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NBS TECHNICAL NOTE 542

Activities of the NBS Spectrochemical Analysis Section

July 1969 to June 1970

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Activities of the NBS Spectrochemical Analysis Section July 1969 to June 1970

Bourdon F. Scribner, Editor

Spectrochemical Analysis Section
Analytical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

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FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of nine Sections and about 100 technical personnel encompassing some 45 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the Sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is a highly important output of our laboratories. In addition, however, it has been our experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information about our programs. A word is perhaps in order about the philosophy of these yearly progress reports. In any research program a large amount of information is obtained and techniques developed which never find their way into the literature. This includes the "negative results" which are so disappointing and unspectacular but which can often save others considerable work. Of importance also are the numerous small items which are often explored in a few days and which are not important enough to warrant publication -- yet can be of great interest and use to specialists in a given area. Finally there are the experimental techniques and procedures, the designs and modifications of equipment, etc., which often require months to perfect and yet all too often must be covered in only a line or two of a journal article.

Thus our progress reports endeavor to present this information which we have struggled to obtain and which we feel might be of some help to others. Certain areas which it appears will not be treated fully in regular publications are considered in some detail here. Other results which are being written up for publication in the journal literature are covered in a much more abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1970 we plan to issue these summaries for all of our Sections. The following is the sixth annual report on progress of the Spectrochemical Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

This is the sixth in a series of annual progress reports of the Spectrochemical Analysis Section of the Analytical Chemistry Division. The Section is concerned with instrumental elemental analysis, especially for those spectroscopic techniques that are capable of multi-element determinations, including optical and x-ray spectroscopy.

Chemical elements are uniquely identified by the characteristic frequency of emitted spectra, and amounts present can be determined by measurement of the intensity of emitted radiation. However, many factors enter into successful spectral analysis and must be carefully controlled. These include, in optical and x-ray spectrometry, the production of radiant energy by excitation, the dispersion of radiant energy into a spectrum, and the measurement of spectral wavelengths and intensities. In general these are methods of comparative analysis in which calibration by synthesized or analyzed standards is required.

The research program of the Section is directed largely toward a better understanding of the phenomena involved in producing and measuring optical and x-ray emitted energy and the improvement of spectrochemical methods, instruments, and calibration procedures. Included in the work of the Section are the development of appropriate standard reference materials, analyses of materials to assist other research projects, and literature surveys such as bibliographies and critical reviews.

The purpose of this report is to review the program, facilities, and accomplishments of the Section for the past year.

In order to specify procedures adequately, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

Bourdon F. Scribner, Chief
Spectrochemical Analysis Section

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ACTIVITIES OF THE NBS SPECTROCHEMICAL ANALYSIS SECTION

July 1969 to June 1970

Edited by Bourdon F. Scribner

Spectrochemical research activities, improvements in equipment, and applications, especially to the certification of NBS Standard Reference Materials, are summarized. In electron probe microanalysis, a comprehensive computer correction program for accurate analysis of materials relative to single elements or simple compounds was developed, an improved lithium-doped silicon detector was found to provide increased resolution, and improvements in microprobe instrumentation produced a high level of stability. Studies of procedures for correction of x-ray fluorescence measurements were made, instrumental changes resulted in marked improvement in performance reliability, and new applications were made. In optical emission spectrometry, studies were made of beryllium determination in an air pollution investigation and trace analyses were made of organic materials to parts per billion (10^{-9}) limits. Methods of pre-concentration of impurities are described for optical emission and isotope dilution spark source mass spectrometric analysis of ingot iron, botanical materials, and high purity reagents. Work on Standard Reference Materials resulted in certification of stainless steel, clays, ferrosilicon, blast furnace irons, white irons, lead bearing metal, and ductile irons. Listings are given of 18 publications and 28 talks by members of the Section during the year.

Key words:

Analysis; computer program; electron probe; microanalysis; optical spectrometry; pre-concentration techniques; spectrochemical analysis; standard reference materials; x-ray fluorescence analysis.

1. INTRODUCTION

In the earlier reports in this series [1-5] we described the facilities and programs of the Section, and references to the past reports will be found in the current report. Copies of the earlier reports are available on request. In each report, the research activities and the output in terms of publications, talks given, and analytical work have been recorded. This report follows the same general format although the order of the main topics has been changed. In the introduction we will summarize the major activities of the Section and briefly describe a new and promising Division-wide computing system now being developed.

A. Facilities

No additions of major equipment were made this year; however, the equipment for the electron probe and x-ray fluorescence have been considerably upgraded for improved performance. The spark source mass spectrometer has been transfered to the Analytical Mass Spectrometry Section, but cooperative work continues in the area of isotope dilution spark source mass spectrometry.

The major equipment of the Section includes the following.

3-meter Eagle mounting grating spectrograph
3.4-meter Ebert mounting grating spectrograph
21-foot Wadsworth mounting grating spectrograph
2-meter multi-channel optical spectrometer
3-meter multi-channel optical spectrometer
1.5-meter multi-channel vacuum optical spectrometer
0.75-meter Ebert mounting, scanning spectrometer
0.75-meter Czerny-Turner mounting spectrograph/spectrometer
Multi-channel x-ray fluorescence spectrometer
Single-channel vacuum x-ray fluorescence spectrometer
Electron probe microanalyzer with 3 x-ray spectrometers

B. Activities

The laboratory is organized into four major groups with personnel as listed in section 6 of this report. The groups are electron probe microanalysis, x-ray fluorescence spectrometry, optical emission spectrometry, and enrichment techniques. At the end of the fiscal year, there were 10 full time and 4 part time employees with 2 summer assistants. During the year, several guest workers contributed to the work of the Section. The guest workers included Dr. Jean Hénoc, from the Centre National d'Etudes des Telécommunications, France; Barry L. Hammond, research associate, from the Naval Ship Research and Development Center, Annapolis, Md.; and Dr. Elias Belkas, Greek Atomic Energy Commission, Athens. Other guests, on a part-time basis, were Dr. Toshiaki Kuroha, Harvey Yakowitz, and Fielding Ogburn from NBS groups.

The activity of the Section continued to be divided approximately equally between (1) general research and development and (2) service activities involving spectrometric analyses for certification of standard reference materials, analyses for other projects at NBS, and development of methods and analyses for other Government laboratories. Research activities are directed toward empirical and theoretical studies of sources of error in optical and x-ray spectrometry, the development of models and devices for correction of measurements to obtain more accurate results, and the improvement of instruments to attain improved performance.

In electron probe microanalysis, work was nearly completed on the development of a comprehensive correction procedure for the accurate analysis of materials relative to standards of single elements or simple compounds. This procedure, now involving correction for fluorescence by the continuum, will be made available with a documented computer program. Experimental measurements on metallic alloys are underway to test the procedure and the measurements will be extended to studies of minerals in the near future. Improvement in the lithium-doped silicon detector provides much better resolution, so that energy dispersion spectrometry is becoming an important tool for quantitative as well as qualitative analysis. Stability of the microprobe has been extended to the point where continuous automatic runs for several hours are practicable, for example, in studies of homogeneity of materials by matrix scanning of up to 100 positions on the sample. The use of the microprobe as an electron scanning microscope as well as a means of determining composition is an important development, especially with the production of color prints showing composite images of topography and composition for selected elements.

Activity in x-ray fluorescence spectrometry continues on correction techniques for interelement interferences and an improved correction procedure has been developed. Modifications of the x-ray fluorescence spectrometer and associated electronics as described in this report have resulted in a large gain in stability and reliability, so that down time is practically eliminated. Applications of x-ray fluorescence analysis continue to be made to homogeneity studies of materials and to a wide variety of analytical problems, including measurements of thickness of thin layers of metallic coatings, measurement of austenite in steel standards, and correlation studies comparing results of x-ray and other methods of analysis of standard reference materials.

Work in optical emission spectrometry is being directed toward pollution studies where this method can provide extremely fast and economical analyses. The spectrometric determination of beryllium in paper swipes for surveillance of possible contamination areas now provides determintions down to as low as 0.1 ng Be. Analyses of 100 samples per day for beryllium is considered feasible on a routine basis by one operator. The study of standard reference materials for homogeneity also represents a relatively high speed and economical method and is applied to the analysis of a variety of materials. The optical emission method is particularly useful for trace analyses when impurities can be concentrated by simple methods. An example is shown of the analysis of glucose where detection limits attained were as low as 1 ng/g ($1\text{x}10^{-7}\%$) for several elements.

Chemical preconcentration procedures are being developed to obtain improved limits of detection or to provide analytes in a form more suitable for analysis by either optical emission spectrometry or isotope dilution spark source mass spectrometry. Methods have been devised for the analysis of ingot iron, botanical materials, and high purity reagents. The procedures are especially designed to employ isolation systems and minimum handling thus keeping contamination to a controllable low level.

Studies of standard reference materials for homogeneity and determination of composition have continued as a large effort this year. The Section contributed effectively to the analysis of 53 standards including low alloy steels, blast furnace iron, white cast iron, stainless steel, silicon steel, clays, glucose, metallo-organic compounds, orchard leaves, and micro-bead standards. Standards of interest for spectrometric analysis, that were issued during the year, are listed in Table 1. These are available with final analysis except for SRM 1155 which is provisional. Certificates for most of these standards have been reproduced in appendices to this report.

A set of low alloy steels, SRM 1261-1265, prepared to replace the earlier group of spectrometric steel standards, will be available soon with provisional certificates of analysis.

Table 1. Standard reference materials of interest for spectrometric applications

SRM No.	Title	Date Issued
1155	Stainless Steel Cr18-Ni12-Mo2 (AISI 316)	August 1969
97a	Flint Clay	October 1969
98a	Plastic Clay	October 1969
59a	Ferrosilicon	November 1969
1143,1144,1147 1148,1149	Blast Furnace and White Iron Standards	December 1969
1132	Lead-Base Bearing Metal (84Pb-10Sb-6Sn)	January 1970
1053a	Cadmium Cyclohexanebutyrate	January 1970
1140,1141,1142	Ductile Iron Standards	February 1970

Analyses made by the groups in the Section during the 12-month period June 1, 1969 through May 31, 1970 are summarized in Table 2.

Table 2. Summary of spectrometric analyses

Method	Samples	Determinations	Reports
Optical emission	566	14,714	113
Electron microprobe	61	2,910	20
X-ray fluorescence	88	1,486	17
Total	715	19,110	150

In addition to the analyses, the x-ray spectrometer is employed for rapid determination of compositions to check the labeling of spectrometric standard reference samples where there may be a question of identity. This work involved 2,551 samples, 7,570 determinations, and 4 reports.

C. Computerized Data Acquisition System

During the past year, we contributed considerable effort to the planning and procurement of a Division-wide computerized data acquisition system. This system will have great potential for rapid and efficient data handling for our Section in view of our digital recording systems already in use [3, p. 1]. A five-member evaluation committee, under the chairmanship of Dr. James DeVoe, drew up a request for proposals and an evaluation procedure that would make possible objective rating of the proposals received. The other members of this committee were Roy Saltman, Ronald Shideler, Fillmer Ruegg, and Stanley Rasberry.

Eight manufacturers submitted proposals. These were carefully reviewed by the evaluation committee, with technical ratings being completed on April 28, 1970. The evaluation was made only on the basis of technical specifications; the committee had no access to cost data until after reporting its ratings. Following that report, cost data were released to the committee and price/performance was completed to permit logical choice of the supplier. Subject to contract negotiations, the computer will be delivered in early 1971.

The primary application for this computer system will be real-time, multi-instrument data acquisition, and supervisory instrument control. A disc, with one-million words storage capacity, will give the system great flexibility in acquiring, sorting, and managing experiment data files. As a background function, the computer will process data for those jobs which do not exceed the capability of the computer.

For jobs exceeding those limits, completed data files will be transferred to magnetic tape for processing on the Univac 1108 at the NBS Computation Center.

Interfacing the experiments to the computer system is in the design phase. The plan, for digital data, is to buffer the data from the laboratory experiments onto a common digital data bus. The data bus will enter an interface device located at the computer site ahead of the computer to buffer the lines and sort the data according to rate; i.e., high speed for direct memory access entry, and low speed for priority-interrupt entry. Within the computer, the data will be sorted, by a single acquisition program, into the file of the appropriate experiment.

An executive program will schedule jobs and allocate memory space according to user demand and job priority, with data acquisition being given high priority.

In our Section, there are seven devices that have data output buffered on either scalers or multi-channel pulse-height analyzers. Included are the electron microprobe, x-ray fluorescence spectrometers, optical emission spectrometers, and a microphotometer. Presently, these instruments log data on paper tape for later processing by either time-shared computer or batch loading. Because they already contain some interfacing electronics, the instruments should be easily interfaced to the digital data bus.

One of our first projects will be to get the electron microprobe on-line to the computer. Some of the experiments now running on the microprobe have high data volume. Furthermore, the automatic control equipment (matrix scanner) now in use gives us less flexibility in experiment design than we require and the computer can supply.

B. F. Scribner and S. D. Rasberry

2. ELECTRON PROBE MICROANALYSIS

With other laboratories in our Section, the electron probe microanalysis laboratory performs both service and research. The aim of the research program is to improve the efficiency of the use of the electron probe by increasing the accuracy, sensitivity, speed, and scope of application of electron probe microanalysis. The research activities cover aspects of theory, technique, computation methods, and instrumental development. The experience acquired in the performance of service work, and the problems which arise in the execution of such tasks, are a valuable guidance for establishing priorities in the research program.

The present report covers the progress achieved in the fiscal year 1969-70. References to the activities prior to this period will serve to connect our present work to the overall plan of research.

A. Instrumental Improvements

To ease the task of the operator, we have relocated, close to the front of the instrument, the most important controls and monitoring devices and we have removed devices previously occupying space upon the microprobe bench (see Figure 1). The illuminator control, meters indicating the ratemeter output from the three crystal spectrometers, and the flowmeter for the detector gas are now mounted on the front of the instrument. Meters for target current and monitor current, the controls for magnetic lenses, and a power line monitor, are relocated on a panel within reach of the operator. The target current amplifier (to be described later in more detail), and the oscilloscope used to observe area scans are also very close to the operator.

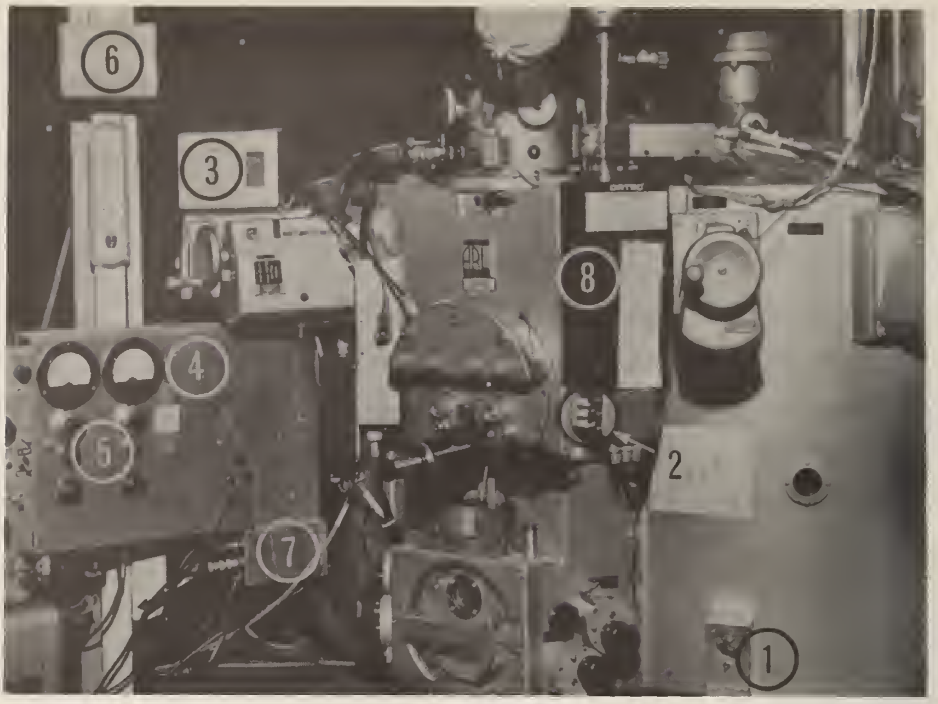


Figure 1. Front view of the electron probe tank, with recent modifications. 1: illuminator control; 2: x-ray countrate meters; 3: flowmeter for flow proportional detectors; 4: meters for monitor- and target current; 5: lens controls; 6: line voltage monitor; 7: first stage of target current amplifier; 8: lithium-drifted silicon detector.

Three new solid-state ratemeters were constructed. One is a periodic integrator, the other two are conventional. We also built two highly stable supplies for the electronic lenses with remote output control; these have no observable drift for periods of several hours.

The vacuum system was also changed. The mechanical pump for the specimen chamber was replaced by a larger pump. Both mechanical pumps were mounted in a cabinet removed from the main body of the microprobe, in order to reduce vibrations. All valves are now manually operated. The specimen chamber can be pumped down in less than half the time needed previously, and the main instrument tank can be evacuated with both pumps operating in tandem. The pumping period needed to bring the main tank from atmospheric pressure to operating conditions is only 20 - 30 minutes.

We are at present constructing a new power supply for the beam voltage which will operate over a continuous range from zero to fifty kilovolts. It is hoped that this supply will combine stability and freedom from noise with ease of repair and adjustment.

B. Qualitative Analysis

Replacement of the Li-doped silicon detector by one of higher energy resolution reduced the width at 50% of peak height from 500 eV to 250 eV (see Figure 2). This improvement substantially reduces the overlap of adjacent peaks. For instance, Cu Kα and Cu Kβ peaks are now fully separated. Furthermore, the peak-to-background ratio is increased by a factor of two.

The availability of the non-diffractive (energy dispersion) spectral read-out [6] has substantially reduced the time spent in qualitative tests. Thus, the silicon detector has proven to be a most valuable addition to the electron probe.

The solid-state detector has good sensitivity and resolution at high energies (20-50 keV). Its usefulness for qualitative purposes can be extended to these energies by working at operating voltages above 20 kV whenever the deterioration of spacial resolution is unimportant (Figure 3).

C. Scanning Electron Probe Analysis

Work on scanning techniques was mainly a continuation of projects started before this fiscal year. A non-linear amplification stage was incorporated in the differential target current amplifier described previously [5,7]. This stage permits the compressing of extremes in current in the input

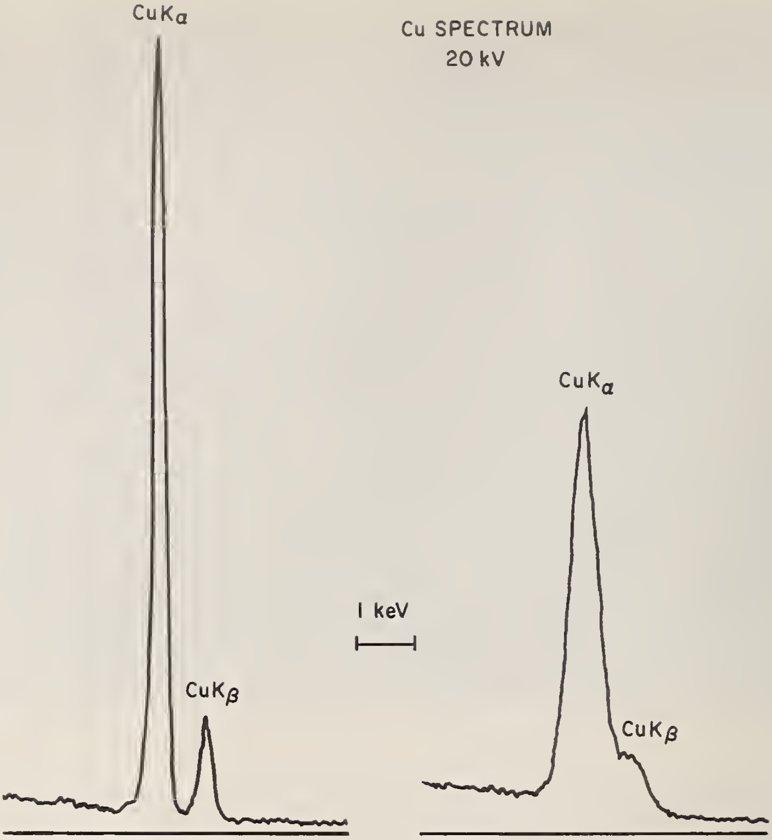


Figure 2. Improvement of energy resolution with silicon detector. Left, new detector. Right, old detector.

signal which would otherwise produce areas of extreme brightness on the scanning images. The non-linear stage can be bypassed if compression is not desired.

The target current amplifier was also used with the secondary electron output signal of a scanning electron microscope (Metallurgy Division, NBS). It could be shown that the principles on which this device is based apply equally to secondary electron signals, and that the use of such an amplifier in scanning electron microscopes can considerably improve the quality of the scanning images based on secondary electron signals [7]. The complete circuit diagram of the amplifier is shown in Figure 4.

