NBS

Technical Note 272

SPECTROCHEMICAL ANALYSIS: OPTICAL SPECTROMETRY,
X-RAY FLUORESCENCE SPECTROMETRY, AND ELECTRON PROBE
MICROANALYSIS TECHNIQUES
JULY 1964 TO JUNE 1965

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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NATIONAL BUREAU OF STANDARDS
Technical Note 272

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SPECTROCHEMICAL ANALYSIS: OPTICAL SPECTROMETRY, X-RAY FLUORESCENCE SPECTROMETRY, AND ELECTRON PROBE MICROANALYSIS TECHNIQUES
JUNE 1964 TO JUNE 1965

Edited by Bourdon F. Scribner

Spectrochemical Analysis Section
Analytical Chemistry Section
Institute for Materials Research

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 seven sections and about 85 technical personnel encompassing some 30 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 highly important. In addition, however, it has been my experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information. At the National Bureau of Standards such publications fit logically into the category of Technical Note. In 1965 we plan to issue these summaries for all of our sections. The following is the first annual report on progress of the Spectrochemical Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

This is the first of a series of annual progress reports of the Spectrochemical Section of the Analytical Chemistry Division. The Section, formerly known as Spectrochemistry, was established in 1948 as an outgrowth of an extensive program of spectrochemical analysis of uranium and related materials and also in recognition of the growing importance of instrumental analysis. While the Section had been primarily concerned with optical emission spectrometry, the growing importance of x-ray spectrometry for elemental analysis led to extension into this complementary field in 1957, and to the addition of research and application of electron probe microanalysis this year.

The purpose of the Section is to develop measurement techniques for determining the composition of materials through the use of optical and x-ray spectra. 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 the production of radiant energy by excitation, the dispersion of the radiant energy into a spectrum, and the measurement of spectral wavelengths and intensities. Because of the complexity of the systems involved no way has yet been found to make absolute measurements of concentrations in analysis; consequently, comparative methods are employed in which spectra of unknowns are measured relative to those of reference materials of known composition.

The research program of the Section is directed generally 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 these activities are the development of standard reference materials, analyses of materials to assist other research projects, and literature surveys such as bibliographies and critical reviews.

In this report, the program, facilities, and accomplishments of the Section for the past year will be reviewed.

In order to specify the 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.

Bordon F. Scribner, Chief
Spectrochemical Analysis Section.

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July 1964 to June 1965

Edited by Bourdon F. Scribner

ABSTRACT

A summary is given of the activities of the Spectro-
chemical Analysis Section for the period from July, 1964
through June, 1965. Activities in optical spectrometry
included studies of excitation by arcs and sparks in
controlled atmospheres and by the laser probe, the measure-
ment of arc temperatures, and atomic absorption spectrometry.
In x-ray spectrometry, methods have been developed for the
analysis of copper alloys in solution, as well as silver-
base, and gold-base dental alloys. An electron probe micro-
analyzer has been installed, and a description is given of
the modifications that have been made to the instrument, the
plans for future investigations, and some applications.
Chemical and physical enrichment methods have been developed
for the analysis of high-purity tin, zinc, and platinum.
Homogeneity tests and analyses have been performed in the
development of standard reference materials. Other activi-
ties included analyses of samples to assist other NBS groups
and government agencies, and literature surveys. Listings
are given of 20 publications and 14 talks by members of the
Section within the year.
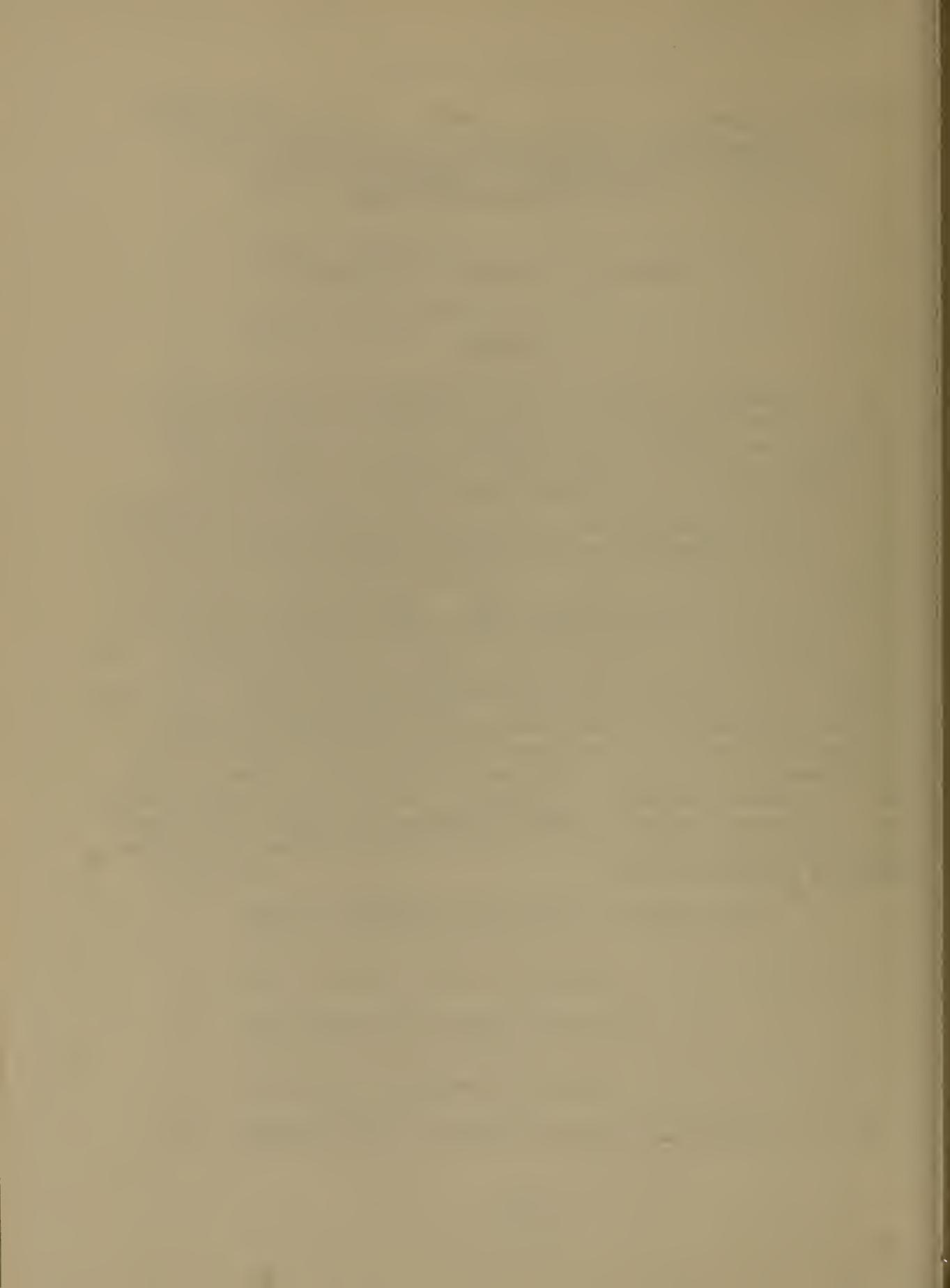
1. PROGRAM AND FACILITIES

A. Program

The Section is organized into several groups of which two are concerned with research and analysis in broad spectrometric fields, one on optical spectrometry and the other on x-ray spectrometry, including electron probe microanalysis. Other groups are concerned with problems across both of these fields: the development of enrichment methods for increased sensitivity; the investigation of problems of calibration; analyses of materials; and literature reference surveys. All groups are involved in the development and analysis of appropriate standard reference materials.

In optical spectrometry major attention is being given to the study of phenomena in the excitation of atomic spectra and the application of this information to the design of new or improved excitation sources. Excitation is a prime problem in optical spectrometry and advances in this field can be expected to stem from the development of excitation sources of steady characteristics, better line to background intensities, or broader applicability.

The marked effects of the gaseous atmosphere around the arc or spark column on the characteristics of the discharge have become evident in recent years and we have an active program in this field. Our study of this problem has involved in one instance the development of a simple means for providing a streamlined flow of a gas mixture around an arc, resulting in a convenient and effective way of controlling the gaseous medium for excitation. The source provides a steadier arc and produces spectra freer of interfering molecular bands. Another area of investigation concerns the effects of the gaseous atmosphere on spark excitation. Here the use of an inert atmosphere with elimination of oxidation effects promises to reduce inter-element effects in the analysis of complex alloys. A device for shielding the spark in a stream of gas was devised and conditions were found which effectively eliminate interelement effects in the analysis of high-temperature alloys.   This work is of considerable

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importance in our general effort toward minimizing the
number of standard reference materials for calibration
in the analysis of alloys.

Another study under way is an examination of the
phenomena involved in arc excitation to provide a better
basis for explaining and predicting the excitation behavior
of complex mixtures. One of the more important parameters
for excitation is the temperature of the source, and
measurement of arc temperature and its effect is under way.

The development of the laser with its high momentary
energies offers an intriguing possibility for vaporization
of materials for spectral excitation. Our study of this
problem has been in the direction of a better understanding
of the factors controlling the reproducibility of laser
pulses, and of the characteristics of this source for
quantitative analysis.

Atomic absorption spectrometry is recognized as one of
the important means of measuring concentrations of atoms
and promises to supplant flame photometry in many cases.
Our effort here is directed toward improving the production
of the atomic species and the quantitative measurement of
concentration. An investigation of simultaneous measure-
ments of several elements using a continuum source is
nearing completion.

In x-ray spectrometry the program involves activity in
x-ray fluorescence spectrometry and in electron probe micro-
analysis. Improved analytical methods have been developed
for the x-ray fluorescence analysis of gold alloys, silver
alloys, and copper alloys. Increased attention is now
being given to the problem of interelement effects and their
correction in order to improve the accuracy of analysis.
The instrumentation for this work is being studied
critically and modifications of equipment are being made to
improve precision of measurement and to extend the method
to the determination of the lighter elements.

The electron probe microanalyzer is one of the most
versatile tools for analysis that has been developed. Not
only can elements in microscopic areas be identified but
quantitative analysis can be made and the distribution of
elements observed over selected areas. During this year

much effort was expended in the installation and modification of an electron probe microanalyzer. It is operating successfully and has been applied to several analytical problems. A beginning has been made in studies of certain fundamental factors that affect the sensitivity and accuracy of analytical measurements with the micro-probe. Immediate attention is being given to the use of specimen current measurements for quantitative analysis, to studies of coincidence loss correction for the detector, and of pulse height variation as a function of counting rate. A general program of research has been planned in this field as discussed later in this report.

The analysis of high-purity metals is one of the critical problems for modern science and technology. Spectrometric methods are useful for trace analysis but the high level of purity now being obtained for some metals has pushed direct methods to the limit in detection of impurities. However, concentration of the impurities by physical or chemical separations offers a means of reaching the required sensitivities. These possibilities are being investigated and a fractional distillation method in arc excitation has been found useful for survey analysis of pure metals.

The analysis activities involve the study of calibration problems and the application of methods of analysis to real samples. These include the study of homogeneity of materials intended for standard reference materials, the analysis of the selected standard reference materials by primary methods, the analysis of materials for other research groups, and the survey of literature to maintain up-to-date reference files and to prepare bibliographies and reviews for publication.

The personnel of the Section this year totalled ten full time and five part time employees with assignments to areas of activity as given in the personnel listing. In addition, the facilities of the Section are made available on occasion to responsible investigators from outside. Four individuals who spent an appreciable length of time as guest workers in x-ray spectrometry are indicated in the listing.

B. Facilities

The Section is located in the NBS Chemistry Building on the ground floor, a circumstance which has proven advantageous for the mounting of vibration-sensitive optical equipment. The laboratories consist of several spectrometer rooms in which temperature and humidity are controlled to $75^{\circ}\pm1F$ and $40\%\pm5$ RH, two general-purpose chemistry laboratories, a dark room, a sample preparation room, and the Section Office. Electrical facilities include heavy-duty single and three-phase a-c power, d-c power, trunk line connection to the Power House for special power needs, and standard frequency service lines. Ventilation is provided by fresh air intakes through blowers, and by an exhaust system largely through exhaust stacks over arc or spark excitation sources and through chemical hoods.

The equipment available to the Section provides unique facilities for the observation of spectral wavelengths and measurement of radiated energies in optical emission and x-ray spectrometry. The optical instrumentation includes high-resolution grating spectrographs, multi-channel photoelectric spectrometers, a single channel scanning optical spectrometer, and comparator-microphotometers for measuring spectrograms. The basic x-ray equipment consists of a single channel spectrometer, a multi-channel spectrometer, and an electron probe microanalyzer recently installed.

The large spectrometers are required mainly to provide high speed and high precision in the spectrochemical analysis of standard reference materials especially for homogeneity testing; their cost has been included in the fees for these materials.

Much attention is being given to up-dating the equipment of the Section in view of marked advances in electronic circuitry and also in anticipation of the move to the new NBS site at Gaithersburg. Some of this modernization has been completed, notably for the multi-channel x-ray spectrometer.

Details on the instruments, their modification, and applications are given in the appropriate sections of this report.

2. OPTICAL SPECTROMETRY

A major interest of this Section in research in optical spectroscopy has been the development of new or improved excitation sources and the study of the properties of existing sources. Atomic spectra can be excited in many ways; any method that produces a high enough temperature to convert a solid or liquid sample into an atomic vapor will usually also provide energy to excite some of the atoms to emit light. Naturally, not all of these sources will have equally desirable properties in terms of the type of spectra excited and the convenience of operation. Certain electrical discharges have been found to have particular utility for spectrochemical analysis, and d-c and a-c arcs and high- and low-voltage sparks have been widely employed for this purpose because of their convenience and general applicability. Flame excitation has also been employed since the earliest days of atomic spectroscopy, but its use is largely restricted to those elements with low excitation energies.

These common excitation sources are satisfactory for the majority of analyses, but they are not always applicable to special problems. It is often necessary to develop new or improved sources to meet particular requirements, such as improved sensitivity, accuracy, or precision; for the determination of the few elements which are not excited in the usual sources; or to analyze samples which are limited in quantity or which have unusual forms. To obtain the best possible analytical results with either old or new sources, it is important to understand the mechanisms by which the samples are vaporized and excited and the influences of changes in the experimental parameters[1].

Until recently, all spectrochemical analyses were based on emission spectra. Observations of atomic absorption spectra have long been employed in astrophysics and some areas of atomic physics, but such observations were not applied to analyses in the laboratory. Atomic absorption spectroscopy has developed rapidly as an analytical method in the past decade. This new technique offers certain advantages, but, as with any new method, it has a number of difficulties which must be defined and, if possible, eliminated.

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A. Controlled-Atmosphere Arc Excitation

In spectrochemical analysis, it is the normal practice to excite the samples in an electrical discharge in air. This is primarily a matter of convenience; although replacement of air around the arc with other gases is known to produce some benefits, the use of controlled-atmosphere excitation has been limited by the practical difficulties involved.

The most obvious advantage of controlled-atmosphere arc excitation is the elimination of CN bands (CN is formed by reaction of the graphite electrodes with nitrogen in the air) which obscure the most sensitive lines of several elements. In addition, the temperature of the electrodes can be reduced by burning the arc in argon or helium, rather than in air or some other reactive gas, since a considerable portion of the heat generated at the electrodes comes from reactions of the carbon with the gases. By reducing the temperature of the electrodes, it is possible in some cases to vaporize volatile impurities while leaving the more refractory matrix behind. Excitation in an active gas may sometimes be desirable; for example, if the sample is excited in chlorine, those elements forming volatile chlorides should be selectively vaporized. The atmosphere around the arc also produces other effects, related to changes in the temperature, electron density, and chemical reactions in the arc, but these are poorly understood at present.

