination by isotope dilution mass spectrometry (IDMS). It consists of a plutonium residue contained in a Teflon bottle. The residue was formed by evaporating an aliquant of a plutonium nitrate solution ($\sim$1 mg Pu) to dryness at $\sim$90 °C. SRM 996 is supplied with recommended procedures for reconstitution and use. It was prepared and certified by three national laboratories: the National Bureau of Standards, the New Brunswick Laboratory of the Department of Energy, Argonne, Illinois, and the University of California Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

.30 Environmental Radioactivity, "Rocky Flats Soil Number 1"--SRM 4353

This Standard Reference Material has been developed in cooperation with member laboratories of the International Committee for Radionuclide Metrology and consists of approximately 90 grams of air-dried, pulverized soil in a polyethylene bottle. The sample was collected from Rocky Flats, CO.

It is intended for use in tests of measurements of environmental radioactivity contained in matrices similar to the sample.

.31 Hydrogen-3 Radioactivity Standard--SRM 4361

This new radioactivity standard is tritiated water in a flame-sealed glass bottle. It has a radioactivity concentration of 1.31 $s^{-1}g^{-1}$ and a half-life of 12.43 years. The instrument used for calibration of each hydrogen-3 source was a $4\pi\beta$ internal gas proportional counter.

.32 Low-energy Photon Standard--SRM 4266

This new radionuclide SRM for calibrating low-energy photon counting systems is vanadium-49. It is a point source of dried vanadium-49, as the chloride, deposited between polyester film and tape, and held in an aluminum annulus. The radionuclide has a halflife of 302.2 days and is for K x-ray emission rate per steradian as determined with the NBS low-geometry NaCl x-ray detector system.

.33 Mixed-Radionuclide Point-Source Standard Efficiency Calibration of Germanium-Spectrometer Systems--SRM 4276

This standard is intended for use in measuring the full-energy-peak efficiencies of spectrometer systems for x and gamma rays from 27 to 1274 keV, provided that the responses to radiations approximately 5 keV apart can be resolved. Emission rates are specified at 18 energies for photon radiations from a mixture of antimony-125-tellurium-125m, europium-154, and europium-155. Uncertainties are estimated and combined at a level corresponding to a standard deviation of the mean, with the intent that the user can propagate this uncertainty along with other uncertainties in the spectrometer calibration.

2.6 Data Base Management System

The new Texas Instruments 990/12 minicomputer system was made fully operational during FY81. Also installed during the year was a new tape drive and 100 M Bytes of hard disk memory. The development of the new COBOL programs for use in processing of SRM orders and inventory control is progressing. The new system is expected to be implemented on a trial basis (in parallel with the old system) in early 1982. The pending implementation of the new system will result in better service to SRM customers through more efficient processing of orders, more effective handling of backorders, quicker and more complete response to customer inquiries, and improved billing procedures.

2.7 ASTM Research Associate Programs

.1 Metal SRM's

For six years the ASTM has supported a Research Associate Program at NBS to assist in the certification of metal and metal-related SRM's. The project is under the sponsorship of ASTM Committees E-2 on Emission Spectroscopy, E-3 on Chemical Analysis of Metals and E-16 on Sampling and Analysis of Metal Bearing Ores and Related Materials. Coordinating Committee S-17, is chaired by Luther Ikenberry of Armco Steel Company -- Mr. James Shultz and Mr. Rosemond K. Bell are the two Research Associates assigned to this program by ASTM. Mr. Robert E. Michaelis of OSRM is the NBS liaison. During the last six years, 100 certifications have been completed and a similar number of projects are underway to provide additional SRM's.

The approach in the metals RAP continues to have NBS emphasize development and production of new metal SRM's involving more challenging measurement problems. The burden for certification of renewals is placed primarily on the Research Associates and cooperating laboratories. NBS helps by providing oversight to each project and homogeneity testing. NBS also stands ready to resolve discrepant cooperator data through direct analysis. Over 225 laboratories throughout the U.S. (and eight foreign countries) have participated in the metals RAP.