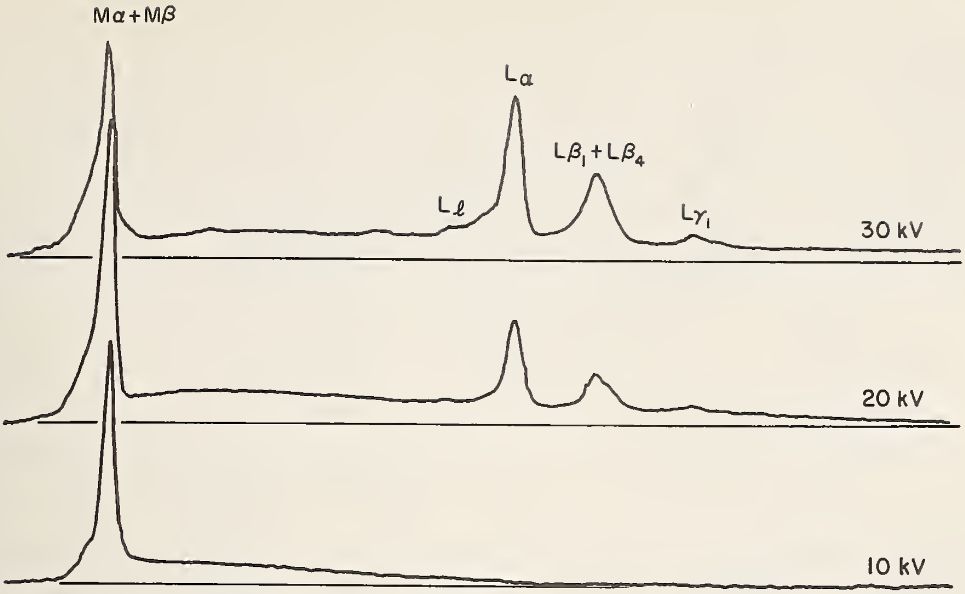


Figure 3. Energy dispersion spectra of rhenium at various voltages.

The experiments with the scanning electron microscope were performed in cooperation with H. Yakowitz (Metallurgy Division, NBS).

We have described [4,7] a method of color representation of x-ray area scans. This method has been perfected this year by adding information from target scans. In the new technique, up to three area scans are represented in primary colors, and a target current scan is added in neutral gray tones. The target current scan adds topographical information to the composite, which is helpful in recognizing the scanned area. It also sharply outlines the contours of the phases which are characterized by the x-ray scan. This procedure overcomes, to a large degree, the lack of sharpness of the x-ray scans caused by statistical factors as well as to the production of secondary x-ray emission.

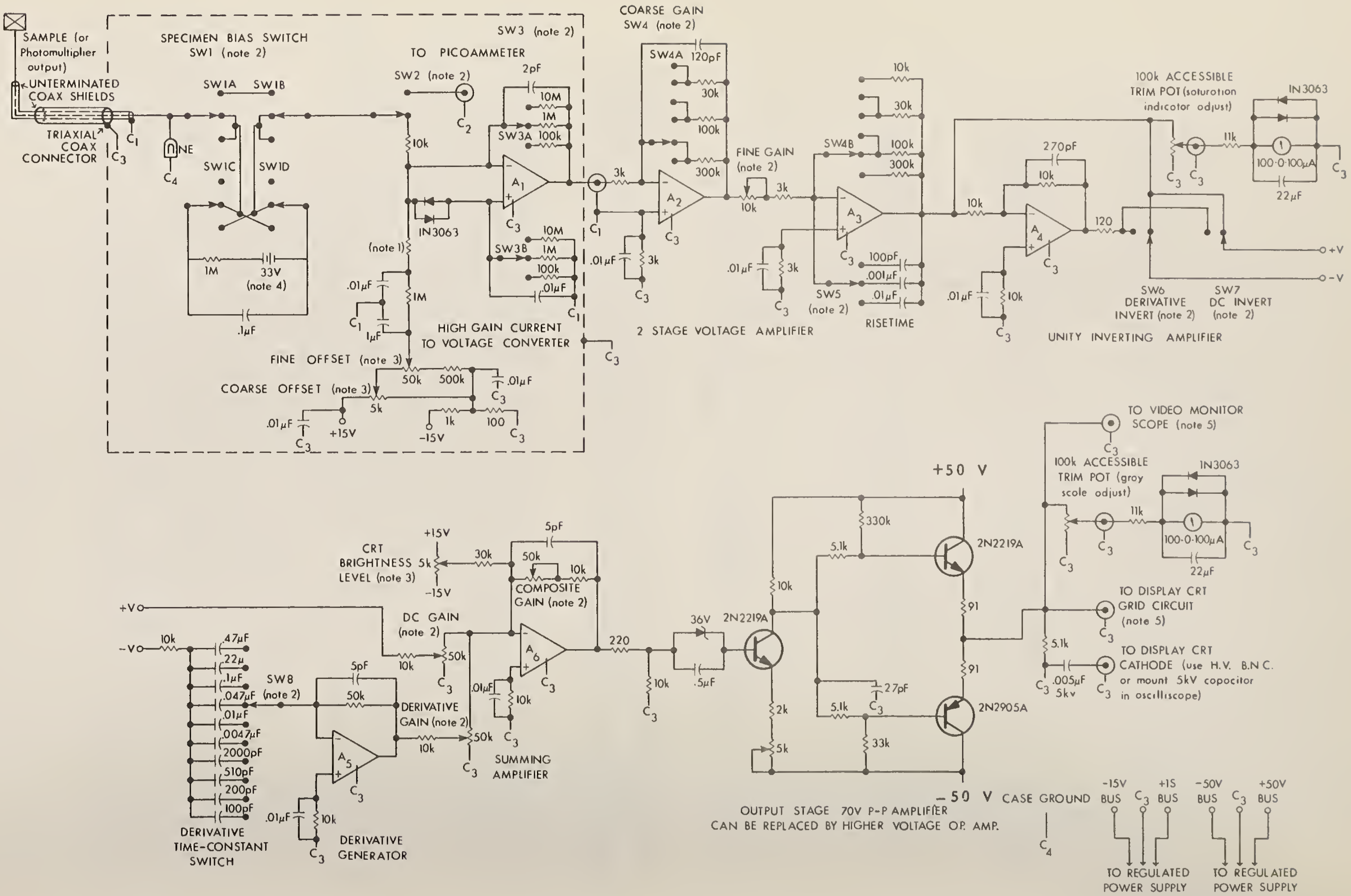


Figure 4. Circuit diagram of the target current amplifier.

The proportions of the representation of topography and of composition can be changed at will by varying the lengths of the corresponding photographic exposures. One obtains, as a result, a true microscopic picture of the scanned area, with the display of the distribution of up to three elements. This technique constitutes a novel kind of microscopy which has already been shown to be very useful for a wide variety of specimens, including alloys and minerals such as lunar specimens.

The first experiments in this technique antedate this fiscal year [5]. We have now established the best exposure conditions. We have also provided the copy camera with a filter holder, and a stage with x-y translation to which the original scanning images are affixed by suction. The stage translation is used for correcting shifts in registration between scanning images (Figure 5). In the course of our work

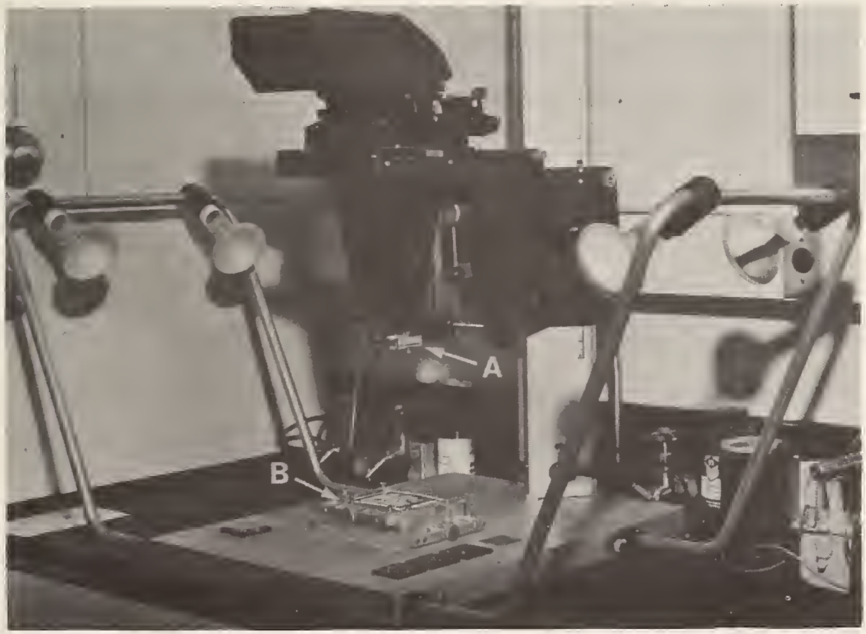


Figure 5. Copying camera for color composites.
A: filter holder, B: stage with x-y translation

in scanning target current images, we discovered two unexpected sources of noise. We found that, after all sources of amplifier noise and noise induction within the instrument were reduced or eliminated, a moiré pattern persisted on the scanning images of uniform surfaces. We found that the oscillations which cause these patterns were caused by ripple in the high voltage power supply; this could be observed even though the supply was within specifications (0.1% ripple).

When the electron beam was cut off, a slight pattern could still be observed, which was traced back to the oscilloscope.

Although these effects do not detract from the accuracy of quantitative analysis, they are undesirable in scanning electron microscopy by means of target current signals. A power supply now under construction should contribute to the improvement of the scanning images. A good case can also be made for the use of cathode-ray tube oscilloscopes of high quality. At moderate magnifications, the sharpness of the scanning electron images is limited by the resolution of the cathode-ray tubes commonly used in microprobes. We hope to explore the advantages which should accrue from the use of high-resolution oscilloscopes having high stability and low noise.

D. Quantitative Analysis

Research in quantitative electron probe analysis includes instrumental and theoretical aspects. We have previously reported on our investigations of spectrometer alignment [3] and of pulse coincidence losses [9]. In this fiscal year, we started a study of the background corrections, which become particularly important when energy dispersion spectrometers are used in quantitative analysis [10].

The theoretical study of the corrections for absorption of primary emission [11], for primary generation of x-rays [12], and for fluorescence due to characteristic lines [13], is now complemented by an investigation of fluorescence caused by continuous radiation. The theoretical treatment is greatly aided by measurements of x-ray intensities obtained under varying conditions from the standard reference materials of Au-Ag and Au-Cu alloys which had been developed and tested for this purpose at NBS [5].

In order to increase the speed and accuracy of the tests for homogeneity of these and other alloys, we had developed an automatic device for analysis of many points on a specimen - the matrix scanner -. This device is described in a previous annual report [3]. A computer program written by S. Rasberry (TOPO) now provides a topographic and statistical characterization of the degree of homogeneity of the tested material. During the present fiscal year, we continued the study of the application of the matrix scanner. The aim of this study is to develop a technique of completely automated and unattended matrix analysis, which could be performed during overnight periods.

The analysis of lunar specimens has greatly stimulated the interest in the quantitative analysis of minerals. We have initiated a systematic study of the application of the theoretical principles of microprobe analysis - which were primarily developed for alloys - to mineral specimens. For this purpose we have assembled a large number of well-characterized mineral specimens (Figure 6) which were obtained through the kindness of several investigators.

The need for techniques for the analysis of small particles and of biological specimens is even more pressing due to the social significance of the studies of pollution and of biological and medical problems. Unfortunately, this is the most difficult area within the realm of quantitative electron

Figure 6. Specimen mount for minerals. The small circles in center contain elements. The larger circles at the periphery contain 45 minerals, mostly in groups of four, which are mounted on removable and exchangeable cylinders. The entire assembly measures 25 mm in diameter.

probe microanalysis. In view of the urgency of progress in this field, we hope soon to broadly attack this important subject, to which we have already given much attention in the past years.

We will now comment, in more detail, on some aspects of the research on quantitative analysis which we have outlined above.

1. Emission of Continuous Radiation

The study of the continuous emission is the basis for the development of a technique of background correction. Moreover, the correction for fluorescence due to the continuum requires the quantitative knowledge of the continuum emission.

A study of the correction for fluorescence by the continuum [14] indicates that the uncertainty in the emission of continuous radiation is the largest potential source of error in this correction. Existing experimental evidence [15,16] is contradictory. Our preliminary experimental data on the atomic number dependence of the intensity of the continuum disagree with those published by Green [15] and tend to support the results obtained by Rao-Sahib and Wittry [16]. Further extensive experimental studies of this subject are under way.

We have not found any reference in literature to the intensity of continuous radiation of targets containing more than one element. Measurements on the gold-copper Standard Reference Materials indicate that the intensity varies (at least at short wavelengths) linearly with the weight-fraction of the components (Figure 7), in agreement with Hénoc's prediction. Further measurements will be made. Experiments on the x-ray emission of undiffused metal couples [17] are also being performed. We are confident that these measurements will provide the necessary basis for an accurate correction of the fluorescent contribution from the continuum.

2. Further Measurements on Standard Reference Materials

The Standard Reference Materials of gold-silver and gold-copper alloys mentioned in previous reports [4,5], are being used to obtain experimental intensity ratios under varying excitation conditions. The results, and comments on the fit of the theoretical models to these results, will be published shortly. This is intended primarily to illustrate the variety of tests that can be performed with the aid of the Standard Reference Materials. At the same time, it is hoped that the results obtained at the NBS laboratory will further the studies of the theory of quantitative electron probe microanalysis.

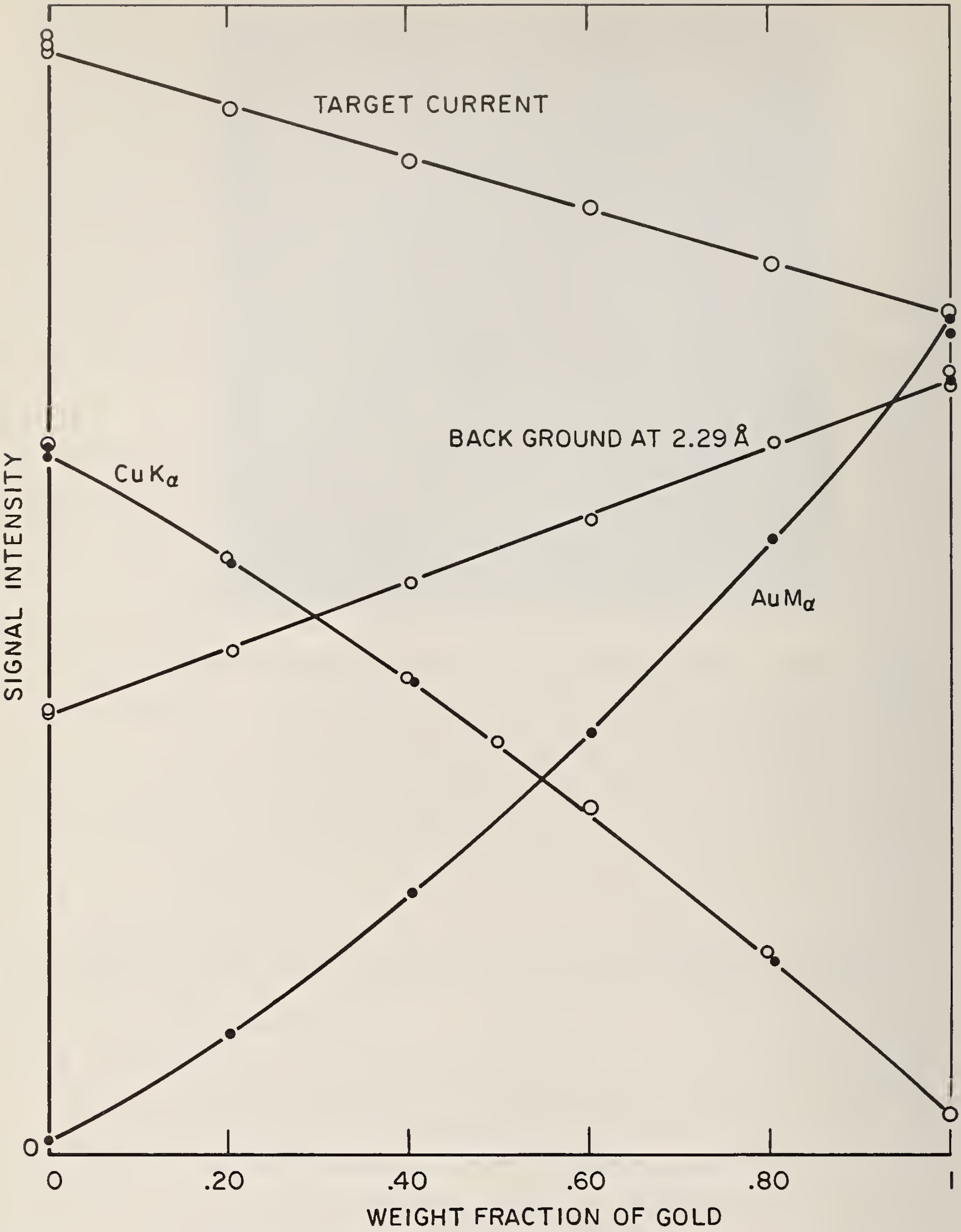


Figure 7. Measurements at 20 kV on copper-gold standard reference materials. The signal intensities are on an arbitrary scale. Both target current and continuous radiation (background at 2.29 Å) vary linearly with weight fraction.

It should be noted that the intensity ratios obtainable on the Standard Reference Materials provide tests on all existing corrections. The measurements of the Au Mα line in both series, and of the Ag Lα lines in the Au-Ag series, provide a test of the absorption correction; fluorescence by the Au L lines affects the intensity of Cu K emission in the Au-Cu series; fluorescence by the continuum also occurs in the Cu K emission; and the atomic number effect influences the intensities of all elements in these series.

3. Quantitative Analysis of Minerals and Ceramics

Over 40 specimens of well-characterized mineral specimens, mostly, but not exclusively, silicates, were obtained from several laboratories which are listed in the acknowledgments. These specimens - some of which are exceedingly small - were skillfully mounted and polished by C. Fiori, of this Section (see Figure 6). Some of these specimens were used in the standardization of analyses of lunar specimens. Systematic measurements and analysis of all of them are presently under way. The purposes of this study are as follows;

a. To estimate the accuracy achievable by theoretical and empirical correction procedures.

b. To estimate the reliability and homogeneity of chemically analyzed minerals as standards.

c. To attempt to establish a simple system for the analysis by means of a limited number of natural or synthetic standards which are easy to prepare or obtain, and which could be issued by the National Bureau of Standards.

The results obtained at present indicate that the theoretical calculations can be applied to mineral and ceramic specimens, and that a system of calibration using a limited number of standards is feasible. This work will be continued in the coming fiscal year.

The work on minerals is partially sponsored by NASA.

4. Quantitative Applications of Energy Dispersion Detector Systems

In view of the success obtained in the qualitative use of energy dispersion spectrometry (particularly with the lithium-doped silicon detector), we began investigating the possibilities of using this technique for quantitative purposes. The following advantages can be obtained:

1. Since deflection of the electron beam does not produce optical defocusing when such systems are used, the matrix analysis can be applied over larger areas than those which can be investigated quantitatively with the use of focusing spectrometers.

2. The combined use of energy dispersion and x-ray dispersion spectrometry permits the simultaneous measurement of a large number of elements. This possibility was successfully exploited in the analysis of lunar specimens.

Since the line-to-background ratios in non-diffractive analysis are less favorable than with diffractive devices, more attention must be given to the background correction. In particular, the concentration limits of detection and determination are lowered. Detailed studies of the background correction are presently under way, as mentioned previously.

The combined use of the solid-state energy-dispersion spectrometer and the crystal x-ray spectrometers proved to be particularly useful in the analysis of mineral specimens, where the simultaneous determination of many elements is a significant advantage. It is difficult to relocate areas of interest on a complex inhomogeneous mineral. Since many minerals (particularly silicates) contain a considerable number of constituents, the complete quantitative evaluation of small grains is, thus, very tedious and sometimes inaccurate when only crystal spectrometers are used. In the analysis of lunar silicates and other minerals, we were able to determine, with sufficient accuracy, the elements Si, Ca, and Fe by means of energy-dispersion spectrometry, even in the presence of Al and Mg, using a single-channel pulse height analyzer for each element. The interference of the Al line with the Si line could be reduced to negligible proportions by judicious setting of a single-channel analyzer across the part of the energy distribution of the Si signal which does not overlap with the distribution of the Al signal. The crystal spectrometers were used simultaneously for the determination of other elements present, such as Na, K, Mg, Al, Ti, and Cr. A maximum of six elements was determined simultaneously. Comparison with the results of analysis of Si, Ca, and Fe, using crystal spectrometers, showed satisfactory agreement. The energy distributions were very stable, so that, even in the case of the determination of Si, no drift was observed.

Another area in which the application of energy dispersion analysis is very promising is the analysis of points distributed in a two-dimensional matrix of locations for the study of homogeneity of materials to be used as standard references. In our instrument, the matrix is generated by electromagnetic deflection of the beam. If this deflection is large, defocusing of the crystal-spectrometer optics is observed [2, p. 52]. The largest matrix we can presently generate at 20 kV is 500 X 500 μm. Measurements using energy-dispersion techniques on a matrix of this size showed the absence of defocusing effects.

We have started a study of the factors which affect the accuracy of measurements performed in matrix scans of long duration. Preliminary experiments indicate that the ratio of monitor current to beam current may be subject to slow drift; therefore, there is some doubt concerning the efficiency of using monitor current as a means of drift correction. The output of the silicon detector appears to be quite stable provided that the specimen current does not drift.

The stability and reproducibility of the beam positions on the specimen are excellent, as can be observed in Figure 8. This figure shows the superimposed contamination marks on a specimen which was scanned for three consecutive times. The total time of scan was 15 hours.