Although the effects of controlled atmospheres have been applied in spectrographic analysis, it has until recently been necessary to enclose the samples in a chamber for this purpose. The use of a chamber introduces practical difficulties, including delays in changing electrodes between samples, the need for flushing the chamber before excitation can be started, and clouding of chamber windows by deposits of sample and electrode vapors. It has recently been shown that samples can be vaporized and excited in arcs in controlled atmospheres by surrounding the electrodes and the analytical gap with a flow of gas, thus eliminating the need for a chamber. The devices which have been described for this purpose all had one or more disadvantages. Either they did not adequately

exclude air, or they required extensive modification of
the arc stand, or they did not provide for rapid change
of electrodes.

Devices have been developed in the Spectrochemical
Analysis Section [2] which make it possible to excite
samples as rapidly and conveniently in controlled
atmospheres as in air, which do not require modification
of the arc stand, and which can be put in place or removed
easily. One of-these is shown in figure 1. It is made of
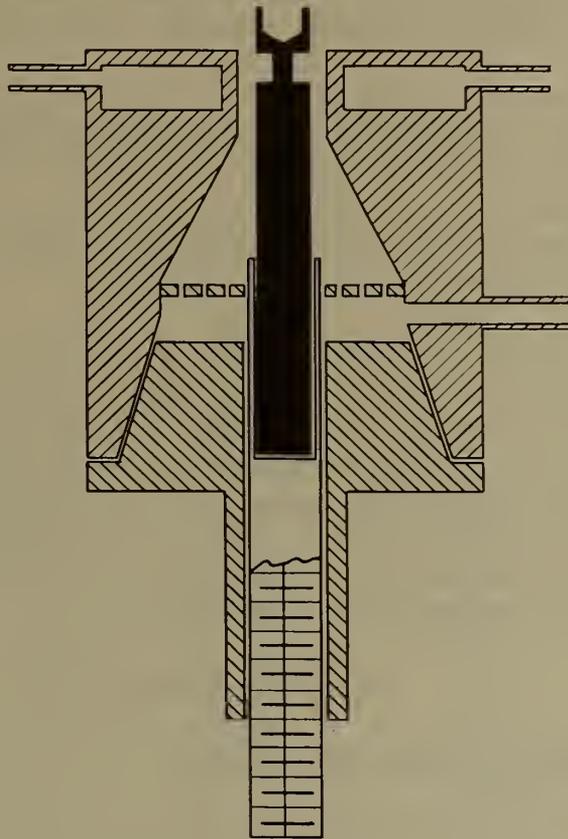
Figure 1. Design of an arc sheath
for excitation in control-
led atmospheres.

copper, except for the threaded electrode holder, which is
stainless steel. The extension rod on the bottom, diameter
$\frac{1}{2}$ in., fits into the lower jaws of the arc stand. The gas
or gas mixture is introduced at the bottom of the chamber,
passes through a pierced plate, and flows around the lower

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electrode to sheathe the arc. The taper of the chamber has been found to be necessary to give adequate exclusion of air. The top of the chamber is water cooled to prevent damage by the heat of the arc. The electrode holder is threaded to permit positioning of the electrode before excitation is started.

The device has been used with gas flows of 5 or 10 1/min, the lower flow providing less complete exclusion of air as shown by the appearance of CN bands in the spectrum. No flushing is needed once the system has been purged of air, and the arc may be ignited within a few seconds after the gas flow has been started. Thus, the system conserves gas.

An additional advantage of the device, compared to excitation in air or in a chamber, is that the concentric flow of gas around the arc stabilizes the position of the discharge, presumably by overcoming the convection currents which ordinarily cause the arc to wander.

This device and others similar in design but differing slightly in construction have been used in a number of analyses. It has also been employed in a study of the gross effects on the spectra of changing the atmosphere around the arc. The observations have been in good agreement with published data obtained with arcs in sealed chambers. The device is also being used in measurements of arc temperatures in various atmospheres (see below).

(M. Margoshes and B. F. Scribner)

B. Inert Atmosphere Spark Excitation

Quantitative spectrochemical analysis is a comparative method. It is not now possible to calculate the relation between element concentration and line intensity, which must be determined by recording the spectra of standards of known composition which are excited in the same way as the samples. The line intensities depend not only on the concentration of the analyte in the sample and the method of excitation and recording of the spectra, but they are also affected by other elements which are present and by the physical form of the sample. For this reason, it is necessary that the standards be as similar as possible to the samples which are to be analyzed.

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Point-to-plane spark excitation is a rapid method for the analysis of metallic samples, since this technique requires a minimum of sample preparation and provides adequate sensitivity and precision for most purposes. However, standards for this method of excitation are difficult to prepare. The analysis of high-temperature alloys has presented especially severe problems in standardization for point-to-plane spark excitation.

The major constituents of high-temperature alloys may be iron, nickel, or cobalt, or a combination of the three, and chromium is also a common major element. Table 1 lists

Table 1. Matrix element composition of some NBS Standard Reference Materials.

| NBS No. | Concentration % | | | |
	Cr	Ni	Fe	Co
1184	19.44	9.47	--	--
1185	17.09	13.18	--	--
1186	16.60	24.50	50.7	0.05[a]
1187	21.62	20.26	27.4	20.80
1188	15.40	72.65	6.60	--
1189	20.30	72.60	1.40	0.06
1190	17.00	51.9	0.6[a]	19.1
1191	19.48	55.15	2.04	13.65
1192	17.88	57.25	1.58	11.40
1203	11.90	75.5	1.4[a]	--
1204	12.75	70.6	3.1[a]	--
1205	13.82	67.5	1.55[a]	--

a. Values not certified.

the contents of some elements in high-temperature alloy standards presently supplied by NBS for calibration of emission and x-ray spectrometers. This variety of matrices, plus wide differences in the chemical and metallurgical properties among the various alloys has required close matching of specimen and standard for accurate spectro-chemical analysis. With more than 200 high-temperature alloys in use [3], it has become prohibitive to have closely matching primary standards available for all alloys.

Instead, we have chosen to develop methods which would make
a smaller number of standards applicable to the analysis of
a variety of alloys.

In recent years several papers have been published
describing the use of controlled atmospheres in point-to-
plane spark analysis of alloys. In particular, Arrak[4] ,
using either argon or nitrogen atmospheres, was able to fit
several types of ferrous-base alloys to a common set of
analytical curves. The present work [5] was undertaken in
order to extend this method to the analysis of high-
temperature alloys.

Controlled-atmosphere excitation has ordinarily been
done by means of air-tight chambers enclosing the sample and
counter-electrode. Use of a chamber sacrifices speed of
analysis, one of the important characteristics of emission
spectroscopy, since considerable time is required to change
samples and replace the air in the chamber with the desired
atmosphere. In the present work, the device shown in
figure 2 was employed to introduce argon or nitrogen into

Figure 2.   Device used for atmosphere
            control in inert-gas spark excitation.

the gap and to force the gas to envelop the counter-
electrode, excitation column, and excited area of the
specimen. The gas is introduced around the counter-
electrode at a flow of 6 1/min. Both the sample and counter-
electrode can be changed as rapidly as in normal operation
in air, and excitation can be started as soon as they are
in place. Two spectrometers were used in this work, and
the high-voltage spark parameters are listed for these two
instruments in table 2. With these parameters there is a

Table 2. High-voltage spark parameters.

	Instrument A	Instrument B
Discharges per cycle	4	2
Inductance, μh	90	36
Capacitance, μf	0.007	0.00725
R.-f. current, amps	6	11.5
Primary resistance, ohms	residual	34
Counter electrode	$\frac{1}{4}$ in. graphite, hemispherical tip, ASTM Type C-5	
Analytical gap, mm	2.5	2.5

transfer of graphite from the counter electrode to the sample
surface. The role of the graphite is not known, but the
electrical conditions giving the desired results have always
caused a deposit of graphite on the sample.

Figure 3 shows calibration curves for the determination
of nickel in high-temperature and ferrous alloys by this
method. With excitation in air the points would be
scattered, and it would not be possible to fit them to a
common curve. Because no element is present at a nearly
constant concentration it was necessary to plot calibration
curves in terms of the concentration ratio. Good results
were obtained with both argon and nitrogen atmospheres, but
in some cases the scatter of the points was somewhat poorer
in nitrogen. Self-absorption was less significant in either
argon or nitrogen than in air, with argon again giving
better results. In argon, a linear calibration curve could
be obtained for the determination of nickel in the range
from 9 to 70%, using the most sensitive resonance line of
this element, without self-absorption being evident. The

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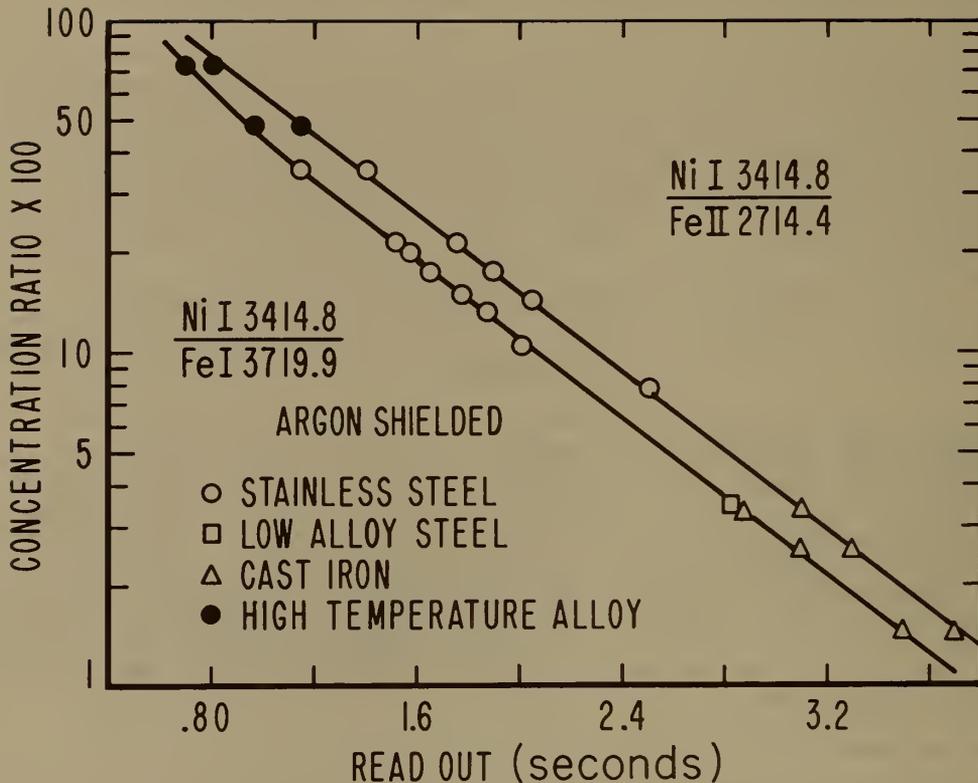
Figure 3. Calibration curves for the determination
of nickel in high-temperature and ferrous
alloys in argon atmosphere.

background intensity was nearly constant, regardless of the
sample, in either argon or nitrogen, while in air the back-
ground varied markedly from one alloy to the next. The
background was lower in nitrogen than in argon, making the
former gas more satisfactory for determination of smaller
element concentrations.

With excitation in air, the emission intensities do
not become constant with time until an equilibrium has been
established between the composition of the specimen, of the

surface being sampled, and of the vapor. It is ordinarily necessary, for this reason, to pre-spark the sample for a period of time ranging from a few seconds to as much as a minute or more in extreme cases before the exposure is started. Once equilibrium has been established, there is only an indirect relation between the composition of the specimen and of the vapor, and line intensities do not necessarily increase in proportion to the content of the element in the sample. In argon or nitrogen atmospheres it has not been found to be necessary to pre-spark the samples. The line intensities reach a steady value virtually as soon as the spark is started. In addition, line intensities are more nearly proportional to concentration.

It seems likely that the observed effects of the controlled atmosphere are due to the fact that the specimen surface does not become oxidized under these excitation conditions. However, it is possible that one effect of the inert atmosphere is to prevent oxide formation in the vapor. More experimental work is needed to define the mechanism of the matrix effect and how it is overcome by controlled-atmosphere excitation. However, the methods which have been developed provide an effective means for reducing the number of primary standards needed for initial calibration in spectrochemical analysis of high-temperature alloys.

(H. C. Dilworth and M. Margoshes)

C. Arc Temperature Measurements

The most important single physical parameter of an excitation source is its temperature. At thermal equilibrium, the population of excited states of an atom or ion is exponentially proportional to the temperature. The degree of ionization of an element is governed by the Saha equilibrium which contains the temperature in both an exponential term and a term in $T^{3/2}$. Little is known about chemical reactions in arc or spark plasmas, other than the fact that chemical compounds are present, as shown by the appearance of some band spectra, but the temperature of the source must be one factor affecting the extent of such reactions.

There have been a number of measurements of arc and spark temperatures in air, but the results obtained by different investigators are not in good agreement. This is partly because these studies have not taken into account the distribution of temperature through the discharge, but have assumed that the plasma could be characterized by a single temperature. In fact, the discharges are generally hotter on the axis than at the periphery, and there are also different temperatures near the electrodes than at the center of the gap. The temperatures measured are usually an average of the temperatures of the different portions of the plasma. This average value will be different depending on how the temperature is measured. For example, there will be considerably more ionization in the hotter portions of the discharge, so temperatures measured from the relative intensities of lines of ions will be higher than those measured from lines of neutral atoms.

The intensity, I, of an emission line under conditions of thermal equilibrium is given by

$$I = K(gf/\lambda^3)e^{-E/kT}, \qquad (1)$$

where K includes several constants as well as a term for the number of atoms or ions of the emitting element, gf is an atomic constant for a particular emission line, E is the energy of the excited state of the line, k is Boltzman's constant, and T is the temperature. Eqn. (1) may be re-written in logarithmic form and rearranged to give

$$\log(I\lambda^3/gf) = \log K - 0.4343E/kT. \qquad (2)$$

Thus, if the left-hand side of the equation is plotted against E for a number of emission lines of a particular atom or ion, the points should lie along a straight line whose slope is inversely proportional to the temperature.