.2 Glass SRM's

In the fall of 1980, ASTM and NBS concluded an agreement whereby ASTM would sponsor a research associate at the Bureau to develop several new glass SRM's in support of the industry. The new Research Associate is Dr. August C. Seifert, former research director at Owens-Corning Fiberglass Corporation, and his liaison at NBS is Mr. Mario J. Cellarosi.

Within ASTM the program is under the guidance of Committee C-14.91, whose chairman is Mr. Henry E. Hagy, of Corning Glass Works. Committee C-14.91 is a special committee established under Committee C-14 on Glass and Glass Products. Mr. Hagy has worked with representatives of many glass companies to develop, by means of ASTM ballot, a priority list of industrial needs for glass reference materials. The top five priorities on the fourteen item list are: 1) thermal expansion glass; 2) ferrous-to-ferric ratio in borosilicate glass; 3) soft borosilicate glass composition; 4) electrical resistivity glass; and feldspathic (3%-10% Al_2O_3) sand.

Work is beginning on the development of SRM's on the priority list. Prior to initiation of the research associate program, ASTM Subcommittee C-14.04, also under the chairmanship of Mr. Hagy, worked together with nine glass companies and the National Bureau of Standards to produce the new glass SRM for liquidus temperature.

.3 SRM's for Particle Metrology

In September 1981, OSRM reached agreement with ASTM to establish a third Research Associate Program in the area of SRM's for particle metrology. A special coordinating committee, S-21 on SRM's for Particle Metrology, has been established by ASTM under the chairmanship of David W. Johnson, Jr. of Bell Laboratories. S-21 represents the interests of over 15 different ASTM parent committees that have an interest in fine particle measurements. Mr. Russell C. Obbink, formerly with Alcoa Laboratories, has been selected as the new Research Associate. Mr. R. Keith Kirby of OSRM is NBS liaison for the program.

2.8 AIF Research Associate Program

During FY81, the Research Associate Program sponsored by the Atomic Industrial Forum (AIF) for Radiopharmaceutical SRM's was renewed.

This project has already resulted in the certification of over 20 different short-lived radionuclide SRM's for use in measurement quality assurance during the manufacturing of radio pharmaceuticals. A cost recovery agreement has been implemented for this project.

Mr. Daniel B. Golas is the Research Associate assigned to the project by AIF and Dr. Dale D. Hoppes, Nuclear Radiation Division is serving as NBS liaison.

2.9 International SRM Activities

.1 International Organization for Standardization

OSRM continues to maintain an important role in international SRM activities. Within the International Organization for Standardization

(ISO), OSRM has been a major contributor to the work of the Council Committee on Reference Materials (REMCO), since its inception. During FY81, George A. Uriano was selected by ISO Council to serve as Chairman of REMCO for three years. Uriano chaired the 7th Meeting of REMCO held in Paris, France during September 22-24, 1981. At that meeting, the revised International Directory of Certified Reference Materials, prepared by OSRM Consultant, J. Paul Cali, was accepted for publication as an official ISO Directory. Dr. Keith R. Eberhardt, Statistical Engineering Division, is currently a member of a REMCO taskgroup preparing a statistical guide for the preparation and use of reference material certificates.

.2 International Union of Pure and Applied Chemistry

During FY81, George A. Uriano was elected to Titular Member, vice-chairman, and secretary of Commission I.4, on "Physicochemical Reference Materials and Standards," of the International Union of Pure and Applied Chemistry (IUPAC). Among the activities of the Commission are: (1) the preparation of an annotated bibliography on accuracy in measurement, (2) preparation of monographs describing reference methods for the realization of physicochemical quantities, and (3) publication of recommendations for reference materials used in physicochemical measurements.