The programming of automated overnight runs of matrices will be greatly aided by connecting the electron probe to the on-line computer facilities which we expect to acquire during the next fiscal year (see Section 1 C).

The experiments on stability during overnight runs were performed in cooperation with H. Yakowitz (Metallurgy Division, NBS).

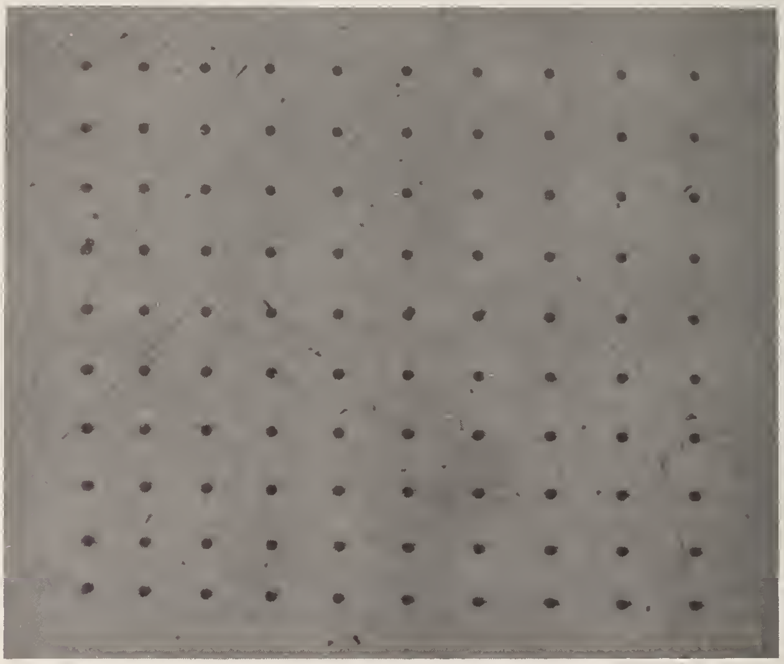


Figure 8. Superimposed contamination marks from a matrix run of 15 hours duration on pure nickel. Size of the matrix: 575 x 667 μm.

E. Computer Program COR for the Correction of Quantitative Microprobe Measurements

This program was written in order to include in the correction procedure all known refinements of the quantitative theory of electron probe microanalysis, avoiding all unnecessary simplifications. The original version of the program is due to Jean Hénoc, who was a guest worker in our electron probe laboratory from October 1969 to October 1970. Further work after Dr. Hénoc's departure was performed by Hénoc in Paris, and by R. L. Myklebust, in our Section.

The purpose of the program is not limited to obtaining the best possible corrections for analytical data. Rather, it is a starting point for studying the effects of uncertainties arising from the theories, from parameters, and constants, and from the approximations frequently used in other programs. The following comments briefly outline the structure of the program.

1. Theories Used in the Correction Procedure

The generation equation (atomic number correction) follows the procedures of Philibert and Tixier [18] for integrating the stopping power of the target for electrons over the range of deceleration. Although several expressions for the mean ionization potential can be used, we usually employ the values proposed by Berger and Seltzer [19]. We follow a procedure advocated by Duncumb and Reed [20] for the calculation of backscatter losses.

The calculation of the absorption of primary x-rays uses the modification by Heinrich [21] of the procedure of Philibert and Duncumb [22]. The mass attenuation coefficients are those proposed by Heinrich [23]. If desired, other values can be substituted.

The correction procedure for fluorescence produced by characteristic lines is that of Hénoc, Maurice, and Zemskoff [17]. The primary intensities of the exciting lines are calculated rigorously, using the full generation calculations. Hence, the approximations for primary intensities used by other authors are avoided. The fluorescence due to each exciting line ($K\alpha$, $K\beta$, $L\alpha_1$, $L\beta_1$, etc.) is calculated separately. In the calculation of the attenuation of emergent fluorescent radiation, a refinement by Criss [24] is employed. We usually apply the data of Fink et al. [25] for fluorescent yield.

The treatment of fluorescence by the continuum is based on previous work by Hénoc. As in earlier versions by Hénoc, the calculation of the intensity of the continuous radiation is based on Green's modifications to Kramer's law [15]. However, this aspect may subsequently be modified. Contrary to previous procedures by Hénoc, COR performs a numerical integration of the fluorescent intensity with respect to wavelength. This not only eliminates the need for the assumption that the variation of attenuation coefficients with wavelength follows a cubic law; it also permits a physically more meaningful interpretation of the factors affecting the magnitude of the fluorescent emission.

2. Internal Structure of the Program COR

A schematic diagram of the structure of COR is shown in Figure 9. Besides the main program, COR contains several subroutines which provide partial steps of calculation to be used in the main program. Thus, the mass absorption coefficients, primary intensities, fluorescent contributions, etc., are calculated in sub-units which can easily be studied. We are at present writing extensive comments to the program and subprograms so as to enable the user to understand them and, if desired, make modifications.

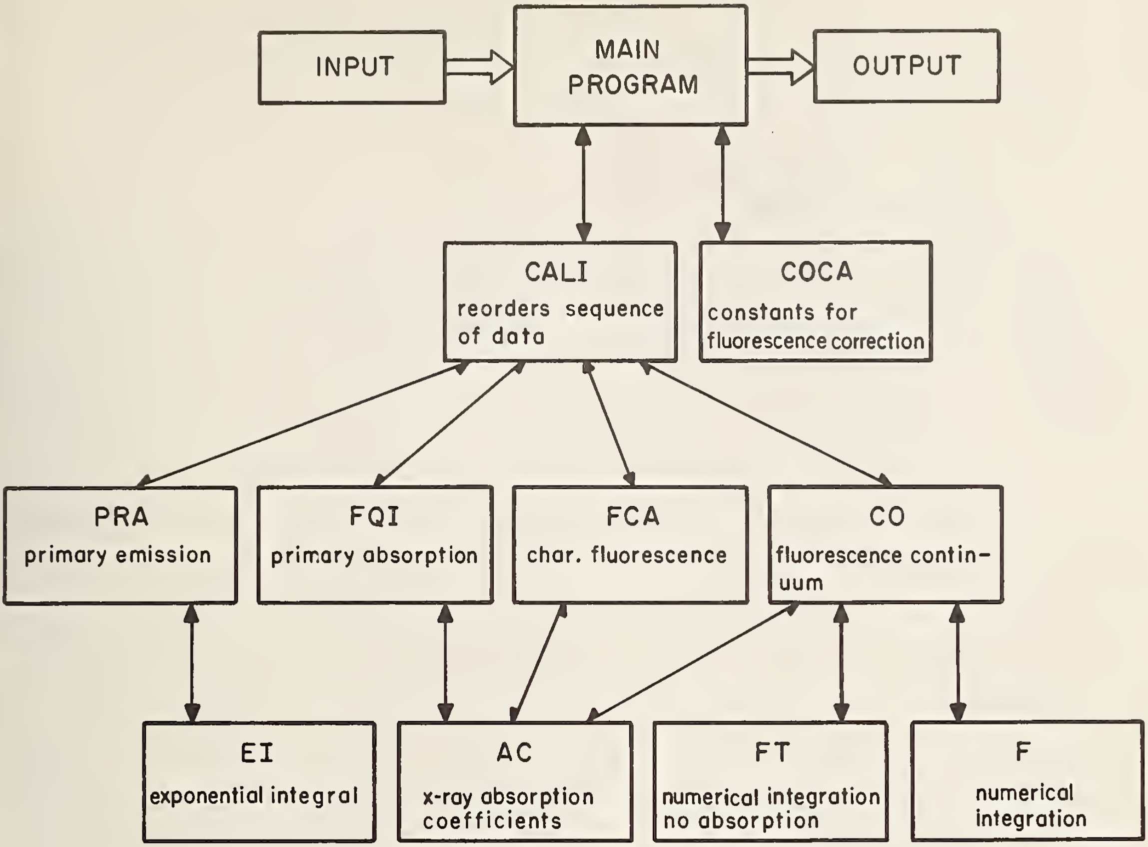


Figure 9. Diagram of the subprograms in the program COR. The subprogram FT is only needed if the printout of the absorption factor for fluorescence from the continuum is desired.

The decision-making processes in the program are an important feature. The program decides by itself which fluorescent correctures must be applied. If operating conditions are chosen improperly, or if relevant parameters (e.g., mass attenuation coefficients) are not known, warning messages are transmitted to the output. These decision-making processes are designed to minimize the possibility of operator errors in the choice of experimental conditions or input.

The iteration procedure is a modification of that proposed by Criss and Birks [26]. The modified Criss iteration has been tested extensively prior to its inclusion in the program

MULTI7. It is rapid and always converges. We strongly feel that this iteration procedure is by far better than other proposed techniques.

3. Input to the Program

The constants for each element contained in the analyzed specimens (name, atomic number, atomic weight, absorption parameters, fluorescent yield) are entered by means of a set of cards. The card file can be completed as the necessity arises. (See examples in Appendix B to this report).

The analytical information for the input can consist of background- and deadtime-corrected intensity ratios, or of the uncorrected photon counts obtained by the instrument. In the second case, the background and deadtime corrections are performed by a sub-program written by R. L. Myklebust. Elements which were not included in the x-ray intensity measurement can be determined by difference (one element only) or on the basis of stoichiometric relations - e.g., oxygen in oxidic materials - or their concentration can be assumed to be known. (e.g., the main constituents when analyzing for impurities). The program can also be used to calculate theoretical intensity ratios for specimens of known composition.

Standards composed of several elements (e.g., for the analysis of minerals) can be employed. Their characteristics are entered via a few cards. The program permits the use of a different excitation voltage or x-ray emergence angle for each element. We believe that we have covered all contingencies which may arise in the analysis of a flat, semi-infinite specimen of homogeneous (within the excited area) composition. There are no provisions, however, for the analysis of data obtained by using an electron beam of non-normal incidence upon the specimen. This case requires further studies of the backscatter losses for oblique beam incidence.

4. Output of the Program

Since Hénoc's departure, R. L. Myklebust has written a new output program for COR, which provides the following information: a label (name or number of specimen, date, etc.), number of sample (when several points or specimens within a system were analyzed), characterization of standards, symbols and atomic numbers of elements included in the calculations, atomic fractions obtained, weight fractions obtained, standard deviations (if several measurements were made on the same point or specimen), absorption losses ($f(\chi)$) for primary and fluorescent emission (by characteristic and continuum excitation), absolute primary intensities for specimens and standards, ratio of fluorescence by characteristic lines to primary intensity, ratio of fluorescence by continuum to primary intensity, sum of computed mass fractions, and number of iterations. Warning labels may also appear in the output. When elements are calculated by stoichiometry, molar weight fractions (e.g., SiO_2, $CaCO_3$, etc.) are also printed.

An example of the program output is shown in Figure 10.

5. Documentation of the Program

Since requirements and preferences for input and output, as well as for certain variables and constants to be used in the program, change from laboratory to laboratory, it is important to thoroughly document programs intended to be used widely. This also reduces the possibility that errors in the program remain indefinitely undiscovered. We are at present adding extensive commentaries to the program which identify each step of the procedure. These will be complemented by a general discussion, which will be included with copies of the program.

```
SYNTHETIC STD = I   SAMPLE = III 15 KV K-VALUES     B+S J-FACTOR   JAN 29, 1970

 SAMPLE NO  2
    STANDARDS
            SIKA1     AT NO 14      F(X)= .9175    I(P)/(F(X)*C)= .26511-02    I(C)/I(P)= .17155-02    F(X),CONT= .6502
            COMPOUND STANDARD FOR ELEMENT 1
                      AT NO 14      F(X)= .7018    I(P)/(F(X)*C)= .26721-02    I(C)/I(P)= .17261-02    F(X),CONT= .3624
            MGKA1     AT NO 12      F(X)= .8825    I(P)/(F(X)*C)= .59589-02    I(C)/I(P)= .88705-03    F(X),CONT= .6088
            COMPOUND STANDARD FOR ELEMENT 2
                      AT NO 12      F(X)= .6579    I(P)/(F(X)*C)= .60674-02    I(C)/I(P)= .11572-02    F(X),CONT= .4449
            ALKA1     AT NO 13      F(X)= .9025    I(P)/(F(X)*C)= .37499-02    I(C)/I(P)= .12522-02    F(X),CONT= .6310
            COMPOUND STANDARD FOR ELEMENT 3
                      AT NO 13      F(X)= .7094    I(P)/(F(X)*C)= .36942-02    I(C)/I(P)= .14366-02    F(X),CONT= .4236
            CAKA1     AT NO 20      F(X)= .9676    I(P)/(F(X)*C)= .90094-03    I(C)/I(P)= .78028-02    F(X),CONT= .7518
            COMPOUND STANDARD FOR ELEMENT 4
                      AT NO 20      F(X)= .9361    I(P)/(F(X)*C)= .84723-03    I(C)/I(P)= .92689-02    F(X),CONT= .4221


    POINT NO 1
K(1)=.1844 K(2)=.0368 K(3)=.0863 K(4)=.1475

    ELEMENT     AT CONC     WT CONC     STD DEV     F(X)     I(P)/(F(X)*C)     I(C)/I(P)     F(X)CON     CHAR FLUOR     F(X)CHA
     SI   14     .1740       .2268       .0000     .7392      .26802-02       .18214-02     .4020
     MG   12     .0433       .0488       .0000     .6464      .60860-02       .12239-02     .4408       .91962-02       .6153
     AL   13     .0870       .1089       .0000     .7188      .37055-02       .15353-02     .4405       .90593-02       .6714
     CA   20     .0869       .1616       .0000     .9370      .84988-03       .90648-02     .4423
     O     8     .6088       .4519       .0000

              TOTAL =     .9980

                   ITERATION NO  4

        STOICHIOMETRY

              OXIDE      CONC.

              SIO2       .4852
              MGO        .0810
              AL203      .2058
              CAO        .2261
```

Figure 10. Typical output of program COR for the analysis of a mineral, using compound standards.

The program is at present used routinely for data reduction. Certain minor features are still being tested. Copies will be available after the documentation and testing are completed.

F. Service Analyses

Besides the homogeneity characterization on the gold-silver and gold-copper Standard Reference Materials, we have performed a large number of service analyses, including the following:

1. Analysis of lunar material from flights Apollo 11 and Apollo 12 (Figures 11-13).

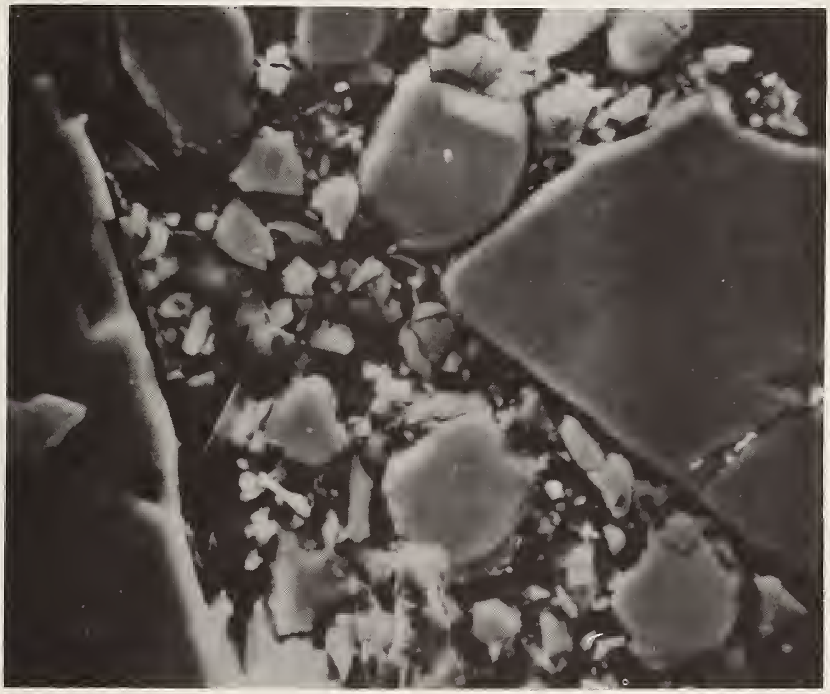


Figure 11. Scanning electron micrograph of a breccia from flight Apollo 11. Magnification: 1200X.

Figure 12. Target current and x-ray scanning images of a rock fragment in breccia from Apollo 11. Magnification: 40 μm/cm. (A) Target current. (B) Si Kα. (C) Fe Kα. (D) Ti Kα. The major phases observable in this series are orthoclase (low iron level), pyroxene (medium iron level, silicon present), and ilmenite (high iron and titanium, silicon absent).

The work was performed both on basalt-like rock fragments and on breccia. On all of these specimens, the analyses started with a general survey, performed by target current scanning, x-ray scanning, and qualitative or semi-quantitative local analysis by means of crystal spectrometers or energy dispersion detectors. By these means, we established which phases were present in each specimen and the approximate composition of each phase. Color composites were also prepared to illustrate the element distribution in several areas of interest.

The following phases were observed in rock specimens:

a. Major phases: pyroxene, feldspar, ilmenite, and (only in Apollo 12 sample) olivine

b. Minor phases: apatite (containing rare earths), cristobalite, troilite, metallic iron, mesostasis (feldspar with high level of potassium), and ulvospinel

In breccia, besides the aforementioned phases, glassy spherules of composition approximating the average composition of the crystalline rocks were also analyzed.

The compositional variations within grains and from grain to grain were quantitatively investigated, by means of the simultaneous determination of six elements over hundreds of points. Some of the results of this work, performed in cooperation with I. Adler, L. Walter, and B. French (Goddard Space Flight Center, NASA), were reported in references [27-28].

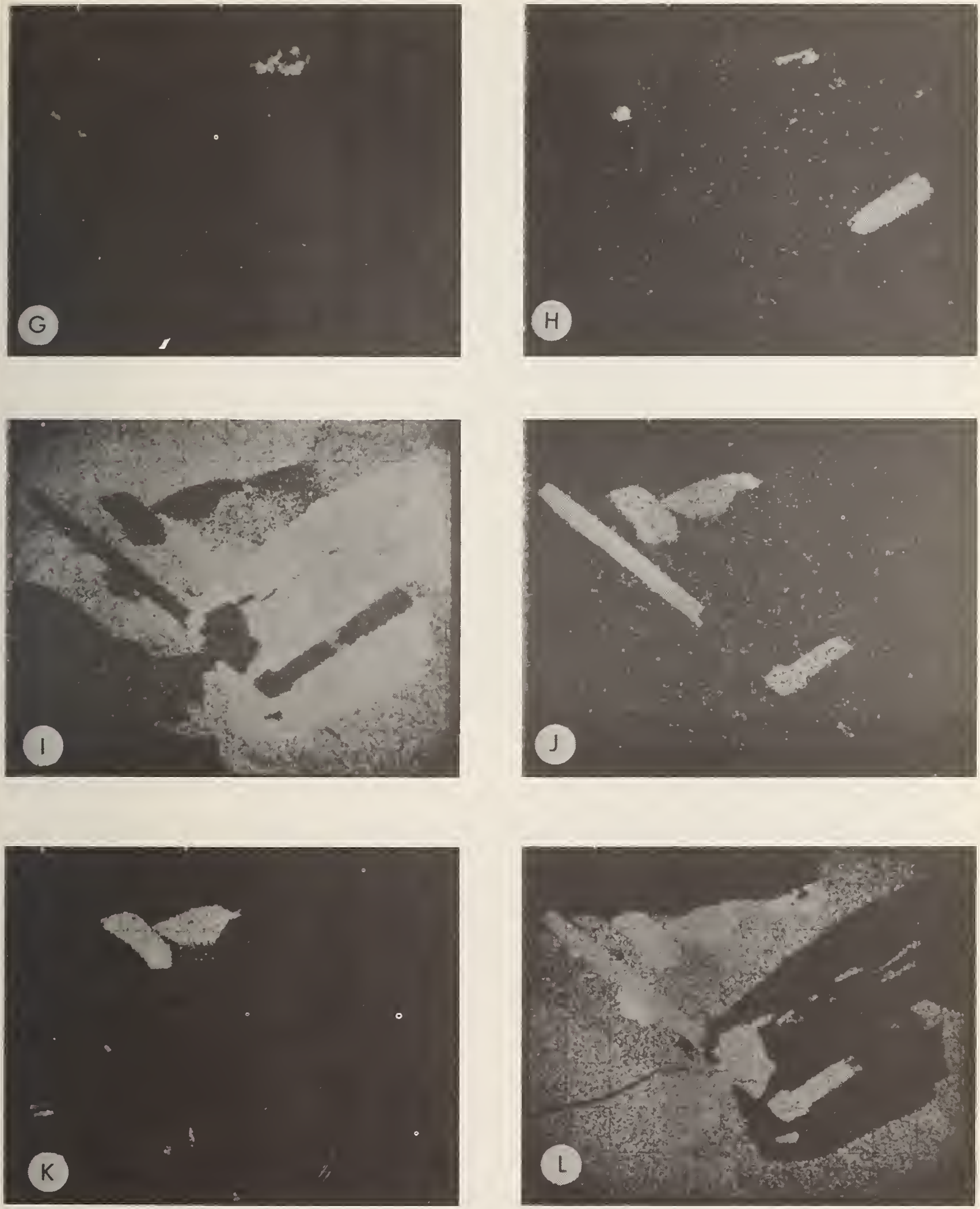
2. Failure analysis: Analyses were performed on various materials affected by corrosion or other failure processes. These include:

a. Sections of an eye-bar and of a hanger-strap from the collapsed Point Pleasant bridge

b. A specimen from a helicopter

c. Corrosion products on Cu-Pd alloys and on aluminum

Figure 13. Target current and x-ray scanning images of a rock fragment from flight Apollo 12. Magnification: 25 µm/cm. (A) Inverted target current. The numbers indicate the phases present in the specimen: 1-olivine, 2-pyroxene, 3-plagioclase, 4-mesostasis (a silicate with high contents of potassium, and some aluminum), 5-ilmenite, 6-ulvospinel, 7-troilite, and



8-metallic iron. (B) Derivative target current image, showing grain boundaries and other topographic features. (C) O Kα. (D) Mg Kα. (E) Al Kα. (F) Si Kα. (G) S Kα. (H) K Kα. (I) Ca Kα. (J) Ti Kα. (K) Cr Kα. (L) Fe Kα.