In order to take into account the distribution of temperatures in the source, it is necessary to measure the line intensities emitted separately in the different portions of the plasma. However, these intensities cannot

be measured directly. Figure 4 shows a diagram of the

$I_A = aI_1$

$I_B = a'I_1 + b'I_2$

$I_C = a''I_1 + b''I_2 + c''I_3$

$I_D = a'''I_1 + b'''I_2 + c'''I_3 + d'''I_4$

$T_4 > T_3 > T_2 > T_1$
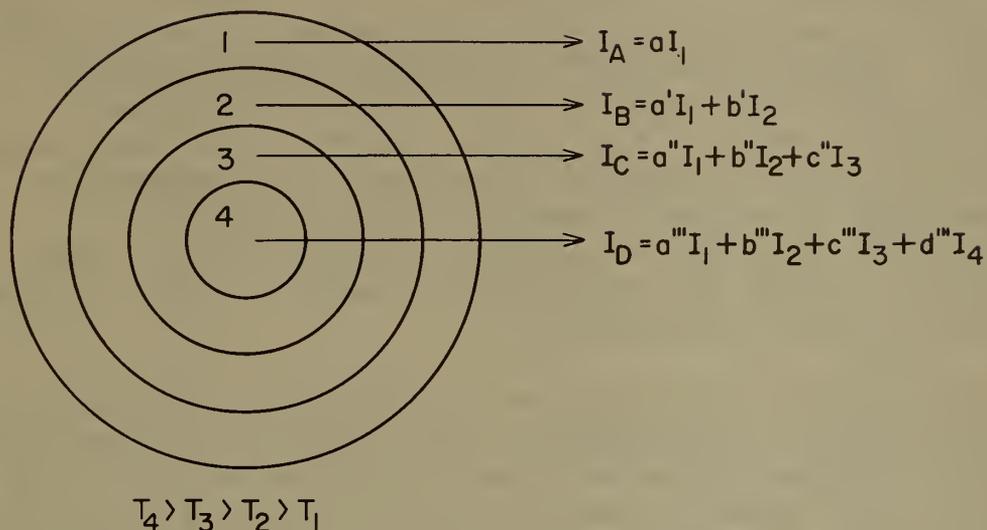
Figure 4. Diagram of cross-section through an arc
          column, indicating contributions from four
          zones to intensities measured along four
          lines of sight.

cross-section through an arc plasma. It is here considered
to be made up of 4 concentric zones, each characterized by
constant properties but with the temperature increasing from
zone 1 to zone 4. The intensity, I_A, measured along line-
of-sight A is a function of the line intensity emitted per
unit of volume in zone 1 and of geometric factors. The
intensity, I_B, viewed along line-of-sight B is given by the
intensities emitted per unit volume in zones 1 and 2 and the
appropriate geometric factors. The intensity per unit
volume as a function of radius, I_r, can be determined from
the intensity per unit volume as a function of the projected
distance along the arc image, I_x, by the Abel inversion:

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$$I_r = -\frac{1}{\pi} \int_r^{r_o} \frac{dI_x}{dx} \frac{dx}{(x^2-r^2)^{1/2}} , \quad (3)$$

where r is the radial distance from the axis of the discharge, r_o is the maximum radius, and x is the distance from the center along the projected arc image.

Measurement of I_x requires that the source be stable in time and space for the interval needed to record the spectra. Measurements with the spark, which changes rapidly with time, require time-resolution of about a microsecond. Arcs do not change rapidly with time, but they ordinarily have a tendency to wander, which makes the observations difficult. However, it is possible to stabilize an arc, and at the same time to control the atmosphere around the discharge, by means of the gas sheath described earlier (see above).

Studies are now under way to determine arc temperature distributions in atmospheres of air, argon, and argon-oxygen mixtures. These atmospheres were selected because they are the ones most commonly used in spectrochemical analysis and because there is evidence that arcs in these atmospheres are in thermal equilibrium. In contrast, an arc in a helium atmosphere, which is also sometimes used for spectrochemical analysis, is apparently not in thermal equilibrium. The temperature of a discharge is a function of all components of the plasma, including the elements in the sample, so the measurements will be made with a number of elements in the electrodes.

In the first experiment, the arc was operated at 10 amps in an atmosphere of argon and with titanium in the lower electrode -- the anode. The image of the arc was rotated 90° by a mirror system and focused onto the slit of the spectrograph, so that the light passed by the slit was a cross-section through the plasma at a point 2 mm above the anode, with a total arc gap of 6 mm. The values of I_x were then determined by measuring points along the line images on the photographic emulsion. The image was magnified 3.5X to permit the I_x measurements to be spaced more closely; approximately 15 measurements could be made across the image of each line.

A group of ten Ti II lines with known gf-values
were measured, and the Abel inversion was done by means of
a computer. Plots were then made of log $(I\lambda^3/gf)$ vs. E
for these lines at a number of radial distances, the slope
of each line found by a least-squares fit to the data, and
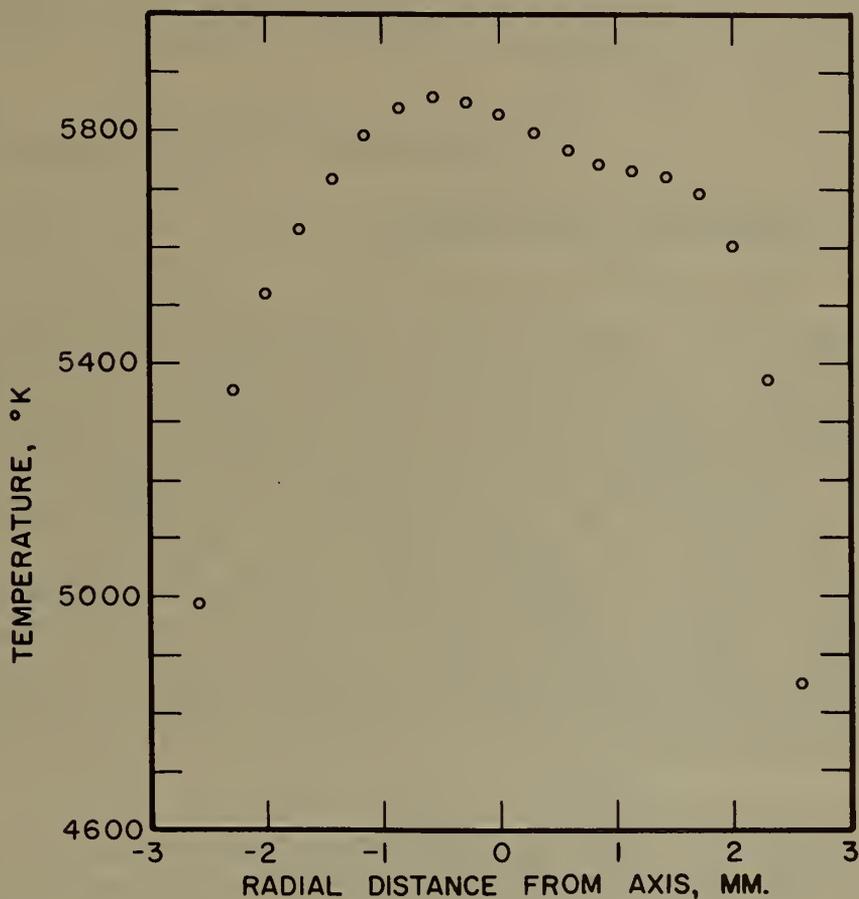the temperatures determined from the slopes. Figure 5

Figure 5. Results of a set of measure-
ments of temperatures in a
20-amp d-c arc in argon.

shows the results of the first measurement. The arc was
found to have a temperature of 5800° K at the center, with
little change over a radius of 1½ to 2 mm but dropping
sharply at larger radii. The difference between the

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temperatures at equal radii on either side of the center is within experimental error.

Now that a method has been established for the determination of arc temperatures as a function of position in the discharge, it should be possible to make detailed studies of the effect of the atmosphere, the sample, and the arc current on this important parameter. Knowledge of these values should make it possible to interpret the effects of these operating conditions on observed emission intensities, and to make a more rational choice of operating conditions for a particular analysis.

(M. Margoshes and H. E. Bond)

D. Atomic Absorption Spectrometry

Atomic absorption spectrometry is a relatively new method of analysis, based on the absorption of characteristic ultraviolet or visible radiation (usually the resonance lines) by atoms. In the normal mode of operation, light from a hollow cathode source passes through a chopper and a flame into a spectrometer, which is set to measure the intensity of one line of the analyte. The sample, in the form of a solution, is sprayed into the flame where it volatilizes to give a concentration of free atoms in the flame which is proportional to the element concentration in the solution. These free atoms absorb a fraction of the characteristic radiation, and the absorbance of the flame is related to the analyte concentration by suitable standards.

Atomic absorption spectrometry has been shown to provide good sensitivity of detection for a number of elements. The equipment is moderate in cost, and analyses can be done rapidly (once the sample is in solution) and with reasonable precision. Because a flame is used to convert the sample into atomic vapor, atomic absorption spectrometry is subject to many of the same interferences as is flame photometry, including disturbances in sample feed rate, shifts in ionization equilibria, and formation of stable chemical compounds in the flame. On the other hand, atomic absorption spectrometry is often more specific than is flame photometry. The resolution achieved is determined by the band-width of the emission line in the

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hollow-cathode lamp, not by the spectrometer, so other elements in the sample are not detected. In fact, it is possible to do isotopic analyses by employing a single isotope in the hollow-cathode lamp. Such analyses have already been done for Li and U.

One presently limiting factor in atomic absorption spectrometry is that it has not been possible to use the same hollow cathode source for the determination of several elements in a sample. The lamps are expensive and have a limited life, and a stock must be kept on hand for the analysis of all elements of interest. The lamp must be changed for the determination of each new element, and it must be warmed for about 15 minutes to reach steady intensity. Recently, lamps have been built containing three or four "compatible" elements, but there are severe limits on which elements may be combined in a single lamp.

Atomic absorption spectrometry with a continuum source, together with a spectrometer equipped to measure the intensities of several lines either simultaneously or in rapid sequence, would seem to offer promise as means of determining a group of elements in the same sample. The absorption lines in the flame are quite narrow -- much narrower than the resolution limit of all but the largest spectrographs -- so there will be some loss of sensitivity and specificity compared to the high effective resolution attained by using a hollow cathode lamp. However, for many purposes the losses will be more than compensated by gains in speed of analysis and by the convenience of not having to stock a large number of lamps.

Our first efforts in this direction, in 1962, were with a tungsten filament lamp. Absorption spectra were detected for several elements, including Na, Sr, and Ca. However, the sensitive lines of most elements are in the ultraviolet, where the tungsten lamp emits little or no light. Some efforts were made at that time with a high-pressure xenon lamp as a source, but the lamps then available were extremely unstable, although they did emit copious ultraviolet radiation. A more stable high-pressure xenon-mercury lamp has since become available, and work has resumed with this source.

An instrument originally designed for emission spectroscopy has been modified for use as an atomic absorption spectrometer. The heart of the spectrometer is a 3/4-m Fastie-Ebert spectrometer equipped with a 1200 groove/mm grating and a photomultiplier detector. With entrance and exit slit widths of 10 microns, the measured resolution is about 0.2 A in the first order. The instrument is equipped with a chopper and a phase-sensitive a-c amplifier. A quartz plate in front of the slit reflects a fraction of the undispersed radiation onto a second photomultiplier, and the line intensity can be measured, if desired, as a ratio to the undispersed radiation.

A notable characteristic of the instrument for the present purpose is its capability of measuring the intensities of up to 12 lines in rapid sequence, at 6 sec/line. A mechanical system, which is fairly easily adjusted to select the lines of interest, positions the rotation of the grating to select the approximate wavelengths of interest. The instrument steps to these positions in sequence and at each point it scans a narrow wavelength region which includes the peak of the line. Individual sensitivity controls are provided for each of the 12 wavelengths which can be measured.

Figure 6 shows calibration curves for the Fe 2522A line obtained with this instrument with a hollow-cathode lamp and the high-pressure Xe-Hg lamp as the source. There is some loss of sensitivity and curvature of the calibration curve with the continuum source, as is to be expected. These effects are caused by the limited resolution of the spectrometer compared to the true width of the absorption line. Under these conditions, it cannot be expected that the curves will follow Beer's law. Some improvement in sensitivity results when measurements are made at higher resolution by using the grating in the second order.

Studies are now under way to define the precision of atomic absorption analysis with the continuum source as compared to hollow cathode sources, and to test the method in the rapid sequential determination of several elements in an alloy, including the matrix element, alloying elements, and impurities.

(M. Margoshes and M. M. Darr)
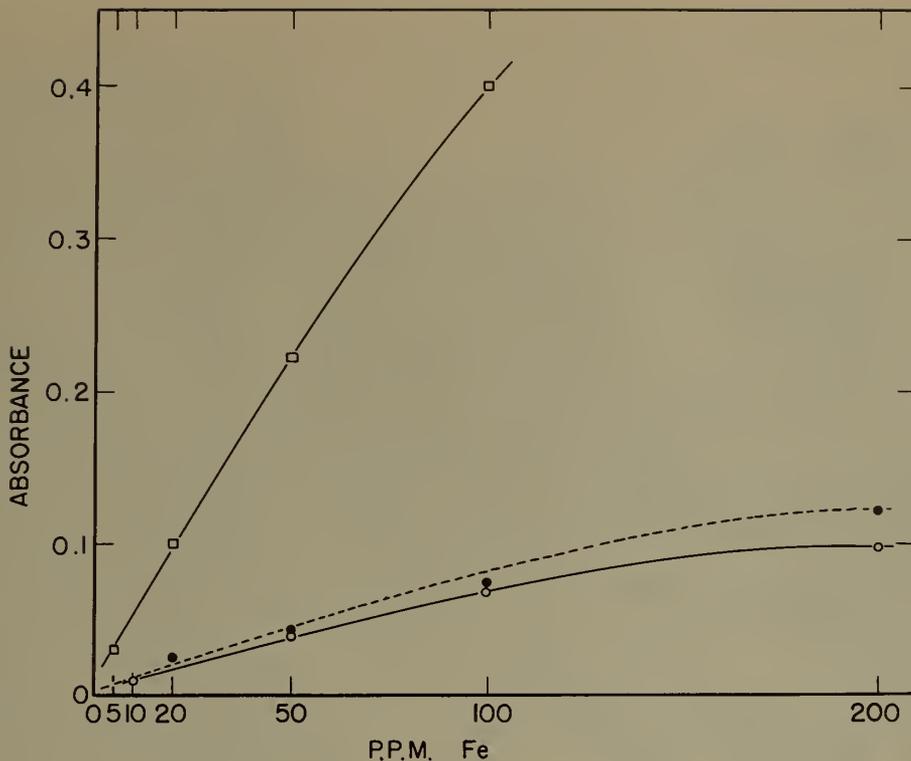
Figure 6.   Calibration curves for atomic
            absorption spectrometry, for
            the Fe resonance line at 2522.85A.
               ○ - with hollow-cathode lamp;
               ● - with high-pressure Xe-Hg
            lamp, grating used in first order;
               □ - with high-pressure Xe-Hg
            lamp, grating used in second order.

E.   Laser Probe Excitation

     In June, 1963, we began the task of determining the
characteristics of a laser probe [6] for qualitative
and quantitative analysis of samples as small as 35 μ in
diameter and 20 μ thick. From the beginning, there have
been three parts to this task:

     1. To experimentally investigate the characteristics
of spectra produced by the laser probe for a wide variety
of instrument parameters and specimen conditions, the direct
object of these experiments being to correct any defects in
the design of the prototype instrument and to define tech-
niques for carrying out several specific types of analyses.

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2. To define the areas where the laser probe can be of most use as an analytical tool.

3. To define the changes in instrumentation and technique needed to make the laser probe adaptable to analyses it cannot already do, e.g., quantitative analysis of a single microspecimen of unknown type.

Four specific features of the laser probe make it particularly attractive as an analytical tool. It consumes a small amount of sample per analysis -- about 0.1 µg. Under usual circumstances, there is no need for surface preparation, which might cause contamination. The method has high absolute sensitivity for those elements considered as sensitive spectrochemically; amounts as small as 10 pg have been determined for some elements. Furthermore, the specimen need not be electrically conductive.

The design of the laser probe is shown in figure 7.
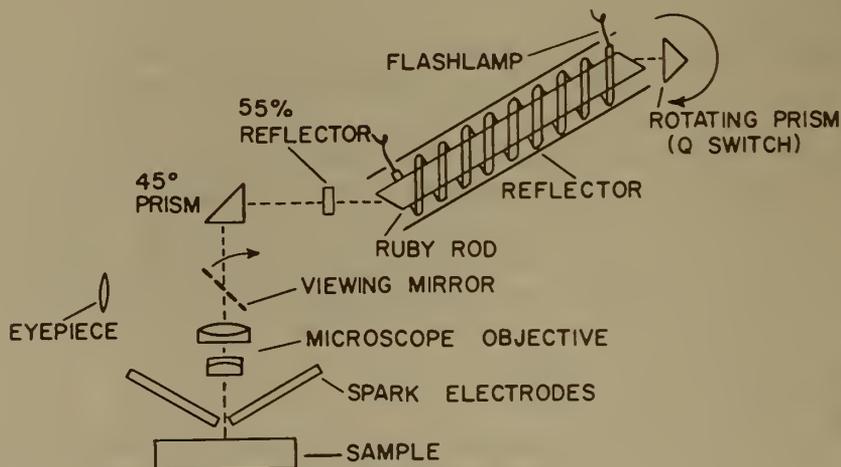
Figure 7. Optical diagram of the
laser probe.