.3 U.S.-Egypt Cooperative Program

Stanley D. Rasberry was part of an NBS team sent to Egypt during September 10-20, 1981 to make arrangements for a cooperative NBS-Egyptian applied science and technology research program sponsored by the U.S. Agency for International Development (AID). The maintenance and distribution of NBS SRM's by the National Institute for Standards of Egypt was discussed. Mr. Rasberry also consulted with the Egyptian Organization for Standardization and Quality Control with regard to the aquisition, installation and operation of a wavelength dispersive, x-ray fluorescence spectrometer intended for analysis of a wide range of materials, including metals, cement, glass, petroleum and gasoline.

.4 Royal Society of Chemistry Meeting

Stanley D. Rasberry was invited to present a paper describing NBS SRM activities before a special meeting on reference materials organized by the Royal Society of Chemistry in London during February 1981. Invited papers were also presented by nine other reference material producers in the U.K. and Europe. Mr. Rasberry met with Dr. Harold Egan, Government Chemist of the United Kingdom and Dr. Peter Ridsdale, Bureau of Analysed Samples Ltd. to review the activities of their organizations of interest to NBS.

.5 DoC Trade Exhibits in Ecuador and Columbia

In March 1981, Robert Alvarez participated in a U.S. Instrument and Related Equipment Catalog Exhibition in Ecuador and Colombia, as an industry technical representative. Sponsored by the International Trade Administration of the Department of Commerce, the exhibition was designed to test market interest, develop trade leads, and locate agents and distributors for the exhibitors' products and services. Alvarez responded to technical inquiries and discussed the use of SRM's in quality control to calibrate instrumentation and validate measurements.

.6 Chemical Institute of Canada Meeting

In June 1981, Robert Alvarez presented a paper entitled, "Recent Developments in NBS Chemical Composition Standard Reference Materials for Quality Control Application," at a Chemical Institute of Canada meeting in Halifax, Canada. He met with National Research Council of Canada scientists to discuss their progress in the development of a sea water certified reference material. This material is to be issued in 1982.

.7 Fourth European Conference on Analytical Chemistry

At the Fourth European Conference on Analytical Chemistry in Espoo (Helsinki) Finland, Robert Alvarez gave a talk on "New NBS Certified Reference Materials for Validating Clinical and Health Related Measurements. The talk highlighted the two NBS human serum SRM's - one certified for concentrations of antiepilepsy drugs; the other for constituents, such as glucose and cholesterol, commonly found in serum and measured for diagnostic purposes.

.8 International Conference on Heavy Metals in the Environment

Thomas E. Gills attended the International Conference on Heavy Metals in the Environment held in Amsterdam in September 1981. This was the third conference in a series concerned with health effects, pathways and cycling, waste control, metal speciation and analytical techniques pertaining to heavy metals in the environment.

.9 U.S.-Italian Cooperative Research on Reference Materials

Thomas E. Gills presented a paper at the University of Pavia (Italy) entitled, "The Use of Nuclear Methods in Certifying Standard Reference Materials." He also negotiated a final agreement on specific research initiatives under the joint NBS-Italian cooperative agreement for the chemical characterization of reference materials.

.10 NBS - WHO Collaboration

NBS continues as a Collaborating Center of the World Health Organization in the area of clinical chemistry. The OSRM is responsible for reviewing WHO technical proposals.

.11 Bilateral Activities

Bilateral SRM activities continue to be of interest and use to OSRM. During FY81, NBS and the French National Bureau of Metrology (BNM) completed an intercomparison of measurements on four different sets of gas SRM's for use in air pollution monitoring. Agreement between the two countries was excellent. The joint NBS/BNM project for certification of octane rating SRM's is also nearing completion. Negotiations have begun with the National Physical Laboratory (NPL) of the United Kingdom to initiate cooperative SRM certification projects.

During FY81, Mrs. Pan Xiurong, State Bureau of Metrology, Peoples Republic of China was a guest worker in OSRM for one month. She is one of the responsible Chinese officials who will be starting a new Chinese Institute for Reference Materials in Beijing.