3. Diffusion couples: Hundreds of measurements were performed on Cu-Zn and Al-V diffusion couples.

4. Binary two-phase alloys: Very accurate measurements were performed on the systems Pt-V and Cr-Ir, as part of a program to investigate the respective equilibrium phase diagrams.

5. Five single crystals of a Cu-Au alloy were analyzed for local variations in composition. A zinc oxide specimen and sapphire crystals were investigated for distribution and composition of localized impurities.

6. A large number of specimens obtained in the research concerning "polywater" were investigated for the distribution of impurities.

7. Extensive work was performed on microbeads of ion-exchange resins loaded with various cations.

8. Other miscellaneous work included the quantitative analysis of evaporated thin films of various alloys, and the investigation of counterfeit documents.

G. Literature Research

We have updated our literature card files to the end of 1969. The classifying of these cards into categories is almost finished. However, due to reduction in personnel, work on the issuance of a bibliography had to be postponed.

K. F. J. Heinrich

3. X-RAY FLUORESCENCE SPECTROMETRY

The program and instrumentation for x-ray fluorescence spectrometry have been reviewed in prior technical notes of this series [1-5]. Continued research in the field of calibration, especially the area of correction techniques for interelement interferences, has given us new insight into this problem. We have produced an improvement to the state of the art on interelement interference correction methodology.

Again, as in the past few years, about one-half of the work of the x-ray fluorescence project has been in the area of support to SRM production and service analyses for a wide variety of projects from both inside and outside NBS. The types of support that have been provided to the Office of Standard Reference Materials include analysis of chemical composition, homogeneity testing, specimen sorting, and rapid verification of composition of labeled specimens. Through consulting, cooperative work, and instrument sharing, this project has assisted in the certification of a number of different SRM's for plating thickness. Our x-ray fluorescence instrumentation was first described and illustrated in 1965 [1]. Since that time, the equipment has been up-graded through gradual replacement of components. Seven of the ten modules shown in 1965 have been replaced and an oscilloscope for pulse monitoring and a system for automatic data acquisition have been added [2-4]. The current instrumentation, Figure 14, includes the following devices:

1. A 50-kV full-wave rectified x-ray generator, consisting of a power supply and a properly shielded and cooled x-ray tube. Two tubes, of a "quick change" design, are currently available, one with a tungsten target, the other with a chromium target.

Figure 14. Single-channel, vacuum x-ray fluorescence spectrometer. The power supply for the x-ray generator and the teletypewriter are to the left. The x-ray spectrometer is in the center and, on the right, are the signal processing electronics and oscilloscope.

2. A vacuum specimen chamber with provisions for introducing, positioning, and exchanging specimens to be measured.

3. A vacuum x-ray spectrometer, including a flat-crystal monochromator, with a choice of two crystals and two detectors (flow proportional and scintillation), and a wide-range goniometer with motor drive.

4. An electronic assembly for processing x-ray signals, including power supplies, preamplifiers, linear amplifier, single-channel pulse-height analyzer, scaler, timer, linear

ratemeter, chart recorder, data scanner for interface to teletypewriter, and a teletypewriter.

5. An oscilloscope for pulse monitoring.

The performance of the new electronics, all solid-state, has been very satisfactory. During the past two years, the equipment has been used almost continuously. Maintenance and down-time (principally related to the x-ray generator) consumed about five days during that period.

A. Research Activities

In seeking improvements in methods for data correction for interelement effects, it is helpful to begin with the binary alloys; with these, interaction relationships are easier to consider and a prerequisite of any valid model is that it will apply to binary cases. A classical set of binary interelement effect curves of relative intensity (R) is given in Figure 15. These curves have been approximated as hyperbolae in the past; but, if one plots C/R versus C, for the same data, (Figure 16) straight lines are not obtained, especially for the fluoresced element, Fe. A hyperbola in Figure 15 would be represented by a straight line in Figure 16. Earlier models were based on equations of the sort:

$$(C/R)_A = \alpha_{AA}C_A + \alpha_{AB}C_B$$

where the R's and C's are as defined before, α's are interaction coefficients, and the subscripts A and B are labels denoting the two elements of a binary. This does not reasonably fit the curvature apparent in Figure 16, consequently we have introduced the calibration equation:

$$(C/R)_A = 1 + \alpha_{AA}\,(C_A - R_A) + \alpha_{AB}C_B$$

with the symbols defined as before.

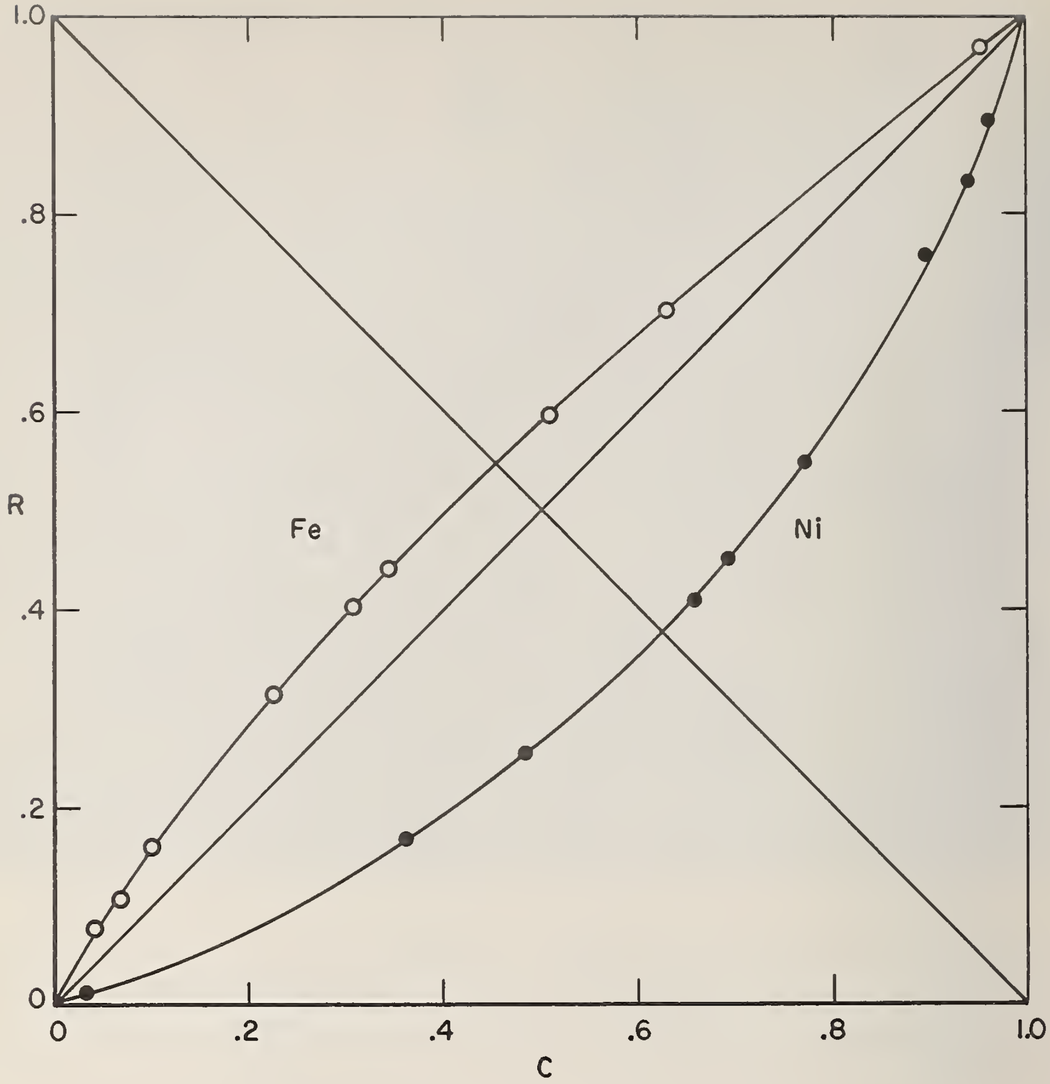


Figure 15. Calibration curves for Fe and Ni in the Fe-Ni binary system. Close examination will show that the interelement effects of fluorescence for Fe and absorption for Ni are not exactly hyperbolic.

Our testing, to date, indicates that this model very accurately calibrates the analysis of binary systems. Current effort is directed toward extending these ideas to multi-element systems.

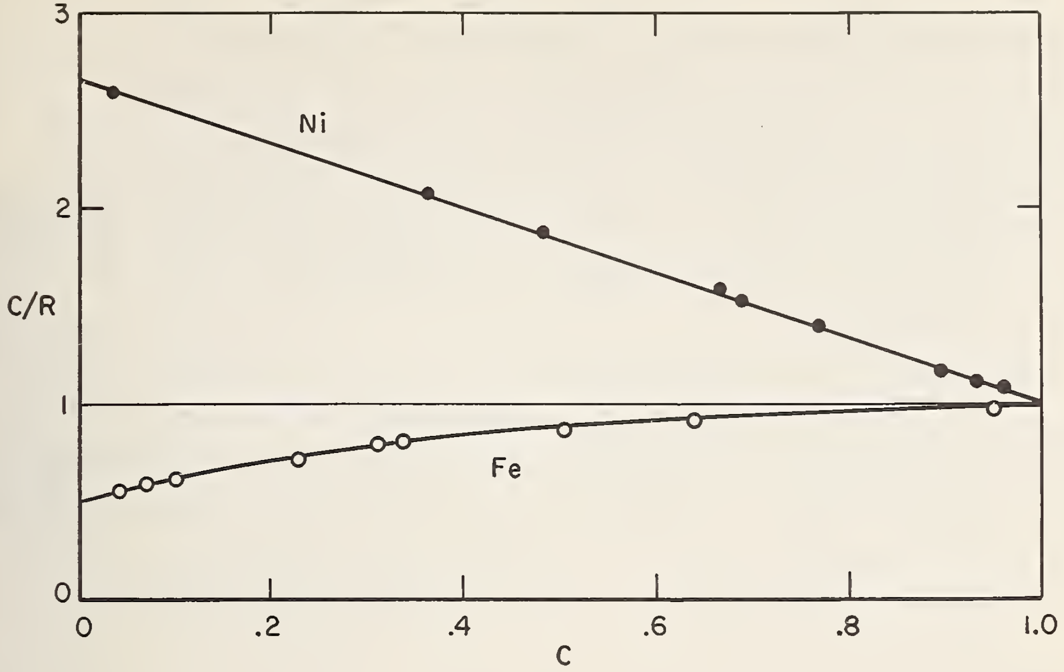


Figure 16. Graphs of C/R as a function of C. The same data as in Figure 15 are used to construct graphs to demonstrate more clearly the departure from a hyperbolic function. Here true hyperbolae would be represented by straight lines.

Frequently, ideas for new extensions of our technique are prompted by requests for service analyses. A recent request for assistance, by the Metallurgy Division, is typical of such cooperative developments. The problem, from the metallurgists' point of view, was to accurately, nondestructively, and economically determine the austenite in discs prepared by powder metallurgy as SRM's for the measurement of retained austenite. The measurement process sought also had an important requirement that the determination be specific to the surface. These SRM's are intended only for surface techniques (optical methods and x-ray diffraction) and differences between surface and bulk determinations have been observed. The requirements for economy and nondestructiveness are present because of the necessity of certifying individual discs.

While austenite cannot be directly determined by x-ray fluorescence, we still had an approach to this problem. The two powders mixed in preparation of the discs were ferrite (which contained no nickel) and austenite (which contained a constant proportion of nickel); therefore, a determination of Ni is directly proportional to the amount of retained austenite present.

Over ranges of a few percent, x-ray fluorescence calibration curves can be generally approximated as linear. In Figure 17 we see a curve for Ni in austenite/ferrite contrasted with a curve for Ni in low alloy steels. The greater slope in the low Ni region in austenite/ferrite is due to

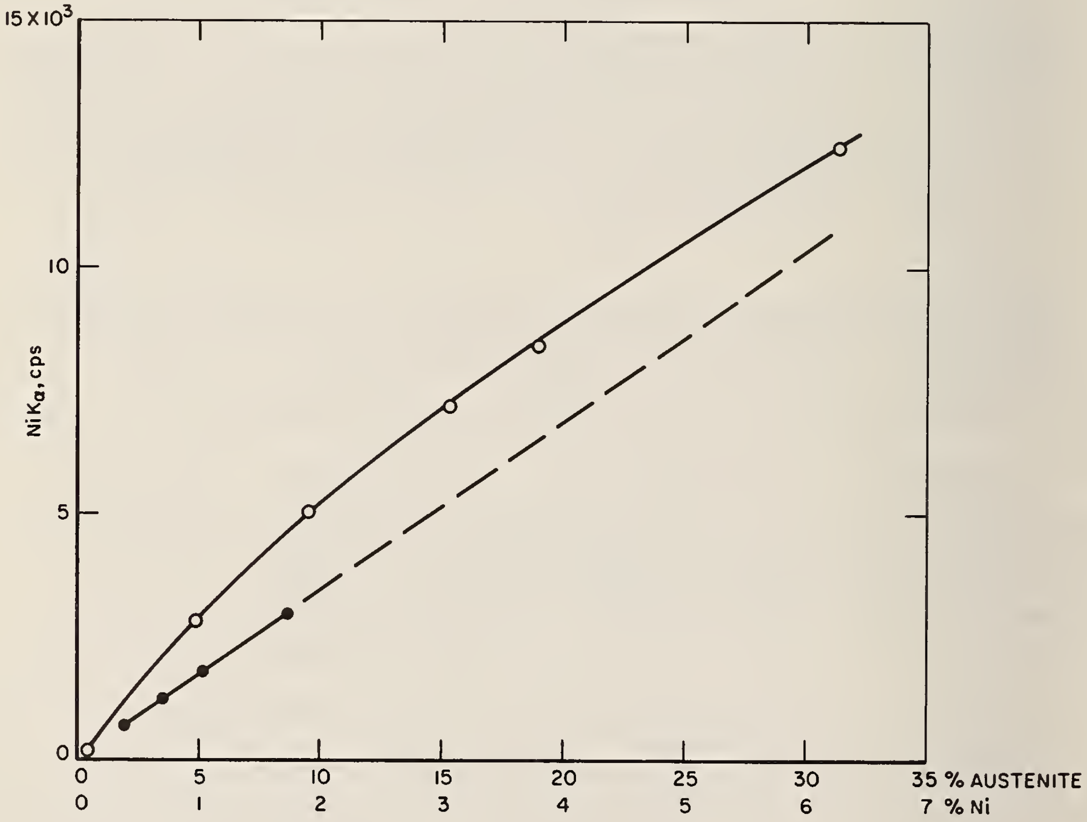


Figure 17. Top curve, Ni calibration in austenite/ferrite matrix. Bottom curve, Ni calibration in low alloy steels.

the localization of Ni in small particles. The Ni x-rays from the particles are relatively less absorbed by the adjacent iron than when both are more finely mixed.

During this year a joint paper with Dr. Marvin Margoshes entitled, "Fitting of Analytical Functions with Digital Computers" was published [29].

B. Applications

Nearly 700 man-hours have gone into performing 9056 separate quantitative determinations. Four of these projects seem especially interesting and worthwhile describing:

1. Zinc Diecast Gears

An outside agency submitted four small zinc diecast gears for analysis and comparison with specification AG40A, ASTM B-86. Figure 18 illustrates the sort of fractures occurring in some gears of this type. Quantitative determinations for six elements in each of the four specimens revealed that one gear was within specification and three gears differed from specification in only one element, lead.

Although Pb was present in these three gears at a concentration of only 0.02%, this exceeds the specification by fourfold. Consultation with a metallurgist revealed that the lead, being insoluble, migrates to the grain boundaries and lubricates them, propagating any cracks along these boundaries.

2. Thickness Determination of Fe-Be Layers

Within our Division, the Mössbauer spectroscopy group provided us with an interesting problem. In the construction of a resonant detector for 14.4 keV Fe^{57} gamma rays, they needed to measure the thickness (in the region of 1000 Å to 2000 Å) of supported layers of Fe-Be which was to become a

Figure 18. Photomicrograph (magnification, 60X) of a section of a zinc die-cast gear. Note the fracture between two of the gear teeth.

part of the detector. They were able to provide standards for this region of thickness and the calibration curve obtained is illustrated in Figure 19.

For this application, the x-ray fluorescence technique requires no specimen preparation and is quite rapid, thus specimens could be measured immediately after production, simplifying quality control. The set-up and measurement times for three unknown specimens was approximately 20 minutes.

3. Homogeneity Analysis of a Research Ingot of Cu-Ni-Fe

In materials research, experimenters should take care not to invest time and money in employing new specimens prior to verification of composition and homogeneity. Even on a non-routine basis, test pieces of experimental ingots can be economically examined by x-ray fluorescence.

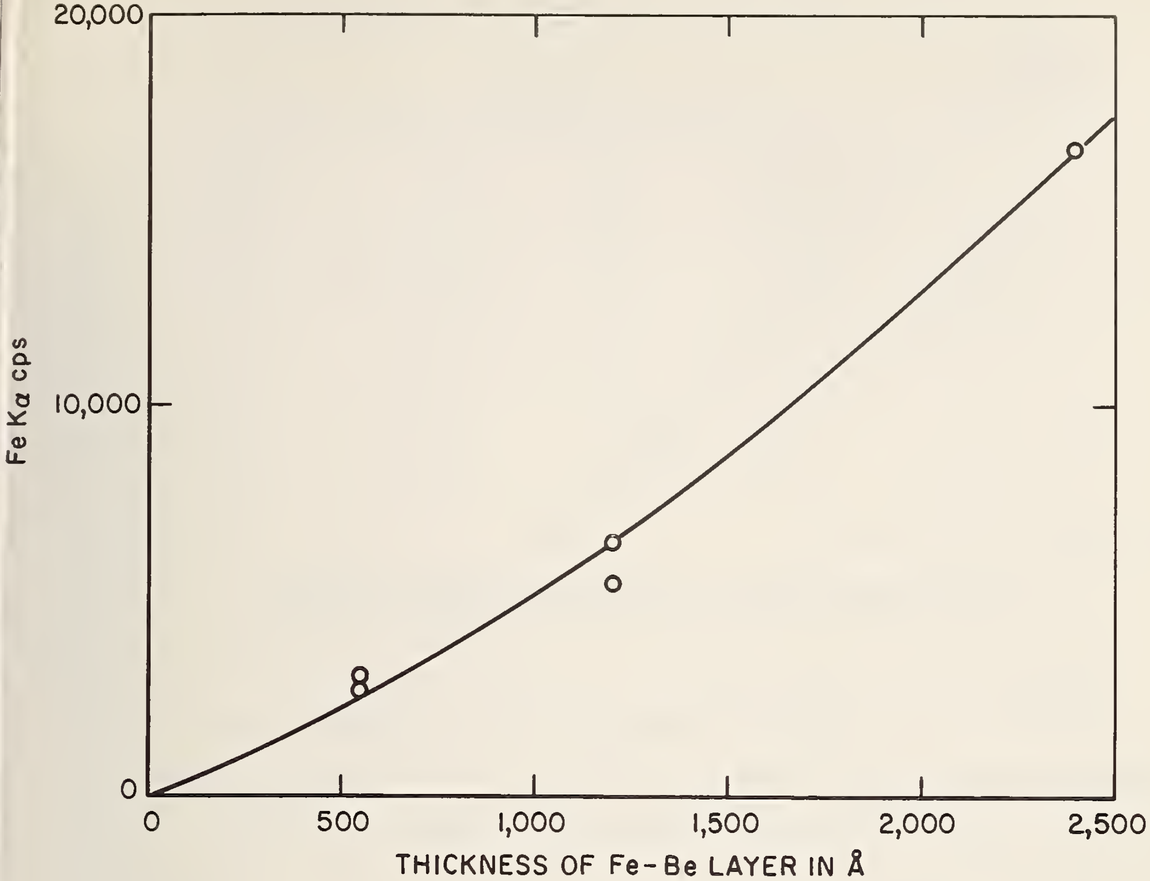


Figure 19. Thickness calibration for thin, supported layers of Fe-Be.

A request, recently received, was fulfilled in one-half man-day, including preparation, measurement, analysis, and report generation. The problem was to analyze the end pieces of two six-inch ingots of Cu-Ni-Fe alloy prior to their use in a research project of another Division. Table 3 shows the results of this analysis.

Limitations in the available calibration standards for these compositions prevented determination of the Cu and Ni with accuracy of better than ±2%, relative. However, the discrepancy apparent between the top and bottom of specimen B represents a real difference and alerts the user of the material that it should not be considered homogeneous.