A photograph of the instrument in position on a spectrograph is shown in figure 8. A Q-switched ruby laser provides the energy for vaporizing the sample. The 6943 Å laser light is focused onto the specimen by a metallurgical microscope which is also used for specimen viewing and sample area selection.

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Figure 8.   Laser probe in position on spectrograph: Left:
            Electronics cabinet containing power supply and
            controls for laser head and cross-excitation
            spark; Top center: Slit-end of 21-ft Wadsworth-
            mount grating spectrograph; Top right: Laser
            probe, consisting of laser head and microscope;
            Lower right: Arc-spark power supply (not used
            with laser probe).

The measured power at the peak of the laser pulse, approxi-
mately 4×10^6 watts, is sufficient to vaporize any material
present at the focal point.   Typical sample pits in steel are
40 to 50 μ in diameter and about 20 μ deep, corresponding to
a sample weight of about 10^{-7} g.   Additional energy for excit-
ing the sample vapor is provided by a spark circuit, with

adjustable voltage, capacitance, inductance, and resistance, connected to graphite electrodes placed just above the specimen. The partially-ionized vapor passes between the charged electrodes, automatically triggering the spark.

Because of the very small amount of sample consumed, the spectra are weaker than in most spectrographic analyses. A critical examination of spectrograph illumination was necessary to insure that the light from the source is used as efficiently as possible. For quantitative analyses, a pair of crossed cyclindrical lenses was used to illuminate the slit evenly with a minimum loss of light. For qualitative analyses, spectra about 4 times as bright are obtained by focusing the spark onto the slit with a spherical lens.

Other efforts to improve the instrument for laser-probe analyses included investigation of optical component failures due to the high radiant flux of the laser beam, temperature control of the laser ruby rod, control of voltage to the flash-lamp used to pump the laser, and mechanical changes to permit easier optical alighment of the source with the spectrograph.

The characteristics of the spectra produced without the electrical spark have also been determined [7]. In general, when not sparked, the vapor cloud formed by the laser pulse which are weaker in intensity than the sparked spectra by a factor of 10 to 15. Although the laser without the spark has been suggested as an analytical tool, most of our studies have been carried out with spark cross-excitation, the laser being used primarily as a sampling device.

When the laser is considered as a sampling device, it is possible that the over-all intensity of a spectrum and the relative intensities of lines in the spectrum will be controlled primarily by the amount and rate of introduction of the sample into the spark. A considerable variation in the spectrum from one exposure to the next, even with the same homogeneous specimen, would be expected if the laser output varied and thereby changed the sampling process. Such variations were observed early in this study.

An apparatus was designed to monitor the laser output vs. time, recording the event on a high-speed oscilloscope [8]. When the laser output was initially checked with this system, it was found to consist of 2 to 10 or more spikes

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and to be quite unreproducible from one pulse to the next.
The variation of the total energy of a pulse was as large as
$\pm$50%. Using the output monitor, the laser output was inves-
tigated as a function of the energy supplied to the flash-
lamp which pumps the laser, the temperature of the ruby-rod,
and the optical alignment of the cavity. Parameters were
determined which yielded a single-spike output with the peak
power and the energy of the pulse reproducible to about $\pm$10%
[9]. The improved control of the energy of the single-spike
pulse gives a visible improvement in the reproducibility of
the size of the sample pits, compared to multiple-spike
operation. However, because of the irregular shape of the
pits, it has not yet been possible to measure sample volumes.

The effect of improved sampling reproducibility was
investigated by comparing the variabilities in spectrum line
intensities produced by single-spike and 4-spike laser
operation. Table 3 shows the results of this experiment.

Table 3. Variability of line intensities
          for laser probe excitation (sample
          size = 12).

A. Coefficients of variation, %, for line
    intensities.

	Mn II 2576	Ni I 3414	Cu I 3273
4 spikes	19	39	38
1 spike	9	11	15

B. Coefficients of variation, %, for intensity
    ratios.

	$\dfrac{\text{Mn } 2576}{\text{Fe } 2926}$	$\dfrac{\text{Ni } 3414}{\text{Fe } 2926}$	$\dfrac{\text{Cu } 3273}{\text{Fe } 2926}$
4 spikes	10	18	14
1 spike	9	12	15

In addition, analytical curves have been established for single- and 4-spike operation using NBS standards of low-alloy steels, high-temperature alloys, and zinc-base die-casting alloys. A representative set of analytical curves is shown in figure 9.
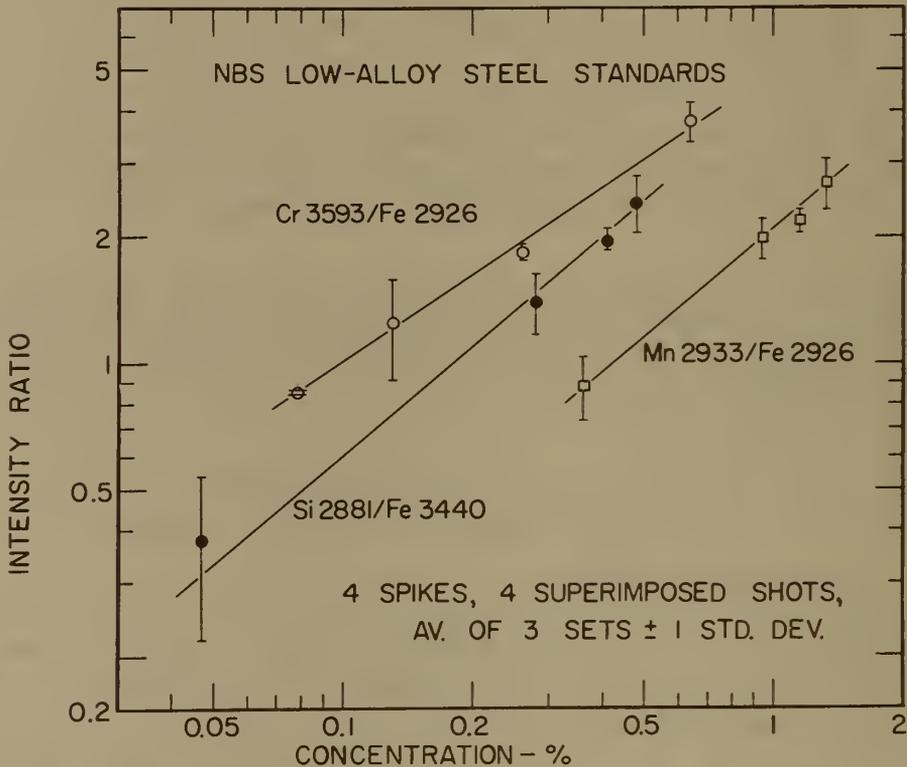
Figure 9. Calibration curves for the
determination of Cr, Si, and Mn
in low-alloy steel with the
laser probe.

The laser probe has been successfully applied to several qualitative analytical problems, including:

Identification of a surface stain and metallic particles on a ceramic disk. For identification of the stain, the laser beam was defocused in order to form a pit 60 μ in diameter and only 10 μ deep.

Identification of the material of a wire 75 μ in diameter.

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Qualitative analysis of individual grains, 40 to 50 in diameter, of silver-alloy powders of the type used in making dental amalgams. For these analyses, the grains were mounted on an adhesive tape.

Qualitative analysis of the components of a semi-conductor micro-diode. The main portion of the diode was $1 \times \frac{1}{2} \times \frac{1}{2}$ mm, the lead wires were $\frac{1}{2}$ mm wide, and the active head was 0.4 mm x 0.2 mm.

The future program includes investigating Q-switching methods employing a saturable absorber in an attempt to increase the power output in a single spike. If successful, this would make it possible to vaporize a larger sample when desired, with a consequent improvement in sensitivity of detection, while retaining the improved reproducibility of single-spike compared to multiple-spike operation. The time-course of events between arrival of the laser pulse at the specimen and the excitation of the vapor in the spark should also be studied, along with the mechanisms involved in vaporization and transport of the specimen. A problem in quantitative analysis is the determination of the constituents of a single micro-specimen of unknown composition. If enough specimen is available, it is possible to first perform a qualitative analysis and then select or prepare standards bracketing the composition of the specimen. This will not be possible when the specimen is so small that only one ex-posure can be made; in spectrographic analysis it is ordinar-ily necessary to run the standards at the same time as the samples, since calibration curves commonly shift from day to day for a variety of reasons, some of which are not known. It may be possible to develop a technique in which the analyses are based on direct measurement of line intensities and the amount of material vaporized, without the need for standards matching the composition of the sample.

(S. D. Rasberry, B. F. Scribner, M. Margoshes)

3. X-RAY SPECTROMETRY

X-ray spectra contain lines having frequencies characteristic of the elements present in the radiating material. The characteristic line emission spectra can be simply related to the atomic number of the emitting elements [10]; their structure is considerably simpler than that of spectra in the visible frequency range. While the fine structure of the emission lines is at present the object of study and speculation, the coarser features were exhaustingly explored several decades ago.

Not surprisingly, the potential of x-ray spectroscopy for elemental analysis was soon recognized, and methods and instrumentation were developed, as described by Siegbahn [11] and Von Hevesy [12]. However, in spite of the discovery by this method of several elements predicted by Mendeleev's theory, x-ray spectrometry was not broadly applied until after World War II, when x-ray detection methods of high efficiency had become available [13].

The ionization leading to x-ray emission is presently achieved in practice by one of three methods: by the impact of particles (electrons, protons, etc.), by the action of ionizing radiation (x-ray fluorescence), or by electron capture in nuclear reactions. In the first method, the specimen acts as the target of an x-ray tube. Consequently, the specimen is exposed to heating, to the impact of electrical charge (which has to be removed by conduction), and to the chemically destructive action (particularly for organic matter) of the impinging particles (commonly electrons). Furthermore, the specimen must be mounted within the vacuum chamber of the instrument. For these reasons, the second method, excitation by x-ray fluorescence is preferred. Here the specimens may be kept outside the primary vacuum enclosure and analysis can be made of a wide variety of materials including liquids, electrical and thermal insulators, and organic materials.

A. Capabilities of X-Ray Fluorescence Spectrometry

1. Elements that can be analyzed: All elements of atomic number three or higher emit x-rays. While the frequency of homologous x-ray lines is strongly dependent

upon the atomic number, the existence of several series of
x-ray lines (K, L, M ...) assures the availability of lines
within a useful frequency range for almost all elements.
The only exception is given by the elements of atomic number
below 12, with all of their x-ray lines within the very
"soft" range of wavelengths greater than 10Å. Commercially
available instruments usually cover the elements of atomic
number 12 (Mg) or higher; instrumentation for the
determination of lighter elements is presently under
development [14].

   2. Range of Concentrations being investigated: The
inherent sensitivity of the method is typically 20 to 200
ppm, depending on the instrument, the nature of the
specimen, and the atomic number of the element to be
determined. Measurements of major components are very
frequently made. Thus, the range of x-ray fluorescence,
although overlapping considerably with that of light
emission spectrometry, tends towards higher concentrations.
It is, however, possible to combine chemical preconcentra-
tion methods with final read-out by x-ray spectrometry.
Fractions of a microgram can be measured in this way, after
separation of one element or a group of elements from the
major constituents.

   3. Precision and Accuracy: With modern equipment and
due precautions, the precision attainable in x-ray
intensities can be made better than that of most conven-
tional chemical analytical methods, if the statistics of
quantum counts are taken into account. Therefore, x-ray
fluorescence analysis is probably the most successful
competitor of quantitative "wet" chemical analysis. The
x-ray intensities received from an irradiated specimen
depend upon the extent of attenuation of both the primary
(exciting) and the secondary (fluorescent) beam. This
attenuation is a function of the concentrations of all
constituents of the specimen. Tertiary emission of x-rays
excited by the fluorescent x-rays may also occur, and its
presence and intensity is also dependent upon specimen
composition. Consequently, analytical curves are generally
nonlinear for binary systems, and the complexity of the
"interelement effect" increases rapidly with the number of
constituents. Unless standards of composition close to that
of the specimens are available, or correction procedures

for these effects can be developed, the accuracy of the
method may be considerably poorer than its precision. The
problems involved in the development of such correction
procedures have been recently discussed in a two-day informal
meeting arranged by our group at the NBS with assistance of
several x-ray spectroscopists of the United States and
Canada. A report covering the meeting is in preparation.
The critical study of proposed techniques for the solution
of this problem is one of our research goals.

The calculation procedures mentioned above assume that
the specimen is completely homogeneous. Inhomogeneity and
particle size variations in particulate specimens constitute
another potential source of errors.

B. Modifications of X-Ray Fluorescence Equipment

The Spectrochemical Analysis Section is at present
equipped with a single channel x-ray fluorescence
spectrometer (the Norelco Three Specimen Position Spect-
rometer), chiefly used for research and development purposes,
and a multi-channel x-ray fluorescence spectrometer (The
Applied Research Laboratories, Inc., PXQ) for rapid routine
or semi-routine analysis of a large number of specimens.
These instruments were purchased in 1957 and 1958,
respectively.

1. Single Channel Spectrometer: This instrument,
figure 10, consists of the following sections:

a. An x-ray generator, consisting of a power
supply and a properly shielded and cooled x-ray tube with
side window.

b. A specimen chamber section with provisions
for introducing, positioning, and exchanging the specimen
to be excited by the primary x-rays.

c. An x-ray spectrometer unit, consisting of a
single crystal for monochromatization of the secondary x-
rays emitted from the specimen, collimators defining the
direction of the x-rays before and after diffraction, a
mechanical assembly assuring proper angular relations
according to Bragg's law of the aforementioned components
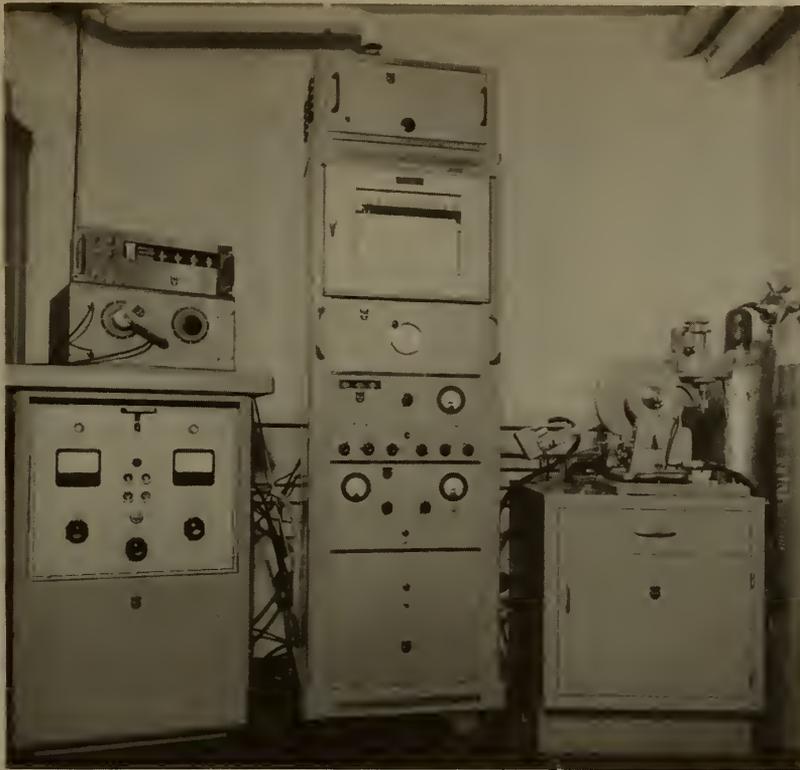
Figure 10.   Single channel x-ray fluorescence
              spectrometer.   The spectrometer unit is
              on top of the cabinet to the right.   The
              middle console houses the voltage supply
              for the detector; the scaler-timer
              combination with ratemeter, the signal
              amplifier and conditioner, and the chart
              recorder for the ratemeter output.   On
              the left, the power supply for the x-ray
              generator, and, on top, a single channel
              pulse height analyzer and an electronic
              timer.

during the diverse operations, and an x-ray detector
receiving the x-rays collimated after diffraction.

d. An electronic assembly for read-out of the
x-ray signal produced by the detector. This assembly
includes the power supply for the detector, signal
amplifiers, a single channel pulse height analyzer, a
scaler-timer combination for quantitative measurements, and
a ratemeter chart recorder for qualitative and semi-
quantitative operations.