3. OSRM STAFF PUBLICATIONS, INFORMATION TRANSFER AND COMMITTEE ACTIVITIES

3.1 Publications, Journal Articles, and Written Reports by OSRM Staff in FY81

--Alvarez, R., "Report on Reference Materials and Standard Solutions," J. Assoc. Off. Anal. Chem. (Vol. 64, No. 2, 1981).

--Kirby, R. K., "Recent Activities of the National Bureau of Standards and the American Society for Testing and Materials in Developing Particulate Standard Reference Materials," Proceedings of the Fine Particle Society Meeting - 1980, University of Maryland, Sept. 18, 1980.

--Kirby, R. K., "The NBS Program for Standard Reference Materials," Proceedings of the NBS-EPA Asbestos Standards Workshop, NBS, Gaithersburg, MD, Oct. 1, 1980.

--Michaelis, R. E. (coauthored with Shultz, J. I.), "Progress Report-NBS ASTM Research Associate Program," distributed March 30, 1981, to ASTM Coordinating Committee S-17 on Reference Materials.

--Michaelis, R. E. (with other OSRM staff members), "NBS Standard Reference Materials, 1980 Status Report, March 1, 1981, distributed at the Pittsburgh Conference and to ASTM Committees E-02, E-03, E-16, and S-17.

--Michaelis, R. E., "Report on the NBS-SRM Program and Other Sources for RM's," 31st Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 9-13, 1981 (published in minutes of meeting by ASTM Committee E-2 on Emission Spectroscopy).

--Michaelis, R. E., "Summary Report on NBS SRM Program," Meeting of ASTM Committee E-2 on Emission Spectroscopy, NBS, Sept. 28, Oct. 1, 1981. (Published in minutes of ASTM Committee E-2, Subcommittee IV on Standard Reference Materials, Sampling, Electrodes, and other Spectrochemical Materials).

--Rasberry, S. D., ed., "Reference Materials," American Laboratory 12 (10), pp. 63-64 (1980).

--Rasberry, S. D., ed., "Reference Materials," American Laboratory 12 (11), p. 146 (1980).

--Rasberry, S. D., ed., "Reference Materials," American Laboratory 12 (12), p. 84 (1980).

--Rasberry, S. D., ed., "Reference Materials," American Laboratory 13 (1), pp. 134-135 (1981).

--Rasberry, S. D., ed., "Reference Materials," American Laboratory 13 (2) pp. 167-168 (1981).

--Rasberry, S. D., ed., "Reference Materials," *American Laboratory* *13* (4) pp. 89-95 (1981).

--Rasberry, S. D., ed., "Reference Materials," *American Laboratory* *13* (6) pp. 79-82 (1981).

--Rasberry, S. D., ed., "Reference Materials," *American Laboratory* *13* (7) p. 83 (1981).

--Rasberry, S. D., ed., "Reference Materials," *American Laboratory* *13* (8) p. 104 (1981).

--Rasberry, S. D., ed., "Reference Materials," *American Laboratory* *13* (9) p. 136-138 (1981).

--Rasberry, S. D., ed., "Current Work and Future Plans in Reference Materials," extended summary in *The Analyst* - England (in press).

--Uriano, G. A. and Rasberry, S. D.,"Clinical Laboratory Use of SRM 909 - Human Serum," *Pathologist* (in press).

--Uriano, G. A., "The Certified Reference Materials Program of the United States National Bureau of Standards," pp. 7 - 24, Proceedings of the International Symposium on the Production and Use of Reference Materials, Nov. 13-16, 1979, published by Bundesanstalt für Materialprüfung (Berlin), B. F. Schmitt, editor (1980).

--Uriano, G. A., "Management Considerations for Planning and Operation of a Coal Reference Materials Sample Bank," Proceedings of the Coal Sample Bank Workshop, March 27-28, 1981, Atlanta, GA (in press).

--Uriano, G. A. (Rasberry, S. D., editor), "Reference Materials," *American Laboratory* *13* (1) p. 134 (1981).