Table 3. Analysis of Cu-Ni-Fe specimens

Specimen	Element (Concentration in Weight Percent)			
	Cu	Ni	Fe	Total
A - Top	81.8	18.2	0.04	100.0
A - Bottom	81.6	19.0	<0.02	100.6
B - Top	81.0	17.6	0.25	98.9
B - Bottom	74.3	23.7	0.15	98.2

4. Replacements for 1100 Series Steel SRM's

During this fiscal year, a large portion of our service to the Office of Standard Reference Materials has centered around evaluation of proposed SRM's 1261-1265, the replacements for the 1100 series low alloy steels and ingot irons. Our contribution to this program has been along three lines; preliminary analysis, homogeneity testing, and analysis for certification. The preliminary analysis is made on a ladle specimen obtained at the time of pouring the steel; the test is made to insure that the material is nominally the composition desired prior to further treatment. Using x-ray fluorescence techniques, we typically determine, quantitatively, 14 elements and report the results within one to two days after receipt of specimen.

Homogeneity studies begin after the material has been processed to slab form and properly sampled for the test. To date, all the preliminary analyses are complete and homogeneity testing remains to be done on only one of the standards, 1264.

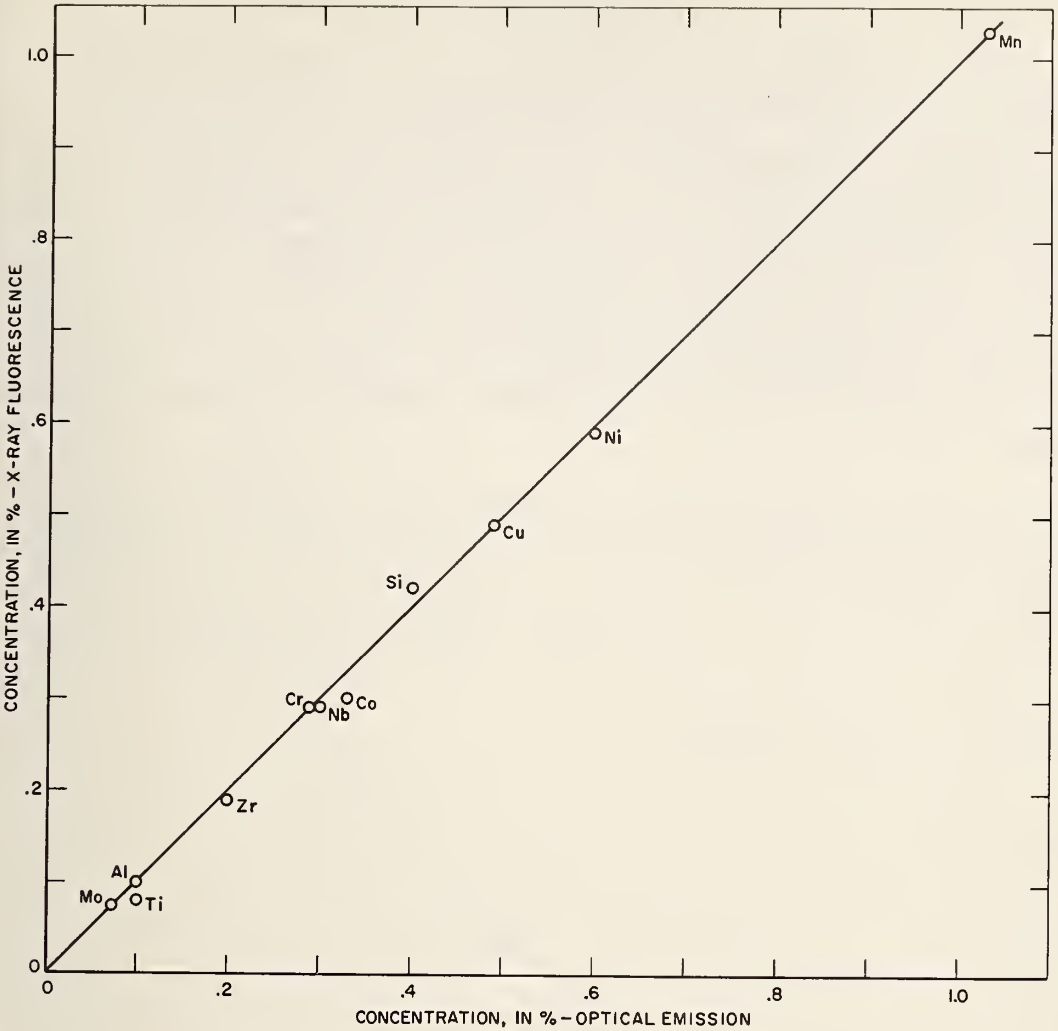


Figure 20. Correlation of x-ray fluorescence and optical emission results in the analysis of proposed SRM 1262.

Analysis for initial certification is accomplished by several methods, including x-ray fluorescence. These tests, which are now underway, are made on the material in its final state; that is, after it has been processed to 1 1/4-inch diameter rods. The x-ray analyses of the new SRM's are made relative to standards previously prepared which were analyzed by general chemical methods. The procedure permits the intercomparison of standards to insure that all are on a consistent basis. If irregularities are observed in plotting the x-ray data, the possibilities of line interferences in spectra or of errors in chemical analyses of the material are examined.

The results of two different methods may be compared to detect errors. As an example, the agreement obtained between x-ray fluorescence and optical emission spectroscopy is demonstrated in Figure 20, for the case of proposed SRM 1262. A similar correlation graph for x-ray fluorescence results and the values (mean of determinations by several methods) which will be published on the provisional certificate are given in Figure 21.

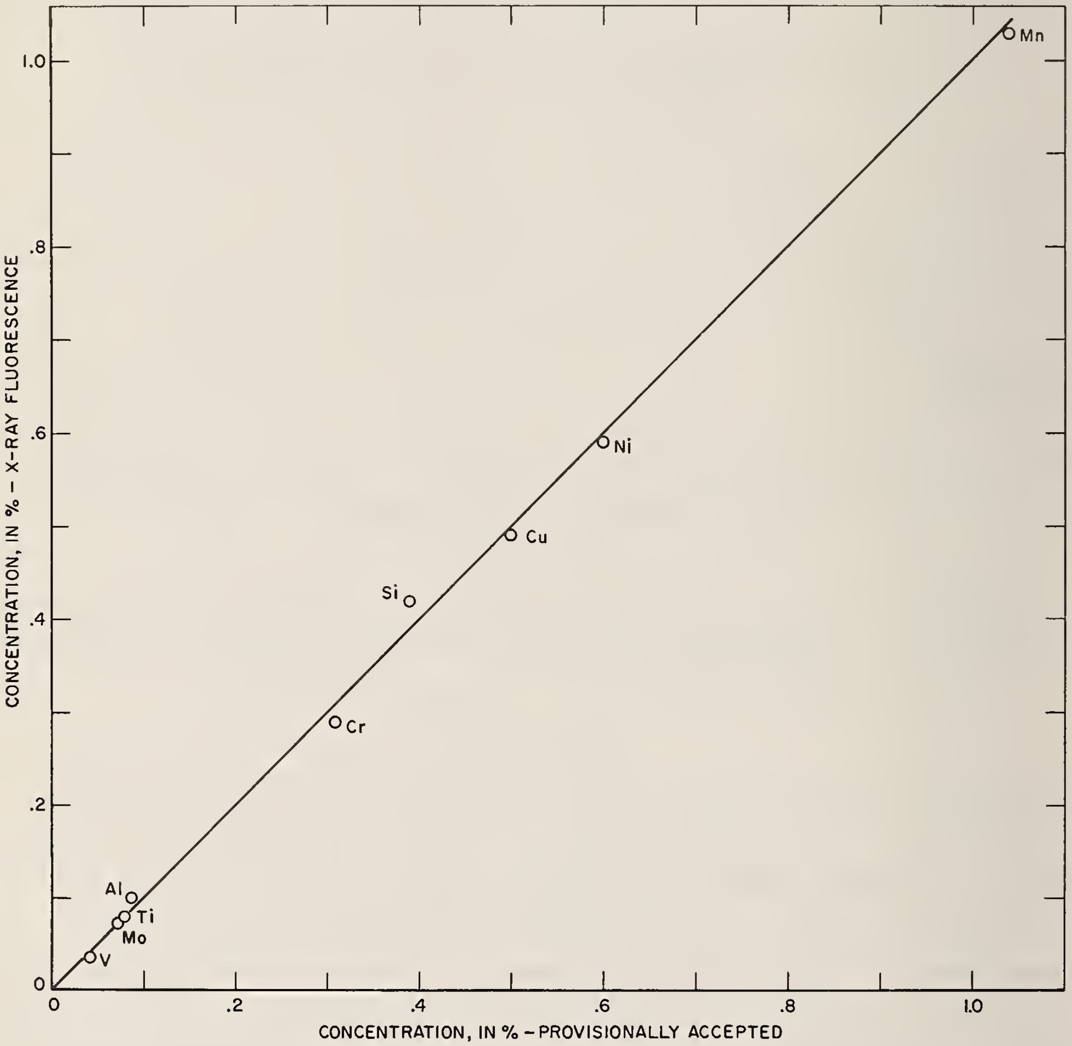


Figure 21. Correlation of x-ray fluorescence results and provisionally accepted values for proposed SRM 1262.

C. Contributions of NBS Personnel

Jerry McKay has assisted in performing quantitative analyses and tests of homogeneity. Jeremy Winick began researching quantitative x-ray fluorescence analysis by the approach of fundamental parameters (absolute methods). We gratefully acknowledge the assistance of Doward Bouchette in supplying data for several intercomparisons between x-ray fluorescence and optical emission. He and James Izlar, of OSRM, assisted in specimen identification and label checking by x-ray methods.

Fielding Ogburn, Jacob Smit, Virginia Pennington, and Carole Shriner (from the Metallurgy Division) have been part-time guest workers carrying out a project of thickness measurements on electroplated metal coatings.

S. D. Rasberry, K. F. J. Heinrich

4. OPTICAL SPECTROMETRY

During the past year, emphasis has been placed on the investigation of optical emission spectroscopic methods for the analysis of air-borne pollutants and of impurities in clinical and botanical materials. These analytical problems are vitally important in view of the increasing environmental hazards that have been recognized. Optical emission spectrometry is especially useful for this type of analysis because of its high speed and relatively simple preparation of samples.

The sensitivity of emission spectroscopic methods can often be extended by preconcentration techniques; these are discussed in Section 5 of this report.

Literature studies have been continued and an extensive reference file on emission spectrometry has been maintained.

Homogeneity testing and analysis of Standard Reference Materials continues to be a major effort in optical spectrometry along with qualitative and quantitative analysis of a diversity of other samples. The effort is due in part to the increasing number and variety of Standard Reference Materials being prepared. Section 4B of this report describes some of the emission spectrochemical analyses performed this year and will give an indication of the variety of problems encountered in this work.

A. Air Pollution Studies

The Spectrochemical Analysis Section has been especially active in the analysis of dusts, deposits, precipitates and similar samples by optical emission. The early spectroscopic work was reported by B. F. Scribner at the United States Technical Conference on Air Pollution, May 1950 [30]. Applications of this work have continued in our laboratory.

The last report in this series [5] briefly described an application of a semi-quantitative analysis of beryllium smears as part of a safety surveillance program. During the past year, we have continued the investigation to extend the sensitivity of the determination of Be in dust deposits and dust collected from the air to the subnanogram range. The samples are collected on 25 mm square or 12 mm diameter filter papers, placed in cupped electrodes, and charred for approximately 15 minutes in a muffle furnace heated at 450°C. Landis and Coons [31] have pointed out the advantages of using alkaline earths as a buffer in arcing small amounts of Be and accordingly, 5 mg of $BaCl_2$ in a 1:1 $BaCl_2$ + graphite mixture is added to the cupped electrode after charring. Standards are prepared by adding aliquots of a beryllium sulfate solution to filter paper, drying, and then handling in the same manner as the samples.

The samples and reference standards are excited in a controlled atmosphere direct current arc and the Be 3130.4 Å line is recorded photoelectrically. The controlled atmosphere device that we use is one developed in this Section [32]. A photograph of the gas sheath device mounted in a multi-purpose arc-spark stand on a photoelectric spectrometer is shown in Figure 22. This device makes it possible to excite samples as rapidly and conveniently in controlled atmospheres, as in air, does not require modification of the arc stand, and can be put in place or removed easily. Two advantages of the controlled atmosphere excitation as opposed to excitation in air are improved stability of the discharge, resulting in more uniform burning of the sample, and elimination of CN bands which obscure the most sensitive lines of several elements. This latter advantage will be particularly useful as the method is expanded to include other elements. Conditions for the spectrometric determination of Be are given in Table 4.

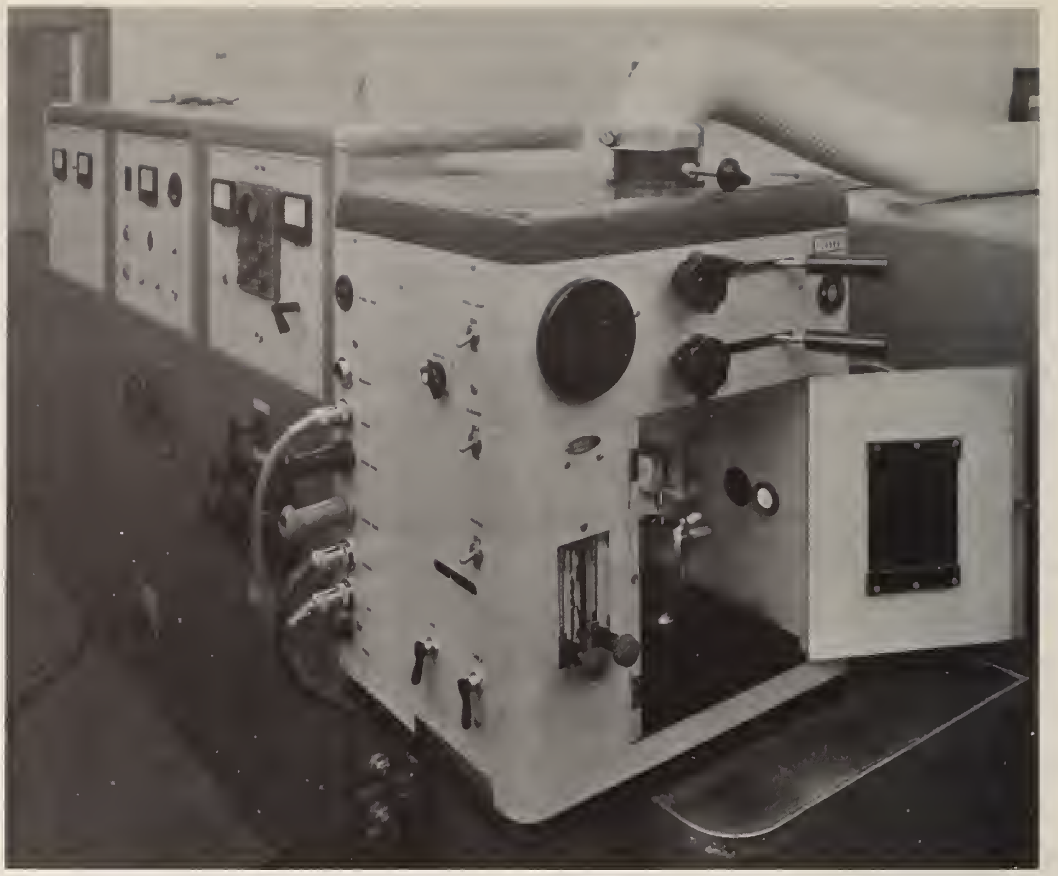


Figure 22. Arc-spark stand mounted on photoelectric spectrometer.

Following the readout of the Be 3130.4 Å line, calibration curves relating intensity vs weight of Be contained in the standards are constructed. This method has enabled us to detect differences in Be content at the 0.1 ng level.

We plan to continue this investigation and to extend the method to include lead, mercury, and other elements of concern in air pollution studies.

B. Analysis of Clinical Materials

The analysis of organic materials, such as plastics, foods, and clinical materials is preceded by careful low temperature ashing of the sample with collection of the ash in a suitable high purity material.

Table 4. Spectrometer conditions for beryllium determinations

Spectrometer	3.0 meter grating spectrometer with a reciprocal linear dispersion of 5.2 Å/mm
Slit width	20 µm entrance slit, 75 µm exit slit
Electrodes	Lower, anode, sample. Undercut thin wall ASTM type S-12. Upper, cathode, ASTM type C-5
Electrode gap	4 mm - adjusted during burn
Atmosphere	70% argon, 30% oxygen, 15 cu ft/hr at 3 lbs/in.^{2}
Excitation	Direct current arc. Start at 5 amp for 5 sec then at 20 amp for complete burn (approximately 90 sec)
Recording	Digital print-out of photoelectric integration

An example of this type of analysis is the analysis of glucose. Three lots of glucose were obtained by the Office of Standard Reference Materials as potential SRM's. The materials were submitted to our Section with the request that they be analyzed for impurity elements. Weighed portions of each lot were ashed with high purity gallium oxide, which was used as a collector, and were analyzed by an emission spectrochemical method using a gas sheath around an 1/8-inch diameter electrode. A short duration 15-amp dc arc burn gave good line-to-background ratios with complete consumption of the samples. Synthetic standards of gallium oxide doped with elements in the ranges desired were arced in the same manner to provide for standardization. Quantitative data for the elements Al, B, Cu, Fe, Mg, Si, and Ca, and limits of detection by this method for 18 elements specifically looked for, but not detected, are shown in Table 5.

Table 5. Determinations of impurities in glucose

Concentrations in parts per million (μg/g)

Element	Sample			L.D.*	Element	Sample			L.D.*
	1	2	3			1	2	3	
Ag	-	-	-	<0.001	In	-	-	-	0.002
Al	<0.05	<0.05	<0.05	0.01	Mg	0.1	0.1	0.1	0.001
As	-	-	-	0.4	Mn	-	-	-	0.002
B	<0.05	<0.05	<0.05	0.01	Mo	-	-	-	0.005
Be	-	-	-	<0.001	Ni	-	-	-	0.002
Bi	-	-	-	0.005	Pb	-	-	-	0.002
Ca	5	5	5		Sb	-	-	-	0.3
Co	-	-	-	0.002	Si	0.1	0.1	0.1	0.05
Cr	-	-	-	0.002	Sn	-	-	-	0.002
Cu	<0.01	<0.01	<0.01	0.001	Ti	-	-	-	0.002
Fe	< .05	<0.05	<0.05	0.005	Tl	-	-	-	0.3
Ge	-	-	-	0.001	V	-	-	-	0.002
Hg	-	-	-	0.4					

* Estimated limits of detection

It will be noted that detection limits as low as 1 to 2 parts per billion are attained for 14 chemical elements.

C. Literature Research

A systematic survey of the literature has been continued largely through scanning of Chemical Abstracts for papers on spectrochemical analysis. References are machine copied and pasted on cards. A periodic check of original journals is made to ensure full coverage of the literature. References are indexed by subject and are employed for publication of bibliographies or review articles. During this year, the bibliography on optical emission spectrometry for the years 1956-60 was prepared for publication. A comprehensive two-year review of Emission Spectrometry was prepared by Margoshes and Scribner and was published in the April 1970 issue of Analytical Chemistry.

D. Applications to Analysis

During the past year, as in previous years, the facilities of this Section for spectrochemical analysis were employed for analytical work as well as for research activities. For the period July 1969 through June 1970, analyses were performed by optical emission spectroscopy involving 566 samples, 14,714 determinations, and 113 reports. Some high points of the analyses will be described.

1. Analyses of Standard Reference Materials

The program of Standard Reference Materials continues to be an important activity of the Spectrochemical Analysis Section. The output of this program consists of standard reference samples of certified composition produced in cooperation with the Office of Standard Reference Materials and other sections of the Analytical Chemistry Division. Starting with the preliminary evaluation of the material and carrying through to the final quantitative analyses, this Section contributes to the certification of many reference materials.

Most of the materials are submitted for a qualitative or semi-quantitative analysis as a step in the preliminary evaluation. This procedure will show whether or not the material is pure enough for the intended purpose or, in the case of alloyed materials, whether it has approximately the desired composition. It will also provide information to permit proper planning of subsequent analytical procedures for certification of composition. Samples carried through this procedure in the past year include glucose, fructose, bilirubin, orchard leaves, potassium dichromate, metallo-organic compounds, irons, and steels.

The next step in the production of Standard Reference Materials is to procure a large quantity of the material and determine its homogeneity. Homogeneity of the intended standard is essential to its use, since each user should receive a specimen corresponding in analysis to the certificate provided for the bulk material. A common procedure is to select samples from chosen points, which represent the extremes in the bulk of the material, and to make analyses at each of these points for elements of interest. An illustration of the sampling procedure for a 5-ton steel ingot is shown in Figure 23.