Considerable progress has been made in the instrumen-
tation for x-ray fluorescence analysis since the
acquisition of the present instrument. It was therefore
decided that a modernization of this equipment was necessary
in order to permit its efficient use for research purposes.
The components which are mentioned below in detail have
been ordered and are presently being installed and tested:

a. A new x-ray tube assembly permitting quick
change of x-ray tubes with diverse target and window
characteristics.

b. A new assembly for the specimen changer and
the spectrometer unit which permits operating the entire
x-ray optics in vacuo or within a helium atmosphere.

c. An arrangement permitting the alternative or
simultaneous use of gas flow proportional detector and a
scintillation detector.

d. A new electronic panel including an improved
pulse height analyzer and a fully electronic timer.

The chief purpose of the these improvements is to
extend the useful range of the instrument to the wavelength
region between 2.5Å and 10Å. This wavelength region is at
present of great practical interest. Work in it should also
give us the proper background for future exploration of the
"ultrasoft" region (10-100Å), which is most interesting
from the point of view of advanced research.

2. Multi-channel Spectrometer: This instrument,
figure 11, differs from the previous instrument by the fact

Figure 11. Multi-channel x-ray spectrometer.
Left, x-ray tube power supply;
center rear, spectrometer proper;
right, signal integrating and
conditioning console; center front,
digital converter, programmer, and
typewriter read-out with tape punch.

that an array of monochromators, arranged radially around
the end-window x-ray tube and the specimen, permits the
simultaneous registration of x-ray intensities at several
wavelengths. All but two of the monochromators are
permanently adjusted to a selected fixed wavelength, so
that the array of elements measurable by the fixed channels
is pre-determined by the original programming. When the
instrument was purchased the programming included soft x-ray
spectrometers for the elements from magnesium (12) to
sulfur (16) as well as one channel for calcium (20). In
the meantime, the interest for routine analysis has shifted
toward alloys containing heavier elements only; moreover,
the analysis of soft radiation necessitates the use of
vacuum or helium paths for the x-rays, and this caused
technical problems in the multi-channel instrument that
were never satisfactorily resolved. It had therefore been
decided to replace the long wavelength channels by channels
for heavier elements. At the same time, other components,
particularly some connected to the power supply, were to
be upgraded as well. This work has been completed. At
present, the multi-channel unit has 18 fixed channels,
tuned to the K alpha lines of the nine elements from
titanium (22) to zinc (30), of zirconium, niobium,
molybdenum, silver, tin, and antimony, and to the L alpha-1
lines of tungsten, gold, and lead. Each of the two
scanning sections covers the wavelength range of 0.4 to
3.5Å; by their use, two additional elements can be added
to the range of the instrument. Present electronics for
read-out permit the simultaneous use of up to 12 channels.

(K. F. J. Heinrich)

C. <u>Accuracy of Solution X-Ray Spectrometric Analysis of
Copper Alloys.</u>

To certify the composition of NBS Standard Reference
Materials, it is desirable to use at least two independent
analytical methods to reduce the possibility of bias in the
results. X-ray fluorescence spectrometry, with its high
precision, can serve as one of the methods if the factors
affecting accuracy are recognized and evaluated. The
ultimate in reliability is attained by using a direct-
comparison method in which the unknown and the synthetic
standard are uniform, identical in composition, and (ideally)
exposed to the excitation source at the same time.

By using solutions of the unknown and synthetic
standards, homogeneity is assured and after a preliminary
analysis of the unknown, a synthetic standard closely
approximating the composition of the unknown can be
prepared. Moreover, differences in absorption and en-
hancement effects between unknown and standard can be
reduced by dilution.

In the comparison of solutions of an unknown and
synthetic standard, several factors may be expected to
contribute to error:

a. For solution cells having thin films as
irradiation windows, the films of the two cells may
distend by different amounts thus changing the surface
and consequently the fluorescent intensity.

b. The acid concentration may differ in the two
cells producing different absorption effects.

c. During the irradiation period, the temperature
increase may be sufficient to affect the density of the
solution.

These factors were investigated for the determination
of copper and zinc in the cartridge and aluminum brasses
which were being analyzed for certification as NBS Standard
Reference Materials. The results of the investigation were
published in a report [15] which will be briefly reviewed
here.

1. Experimental

A commercial, multichannel spectrometer of the
curved cyrstal type, the main features of which were
described earlier, was used for this study. Additional
details are given in table 4.

The solutions were contained in cells of methyl
methacrylate plastic with an opening of 25 mm across
which was cemented $\frac{1}{4}$-mil Mylar film as an irradiation
window. The volume of the cells was approximately 11 ml.

Table 4. X-ray spectrometer settings.

Element	Wavelength Å	Crystal Radius	Material	Atmosphere	Detector
Copper	K_α 1.542	10 cm (4 in.)	LiF	Air	Proportional
Zinc	K_α 1.437	28 cm (11 in.)	LiF	Air	Proportional

2. Effect of Film Position

The effect of changes in film position was determined by using the solution cell and micrometer head assembly as shown in figure 12. The micrometer head could
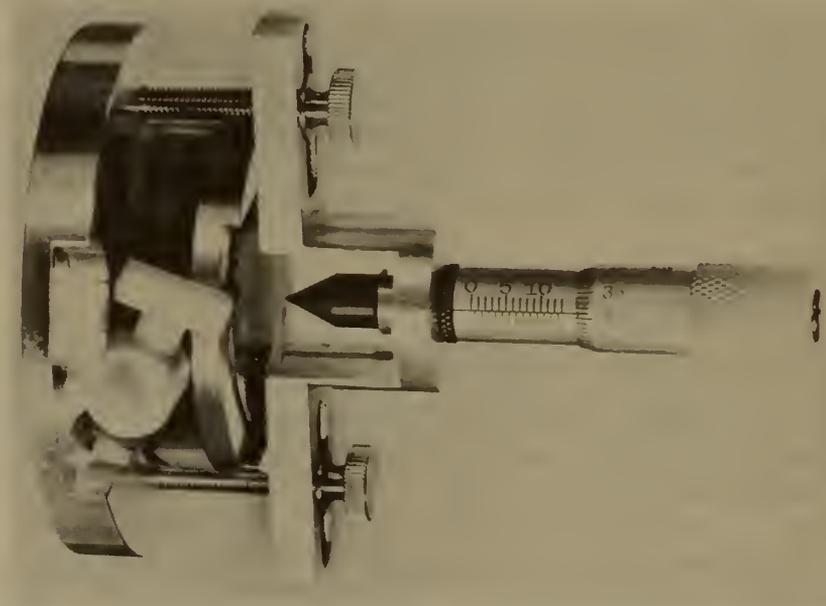

Figure 12. Apparatus to measure the position of the film.

be read to 0.01 mm. The position of the film could be changed by operating a small syringe attached temporarily to the stopcock. The cell during excitation was mounted on its edge, and the solution caused the film to distend 0.4 mm by hydrostatic pressure. Bowing the film an additional 0.10 mm from this position caused the zinc K_α intensity to change 0.19% and the copper K_α intensity to change 0.069%.

3. Effect of Acid Concentration

A 0.38% decrease in zinc intensity resulted from the addition of 1.6 millimoles of nitric acid to 10 ml of a solution of brass which was 1 molar with respect to nitric acid and had a concentration of 10 mg of brass per ml. Under the same conditions, a similar increase in nitric acid concentration resulted in a 0.48% decrease in copper intensity.

4. Effect of Temperature

A calibrated thermistor was placed in a cell to measure the temperature rise resulting from a two-minute irradiation period. The observed temperature rise of $0.1^\circ C$ did not significantly affect the intensity measurements.

5. Analytical Results

Comparing solutions of unknown brass samples with a closely-matched synthetic standard and closely controlling acid concentration and film position, the results shown in table 5 were obtained.

6. Discussion

Improvement in precision for this method lies in better control of instrument instability.

Since the accuracy of this method depends on closely matching the composition of solutions of samples and synthetic standards, a preliminary examination of the sample should be made. It is necessary to note particularly the presence of elements having principal x-ray radiations lying several tenths of an Angstrom shorter than the absorption edge of the analytical line of the analyte and also those elements which have large mass absorption coefficients at the wavelength of the analytical line.

(R. Alvarez)

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Table 5. Comparison of chemical and x-ray
results.

NBS Sample Number	Element	Chemical Results [a] %	X-Ray Results [b] %	Standard Deviation of the Mean [c]	Coefficient of Variation of the Mean [d]
C1100	Cu	67.4_3	67.3_3	0.07	0.10
	Zn	32.2_0	32.2_5	0.03	.09
C1101	Cu	69.5_0	69.6_0	0.07	.10
	Zn	30.3_4	30.2_8	0.04	.12
C1102	Cu	72.8_5	72.8_6	0.06	.08
	Zn	27.1_0	27.0_6	0.03	.12
C1118	Cu	75.0_7	75.0_6	0.09	.12
	Zn	21.9_1	21.9_7	0.04	.16
C1119	Cu	77.1_2	77.2	0.05	.07
	Zn	20.5_3	20.4_9	0.03	.15
C1120	Cu	80.1_4	80.2_9	0.05	.06
	Zn	18.1_0	18.1_2	0.02	.12

[a] Average reported on provisional certificate. Cu determined
by electrodeposition; Zn by a double precipitation with
H_2S followed by ignition to the oxide.

[b] Mean of 8 runs.

[c] Standard deviation of the mean $s = \sqrt{\dfrac{\Sigma d^2}{n(n-1)}}$, where d is
the difference of the determination from the mean, and n
is the number of runs.

[d] Coefficient of variation of the mean, C.V. $= \dfrac{100\ s}{C}$, where
C is the average concentration in percent.

D. Interelement Effects in the X-Ray Spectrometric
   Analysis of Gold Alloys.

In x-ray fluorescence analysis the concentration of an
element is in general not a linear function of the emitted
x-ray line intensity. Interelement effects of absorption,
enhancement, and line overlap generally produce nonlinear
calibration curves when curves are developed for a wide
range of compositions. If all specimens in the analysis
have nearly the same matrix, that is, the composition range
is small, it is usually possible to plot a single, linear
calibration curve for each element determined.

This was the case (figure 13) in the method of x-ray
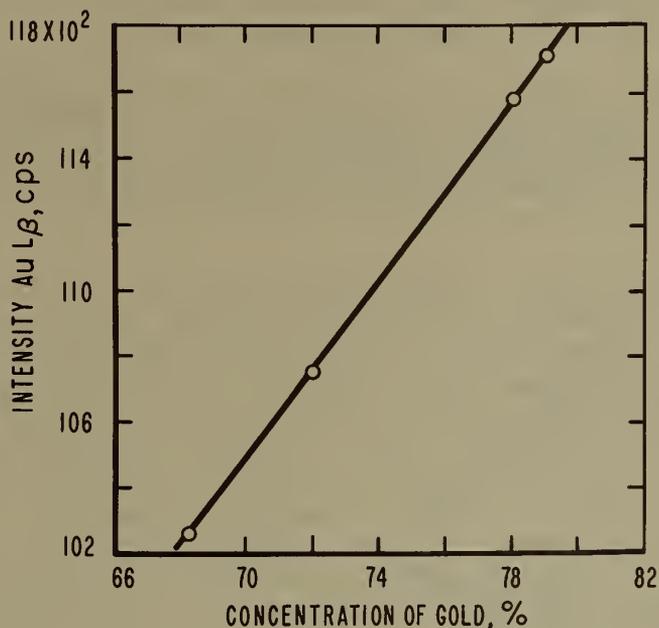
Figure 13. Calibration curve
            for gold in gold
            alloys, linear case.

spectrometric analysis of noble metal dental alloys
developed by Mulligan, Caul, Rasberry, and Scribner in the
Spectrochemical Analysis Section and recently published[16].
The method was specifically established for the quantitative
determination of Au, Ag, Cu, Pt, Pd, and Zn in a set of
dental gold alloys having the limited range of concentrations,
in percent: Au 68 to 79, Ag 8 to 14, Cu 6 to 12, Pt 0 to 6,
Pd 0 to 3, and Zn 0 to 2. Linear calibration curves are
used and the agreement with chemical analyses, $\pm$ 0.2%, is

satisfactory for quality control. It has marked
advantages of speed and simplicity compared to chemical
analysis.

Recently, J. D. Eick, research associate of the
American Dental Association in the NBS Dental Section,
attempted to apply the method to the analysis of a set of
dental gold alloys having a wider range of compositions.
The precision in this analysis remained good; however, the
values for Au and Ag were inaccurate for specimens having
compositions outside the range of compositions in the
original work. Errors as great as + 8% Au concentration,
and -2% Ag concentration occurred in the analysis of Au - Ag
binaries in which the concentration of Ag was a factor of
3 greater than in the case of the original work. These
inaccuracies appeared to increase systematically when the
amount of Ag was increased in the binaries.

A detailed study of the surface preparation of the
specimens was undertaken by Eick in an effort to account
for the analytical discrepancies. No improvement over
the originally suggested surface preparation technique
could be obtained with more refined techniques.

When it was seen that additional or different surface
preparation offered no solution to the problem, the first
approximation assumption of linearity was dropped and the
problem was considered as a matrix effect problem. To
correct for possible matrix effects, concentration was
treated as a function of line intensity affected by a
summation of contributions from every element in the
matrix. This function can be made linear by multiplication
of each summation term by the appropriate correction
coefficient. To empirically determine these coefficients
for any specific series of specimens, a mathematical
technique given by Lucas-Tooth and Price in 1961 [17] was
applied. This treatment requires the solution of N+2
simultaneous equations, where N is the number of elements
present. All of the required computations were
programmed for digital computer processing.