--Uriano, G. A. and Rasberry, S. D., ed., "Annual Report 1981-Office of Standard Reference Materials (1981).

--Zeisler, R., Greenberg, R. R., Gills, T. E., and Lindstrom, R. M., "Nuclear Activation Techniques Used for the Determination of 18 Trace Elements in New Standard Reference Water," Proceedings of the American Chemical Society, Division of Environmental Chemistry, Houston, TX, March 23-28, 1980.

3.2 Technical Lectures/Talks Given by OSRM Personnel

--Alvarez, R., "The Role of Standard Reference Materials in a Reliable Measurement System," VII Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, Sept. 28 - Oct. 3, 1980.

--Alvarez, R., "Standard Reference Materials for the Analysis of Food and Plant Tissue," VII Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, Sept. 28 - Oct. 3, 1980.

--Alvarez, R., "New NBS Standard Reference Materials for AOAC Use," Association of Official Analytical Chemists, Washington, D.C., Oct. 20, 1980.

--Alvarez, R., "General Referee's Report on Reference Materials and Standard Solutions," 94th Annual Meeting, Association of Official Analytical Chemists, Washington, D.C., Oct. 20, 1980.

--Alvarez, R., "National Bureau of Standards Standard Reference Materials for Accurate Analysis of Materials," Science and Technology Enrichment Program, Montgomery County, MD (two talks):
E. B. Wood, Jr. High School, Rockville, MD, Dec. 9, 1980.
E. B. Lee, Jr. High School, Silver Spring, MD, Feb. 2, 1981.

--Alvarez, R., "New Developments in NBS Standard Reference Materials - 75 Years Later," 15th Middle Atlantic Regional Meeting, Amer. Chem. Soc., Washington, D.C., Jan. 7, 1981.

--Alvarez, R., "NBS Standard Reference Materials for Validating Nutrient Element Determinations in Foods," 15th Middle Atlantic Regional Meeting, Amer. Chem. Soc., Washington, D.C., Jan. 8, 1981.

--Alvarez, R., "National Bureau of Standards Standard Reference Materials for Industrial Quality Control (in Spanish)," Catalog Exhibition for U.S. Scientific Instruments and Related Equipment, U.S. Embassy, Quito, Ecuador, March 12-13, 1981 (talk given each day).

--Alvarez, R., "Recent Developments in NBS Chemical Composition Standard Reference Materials for Quality Control Application," The 64th Canadian Chemical Conference and Exhibition, The Chemical Institute of Canada, Halifax, N.S., Canada, June 1, 1981.

--Alvarez, R., "New NBS Certified Reference Materials for Validating Clinical and Health-Related Measurements," Fourth European Conference on Analytical Chemistry, Euroanalysis-IV, Helsinki, Finland, Aug. 24, 1981.

--Gills, T. E., "Status of NBS Nuclear Standards for FY81," Meeting of ASTM Committee on Nuclear Fuel Cycle, Reno, Nevada, Sept. 1981.

--Gills, T. E., invited talk "The Use of Nuclear Methods in Certifying Standard Reference Materials," University of Pavia, Pavia, Italy, Sept. 22, 1981.

--Kirby, R. K., "Standard Reference Materials and Quality Assurance of Chemical Analysis," 1981 Measurement Science Conference, Anaheim, CA, Jan. 30, 1981.

--Kirby, R. K., "SRM/Transfer Standards," NBS Measurement Seminar on Thermal Resistance of Insulating Materials, NBS, Gaithersburg, MD, July 16, 1981.

--Kirby, R. K., "Standard Reference Materials," 23rd Rocky Mountain Conference, Denver, CO, Aug. 4, 1981.

--Michaelis, R. E., "Testing and Characterization of SRM's," Inorganic Analytical Research Division Seminar, NBS, Oct. 16, 1981.

--Michaelis, R. E., "Report on the NBS-SRM Program and Other Sources for RM's," 31st Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 9-13, 1981.