A cylindrical ingot, the cross section of which is shown in the upper left corner, is forged or rolled to a slab 5 in. thick by 17 in. wide. Previous experience has shown that areas of heterogeneity are most likely to exist in the portions corresponding to the top, bottom, and middle of the ingot; therefore, these portions are cut from the slab and discarded prior to homogeneity tests. Slices are then cut from the remaining slab pieces at the top, middle, and bottom and appropriate samples are taken from the slices to test for

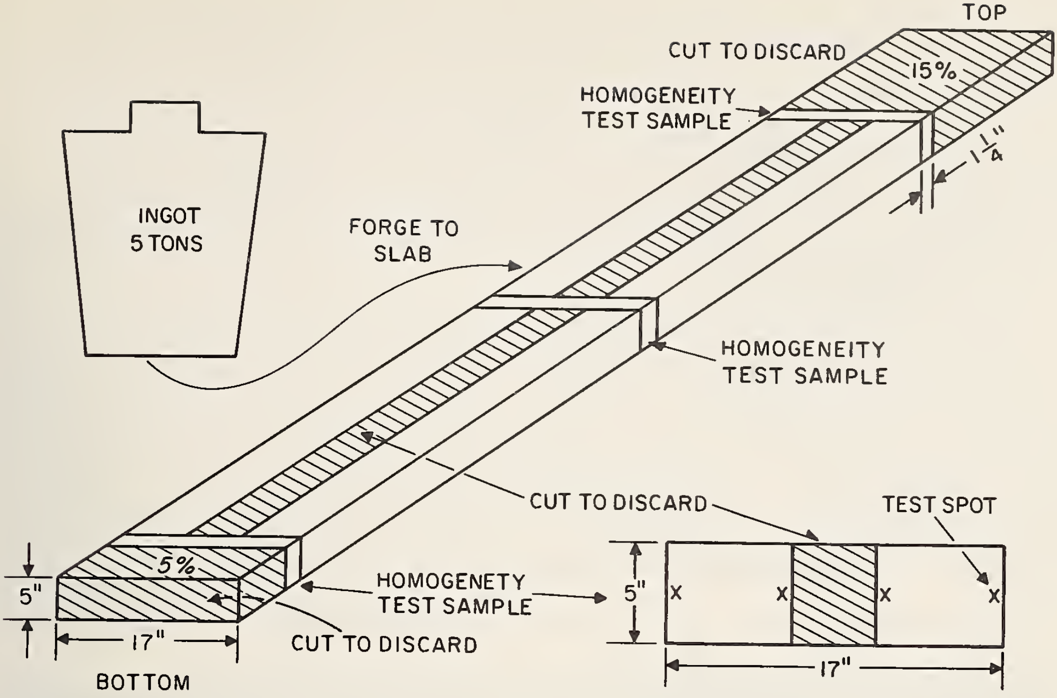


Figure 23. Sketch showing sampling of steel slab for homogeneity studies.

homogeneity. A cross section of one of the slices is shown in the lower right corner with the positions for sampling also shown. The twelve samples, so chosen, are representative of the extremes of the trimmed slab; i.e., top, middle, bottom, inside, and outside.

Emission spectrochemetric methods are generally employed for the homogeneity testing. Data from the emission spectrometer are recorded directly in digital form and entered into a computer for statistical treatment. Analysis of variance serves appropriately for determining that part of variation in concentration attributable to segregation in the sample. Materials analyzed for homogeneity in this manner in the past year include four special low alloy steels, three stainless steels, two tin-lead solders, and two cast irons.

In addition to acceptance testing and homogeneity testing, we also participate in the quantitative analysis necessary for certification of Standard Reference Materials. Analyses by at least two independent methods relative to standards synthesized from pure materials, along with other analyses made at NBS, and by cooperators, provide for the provisional and final certification.

A final check on the analyses and the performance of the standards in optical emission analysis is made by intercomparison of the SRM's in a group and comparison with other standard materials. The results are studied by correlation methods to observe discrepancies that might point to errors in assigned concentration values or to interferences in the spectroscopic method. The correlation studies are similar to those described in Section 3 of this report.

Examples of certificates for Standard Reference Materials issued in the past year, to which this Section contributed, are given in the Appendix.

2. Other Analyses

Spectrochemical analyses are performed by this Section for other NBS laboratories and other Government agencies as part of a general service work program. The majority of analyses made are rapid surveys by optical spectroscopy in which 51 chemical elements are sought. An occasional request is made for rare earths and the alkalies to extend the list of elements to 70. This type of analyses is semi-quantitative with the concentration of elements found reported in ranges of factors of 10, e.g., 0.001 to 0.01%, 0.01 to 0.1%, etc. The information provided will quite often be sufficient for the problem; if not, it will provide the basis for planning of additional quantitative analysis by spectrochemical or other means. Typical samples analyzed in the past year by this method were dust, boiler scale, metallic oxides, paint pigment, solder flux, gold plate, and ceramic tubes.

Qualitative analysis may also be made on extremely small and single particles of material by use of the laser probe and a high aperture spectrograph. A recent application of this type of analysis involved an investigation by T. Kuroha of inclusions in high purity Teflon containers. The inclusions, which were in the order of 100 microns in diameter, were analyzed directly in the Teflon substrate and the qualitative information derived was sufficient to identify the particles as plain steel, stainless steel, and aluminum alloys. A photograph of the laser head mounted on the optical bar of the high aperture spectrograph is shown in Figure 24. A more detailed description of this equipment was given in the last publication of this series [5].

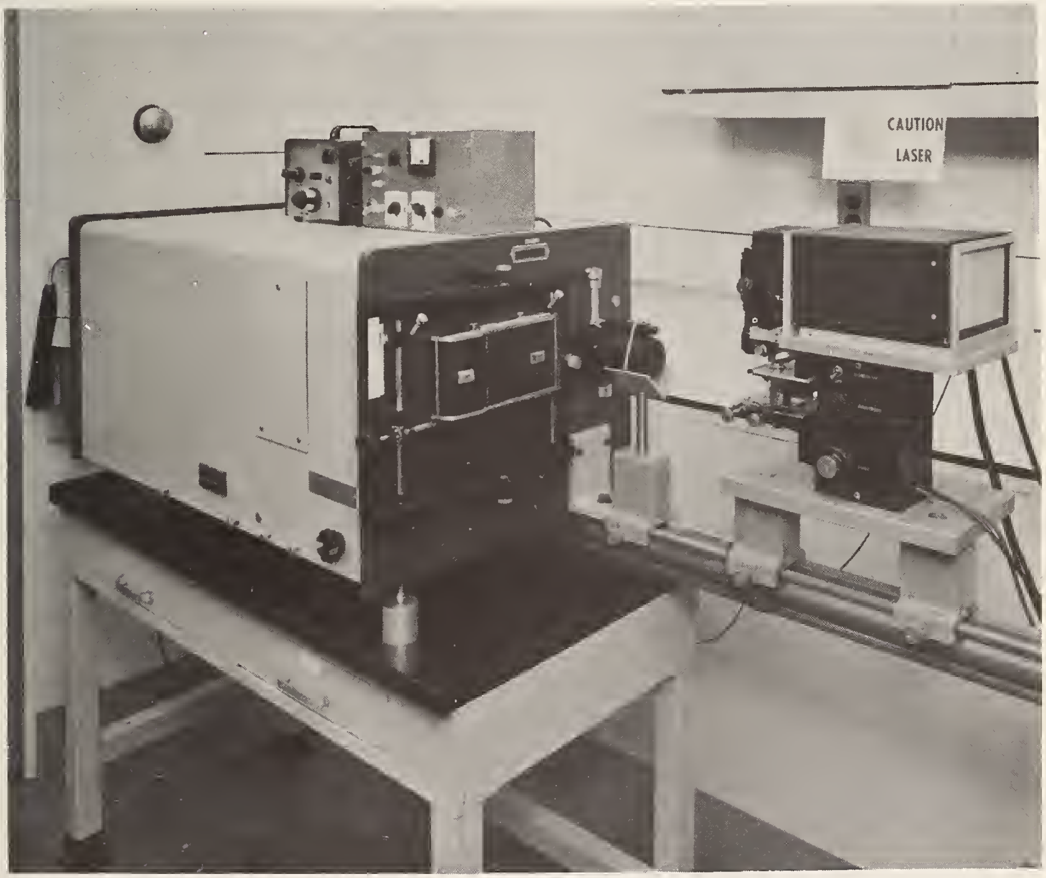


Figure 24. Apparatus for laser-probe analysis. Left, high-speed spectrograph. Right. laser probe mounting.

In addition to the qualitative and semi-quantitative survey type analyses, we are frequently called upon to perform quantitative analyses for compliance to chemical composition specifications. These analyses are usually part of a detailed failure study made at NBS or by other agencies such as the Transportation Safety Board. An example of this is an investigation of the cause of an aircraft disk brake assembly failure. As a first step in the investigation, the samples identified as stationary disk and rotating disk were submitted for analysis to verify compliance to alloy specifications. In this case, both parts were found to be the alloys specified and the investigation has been continued to find other possible causes of failure. Similarly, other analyses were made in the past year on bridge steel members, railroad tank car plate, aluminum sheet and castings, stainless steel tubing, and steel construction rod.

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5. PRECONCENTRATION TECHNIQUES

This part of the report outlines procedures by which analytes are separated or preconcentrated from the matrix material for instrumental determination by optical emission or spark source mass spectrography. These procedures are developed to obtain improved limits of detection or to provide the analytes in a form more suitable for the spectrochemical excitation or ionization step. For instance, in optical emission spectrochemical methods, the matrix may be removed and replaced by a smaller amount of material having a simpler spectrum when excited in a dc arc; or a group of trace elements may be separated and transferred onto electrodes for excitation by a high-voltage spark discharge. In both cases, the analysis is accomplished by comparison with synthesized standards. For spark source mass spectrography, the analytes are usually isotopically diluted before being placed on a wire substrate for sparking.

Most of the applications are to a variety of materials that are issued as NBS Standard Reference Materials after comparing the results of various analytical methods. When results obtained, using such fundamentally different procedures as optical emission and spark source mass spectrography, are in agreement, the validity of the results and of the methods that produced them are reinforced. Moreover, because of the desirability of completely characterizing a composition SRM, these methods which yield results for a number of analytes simultaneously are particularly valuable and efficient.

A. Optical Emission

1. Ingot Iron

An optical emission method was developed for determining cobalt, chromium, copper, and manganese in an ingot iron material, subsequently issued as SRM 1265. "Less than" values were reported for the aluminum and titanium contents, which were less than the lowest concentrations in the synthesized standards. In the procedure, sample weights of 100 mg were dissolved in 6 M HCl and a few drops of HNO_3 were added to oxidize Fe^{++} to Fe^{+++}. The iron was then extracted with methyl isobutyl ketone that had been equilibrated by shaking with an equal volume of 6M HCl. After making up the aqueous phase to 25 ml, 5 ml aliquots were pipetted into 100-ml Teflon evaporating dishes. To each dish were added 400 µl of gallium nitrate solution, containing 5 mg of gallium per ml, and 250 µl of indium nitrate solution containing 1 µg of indium per ml. The indium solution was added to serve as an internal standard. The solutions were evaporated to approximately 1 ml in a clean environment evaporator, which is shown in Figure 25. After adding one drop of HNO_3 and 0.5 ml of 12M $HClO_4$ to each solution, they were evaporated to dryness and the residues ignited at 250°C for 30 minutes.

Figure 25. Clean environment evaporator.

Synthesized standards were prepared by adding known amounts of the impurity elements to the same quantities of gallium and indium solutions used for the samples. Following the procedure used for the samples, the solutions were dried and ignited at 250°C for 30 minutes.

The powders from the sample treatment and from the preparation of the reference standards were transferred to graphite electrodes and excited in a dc arc. The spectra produced were photographically recorded and the intensity ratios of selected pairs of analytical lines and indium internal standard lines were determined photometrically. Concentrations of the elements were read from analytical curves relating log intensity ratio to concentration. Table 6 shows details of the spectrographic procedure.

Table 6. Spectrographic details for determination of impurities in iron

Spectrograph	Ebert, 3.4 meter grating spectrograph with a reciprocal linear dispersion of 5 Å per mm
Slit width	30 micrometers
Electrodes	Lower, anode, sample. Undercut thin wall ASTM type S-13. Upper, cathode, ASTM type S-1
Electrode gap	4 mm - adjusted during burn
Atmosphere	70% argon, 30% oxygen
Excitation	Direct current arc. Start at 5 A for 10 seconds then at 15 A for complete burn plus 5 seconds
Recording	Photographic using SA1 emulsion
Developing	Routine D-19

The results obtained by this method are shown in Table 7.

Table 7. Analysis of ingot iron SRM 1265 by optical emission spectrography

Element	Average concentration percent by weight	95% Confidence limits	Number of determinations
Cr	0.0073	±0.0006	6
Co	.0070	± .0006	6
Mn	.0069	± .001	6
Cu	.0066	± .0006	6
Al	<.001		6
Ti	<.002		6

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2. Botanical Materials

A spectrochemical method for analyzing samples of ground orchard leaves is being developed. The samples are mixed with gallium oxide and weighed into graphite electrodes. They are then ashed, covered with high-purity graphite powder, and excited with a dc arc. Better burns and lower background is achieved with a gas sheath [32]. When the ash content is very low, several ashed portions can be combined in one electrode.

3. Miscellaneous

The copper spark method [33] is a spectrochemical technique for determining trace elements in a solution that has been evaporated on the ends of a pair of electrodes. The analytes are subsequently excited by a high-voltage spark discharge. High-purity graphite has also been used in the general method instead of copper [34]. In applying this technique to analytical problems, the procedures for separating the trace analytes from the matrix often produce a considerable amount of residue. Under these conditions, the residue on the electrode surfaces can be dislodged by the high-voltage spark before excitation.

In separating the trace elements from the matrix, they are usually present as extremely dilute solutions and are therefore susceptible to "sorption" losses. Moreover, the manipulations required for preconcentrating the analytes and evaporating the solution on the electrodes increases the possibility of contamination. Electrodeposition of certain trace elements from a solution of the matrix directly on the electrode surface would be less subject to such errors. Previous work from our laboratory describing the electrodeposition of trace amounts of silver on graphite electrodes was reported at an NBS Symposium for Trace Characterization [35]. At that time, initial experimentation was performed on electrodepositing trace amounts of cadmium on mercury-plated copper electrodes.

During this period, additional experiments were performed to establish conditions for quantitatively electrodepositing bismuth, cobalt, tin and zinc by using ^{207}Bi, ^{60}Co, ^{119m}Sn and ^{65}Zn as tracers. In addition, a number of other cathode-active elements present at concentrations of 0.1 μg/ml in 5 ml of solution appeared to be quantitatively deposited. This investigation will be continued and results made available at a later date.

R. Alvarez, M. Darr, E. Belkas

B. Isotope Dilution

1. Ingot Iron

In last year's annual report [5], we outlined a stable isotope dilution - spark source mass spectrographic method (ID-SSMS) for analyzing ingot iron. Silver, copper, molybdenum and nickel were simultaneously determined in the 100-mg samples of NBS-SRM 1165 using a chemical preconcentration step to separate the spiked analytes from the matrix. The concentrations ranged from 0.0005% for Ag to 0.025% for Ni. Cobalt, a mononuclidic element, was also determined at the same time by adding known amounts of Co to half of the samples used for the isotope dilution determinations and measuring the $^{59}Co/^{60}Ni$ and $^{59}Co/^{58}Ni$ ratios. Details of the method, including a comparison of the results obtained with the certified values, were published recently in Analytical Chemistry [36].

Applying this method to the analysis of an ingot iron material intended as a renewal NBS Standard Reference Material, the basic procedure was altered to investigate whether other elements could be separated and thus determined. Titanium was of particular interest. After extracting the iron into the organic phase, the aqueous phase was evaporated to a few tenths of an ml instead of being electrolyzed as in the published procedure. The residue was transferred to high-purity gold wires and ignited at 450°C for 20 minutes in a tube furnace equipped with a quartz tube liner. The wires were then sparked in the mass spectrograph and the spectrum was phototraphically recorded. A line corresponding to SO^+, which has a mass/charge ratio of 48, was found. This species, which is an ion fragment from the sulfate in the residue, interfered with an intensity measurement of the line on the emulsion produced by the ^{48}Ti. The sulfate in combination with alkali cations is not removed by ignition. Some of the sulfate came from the ^{47}Ti spike solution since H_2SO_4 had been used to dissolve the enriched isotope material. Moreover, during the subsequent dilutions of the 1 mg/ml ^{47}Ti stock solution, the acid strength had been maintained with H_2SO_4 to prevent hydrolysis. Had we anticipated the production of SO^+ with this procedure, these dilutions could have been performed with $HClO_4$. Because of interferences of this type and those from combinations of anions and cations, we have preferred to incorporate an electrodeposition step in the previous analytical procedures that we have developed. This has the advantage of providing the isotopically altered analytes relatively free of other anions and extraneous cations, thus greatly simplifying the photographically recorded spectrum.

Although Ti was not determined, other spiked analytes yielded interference-free lines on the emulsion. The results given in Table 8 were calculated from the general isotope dilution equation:

$$C = \frac{W\ K\ (A_{sp} - B_{sp}\ R)}{M\ (BR - A)}$$

where C is the concentration in µg/g, W is the weight of isotopically enriched material ("spike") added in µg, M is the weight of sample in g, A and B are the natural abundances of the analyte isotopes a and b, A_{sp} and B_{sp} are the abundances of isotopes a and b in the spike, R is the measured altered ratio of isotope a to isotope b, and K is the ratio of the natural atomic weight to the atomic weight of the spike.

Table 8. Analysis of ingot iron SRM 1265 by isotope dilution - spark source mass spectrography

Element	Average conc. percent by weight	95% Conf. limits	No. of Deter's
Cu	0.0058	0.0003	8
Cr	.0075	.0002	9
Ni	.040	.001	9
Mo	.0041	.0005	6

In the analytical procedure, most of the iron and some of the molybdenum are extracted with MIBK, and if the molybdenum present in the sample and the molybdenum spike were not in equilibrium, erroneous results would be obtained. This attainment of equilibrium, a sine qua non of the method, is usually ensured by cycling analytes and spikes through oxidation-reduction states. However, in attempting to determine several trace elements simultaneously, indiscriminate use of reagents, other than those of highest purity, would prohibitively increase the method blank for common elements thus precluding their determinations. We were interested in determining silver, which, unfortunately, proved to be less than 0.1 ppm in the samples.

Because of the several stable valence states that molybdenum possesses, there is even more concern regarding the attainment of equilibrium between that analyte and its spike. Consequently, two additional experiments were run in which the spiked samples were dissolved as before but then evaporated to dryness and treated with concentrated nitric acid. Individual results of 0.0039% and 0.0042% were obtained, which agree with the average value of 0.0041% reported in Table 8.

In another series of experiments designed to determine titanium, the isotopically altered trace elements were electrodeposited at an increased current density compared to that usually employed. Although under these conditions titanium was electrodeposited, as was evident from the mass spectrum, it could not be determined because of interference from the doubly charged ^{96}Mo on the singly charged ^{48}Ti. The relative amount of molybdenum compared to titanium on the gold wires was greater in this case than in the evaporation procedure. This interference from the doubly charged ^{96}Mo was eliminated by extracting the solution with methyl isobutyl ketone before electrolysis. But obviously, with this extraction step, we would be substituting molybdenum for titanium as an analyte.

A secondary problem was the appearance of titanium as a contaminant, possibly from the porous Vycor plug of the electrolysis cell. Two of the cells in a clean environment enclosure are shown in Figure 26. In this cell design, a porous Vycor glass plug separates the anode compartment from the cell proper containing the sample solution and gold wire cathodes. The plug is of small diameter, 3.5 mm, to minimize contaminating the sample solution from the porous glass itself and also from the electrolyte in the anode compartment. However, because of the increased current used in these experiments and the large resistance of the porous glass plug, the liquid in the anode compartment was heated to perhaps 80°C. Under these conditions, the sample solution may have become contaminated. A change in cell design using a salt bridge having a greater surface area should remedy this problem.

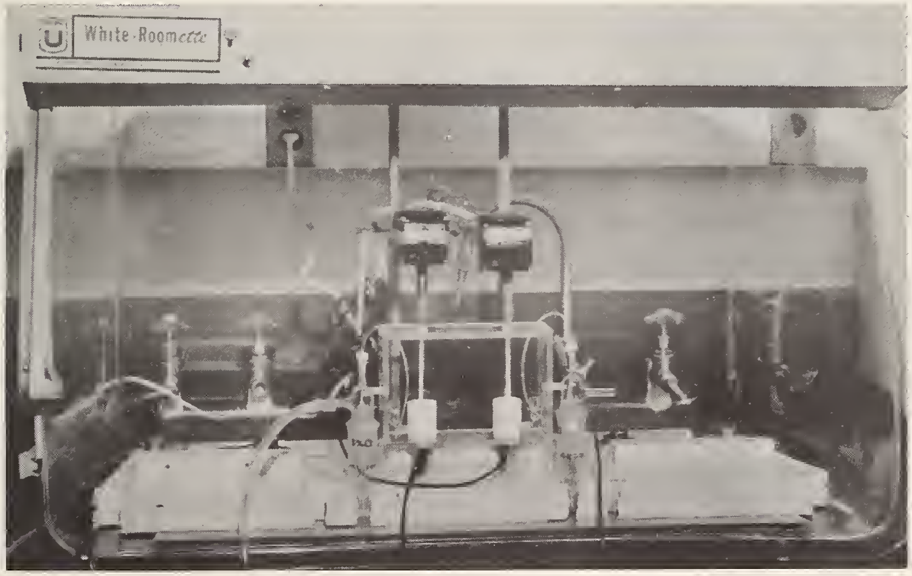

Figure 26. Electrolysis cells in enclosure.

An ID-SSMS method was developed for determining a number of chemically diverse elements in low-alloy steel. Copper, silver, cerium, neodymium, selenium, tellurium and zirconium ranging from 0.040% for Cu to 0.00031% for Nd were determined in a steel material subsequently issued by NBS as SRM 1261. The procedure will be detailed in a manuscript being prepared for publication.