As corrected by this mathematical treatment, the
analytical method now provides analyses which agree with
chemical analyses to ± 0.2% concentration, over an extended
range of compositions, figures 14 and 15. Currently, Eick
is analyzing 300 specimens using this method and the x-ray
equipment in our laboratory.
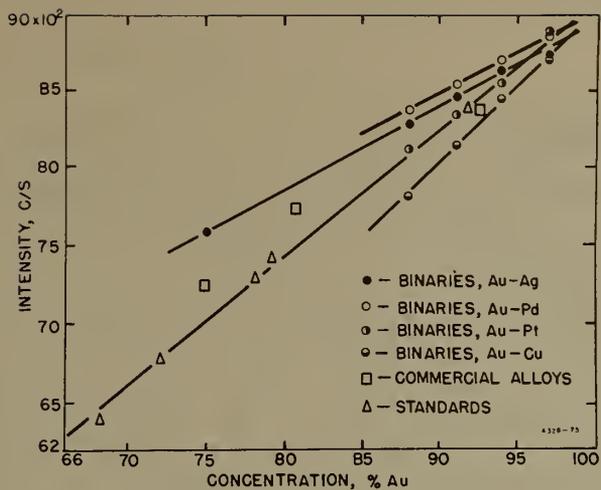
Figure 14. Analytical curve for
           gold alloys, nonlinear
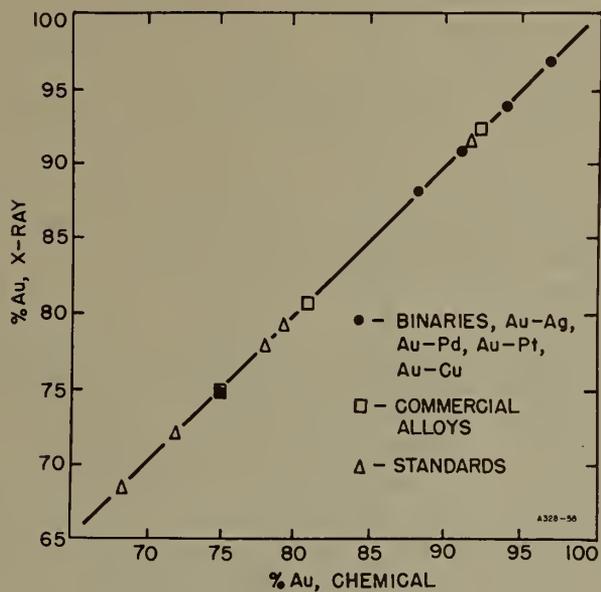   case, uncorrected.

Figure 15. Comparison of gold
           determinations by chemical
           and x-ray method. X-ray
           results corrected by the
           Lucas-Tooth method.

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A detailed account of the experimental work and the
final form of the correction to the method has been prepared
for publication [18].

(S. D. Rasberry, and J. D. Eick)

E. X-Ray Spectrometric Analysis of Silver Alloys

Conventional silver-base alloys for amalgamation with
mercury and use in dental restorations have the nominal
composition, in percent, of silver 69, tin 26, copper 4,
and zinc 1. Quantitative determination of these four
elements by traditional methods of solution chemistry is a
time-consuming task when undertaken for more than a few
specimens. Every three years, the Research Group of the
American Dental Association, in the Dental Section of NBS,
requires analyses of 80-100 of these alloys, an undertaking
which requires six months for a chemist to complete. In
cooperation with the Dental Section, we have undertaken to
establish a method for analyzing these alloys, using x-ray
fluorescence spectrometry. We are currently testing the
precision and accuracy of a tentative method. Preliminary
results indicate that analyses of sufficient accuracy can
be obtained for 100 specimens in two man-weeks.

The alloys, as commercially prepared for dental use,
are fine-grain turnings which vary in particle size by
about one order of magnitude, from 40 to 400 microns. For
the first preparation technique tried, a loose packing of
the grains, no simple function would relate intensities to
concentrations, probably due to the grain size variations.
Simple solution analysis was attempted with little success,
because of tin precipitation. Chemical separation techniques
were not considered practicable because of the increased
sample preparation time. Centrifugally-cast molten alloy
techniques were investigated; however, inaccuracies were
apparent for the more volatile elements, suggesting
volatilization losses. A pelletizing technique, with boric
acid binder, was also tried; however, samples could not be
reproducibly made. A fifth sample preparation technique,
perhaps the simplest to apply, was examined. In this
technique the grains were pressed at 20,000 psi, with no
binder, to form a solid disk with diameter of $\frac{1}{2}$ in. and about
3/16 in. thick. In our preliminary examination, these
briquettes have proven to be representative of the specimen,
reproducible in preparation, and easy to handle, store and
fabricate.

Instrumental techniques for this analysis were directed toward rapid analysis by use of the multichannel x-ray fluorescence spectrometer previously described. We are currently undertaking to optimize the spectrometer program for this analysis.

Analytical curves relating intensities of K_α lines to concentrations of Ag, Cu, and Zn were found to be linear as shown in the example in figure 16. However, the
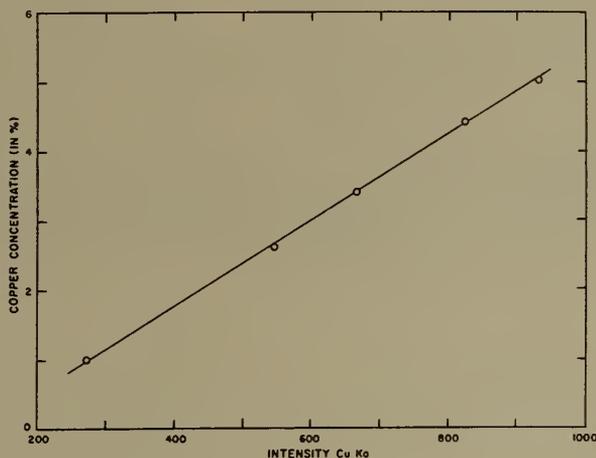
Figure 16. Linear calibration curve for copper in silver alloys.

function for SnK_α was found to be nonlinear because of interference from the unresolved AgK_β line. To mathematically resolve the intensity of SnK_α from AgK_β, the ratio of intensities $(SnK_\alpha + AgK_\beta)/AgK_\alpha$ was plotted versus the ratio of concentrations Sn/Ag. The term AgK_β/AgK_α in the intensity ratio is a constant, yielding a simple intensity ratio plus constant, versus a concentration ratio. This analytical curve is linear and can be used to determine Sn in an unknown, after Ag has been determined (figures 17 and 18). Computer programs to handle the bulk of the data reduction are presently being written.
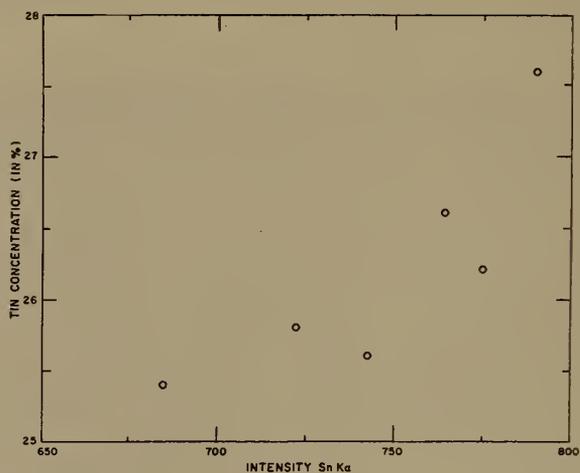
Figure 17.   Non-linear calibration
curve for tin in silver
alloys.
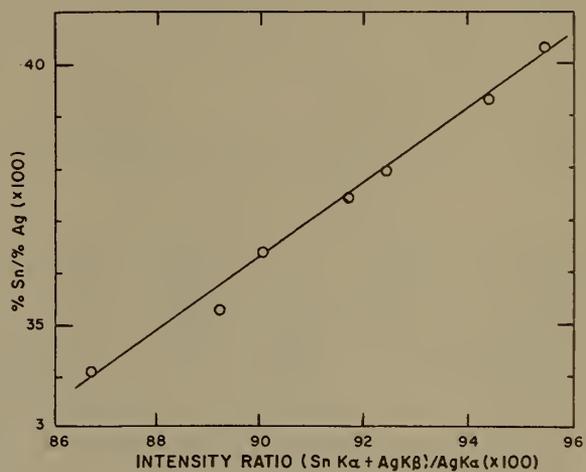
Figure 18.   Corrected calibration
curve for tin in silver
alloys.

All that remains to complete the study of this method is a careful determination of precision and accuracy of the method. When this is completed, details of the work will be prepared for publication.

(S. D. Rasberry and A. M. Yezer)

F. Determination of Coating Thickness

A preliminary study of nickel plating thickness measurement by x-ray fluorescence was performed using the Norelco single channel spectrograph. This work was requested by F. Ogburn, Electrolysis and Metal Deposition Section, NBS, Metallurgy Division, who provided specimens of steel with nickel platings of known thickness, from 0.0001 in. to 0.002 in. Both Ni K alpha and Fe K alpha radiation were employed. It was established that the Ni K alpha radiation is useful from a coating thickness far below the range provided to us, to about 0.0002 in., and that a range from 0.0001 in. to 0.001 in. could be covered by the Fe K alpha radiation. Instability problems associated with the scintillation detector of the unit precluded an assessment of the precision of the method; no further work is projected until installation of the vacuum spectrometer.

(K. F. J. Heinrich and S. Schuhmann)

4. ELECTRON PROBE MICROANALYSIS

Analysis of a micro-volume within a specimen is achieved with the electron probe microanalyzer by directing to the specimen surface a finely focused beam of electrons. Under typical conditions, the resulting x-ray emission is limited to a depth of one to three microns and comparable diameter. The electron beam can be made to scan over a small area on the specimen by applying electrostatic deflection. The brightness of the oscilloscope beam which scans in synchronism with the electron probe beam is modulated by the x-ray signal, and the x-ray image thus formed on the oscilloscope screen is recorded photographically.

Besides the purely qualitative information obtained by these x-ray images, semiquantitative recordings of line scans on the specimen and wavelength scan recordings can be performed, usually on a chart recorder. Quantitative determinations are based on counts of x-ray quanta on a scaler-timer combination.

Auxiliary signals other than x-rays complete the information obtainable with this instrument. The observation of electron backscatter, either directly or by specimen current measurements, provides an excellent image-forming function, figure 19, which combines topographic and atomic number information, since backscatter of electrons increases with increasing atomic number. Another signal of considerable utility is the emission of visible light under excitation by electrons (cathodoluminescence). Thus, the instrument offers a wide choice of read-out functions and read-out modes, and a judicious selection of procedure must precede the analysis of each specimen.

Much effort was expended this year in the procurement, installation, and modification of a suitable electron probe; this instrumentation will be discussed in detail.

A. Basic Equipment

The Applied Research Labs., EXM Microanalyzer, figure 20, as originally received from the manufacturer is composed of the following elements:

target current
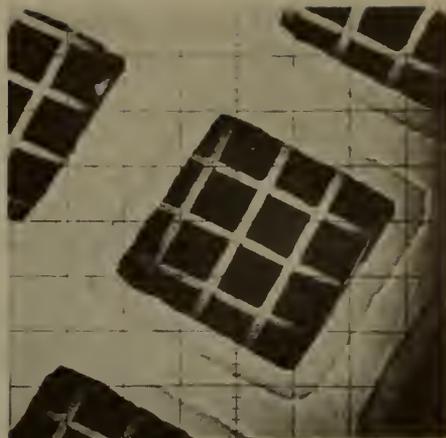
inverted target current
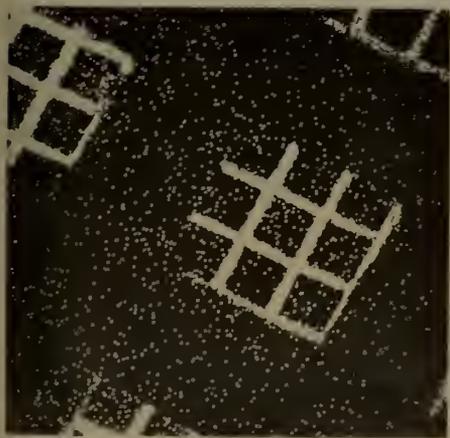
Ag Lₐ x-ray
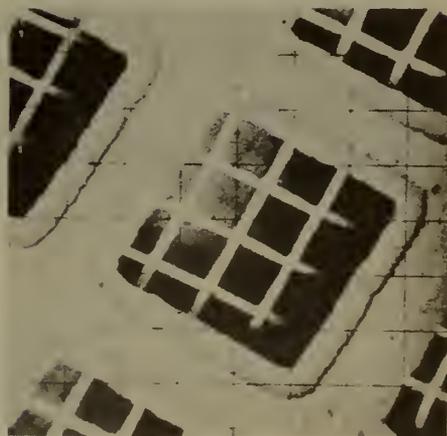
back scattered electron

Figure 19. Electron and x-ray scanning images. Large grid: copper wire, 30 μ diameter, open space 85 μ wide. Small grid: silver wire 4 μ diameter, open space 20 μ wide.
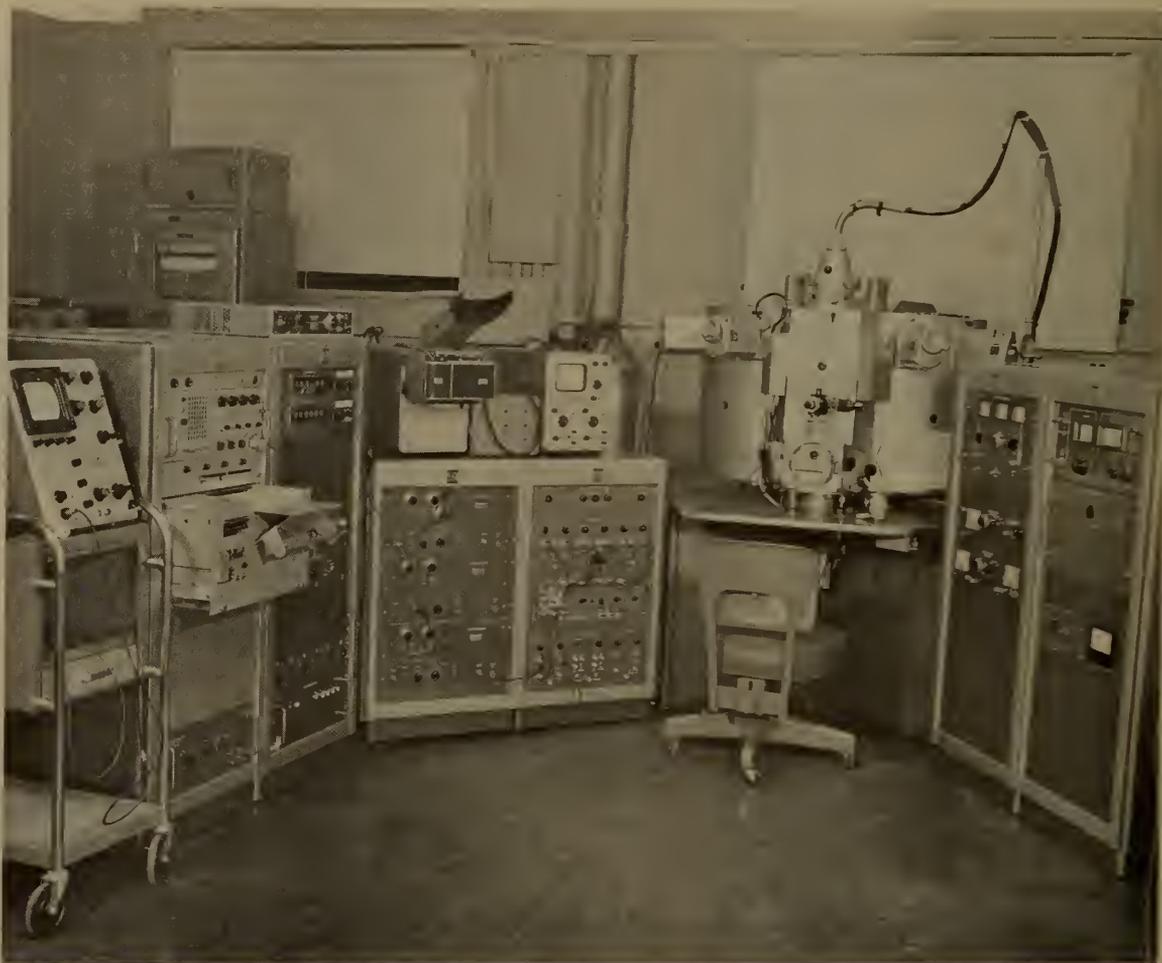
Figure 20.   Electron Probe Microanalyzer. From left to
right: Test scope used for trouble-shooting
and installation. Recorder bay with 4-
channel recorder, and detector power supply.
Scaler panel, with scaler, timer, scaler power
supply, and current meter. Scanning bays,
with AC and DC amplifiers, scan drivers,
signal switch board, linear amplifiers and
pulse height analyzers, and two oscilloscopes,
with oscilloscope camera. Main console,
containing electron optics, sample chamber,
microscope, and three x-ray monochromators.
Power consoles, with power supplies for
electron emission and acceleration, and for
electromagnetic lenses; and vacuum gages.