--Michaelis, R. E., "Standard Reference Materials," representatives of National Research Laboratory of Metrology, Tokyo, Japan, at NBS, April 26, 27, 1981.

--Michaelis, R. E., "Summary Report on NBS SRM Program," Meeting of ASTM Committee E-2 on Emission Spectroscopy, NBS, Sept. 28, Oct. 1, 1981.

--Rasberry, S. D., invited lecture "NBS: Current Work and Future Plans in Reference Materials, Royal Society of Chemistry, London, England, Feb. 4, 1981.

--Rasberry, S. D., "Standard Reference Materials: Present and Future," Spectroscopy Society of Pittsburgh, Duquesne University, Pittsburgh, PA, February 19, 1981.

--Rasberry, S. D., "X-ray Fluorescence Spectrometry - A Technique for Rapid Analysis," Egyptian Organization for Standardization and Quality Control, Cairo, Egypt, Sept. 14, 1981.

--Rasberry, S. D., "Standard Reference Materials in Support of Measurement Quality," National Institute for Standards, Cairo, Egypt, Sept. 15, 1981.

--Rasberry, S. D., "The Future of the SRM Program," ASTM Committee E-2 Meeting held at NBS Sept. 28-Oct. 1, 1981.

--Uriano, G. A., "The NBS Standard Reference Materials Program," Seminar, Dept. of Energy, Div. of Fossil Fuel Research, Germantown, MD, Jan. 21, 1981.

--Uriano, G. A., invited talk "Management Considerations for Planning and Operation of a Coal Reference Materials Sample Bank," DoE-GRI Coal Sample Bank Workshop, Atlanta, GA, March 27, 1981.

--Uriano, G. A., "The NBS Standard Reference Materials Program," U.S. House of Representatives, Science and Technology Committee, National Bureau of Standards, June 8, 1981.

--Uriano, G. A., "A New International Directory of Certified Reference Material Producers," Council Committee on Reference Materials, International Organization for Standardization, Paris, France, Sept. 22, 1981.

3.3 Standards Committee and Other Standards Activities

- Alvarez, R. - Association for Official Analytical Chemists (AOAC)
  - AOAC Subcommittee on Reference Materials and Solutions
  - AOAC General Referee for Reference Materials
  - American Society for Testing & Materials (ASTM)
    - E-02 - Emission Spectroscopy
    - E-02.05 - Copper, Nickel, and High Temperature Alloys

- Gills, T. E. - American Society for Testing and Materials (ASTM)
  - C-26 on Nuclear Fuel Cycle
  - C-26.05 Test Methods
  - C-26.01 Editorial and Terminology

- Kirby, R. K. - American Society for Testing and Materials (ASTM)
  - E-29 on Particle Size Measurement
  - E-37 on Thermal Measurement
  - E-37.02 on Standard Reference Materials
  - E-37.05 on Thermal Properties
  - S-21 Coordinating Committee for Standard Reference Materials for Particle Metrology
  - C-14 on Glass and Glass Products
  - C-14.91 on Standard Reference Materials

- Michaelis, R. E. - American Society for Testing and Materials (ASTM)
  - S-17 SRM's for Metals, Metal Bearing Ores, and Related Materials
  - E-02 on Emission Spectroscopy
  - E-02 (Executive Committee)
  - E-02.02 on Statistics, Calibration, Standardization, and Interlaboratory Testing
  - E-02.04 on Standard Reference Materials, Sampling, Electrodes, and other Spectrochemical Materials
  - E-02.05 on Copper, Nickel; and High Temperature Alloys
  - E-02.06 on Lead, Zinc, Tin, and Precious Metals
  - E-02.07 on Aluminum, Magnesium and Their Alloys
  - E-02.08 on Refractory Metals, Beryllium and Their Alloys
  - E-02.09 on Ferrous Alloys
  - E-02.10 on Miscellaneous Non-Metallic Materials