2. High-Purity Reagents

The purity of reagents is fundamental to reliable trace element determinations by most analytical methods. Samples of high-purity perchloric acid were analyzed by an ID-SSMS procedure to determine their suitability as reagents for high-purity materials. Approximately 50 ml of each sample was spiked with enriched isotope solutions of fourteen elements of interest.

An aliquot of the spiked solution was evaporated to a small volume and transferred to a pair of high-purity gold wires. The wires were then ignited in a tube furnace to remove hydrocarbons and residual perchloric acid. The mass spectra were photographically recorded and the results were calculated from the measured isotope ratios and the other experimental data. The results for two lots of $HClO_4$ are listed in Table 9.

All fourteen impurity elements were determined simultaneously. In this method, if the enriched isotope spikes and impurity elements are in physical and chemical equilibrium, possible losses that may occur during the preconcentration and handling steps do not affect the final results. This should be true for these elements under these experimental conditions. Moreover, providing that enough material is recovered to detect the "spiking" isotope, either an actual concentration or upper limit can be reported.

Table 9. Analysis of high-purity perchloric acid by isotope dilution - spark source mass spectrography

Concentrations in parts per billion (ng/g)

	Lot "A"	Lot "B"
Ag	< 0.5	< 0.5
Ca	40	7
Cd	2	4
Cr	22	18
Cu	2	3
Fe	15	10
Mg	14	4
K	7	9
Ni	4	< 0.5
Pb	14	16
Sn	< 2	< 1
Zn	22	17
Ba	<10	10
Ti	3	2

3. Botanical Materials

Orchard Leaves is the first of a series of plant Standard Reference Materials being issued by NBS to calibrate analytical procedures. A number of trace elements, essential to plants, are being determined by ID-SSMS. In addition, the method yields upper concentration limits for a number of elements. Of particular significance is the presence of an abnormally high concentration of lead. The relative contributions from lead arsenate, fallout from internal combustion engine emissions, or possible contamination from the comminuting operation is not known at this time.

R. Alvarez, P. J. Paulsen*, C. W. Mueller*

*Analytical Mass Spectrometry Section

6. PERSONNEL AND ACTIVITIES

A. Personnel Listing

Spectrochemical Analysis Section

Bourdon F. Scribner, Section Chief
Karen L. Loraski, Section Secretary
Barbara W. Pastine, Chemist (part time)
Charlotte P. Fleming (part time clerical)

Group I. Electron Probe Microanalysis

Kurt F. J. Heinrich, Chemist
Donald L. Vieth, Metallurgist (On extended leave)
Robert L. Myklebust, Chemist
Jean R. Hénoc, Physicist, C.N.E.T., France (Guest Worker)
Barry L. Hammond, Chemist, U.S. Navy (Research Associate)
Charles E. Fiori, Electronic Technician
Katherine C. Burress (Summer Assistant, 1969)
Harvey Yakowitz, NBS Metallurgy Division (Guest Worker, part time)

Group II. X-Ray Fluorescence Spectrometry

Stanley D. Rasberry, Physicist
Jerome S. McKay, Jr. (Laboratory Assistant, part time)
Jeremy R. Winick (Summer Assistant, 1969)
Fielding Ogburn, NBS Metallurgy Division (Guest Worker, part time)

Group III. Optical Spectrometry

Joseph L. Weber, Jr., Physicist
Virginia C. Stewart, Chemist
Doward M. Bouchette, Physical Science Technician
Kimberly V. Koppe (Summer Assistant, 1969)
Toshiaki Kuroha, Section 310.09 (Guest Worker, part time)

Group IV. Enrichment Techniques - Optical and Mass Spectrometry

Robert Alvarez, Chemist
Martha M. Darr, Chemist
Elias Belkas, Chemist, Greek Atomic Energy Commission (Guest Worker)

B. Publications

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2. Paulsen, P. J., Alvarez, R., and Kelleher, D. E.
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3. Margoshes, M.
Remarks on Linearization of Characteristic Curves in Photographic Photometry, Appl. Optics 8, p. 818 (April 1969).

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Fitting of Analytical Functions with Digital Computers in Spectrochemical Anlaysis, Anal. Chem. 41, p. 1163 (Aug. 1969).

5. Heinrich, K. F. J. and Yakowitz, H.
Propagation of Errors in Correction Models for Quantitative Electron Probe Microanalysis in Proceedings V International Congress on X-ray Optics and Microanalysis, Tuebingen, West Germany, Sept. 1968, 151-159 (Springer-Verlag, Berlin, Heidelberg, New York, Dec. 1969).

6. Heinrich, K. F. J.
Advances in the Metallurgical Application of Electron Probe Microanalysis, Ibid., 415-523.

7. Scribner, B. F. (Editor)
Activities of the NBS Spectrochemical Analysis Section July 1968 through June 1969, NBS Tech. Note 502 (Dec. 1969).

8. Heinrich, K. F. J.
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18. Myklebust, R. L. and Heinrich, K. F. J. Rapid Quantitative Electron Probe Microanalysis with a Non-Diffractive Detector System, ASTM Special Tech. Publication (In press).

C. Talks Given

1. Hénoc, J. R., "Quantitative Microanalysis," Fourth National Conference on Electron Microprobe Analysis, Pasadena, Calif., July 16, 1969.

2. Heinrich, K. F. J., "Standard Reference Materials for Quantitative Electron Probe Microanalysis," Fourth National Conference on Electron Microprobe Analysis, Pasadena, Calif., July 16, 1969.

3. Myklebust, R. L., "Qualitative and Semi-Quantitative Analysis with Non-Dispersive X-ray Detectors," Fourth National Conference on Electron Microprobe Analysis, Pasadena, Calif., July 18, 1969.

4. Ahearn, A. J., "Quantitative Analysis of Solids by Spark Source Mass Spectrometry," International Conference on Mass Spectroscopy, Kyoto, Japan, Sept. 9, 1969.

5. Scribner, B. F., "Literature Search and Information Retrieval in Atomic Spectrometric Analysis," Eighth National Meeting of the Society for Applied Spectroscopy, Anaheim, Calif., Oct. 7, 1969.

6. Paulsen, P. J., "Determination of Trace Elements in Iron Using Isotope Dilution Spark Source Mass Spectrometry," Eighth National Meeting of the Society for Applied Spectroscopy, Anaheim, Calif., Oct. 9, 1969.

7. Alvarez, R., "The Analysis of Ultrapure Liquid Reagents by Isotope Dilution and Spark Source Mass Spectrometry," Eighth National Meeting of the Society for Applied Spectroscopy, Anaheim, Calif., Oct. 9, 1969.

8. Rasberry, S. D., "Improvements in Empirical Interelement Corrections in X-ray Fluorescence Analysis," Eighth National Meeting of the Society for Applied Spectroscopy, Anaheim, Calif., Oct. 10, 1969.

9. Heinrich, K. F. J., "Electron Probe Microanalysis," First Georgetown Conference on Surface Analysis," Washington, D. C., Oct. 10, 1969.

10. Heinrich, K. F. J., "Present State of Quantitative Electron Probe Microanalysis," Institute for Analytical Chemistry and Microchemistry, Techn. Hochschule, Vienna, Oct. 22, 1969.

11. Heinrich, K. F. J., "Present State and Perspective of Microprobe Analysis in the USA," "Microsonde" working group of France, Saint Germain-en-Laye, France, Oct. 31, 1969.

12. Alvarez, R., "Analysis of NBS Standard Reference Materials by Isotope Dilution Procedures and Spark Source Mass Spectrometry," American Chemical Society (Southeastern Regional Meeting), Richmond, Va., Nov. 7, 1969.

13. Myklebust, R. L., "Standards and Calibration in Microprobe Analysis," 1969 Eastern Analytical Symposium, New York, N. Y., Nov. 21, 1969.

14. Scribner, B. F., "The Role of NBS Standard Reference Materials in Modern Science and Technology," American Chemical Society, Upper Montclair, N. J., Dec. 11, 1969.

15. Rasberry, S. D., "The Application of Computers in Spectrochemical Analysis," Society for Applied Spectroscopy, Allentown, Pa., Jan. 9, 1970.

16. Weber, J. L., Jr., "Current Work of the Spectrochemical Analysis Section on NBS Standard Reference Materials," Society for Applied Spectroscopy, Clarksville, Md., Jan. 27, 1970.

17. Scribner, B. F., "Advances in Microanalysis by Optical and X-ray Spectrometry," University of Florida, Gainesville, Fla., Jan. 28, 1970.

18. Alvarez, R., "Spark Source Mass Spectrographic Analysis of Ingot Iron for Ag, Cu, Mo, and Ni by Isotope Dilution and for Co by an Internal Standard Technique," 159th National Meeting of the American Chemical Society, Houston, Texas, Feb. 23, 1970.

19. Rasberry, S. D., "Reduced-Regression Interelement Corrections in X-ray Fluorescence Analysis," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 2, 1970.

20. Alvarez, R., "Chemical Techniques for Spark Source Mass Spectrometry," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 5, 1970.

21. Heinrich, K. F. J., "Applications of Electron Probe Microanalysis to Lunar Specimens," Argentine Atomic Energy Commission, Buenos Aires, March 9, 1970.

22. Heinrich, K. F. J., "Progress in Quantitative Electron Probe Microanalysis," Fifth Middle Atlantic Regional Meeting Program of the American Chemical Society, Newark, Del., April 1, 1970.

23. Myklebust, R. L., "A Non-Diffractive Detector System for Rapid Qualitative or Quantitative Electron Probe Microanalysis," Fifth Middle Atlantic Regional Meeting of the American Chemical Society, Newark, Del., April 1, 1970.

24. Heinrich, K. F. J., "Electron Probe Microanalysis," Society for Applied Spectroscopy and the American Chemical Society, Cleveland, Ohio, April 8, 1970.

25. Heinrich, K. F. J., "Topographic and Chemical Scanning Microprobe Analysis," Washington Society for Electron Microscopy, Catholic University, Washington, D. C., May 7, 1970.

26. Heinrich, K. F. J., "Application of Energy Dispersion Spectrometry to Electron Probe Microanalysis," Murray Hill Laboratories, Bell Telephone Co., Murray Hill, N. J., May 26, 1970.

27. Alvarez, R., "Simultaneous Trace Element Determination in High-Purity Liquid Reagents by Isotope Dilution and Spark Source Mass Spectrometry," American Chemical Society and The Chemical Institute of Canada, Toronto, Canada, May 27, 1970.

28. Myklebust, R. L., "Rapid Quantitative Electron Probe Microanalysis with a Non-Diffractive Detector System," 73rd Annual Meeting, American Society for Testing and Materials, Toronto, Canada, June 24, 1970.

D. Committee Activities

B. F. Scribner

Member, ASTM Committee E-2 on Emission Spectroscopy
Member, ASTM Committee E-13 on Absorption Spectroscopy
Chairman, Student Awards Committee, Eastern Analytical Symposium, 1969
Member, Advisory Board, Spectrochimica Acta, Atomic Section
Member, Committee on Honorary Members, SAS, 1969
Member, Nominating Committee, National Capital Section, Optical Society of America, 1969
Member, Analytical Services Committee, NBS Analytical Chemistry Division

K. F. J. Heinrich

Past-President, Electron Probe Analysis Society of America, 1970
Assistant Editor, Mikrochimica Acta
Secretary, Organizing Committee, 10th Symposium on Electron, Ion, and Laser Beam Technology, NBS, 1969

R. Alvarez

Member, ASTM Committee E-2 on Emission Spectroscopy
Member, Awards Committee, Baltimore-Washington Section, SAS, 1970

J. L. Weber, Jr.

Member, ASTM Committee E-2 on Emission Spectroscopy, Subcommittees IV, VII, and IX
Member, ASTM Committee B-7 on Light Metals and Alloys, Cast and Wrought
Secretary, Baltimore-Washington Section, SAS, 1969-70
Column Editor, Applied Spectroscopy

S. D. Rasberry

Member, Laser Task Group, ASTM Committee E-2
Delegate, Baltimore-Washington Section, SAS, 1970-72
Member, Membership Education Committee, SAS, 1970
Member, Computer Evaluation Committee, NBS Analytical Chemistry Division

M. M. Darr

Member, ASTM Committee E-2 on Emission Spectroscopy, Subcommittee XII

7. ACKNOWLEDGMENTS

We have benefited greatly by the cooperation and assistance of persons from other groups and it is a pleasure to acknowledge these contributions to our work.

Dr. J. Hénoc, guest worker from the Centre National d'Etudes des Telécommunications, France was the main author of the computer program COR and contributed extensive discussions on various aspects of the theory of quantitative electron probe analysis.

Barry Hammond, research associate from the U. S. Naval Ship Research and Development Center, Annapolis, Md. contributed effectively to the electron probe measurements.

Mineral specimens were supplied for electron probe studies by K. Frederiksson and J. White, Smithsonian Institution, Washington, D. C.; by A. L. Albee, California Institute of Technology; by T. R. Boyd, Geophysical Laboratory, Washington, D. C.; and by C. Kieft, Institut voor Aardwetenschappen, Vrije Universiteit, Amsterdam, Netherlands.

Valuable contributions were made to our research program in optical emission spectrometry by Dr. Elias Belkas, International Atomic Energy Agency Fellow, from the Greek Atomic Energy Commission, "Democritos", Athens, Greece.

From our own organization, L. A. Marzetta, Measurement Engineering Division, provided valuable assistance in the design of electronic instrumentation, and Morris Schwartzmann of the same group contributed to the repair of electronic equipment.

Alex Fussinger of the Chemistry Division Contact Shop has been especially cooperative in the fabrication of small parts without detailed designs.

The Technical Services Section of our Division, and especially T. M. McLeod, have provided much helpful assistance on instrument problems.

Mrs. Rosemary Maddock and her group have continued to give much assistance to us in the planning of illustrations and slides for publications. In our bibliographic work, Virginia Stewart, Barbara Pastine, and Charlotte Fleming have been most helpful.

Finally, Karen Loraski, our Section Secretary, has provided invaluable assistance to members of the Section in a variety of activities, especially in the preparation and the typing of complex manuscripts and reports.

8. LIST OF REFERENCES

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APPENDIX A

CERTIFICATES FOR NBS STANDARD REFERENCE MATERIALS RECENTLY ISSUED

S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

STANDARD REFERENCE MATERIAL 1155

Stainless Steel

Cr 18-Ni 12-Mo 2 (AISI 316)

(This material also is available in chip form as SRM 160b, primarily for application in chemical methods of analysis)

Element	Percent by Weight
Carbon	0.046
Manganese	1.63
Phosphorus	0.020
Sulfur	.018
Silicon	$.50_2$
Copper	.169
Nickel	12.1_8
Chromium	18.4_5
Vanadium	0.047
Molybdenum	2.38
Cobalt	0.10_1
Lead	.001

SIZE AND METALLURGICAL CONDITION: Samples are 1¼ in (3.2 cm) in diameter and ¾ in (1.9 cm) thick, and are issued in the annealed condition.

PROVISIONAL CERTIFICATION: The provisional value listed for an element is the present best estimate of the true value based on the use of methods at NBS of high reliability. To check for possible systematic errors, other SRM's were chemically analyzed concurrently. The provisional value is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for values having subscripted numbers the deviation is not expected to be more than ± 5 in the subscripted numbers. Based on the results of homogeneity testing, maximum variations within and among samples are less than the estimated accuracy figures given above.

Washington, D. C. 20234
August 4, 1969

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

PLANNING, PREPARATION, TESTING, ANALYSIS: For many metal SRM's it is desirable to make the material available both in the form of chips primarily for chemical analysis and solids primarily for optical emission and x-ray spectrochemical methods of analysis. Prior to the preparation of the renewal SRM 160b (chip form) plans were made to also provide this material as SRM 1155 (solid form).

The material for this standard was prepared at Duquesne Works, U. S. Steel Corporation, Pittsburgh, Pennsylvania.

Homogeneity testing was performed at NBS by D. M. Bouchette and J. L. Weber, Jr. and was found to be satisfactory for the elements certified.

Analyses for certification were performed in the laboratories of the Analytical Chemistry Division of the National Bureau of Standards by J. R. Baldwin, C. E. Champion, T. D. Gills, E. J. Maienthal, T. J. Murphy, R. A. Paulson, W. R. Shields, B. A. Thompson, and S. A. Wicks.

The overall direction and coordination of the technical measurement leading to certification were performed by J. K. Taylor.

The technical and support aspects involved in the procurement, preparation and issuance of this SRM were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

Certificate of Analysis

STANDARD REFERENCE MATERIAL 97a

Flint Clay

(Results based on sample dried for two hours at 140 °C)

Analyst	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	K_2O	Na_2O	Li_2O	ZrO_2	BaO	MgO	CaO	SrO	Cr_2O_3	Loss on Ignition
1[1]	43.74	38.65	0.45^{a} $.46^{b}$	1.88^{c} 1.89^{d}	0.34	0.53^{e}	0.033^{e}	0.12^{e}	0.063^{f}	0.078^{e}	0.16^{g}	0.11^{g}	0.17^{g}	0.028^{h}	13.32
2[2]	43.68	38.95	.45	1.95	.35	$.51^{e}$	$.041^{e}$	$.10^{g}$	....	.07	$.14^{g}$	$.11^{g}$	$.18^{g}$	.03	13.31
3........	43.60	38.79	$.43^{a}$	1.87^{d}	$.38^{i}$	$.46^{e}$	....	......	....	....	......	......	......	....	....
Average..	43.67	38.79	0.45	1.90	0.36	0.50	0.037	0.11	....	0.07_5	0.15	0.11	0.18	0.03	13.32

References: [1] G.E.F. Lundell and J.I. Hoffman, NBS J. Res. 1, 91 (1928) RP5.
[2] L. C. Peck, Geological Survey Bulletin 1170, (1964).

[a] o-phenanthroline photometric method.
[b] Iron reduced with $SnCl_2$ and titrated with standard potassium dichromate solution.
[c] Cupferron gravimetric method.
[d] H_2O_2 photometric method.
[e] Flame emission spectrometric method.
[f] Pyrocatechol violet photometric method.
[g] Atomic absorption method.
[h] Diphenylcarbazide photometric method.
[i] Molybdenum-blue photometric method.

List of Analysts

1. R. K. Bell, B. B. Bendigo, T. C. Rains, T. A. Rush, E. R. Deardorff, J. R. Baldwin, R. A. Paulson, W. P. Schmidt, and S. D. Rasberry, Analytical Chemistry Division, Institute for Materials Research, National Bureau of Standards.
2. L. C. Peck, United States Geological Survey, Denver, Colorado.
3. L. M. Melnick, J. D. Selvaggio, and D. G. Cunningham, Applied Research Laboratory, United States Steel Corporation, Pittsburgh, Pennsylvania.

The material for the preparation of this standard was provided by the A. P. Green Fire Brick Company, Mexico, Missouri.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanships of O. Menis and J. I. Shultz.

The technical and support aspects involved in the preparation, certification and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
October 8, 1969

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

Certificate of Analysis

STANDARD REFERENCE MATERIAL 98a

Plastic Clay

(Results based on sample dried for two hours at 140 °C)

Analyst	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	K_2O	Na_2O	Li_2O	ZrO_2	BaO	MgO	CaO	SrO	Cr_2O_3	Loss on Ignition
1[1]......	48.98	33.13	1.34[a] 1.37[b]	1.56[c] 1.63[d]	0.11	1.07[e]	0.080[e]	0.075[e]	0.042[f]	0.031[e]	0.42[g]	0.31[g]	0.041[g]	0.030[h]	12.40
2[2]......	48.91	33.31	1.35	1.64	.10	1.08[e]	.083[e]	.064[g]	......	.03	.43[g]	.31[g]	.037[g]	.04	12.49
3........	....	33.12	1.28[a]	1.61[d]	.11[i]	0.98[e]	....	....	......	....	......	......	......	....	....
Average..	48.94	33.19	1.34	1.61	0.11	1.04	0.082	0.070	......	0.03	0.42	0.31	0.039	0.03	12.44

References: [1] G.E.F. Lundell and J.I. Hoffman, NBS J. Res. 1, 91 (1928) RP5.
[2] L.C. Peck, Geological Survey Bulletin 1170, (1964).

[a] o-phenanthroline photometric method.

[b] Iron reduced with $SnCl_2$ and titrated with standard potassium dichromate solution.

[c] Cupferron gravimetric method.

[d] H_2O_2 photometric method.

[e] Flame emission spectrometric method.

[f] Pyrocatechol violet photometric method.

[g] Atomic absorption method.

[h] Diphenylcarbazide photometric method.

[i] Molybdenum-blue photometric method.

List of Analysts

1. R. K. Bell, B. B. Bendigo, T. C. Rains, T. A. Rush, E. R. Deardorff, J. R. Baldwin, R. A. Paulson, W. P. Schmidt, and S. D. Rasberry, Analytical Chemistry Division, Institute for Materials Research, National Bureau of Standards.
2. L. C. Peck, United States Geological Survey, Denver, Colorado.
3. L. M. Melnick, J. D. Selvaggio, and D. G. Cunningham, Applied Research Laboratory, United States Steel Corporation, Pittsburgh, Pennsylvania.

The material for the preparation of this standard was provided by the A. P. Green Fire Brick Company, Mexico, Missouri.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmenship of O. Menis and J. I. Shultz.