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a. The main console, containing the vacuum enclosure and vacuum pumps, the electron gun and anode assembly, two electromagnetic lenses for focusing the electron beam, the specimen manipulator and light microscope for specimen observation, and three x-ray spectrometers each with two interchangeable crystals.

b. The service console, containing power supplies for filament current and high voltage for electron acceleration, power supplies for the electromagnetic lenses, and vacuum measurement equipment.

c. The scanning console, containing the sweep generators and amplifiers, modular equipment for manipulation of AC and DC signals, two oscilloscopes for viewing and photographing of scanning images, and three linear amplifiers with pulse-height analyzers.

d. The read-out console, containing the power supply and attenuators for the x-ray detectors in the main console, a microammeter for measuring the beam and target currents, and the scaler-timer assembly with associated power supply.

B. Modifications of the Equipment

A program of modifications of the equipment and additions to the equipment was undertaken in order to improve its reliability and versatility. The following major changes have been made:

a. The d-c amplifiers were modified to provide greater sensitivity and facilities for inversion of black-white values of target current scanning images.

b. The integrators were modified to provide variable time constants when used as ratemeters, and to provide signals indicating unbalance condition of the operational amplifiers.

c. Extensive re-wiring was performed in order to diminish the amount of external connections necessary for operation.

The following elements were added:

a. A periodic integrator, built by the NBS electronics laboratory, according to schematics developed elsewhere [19].

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b. A concentration mapping [19] device also built by the NBS electronics laboratory.

c. A phototube detector for scanning cathodoluminescence images (NBS electronics laboratory).

d. A Sanborn four-channel recording system model 854-5460, including four linear amplifiers, with heated recording stili, for simultaneous recording of up to four signals.

e. A voltage-to-frequency converter for quantitative measurement of beam and target (specimen) currents.

f. An operational amplifier (solid state) for current-to-voltage conversion of target and beam current, to be measured by item e, and for obtaining high-contrast target current scanning images. (NBS electronics laboratory).

g. A Tektronix type 564 Storage Oscilloscope, with a dual trace linear amplifier 3A6 and a timebase with delay line 3B4. This scope is used for diverse testing functions, and particularly for observation of the height and shape of the amplified x-ray pulses.

h. A monitor circuit with variable delay line enabling a direct observation of the single-channel pulse-height analyzer performance on the pulse display of the oscilloscope mentioned under g. This is accomplished by blocking out that part of the oscilloscope trace corresponding to the pulses which are accepted by the pulse height analyzer window. This device was developed in our laboratory and will be described in a technical note soon to be published elsewhere.

Extensive re-wiring with provision for centralized switching facilities is planned in the near future. This will markedly reduce the excessive amount of patching currently necessary for operation, while conserving the flexibility of the instrument.

The following additions to the microprobe laboratory are planned for the near future.

a. Equipment for the detection and measurement of ultra-soft x-radiation will be installed by the manufacturer in July. This will extend our capabilities to the elements fluorine, oxygen, nitrogen, carbon, and boron.

b. Externally variable detector slits for better adjustment of the signal-to-noise ratios and solid state pre-amplifiers for noise-free signal amplifications will at the same time be installed in all spectrometers.

c. A second voltage-to-frequency converter, and two additional scalers, will permit (1) simultaneous scaling for up to three x-ray signals, (2) scaling of up to two x-ray signals for fixed integrated beam or specimen current, or (3) scaling of target current, plus one x-ray signal, for integrated beam current.

d. A multi-channel pulse-height analyzer with a 1600-channel memory will be installed. This instrument will permit efficient pulse height analysis and study of detector characteristics. In addition, the memory banks will permit the storage of a two-dimensional array of fixed-time counts. This analyzer will include typewriter print-out and tape-punching in the ASCII code of the memory contents, as well as paper tape feed into the memory, and will therefore serve as an interfacing device from the microprobe to computer facilities.

e. A precision microammeter, sensitive to 10^{-13} amp full scale, with provisions for measuring current, voltage, and integrated current, will be purchased.

f. The auxiliary equipment for specimen preparation and inspection, presently consisting of specimen polishing tables and a Leitz Ortholux microscope will be expanded by the acquisition of an ultra-microtome and an ultra-vacuum metal evaporizer.

C. Program of Investigations

The program of activities in the field of electron probe microanalysis will cover investigation of methods and instrumentation, exploration of new fields of application, and analyses in areas of interest to the NBS and other Government agencies that lack capabilities in this technique. Topics considered for investigation in the near future are:

a. Use of specimen current measurements for quantitative analysis; methods and instrumentation.

b. Instrumental characteristics of x-ray detectors; coincidence loss correction, and pulse height variation as a function of counting rate.

c. Standard reference materials for calibration in quantitative microanalysis.

d. X-ray line shifts, intensities, and band shape variations as a function of composition; their influence on measurements for quantitative analysis.

e. Use of memory storage and of analog computers for rapid quantitative analysis of specimen homogeneity.

f. Development of graphic techniques for read-out of scanning operations (concentration mapping), and development of the corresponding instrumentation. Later objectives should include the study of spectra in the ultra-soft range (10-100 Å), and use of signals other than x-rays (cathodoluminescence, infrared emission, etc.)

D. Applications

Considerable time and effort has been spent in satisfying the demands for microanalyses for the NBS as well as for other agencies requesting such service from the NBS. The following list will illustrate the type of service performed:

a. Analysis of a specimen of platinum-rhodium standard, for identification of material in grain-boundaries.

b. Analysis of two specimens of micro-film.

c. Analysis of two specimens of gallium arsenide, for dopants.

d. Analysis of turbine inlet guide vane specimens. Figure 21, study of cracked zone.

e. Analysis of fragment of airplane landing gear piston assembly. Composition of a welded area, inclusions, and cracks.

f. Analysis of corroded Monel metal. Identification of phase in grain boundaries of corroded area.

g. Identification of a metallic particle extracted from the eye of a patient.

h. Comparison of three metal particles with a standard steel specimen.

This representative, although incomplete, list illustrates the range of problems of interest to the NBS that can be handled with the microprobe.

A

Cr K$_\alpha$

B

Al K$_\alpha$

Figure 21. Chromium (A) and aluminum (B) x-ray scans of a cracked segment of a turboprop inlet guide vane; showing enrichment of these elements (brightness) within the crack due to preferential oxidation.

The preceding list represents the non-recurrent type of analysis of a single or few specimens. Systematic studies of certain problem areas have also been underway, notably that of homogeneity of NBS standard reference materials. A study of microstructure and homogeneity of dental alloys is presently in preparation. Exploratory work is also being done on possible applications of the microprobe to the analysis of archeological specimens of interest to the Conservation Laboratory of the Smithsonian Institution.

(K. F. J. Heinrich)

5. ANALYSIS OF HIGH-PURITY METALS: ENRICHMENT METHODS

A primary research effort of the Analytical Chemistry Division is to develop methods for detecting and quantitatively measuring slight traces of impurities in matter. High-purity materials are essential for applications in metallurgy, nuclear engineering, quantum-light generators, and solid state devices. The development of NBS Research and Standard Reference Materials in these areas emphasizes the importance and need for sensitive and accurate methods for the analysis of high-purity materials. For a preliminary characterization of high-purity materials as suitable reference materials, it is desirable to know which elements are present, their concentrations, and homogeneity. For this preliminary examination, the spectrochemical method should have high-sensitivity for many elements, be rapid, and be relatively free from contamination. Since the concentrations of many elements in the materials are often below the levels at which they can be detected by conventional spectrochemical methods, enrichment procedures, either physical or chemical, are required. These will be discussed for the analysis of three high purity metals: tin -- important in solid state devices, zinc -- a proposed standard reference material for freezing point and composition, and platinum -- a proposed research material.

A. Physical Enrichment

If a simple enrichment process can be performed without the necessity of dissolving and separating the elements to be determined, the requisite rapidity can be realized. It was felt that this could best be accomplished by fractionally distilling the impurity elements from the matrix. While not new, the method is quite effective in extending the sensitivity to low concentration. In this procedure, the sample is arced continuously as the camera is being racked at definite intervals. Since the spectral lines of volatile elements appear first and the more refractory elements appear later, the exposure can be selected which yields the best spectral line to background ratio. It was found that by flowing an argon-oxygen gas mixture past the arc instead of arcing in air, and using higher spectral orders, greater sensitivities for some elements could be realized.

1. Analysis of Tin

As applied to the analysis of high-purity tin, a cylindrical sample pellet approximately 4 mm in diameter by 4 mm long was placed in a cupped, graphite electrode and arced to completion with a direct current of 20 amp using a

graphite counter electrode and an analytical gap of 3 mm.
As the sample was arced, the camera was racked at 20
second intervals and the spectra recorded on Eastman Kodak
SA No. 1 photographic plates. First order spectra were
taken in the wavelength region from 2200 to 4700 Å; the
reciprocal linear dispersion was approximately 5.0
Angstroms per mm. A slit width of 15 microns was used.

"Addition standards" were made by melting weighed
amounts of an NBS standard reference material of tin,
No. 435, with the high purity tin sample to be analyzed
in a quartz tube under cottonseed oil. By drawing the
molten metal into Pyrex tubes, rods 4 mm in diameter were
formed from which the sample pellets were cut. This
provided a series of reference samples containing known
amounts of Cu, Pb, As, Sb, Ni, Zn, Ag, Bi, Cd and Co. The
surfaces of the samples were cleaned by treatment with
dilute, distilled HCl. It was found that Cd, Bi, Ag, Pb,
and Cu could be detected at an approximate concentration
of 0.1 ppm, Ni at 0.2 ppm and Sb at less than 0.5 ppm.

Preliminary experimentation using a 20% oxygen-80%
argon mixture surrounding the electrodes, and super-
imposing the spectra from the first 20 second arcings of
two sample charges, indicated that bismuth could be detected
at a concentration of less than 0.1 ppm.

2.   Analysis of Zinc

A sample of zinc, a proposed standard reference
material for composition and melting point standard, was
examined using this method. Six metallic impurities, Ag,
Cd, Fe, Mg, Pb and Si, were detected with concentrations
totaling approximately $1._2$ ppm. To cut the 4-mm diameter
sample pellets, a special tool consisting of a steel tube
edged with a tool steel cutter was used. It was found
necessary to remove approximately 8% of the surface area of
the pellet by dissolving in dilute, distilled HCl to
eliminate contamination from the sampling operation.

3.   Analysis of Platinum

Two samples of platinum, proposed research materials,
have been examined by this method. The two lots, largely in
0.020-inch diameter wire form, will serve for inter-
laboratory comparisons of analyses and electrical
measurements. One material, designated as Pt No. 174471,
contains 1 to 10 ppm of at least 13 elements. In addition
to the elements Ir, Rh, Pd, Ag, Au, Ca, Pb, Mg, and Cu
incorporated in the master alloys from which the final
melt was made, Fe, Si, Al and Zr were detected. The Zr,

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from the ZrO_2 crucible which was used by the manufacturer, has such poor spectral sensitivity that it usually is not detected in the spectrochemical procedures ordinarily employed. A 100-mg sample charge was arced using a current of 15 amp, and other conditions as had been used for the analysis of tin. An atmosphere of 20% oxygen-80% argon was found superior to that of air for the detection of zirconium. The other material, Pt No. 273, is a lot of highest commercial purity; here Cu, Si, Fe and possibly Ir were detected.

In addition, several other materials, intended to be of high-purity, were examined by this procedure: magnesium, for experimentation prior to atomic weight determination; copper made at NBS, Boulder for electron scatter measurements; and samples of lithium-gallium and lithium-aluminum purchased as being "free" of iron, cobalt, nickel, and chromium. The copper was found to be of superior purity -- only magnesium was detected, at less than 0.2 ppm. The "high purity" magnesium metal was found to be less pure than a magnesium reference material in our stock; some of the latter metal was supplied to the research group for its use. (In many instances research groups are not aware of the better sources of high purity materials and we have furnished information on the sources or supplied the material from our stock). The lithium compounds were found to be impure, with Fe, Co, Ni, and Cr each greater than 0.001%.

B. Chemical Enrichment

Chemical enrichment-spectrographic methods involve dissolving the sample and employing separation techniques such as ion-exchange, solvent extraction, electrolysis, or selective precipitation to separate the impurity elements from the major constituent and provide a concentrate. By comparing the concentrate containing the impurity elements with synthetic standards, quantitative determination of the elements can be made without the necessity of separating the individual elements. The requirements for dissolving the sample, stringently purifying the reagents used, avoiding contamination from the environment, and investigating possible losses of the separated traces by absorption effects make these methods time-consuming and unsuitable as rapid survey methods for high purity materials. However, they are important for quantitative analysis of a selected material. Several chemical enrichment procedures are under investigation.

1. Analysis of Tin

An extraction procedure described by Stokely and

Moore [20] was adapted for spectrochemical use. 200 mg of tin as a chloride solution having a concentration of 10 mg of tin per ml, was extracted with three 20-ml portions of 0.5 M TTA in methylisobutylketone that had previously been equilibrated with 3N HCl. A shaking period of two minutes was used for each portion. The aqueous layer was placed in a quartz dish and 1 ml of a high purity gallium sulfate solution was added equivalent to 20 mg of Ga_2O_3 per ml. After evaporating the solution to dryness, the dish was ignited at 900°C for 15 minutes. The gallium oxide residue was then arced to completion and compared to synthetic standards. The removal of antimony and iron, two important impurities in tin, during the extraction step constitutes a drawback of this method.

2. Analysis of Platinum

For the possible determination of iron, aluminum, and tin in platinum, a procedure is being investigated in which $Ga(OH)_3$ is precipitated and acts as a "gatherer" for these elements. In this method, approximately 500 mg of platinum was dissolved in 30 ml of aqua regia. The solution was evaporated to dryness in a quartz evaporating dish and excess nitrate removed by adding HCl several times and evaporating almost to dryness. The residue was dissolved in 2 ml HCl and the volume made up to 50 ml; 20 ml of this solution was heated and ammonium hydroxide added to form the platinum ammine complexes. The solution was then made slightly acidic with HCl and 1 ml of a gallium sulfate solution was added equivalent to 20 mg of gallium oxide. On adding ammonium hydroxide, a precipitate of gallium hydroxide formed which could be ignited to the oxide after centrifuging, and then compared to synthetic standards. At present, some platinum is found in the oxide and further investigation of the method is necessary.

(R. Alvarez)

6. STANDARDS, ANALYSIS, AND LITERATURE ACTIVITIES

The Section provides analytical assistance to other research groups at NBS, to other Government agencies, and to the general public. These activities include (1) developing standard reference materials, especially standards for calibration in spectrochemical analysis; (2) providing analyses in optical spectrometry, x-ray fluorescence spectrometry, and electron probe microanalysis; and (3) providing literature surveys in these fields through bibliographies and critical reviews.