Rasberry, S. D. - American Society for Testing and Materials (ASTM)
E-02 on Emission Spectroscopy
C-14.91 on SRM's for the Glass Industry
U.S. Pharmacopeia (Delegate)
Agency for International Development (Standards Assistance to Egypt)

Seward, R. W. - American Society for Testing and Materials (ASTM)
E-13 on Molecular Spectroscopy
E-13.01 on UV and Visible Spectroscopy

Uriano, G. A. - American Society for Testing and Materials (ASTM)
E-02 on Emmission Spectroscopy
U.S. Delegate to ISO Council Committee on Reference Materials (REMCO)
Chairman of ISO/REMCO
Consultant to Standards Committee, American Association for Clinical Chemistry
Vice Chairman, Secretary and Titular Member of Commission I.4 on Physico-chemical Reference Materials and Standards, International Union of Pure and Applied Chemistry
Consultants' Panel on Analytical Quality Control, International Atomic Energy Agency, United Nations

3.4 NBS Special Publication 260 Series

The OSRM is responsible for the publication and dissemination of information on all phases of the preparation, measurement, certification, and utilization of SRM's. One of the major mechanisms for carrying out this responsibility is the publication and distribution of the NBS Special Publication 260 Series on SRM's. Since 1964 over 70 SP 260 reports--authored primarily by technical division staff--have been published, describing the preparation and use of a variety of SRM's and associated measurement methods. In FY81, the following SP 260's were published by OSRM:

--Marinenko, R. B., Biancaniello, F., Boyer, P. A., Ruff, A. W., DeRobertis, L., Standard Reference Materials: Preparation and Characterization of an Iron-Chromium-Nickel Alloy for Microanalysis, NBS Spec. Publ. 260-70 (May 1981) $2.50.

--Seward, R. W. and Mavrodineanu, R., Standard Reference Materials: Summary of the Clinical Laboratory Standards Issued by the National Bureau of Standards, NBS Spec. Publ. 260-71 (in press).

--Reeder, D. J., Coxon, B., Enagonio, D., Christensen, R. G., Schaffer, R., Howell, B. F., Paule, R. C., Mandel, J., Standard Reference Materials: SRM 900, Antiepilepsy Drug Level Assay Standard, NBS Spec. Publ. 360-72 (June 1981) $4.25.

--Interrante, C. G. and Hicho, G. E., Standard Reference Materials: A Standard Reference Material Containing Nominally Fifteen Percent Austenite (SRM 486), NBS Spec. Publ. 260-73 (in press).

NOTE: To order these publications, send order with remittance (add 25 percent for other than U.S. mailing) to Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

For further information, contact the Office of Standard Reference Materials, Room B-311, Chemistry Building, National Bureau of Standards, Washington, D.C. 20234. Telephone (301) 921-2045.

3.5 FY81 Technical Exhibits With Staffed SRM Displays

-- Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 9-13, 1981, Atlantic City, NJ.

-- Western Technology Conference (WESTEC), Los Angeles, CA, March 23-27, 1981.

-- American Chemical Society Meeting, Atlanta, GA, March 29 - April 4, 1981.

-- Air Pollution Control Association Meeting, Philadelphia, PA, June 23-25, 1981.

-- American Association for Clinical Chemistry Annual Meeting, Kansas City, MO, July 19-25, 1981.

-- Federation of Analytical Chemistry and Applied Spectroscopy Societies, Philadelphia, PA, Sept. 20-25, 1981.

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11. 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 report summarizes the technical activities of the Standard Reference Materials (SRM) program of the National Bureau of Standards. Status reports for SRM research and production projects are included in the areas of electrical properties, thermal properties, radioactivity, chemical composition, chemical stability, mechanical properties and optical properties. Projects covered are carried out by technical centers in the National Measurement Laboratory, National Engineering Laboratory, and the Institute for Computer Sciences and Technology. Also covered are a number of cooperative projects with other laboratories and SRM activities of a number of industrial research associates.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Analytical Chemistry; compositional analysis; physico-chemical properties; quality assurance; reference methods; Standard Reference Materials

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