The technical and support aspects involved in the preparation, certification and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
October 8, 1969

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

APPENDIX A-4

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

Certificate of Analysis

STANDARD REFERENCE MATERIAL 59a

Ferrosilicon

	Si	Fe	C	Mn	P	S	Cu	Ni	Cr	Al	B	Ca
ANALYSTS			Combustion-gravimetric		Photometric	Combustion-Iodate	Photometric					
1	48.12^{a}	50.00^{b}	0.044^{c}	0.75^{d}	0.015	0.001^{c}	$0.052^{e,f}$	0.032	0.084^{g}	$0.35^{h,i}$	0.059^{j}	0.039^{k}
2	48.12^{l}	50.06^{m}	$.044^{n}$	$.76^{o}$	.016	$.001^{n}$	$.051^{p}$	.032	$.079^{q}$	$.35^{r}$	$.063^{s}$	$.048^{t}$
3	48.13^{l}	50.09	.050	.76	.017	.002	—	.039	.079	.35	.05	—
4	48.08^{a}	50.08^{u}	$.045^{v}$	$.74^{w}$	.015	—	$.056^{x}$	—	$.076^{g}$	$.37^{y}$	$.060^{z}$	$.038^{z1}$
5	48.07	50.00	$.046^{v}$	.76	.016	.003	$.049^{e}$	$.028^{e}$	$\left\{\begin{matrix}.080^{z2}\\.085^{e}\end{matrix}\right\}$	.35	.057	$.042^{e}$
Average	48.10	50.05	0.046	0.75	0.016	0.002	0.052	0.033	0.080	0.35	0.058	0.042

[a] 0.5g sample fused with Na_2O_2, double dehydration with HCl.

[b] 1-g sample dissolved in nitrohydrofluoric acids and fumed with H_2SO_4. Iron precipitated with NH_4OH, acidified with HCl, reduced with $SnCl_2$ and titrated with standard solution of $K_2Cr_2O_7$.

[c] Iron accelerator.

[d] Persulfate-arsenite titration method.

[e] Atomic absorption method.

[f] Same value by isotope dilution.

[g] Chromium oxidized with ammonium persulfate and titrated potentiometrically with ferrous ammonium sulfate solution.

[h] Polarographic method.

[i] Same value by atomic absorption.

[j] Isotope dilution.

[k] Flame emission spectrophotometric method.

[l] Double dehydration with $HClO_4$.

[m] Iron reduced with $SnCl_2$ and titrated with standard solution of $K_2Cr_2O_7$.

[n] Iron and tin-coated copper accelerators.

[o] Sodium pyrophosphate method.

[p] Diethyldithiocarbamate photometric method.

[q] Diphenylcarbazide photometric method.

[r] Sodium hydroxide separation of aluminum, followed by titration with 1,2-diaminocyclohexanetetraacetic acid.

[s] Azure C photometric method.

[t] EDTA titration.

[u] Iron titrated with standard solution of $KMnO_4$.

[v] Combustion-conductometric method.

[w] KIO_4 photometric method.

[x] Neocuproine photometric method.

[y] Cupferron-NH_4OH-Al_2O_3 gravimetric method.

[z] Spectrographic method.

[z1] Calcium precipitated as oxalate and titrated with standard solution of $KMnO_4$.

[z2] Spectrometric method.

Washington, D. C. 20234
November 6, 1969

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

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1. R. K. Bell, J. R. Baldwin, T. C. Rains, T. A. Rush, S. A. Wicks, E. R. Deardorff, W. R. Shields, E. J. Maienthal, T. J. Murphy, K. M. Sappenfield and L. Moore, Analytical Chemistry Division, Institute for Materials Research, National Bureau of Standards.
2. J. C. Cline and R. A. Pontello, Interlake Steel Corporation, Beverly, Ohio.
3. L. Risi, Shieldalloy Corporation, Newfield, New Jersey.
4. G. Porter, H. H. Hall and J. T. Waller, Ferroalloys Division, Union Carbide Corporation, Marietta, Ohio.
5. H. R. Grady, Vanadium Chemical Research, Foote Mineral Company, Exton, Pennsylvania.

Homogeneity testing was performed at NBS by S. D. Rasberry and C. Gifford and was found to be satisfactory for the elements certified.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmenship of O. Menis and J. I. Shultz.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

The material for this standard was furnished by the Interlake Steel Corporation, Beverly, Ohio.

APPENDIX A-5

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

Certificate of Analysis

STANDARD REFERENCE MATERIALS
1143, 1144, 1147, 1148, and 1149
Blast Furnace and White Iron Standards

SRM No.	1143 Blast Furnace Iron 1	1144 Blast Furnace Iron 2	1147 White Iron (4j)	1148 White Iron (5L)	1149 White Iron (6g)
Element		Percent by Weight			
Carbon	3.91	4.27	3.60	2.89	3.28
Manganese	0.41_4	1.33	0.78,	0.66	1.05
Phosphorus	$.15_8$	0.11_2	$.16_0$	$.30_0$	0.56_4
Sulfur	.028	.021	$.05_9$	[.1][b]	$.12_7$
Silicon	1.68	$.27_6$	1.31	1.82	1.04
Copper	0.144	.090	0.23_0	0.99	0.49
Nickel	$.11_5$	.021	.070	.091	$.13_8$
Chromium	$.14_5$	.019	.093	$.14_6$	$.36_3$
Vanadium	.008	.004	$.03_2$	$.03_6$	$.05_5$
Molybdenum	(.005)[a]	.007	$.07_8$	$.02_2$	$.03_6$
Titanium	.17	.44	$.04_9$	$.05_0$	$.06_2$
Arsenic	(.004)	(.004)	$.02_2$	(.002)	$.03_6$
Tellurium	$.02_0$	$.02_0$	$.01_6$	$.01_5$	$.01_3$

[a] Values in parentheses are not certified but are provided for additional information on the composition.
[b] This element exhibits excessive segregation and is not certified.

SIZE AND METALLURGICAL CONDITION: Samples are approximately 1¼ in (3.2 cm) square and ½ in (1.3 cm) thick; they were chill-cast by a rapid unidirectional solidification technique.

CERTIFIED PORTION: The certified portion for each sample is that extending upward 5/16 in (0.8 cm) from the chill-cast or test surface (the largest surface opposite the numbered surface). This portion only was analyzed in the cooperative program for certification.

FINAL CERTIFICATION: The value listed for an element is the best estimate of the true value based on the results of the cooperative analytical program. The value listed is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 in the subscript figure. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than the accuracy figures given above.

Washington, D. C. 20234
December 22, 1969

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

PLANNING, PREPARATION, TESTING, ANALYSIS: These standards are made available as a result of the cooperative program among the National Bureau of Standards, the American Cast Iron Pipe Company, the Ductile Iron Society, and the General Motors Corporation.

The material for the standards was melted and cast at the American Cast Iron Pipe Company, Birmingham, Alabama, with use of the NBS chill-cast mold assembly. The preparation and homogeneity testing plan was similar to that described in NBS Misc. Publ. 260-1, Standard Reference Materials: Preparation of NBS White Cast Iron Spectrochemical Standards, Robert E. Michaelis and LeRoy L. Wyman, June 19, 1964.

Homogeneity testing was performed at the Research Laboratories, General Motors Corporation, Warren, Michigan, by A. C. Ottolini under the direction of M. D. Cooper.

Cooperative analyses for certification were performed by members of the Ductile Iron Society under the direction and coordination of W. R. Kennedy, American Cast Iron Pipe Company, Birmingham, Alabama. Cooperating in the program were R. E. Deas and R. N. Smith, American Cast Iron Pipe Company, Birmingham, Alabama; F. R. Bryan, Ford Motor Company, Detroit, Michigan; C. M. Davis and C. H. Albright, International Nickel Company, Inc., Suffern, N. Y.; and C. P. Gaskill, U. S. Pipe and Foundry Company, Burlington, New Jersey.

Analyses for final certification at the National Bureau of Standards were performed in the laboratories of the Analytical Chemistry Division by D. A. Becker, B. B. Bendigo, D. M. Bouchette, E. L. Garner, T. D. Gills, W. D. Kinard, P. D. LaFleur, E. June Maienthal, J. S. McKay, Jr., T. J. Murphy, S. D. Rasberry, W. R. Shields, and J. L. Weber Jr.

Technical measurements at NBS for final certification were coordinated by J. I. Shultz and J. L. Weber, Jr., under the chairmanship of B. F. Scribner.

The technical and support aspects involved in the preparation, certification, and issuance of these Standard Reference Materials were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

CAUTIONS:

1. Determinations made on other than the chill-cast or test surface are not recommended because of the unidirectional solidification structure.

2. These chill-cast standards are designed for calibration in the analysis of samples prepared in the same manner; samples prepared by other casting techniques or having other than a white structure may result in considerable bias.

3. Because the samples exhibit a change with respect to the columnar structure, both among standards and from bottom to top of the certified portion of the samples, the surface preparation for x-ray spectroscopic analysis may be critical. (A metallographic polishing technique is recommended.)

4. Because of the poor heat conductivity of the white irons, difference in volatility rates for certain elements in emission spectroscopic analysis may occur depending on the location of the burn and the source parameters. Sample and standard should be handled in the same way with respect to location of the burn.

APPENDIX A-6

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

Certificate of Analysis

STANDARD REFERENCE MATERIAL 1132

Lead-Base Bearing Metal

(84Pb-10Sb-6Sn)

This material also is available in chip form as SRM 53e, primarily for application in chemical methods of analysis.

Element	Percent by Weight
Antimony	10.2_6
Tin	5.84
Copper	0.054
Bismuth	.052
Arsenic	.057
Nickel	.003
Iron	<.001

SIZE: Samples are 1¼ inches (31.4 mm) in diameter and ¾ inch (19.0 mm) thick.

CERTIFICATION: The value listed for an element is the best estimate of the true value based on methods at NBS of high reliability and on the results of outside cooperating laboratories. The value listed is not expected to deviate from the true value by ± 1 in the last significant figure reported. For values having a subscribed number, the deviation is not expected to be more than ± 5 in the subscribed number. Based on the results of homogeneity testing, maximum variations within and among samples are less than the estimated accuracy figures given above.

The technical and support aspects involved in the procurement preparation and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
January 30, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

PLANNING, PREPARATION, TESTING, ANALYSIS: For many metal SRMs it is desirable to make the material available both in the form of chips or powder primarily for chemical analysis, and solids primarily for optical emission and x-ray spectrometric methods of analysis. Prior to the preparation of the renewal SRM 53e, plans were made to provide this material as SRM 1132, solid form.

Material for this standard was prepared by Alcan Metal Powders, Inc., Elizabeth, New Jersey, to specifications for lead-base bearing alloy SAE 13. About 1500 pounds was atomized to powder of minus 140 mesh size. At NBS the material was sized between 170 and 325 mesh sieves and thoroughly blended. Some 1000 pounds was reserved as SRM 53e. About 500 pounds of the powder material was converted to 100% dense rods for this standard at Whitaker Metals Corporation, West Concord, Massachusetts, first by cold compaction at 13 tons psi to billets, then followed by cold extrusion to size without use of a lubricant.

Homogeneity testing of this material and SRM 53e was performed at NBS by R. K. Bell and S. D. Rasberry and was found to be satisfactory for the elements certified.

Analyses for certification were performed in the laboratories of the Analytical Chemistry Division of the National Bureau of Standards by R. K. Bell and E. June Maienthal. Since this SRM 1132 was found to be identical to SRM 53e for all practical purposes, the same values are used for both standards. Cooperating in the analyses of the 53e material was J. H. Kanzelmeyer and J. J. Aldrich, St. Joseph Lead Company, Zinc Smelting Division, Monaca, Pennsylvania; and L. W. Anderson and D. J. Henrie, American Smelting and Refining Company, South Plainfield, New Jersey.

APPENDIX A-7

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

Certificate of Analysis

STANDARD REFERENCE MATERIALS

1140, 1141, 1142

Ductile Iron Standards

SRM No.	1140 Ductile Iron 1	1141 Ductile Iron 2	1142 Ductile Iron 3
Element		Percent	
Carbon	3.18	3.64	2.94
Manganese	0.72_5	0.48_0	0.18_3
Phosphorous	$.007_0$	.073	$.21_0$
Sulfur	.010	.020	.015
Silicon	1.92	1.11	3.33
Copper	0.096	0.20_4	1.02
Nickel	.028	$.54_8$	1.63
Chromium	.030	$.13_8$	$.05_5$
Vanadium	.030	.009	.006
Molybdenum	$.09_5$	.051	.023
Titanium	$.09_6$	.013	.008
Aluminum	(.01)	(.005)	.089
Arsenic	$.07_2$	$.03_6$	$.01_0$
Magnesium	.019	.044	$.09_7$
Cerium	(.09)	(.05)	(.015)
Yttrium	(<.002)	$.04_0$	.01
Lead	$.005_2$	(.0009)	(.0005)
Bismuth	$.001_5$	(.00008)	(.00002)

[a] Values in parenthesis are not certified but are provided for additional information on the composition.

SIZE AND METALLURGICAL CONDITION: Samples are approximately 1 1/4 inches (3.2 cm) square and 1/2 inch (1.3 cm) thick; they were chill-cast by a rapid unidirectional solidification technique.

CERTIFIED PORTION: The certified portion for each sample is that extending upward 5/16 inch (0.8 cm) from the chill-cast or test surface (the largest surface opposite the numbered surface). This portion only was analyzed in the cooperative program for certification.

FINAL CERTIFICATION: The value listed for an element is the best estimate of the true value based on the results of the cooperative analytical program. The value listed is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5 in the subscript figure. Based on the results of homogeneity testing, maximum variations within and among samples are estimated less than the accuracy figures given above.

Washington, D. C. 20234
February 24, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

PLANNING, PREPARATION, TESTING, ANALYSIS: The three ductile iron standards are made available as a result of the cooperative program between the National Bureau of Standards and the American Cast Iron Pipe Company. The standards were developed at the request of the Ductile Iron Society and the American Foundrymen's Society.

The material for the standards was melted and cast at the American Cast Iron Pipe Company, Birmingham, Alabama, with use of the NBS chill-cast mold assembly. The preparation and homogeneity testing was similar to that described in NBS Misc. Publ. 260-1, Standard Reference Materials: Preparation of NBS White Cast Iron Spectrochemical Standards, Robert E. Michaelis and LeRoy L. Wyman, June 19, 1964.

Homogeneity testing was performed at NBS by D. M. Bouchette and was found to be satisfactory for the elements certified.

Cooperative analyses for certification were performed at the American Cast Iron Pipe Company, Birmingham, Alabama by I. Glaze, J. B. Hobby, W. R. Kennedy, and R. N. Smith.

Analyses for final certification at the National Bureau of Standards were performed in the laboratories of the Analytical Chemistry Division by J. R. Baldwin, D. M. Bouchette, M. M. Darr, E. L. Garner, P. D. LaFleur, G. J. Lutz, E. J. Maienthal, M. Margoshes, L. I. McClendon, T. J. Murphy, T. C. Rains, S. D. Rasberry, T. A. Rush, B. A. Thompson, and J. L. Weber, Jr.

Technical measurements performed at NBS for final certification were coordinated by J. I. Shultz and J. L. Weber, Jr. under the chairmanship of B. F. Scribner.

The technical and support aspects involved in the preparation, certification, and issuance of these Standard Reference Materials were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

CAUTIONS:

1. Determinations made on other than the chill-cast or test surface are not recommended because of the unidirectional solidification structure.

2. These chill-cast standards are designed for calibration in the analysis of samples prepared in the same manner; samples prepared by other casting techniques or having other than a white structure may result in considerable bias.

3. Because the samples exhibit a change with respect to the columnar structure, both among standards and from bottom to top of the certified portion of the samples, the surface preparation for x-ray spectroscopic analysis may be critical. (A metallographic polishing technique is recommended).

4. Because of the poor heat conductivity of the ductile irons, difference in volatility rates for certain elements in emission spectroscopic analysis may occur depending on the location of the burn and the source parameters.

APPENDIX B

INPUT DATA FOR THE PROGRAM COR FOR CORRECTION OF QUANTITATIVE ELECTRON PROBE MEASUREMENTS

In its present form, COR requires two groups of cards for input, which will be called, respectively, Permanent Table and Run Input.

The Permanent Table contains all necessary constants for the elements contained in the specimen and the standards. These constants are invariant with respect to operating conditions, and are not changed after they have been established for an element, unless mistakes were made in punching the cards. Eventually, this information will be incorporated permanently in the memory of the program and will no longer be considered input. At present, the Permanent Table is entered with every run for two reasons: a. Elements are added to the Table as required for our analysis. We now have 41 elements in it. However, since the main program is stored on a magnetic drum, it would not be convenient to make piecemeal additions for each new element to the contents of the drum; b. The table is systematically checked for mistakes and will be made part of the memory after this check. In summary, the fact that the Table is part of the input is temporary, and in no way related to the structure of the program.

The Run Input contains all the necessary information which may change from run to run. This includes operating conditions (voltage, x-ray emergence angle, choice of line), dimension statements (numbers of specimens, points on each specimen, etc.) and commands for decision-making switches (choice of input, stoichiometry, difference, etc.), as well as a label for each case.

In the present configuration, the Run Input also contains Kramer's constant for continuous x-ray production, which logically should be in the Permanent Table or even in the main program. This anomaly is justified by the uncertainty in the values for this constant as a function of atomic number. Since we are presently working on the determination of this constant (or constants, if there is indeed an atomic number dependence), its inclusion in the Run Input facilitates its change for experimental calculations.

A. Examples of Permanent Table Input

I. Element of low atomic number (e.g., Na):

Card	Input
1	Atomic number, number of absorption edges listed in table, atomic weight, constants for absorption coefficients C_K and n_K, n_{KL}
2	Wavelength of K- absorption edge, K jump ratio, K fluorescence yield, number of lines related to this edge
3	Wavelength of Kβ, weight of line Kβ
4	Wavelength of Kα, weight of line Kα
5	Wavelength of L_I absorption edge (if larger than 99 Å, use "99")

II. Element of high atomic number (e.g., Au):

Card	Input
1	Atomic number, number of absorption edges listed in table, atomic weight, Coster-Kronig coefficients f_{12}, f_{13}, f_{23}, constants for absorption coefficients C_{KL} (if $Z > 50$), n_{KL}
2	Wavelength of K absorption edge, K jump ratio, K fluorescence yield
3	Wavelength, jump ratio, and fluorescence yield of L_I edge, number of lines generated by L_I (2)
4	Wavelength and weight of $L\beta_3$
5	Wavelength and weight of $L\beta_4$
6	Wavelength, jump ratio, and fluorescence yield of L_{II} edge, number of lines generated by L_{II} (2)
7	Wavelength and weight of $L\gamma_1$
8	Wavelength and weight of $L\beta_1$
9	Wavelength, jump ratio, and fluorescence yield of L_{III} edge, number of lines generated by L_{III} (3)
10	Wavelength and weight of $L\beta_2$
11	Wavelength and weight of $L\alpha_1$
12	Wavelength and weight of $L\alpha_2$

13	Wavelength, jump ratio, and fluorescence yield of M_{I} edge
14	Wavelength, jump ratio, and fluorescence yield of M_{II} edge
15	Wavelength, jump ratio, and fluorescence yield of M_{III} edge, number of lines generated by M_{III} edge (I)
16	Wavelength and weight of $M\gamma$
17	Wavelength, jump ratio, and fluorescence yield of M_{IV} edge, number of lines (1)
18	Wavelength and weight (=1) of $M\beta$
19	Wavelength, jump ratio, and fluorescence yield of M_{V} edge, number of lines (1)
20	Wavelength and weight (=1) of $M\alpha$
21	Wavelength of the N_{I} absorption edge

The Permanent Table is preceded by a card indicating the number of elements contained in the Table.

B. <u>Input for a Run</u>

The sequence of cards varies depending on the following alternatives:

1. We may either calculate intensity ratios for known compositions or vice versa.

2. In the second case, for measured elements, we may either input the uncorrected experimental data, or intensity ratios corrected for background and dead-time. If uncorrected data are entered, the dead-times of the spectrometers must be entered for use in the subprogram which performs the corrections.

3. If one phase (or point) is measured more than once, we may either obtain the individual results or the averages for each element, with the standard deviation of the signal.

4. Elements which were not measured can be calculated either by difference or on the basis of known stoichiometric relations. In case stoichiometric relations are used, the valences of the appropriate elements must be entered.

5. Two output formats are available: a short format (see Figure 10) or a test output format which contains detailed information concerning intermediate steps.

For all elements present, the atomic number and Kramer's constant must be entered. For the measured elements we need, besides the experimental data (or intensity ratio), the operating voltage, the choice of line, and the x-ray emergence angle.

6. If composite standards are used, we must enter the atomic number, the concentration, and Kramer's constant for each element.

7. All elements present in specimens and standards must be listed in the Permanent Table.

Although the total input requirements seem impressively large, they are necessary for any complete procedure which includes the aforementioned options, without making use of approximation which this program seeks to avoid. Once the

Permanent Table is completed and the problem of Kramer's constant is resolved, the input requirements will be similar to those of simpler programs in current use.

Users who always work under the same operational conditions (such as x-ray emergence angle) will be able to further simplify the input, particularly if they do not intend to use stoichiometric relations and multi-element standards.

Latest developments in the subject area of this publication, as well as in other areas where the National Bureau of Standards is active, are reported in the NBS Technical News Bulletin. See following page.

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