A. Standard Reference Materials

1. Standards Program

The program of standard reference materials and calibration in spectrochemical analysis has been a major activity of the Section. The output of this program has consisted of standard reference samples with certified composition, and the determination of information on applying the reference samples, including methods of analysis.

Until recently the actual preparation of standard reference metals and alloys of solid forms was a part of the program of the Section; however, the preparation work was transferred to the new NBS Office of Standard Reference Materials in 1964. The Section continues its activity on the analysis of proposed reference materials in cooperation with other Sections of the Analytical Chemistry Division.

The analysis of reference materials consists of two phases, first, a study of homogeneity of the material, and second, accurate analysis by two or more cooperators or techniques. Homogeneity of the intended standard is essential to its use, since each user should receive a specimen corresponding in analysis to the certificate provided. In spectrochemical analysis the amount of specimen consumed in an analysis may be of the order of a milligram or less and the analysis may be affected by the physical state of the material. Consequently, much effort has been devoted in our Section to the design of optimum procedures for study of homogeneity. For spectrochemical analysis, experiments have been designed to obtain the maximum of information from the minimum of testing, using photoelectric spectrometers for high precision. The information is read out in the form of punched cards or tape and submitted to a computer for statistical analysis of the data. Analysis of variance serves appropriately for

determining that part of variation in concentration attributable to segregation in the sample. Two large photoelectric spectrometers are installed in our laboratory primarily for homogeneity testing, although they are also used for general analytical service and research work.

The Baird-Atomic Direct Reader, figure 22, is a 3-meter Eagle mount of a concave grating with a reciprocal
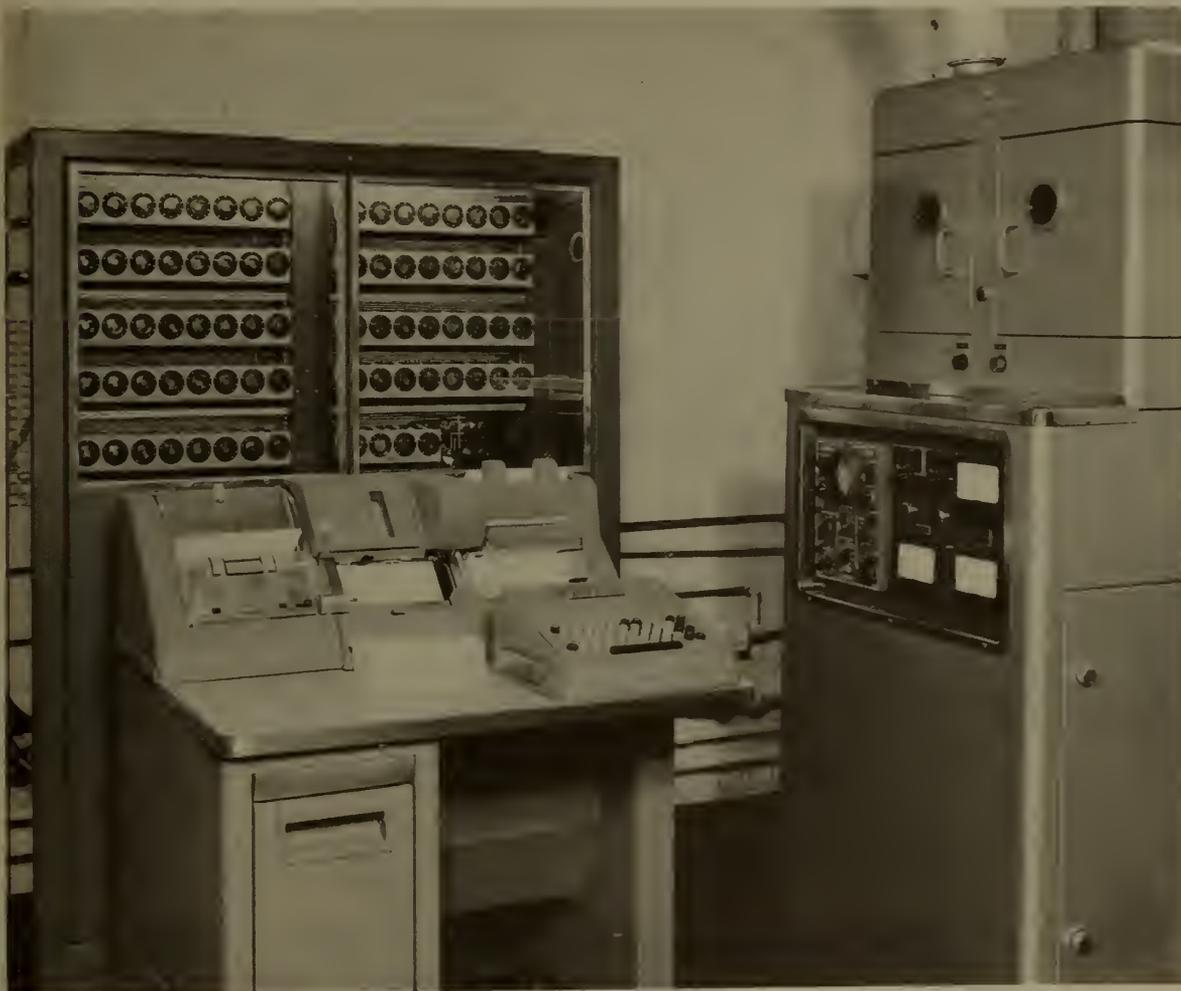

Figure 22.   Direct reading spectrometer with automatic read-out system. Left background, electronic digitizer for spectrometer read-out; foreground, punched-card read-out unit; right, control end of 3-meter grating spectrometer.

linear dispersion of 2.8 Angstroms per mm in the first
order. An array of 58 exit slits and phototubes provides
for intensity measurements of 36 chemical elements.
Eighteen elements may be measured simultaneously relative to
an internal standard element and the results are displayed
on digital counting tubes. The information on spectral
line intensities is printed and punched on an IBM card
within 10 seconds after the spectral exposure is ended. In
a typical homogeneity study, some 30 samples may be
analyzed, resulting in 30 record cards. These are trans-
ferred to a computer which, by previous programming,
converts intensity ratios to concentration and subjects
the data to analysis of variance. All proposed metallic
alloy standard reference materials in production at NBS are
investigated for homogeneity by this method prior to
acceptance for final analysis and distribution. Much of
this homogeneity testing has been done by D. M. Bouchette.

Similar operations are performed on an Applied Research
Analysis spectrometer, figure 23, but with different
excitation sources and with readout to typewriter and
punched tape. X-ray fluorescence spectrometry is also
applied in homogeneity studies and in analysis using the
multi-channel x-ray spectrometer previously described
in this report. The electron probe microanalyzer is a very
sensitive tool for study of homogeneity and is applied in
critical cases.

Following the homogeneity studies, analyses of proposed
standards are made in cooperation with other laboratories
in the Division. Here the spectrochemical analysis must
be made by a primary method relative to standards
synthesized from pure materials. The samples are converted
to finely divided powders or to solutions to homogenize the
sample and to provide a form for comparison with the
synthesized standards. Powders are usually analyzed by arc
excitation; solutions by the plasma jet, by atomic
absorption, or by a spark with the rotating electrode
technique.

2. Analyses Made of Standard Reference Materials

Analyses of standard reference materials during the
12-month period from June, 1964 through May, 1965 included 39

Figure 23. Multi-channel optical spectrometer. At left,
excitation source console; center, 2-meter
grating spectrometer with spark stand in
front; right, recording console with chart
recorder controls, and array of spectral
line integrators.

samples, with 128 qualitative determinations, and 1969
quantitative determinations, and 19 reports written.
(Other analyses made are described below.)

B. General Spectrochemical Analyses

Spectrochemical analyses are made of a wide variety
of materials to assist other NBS laboratories and other
Government agencies where their facilities are not capable
of doing the work.

1. Types of Analyses

The large bulk of analyses are rapid surveys by
optical spectroscopy in which 50 chemical elements are
sought. Occasionally the rare earths and alkalies are
included to extend the list of elements to 70. In the
analytical report the concentrations of the elements
found are given within ranges of factors of 10, e.g. 0.001
to 0.01%, 0.01 to 0.1% etc. This analysis often may provide
sufficient information for the problem; if not, it provides
the basis for efficient planning of further quantitative
analysis by spectrochemical or other methods.

A large grating spectrograph, a 21-foot Wadsworth
concave grating mounting, has been used in the past for much
of the optical emission analytical work. About a year ago
a 3.5-m Ebert mount plane grating spectrograph, figure 24,
was installed to modernize and improve the facilities for
this work. This instrument provides for rapid interchange
of selected gratings and permits observation of spectra at
higher grating orders for better resolution. The arc-spark
stand mounted with this instrument provides for convenient
operation of the excitation source in various gas mixtures.

Qualitative analysis may also be made by scanning
through the x-ray spectrum and this complements the optical
method. The x-ray method is less sensitive for some of
the metallic elements but more sensitive for metalloids
and halogens.

Quantitative analyses are made by both optical and x-ray
fluorescence spectrometric methods using equipment described
earlier. The problem is relatively simple for the analysis
of metals and alloys when a solid sample with a diameter
of 1 to 2 cm is provided, and when adequate reference
samples are available. However, many samples are in the
form of powders, solutions, thin wires, or thin films.
In these cases the samples may be analyzed in the form of
dry powders or solutions, relative to standard samples
synthesized from pure elements or salts.
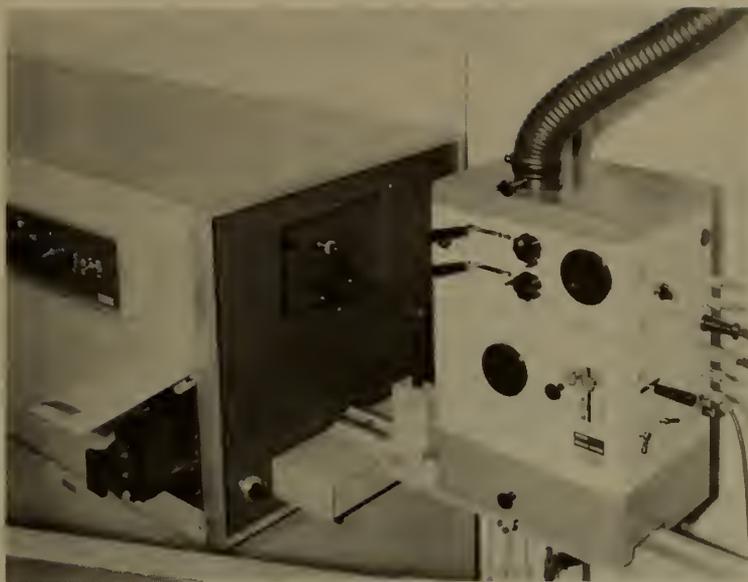
Figure 24.   Optical spectrograph, 3.4-meter Ebert.
(Control end) At the right, an arc-
spark stand for spectral excitation in
controlled atmospheres.

    Spectrochemical methods in general may be considered
micro or semi-micro methods since a sample of 10 mg or less
may suffice for the analysis. Recent developments in both
optical and x-ray analysis have reduced the required sample
size to very small amounts thus extending the methods to
the sub-micro range. The laser probe consumes a sample
weighing about 0.1 μg and can provide information on 50 or
more elements in this sample. The electron probe micro-
analyzer can analyze a volume of a few cubic microns
weighing a picogram (10^{-12}g) or less. It also provides
remarkable information on the distribution and
concentration of chemical elements in a surface. For
further details on these new analytical tools and service
applications see section 2-E and section 4 of this report.

2. General Analyses Made

Spectrochemical analyses, other than those made of standard reference materials, during the 12-month period from June, 1964 through May, 1965 included 409 samples with 12,268 qualitative determinations and 396 quantitative determinations, and 144 reports written.

(B. F. Scribner and E. K. Hubbard)

C. Literature Surveys

Since its inception the Section has served as a focal point for information on the literature of optical spectroscopy. Bibliographies on optical spectrochemical analysis have been prepared and have been published through the American Society for Testing Materials [21]. Biennial reviews in this general field [22] and in flame photometry [23] have been published in Analytical Chemistry.

To collect information on the literature, systematic surveys are made using Chemical Titles, Chemical Abstracts, and final checking against selected journals. Card files are maintained with the abstract typed or pasted on 5 X 8 in. cards. At periods of about five years, the material is indexed and prepared for publication. At the present time preparation is nearly complete on the next volume of the Index to the Literature on Spectrochemical Analysis, for the years 1956-60. Similar literature reference files are maintained for x-ray spectrometry and electron probe microanalysis. A bibliography on electron probe micro-analysis, previously prepared at the E. I. du Pont de Nemours, Experiment Station, Wilmington, Del., is being kept up-to-date. This year a supplement to the original bibliography was made available through the cooperation of the du Pont laboratory. The complete bibliography in off-set form is available on request from Dr. K. F. J. Heinrich of our Section.

Attention is currently being given to the possibility of issuing the bibliographies at shorter intervals.

(B. F. Scribner, M. Margoshes,
K. F. J. Heinrich, and V. C.
Stewart)

7. PERSONNEL AND ACTIVITIES

A. Personnel Listing

Spectrochemical Analysis, Bourdon F. Scribner, Section Chief

Group I. Optical Spectroscopy

    Marvin Margoshes, Chemist
    Martha M. Darr,   Chemist
    Stanley D. Rasberry, Physicist
    Howard E. Bond (Physicist, Summer Student 1964)

Group II. X-Ray Fluorescence Spectrometry and Electron
           Probe Microanalysis

    Kurt F. J. Heinrich, Chemist
    Shuford Schuhmann, Chemist (Temporary)
    Detlef F. Gerlach, Chemist (Summer Student 1965)
    Gerald A. Wolfson, Electronic Technician

        Part Time Guest Workers:
    Michael Duke, Chemist, U. S. Geological Survey
    Harvey Yakowitz, Metallurgist, NBS Metallurgy
               Division
    Donald L. Vieth, Physicist, NBS Metallurgy Division
    John D. Eick, Chemist, Dental Research Group

Group III. Calibration and Analysis

    Harold C. Dilworth, Chemist (Resigned)
    Elizabeth K. Hubbard, Physicist
    Doward M. Bouchette, Physical Science Technician
    Anthony M. Yezer, Summer Student 1964

Group IV. Enrichment Techniques

    Robert Alvarez, Chemist

Group V. Literature Survey

    Virginia C. Stewart, Chemist

Group VI. Clerical

    Frances L. Hilten, Administrative Aid

B.   Publications

1.   Michaelis, R. E., Yakowitz, H., and Moore, G. A.
       Metallographic Characterization of an NBS
       Spectrometric Low Alloy Steel Standard.
       J. Research NBS, 68A, 343-354, July-August 1964.

2.   Margoshes, M., and Scribner, B. F.
       Simple Arc Device for Spectral Excitation in
       Controlled Atmospheres.
       Appl. Spectry., 18, No. 5, 154-155, 1964.

3.   Michaelis, R. E., Wyman, L. L., and Flitsch, R.
       Standard Reference Materials: Preparation of NBS
       Copper-Base Spectrochemical Standards.
       NBS Misc. Publ. 260-2, October 15, 1964.

4.   Scribner, B. F., Margoshes, M., and Rasberry, S. D.
       Laser Microprobe for Analysis of Very Small Samples,
       in "Research on Crystal Growth and Characterization
       at the National Bureau of Standards, January to
       June, 1964", NBS Technical Note 251, Oct. 19, 1964,
       National Bureau of Standards, Washington, D. C.

5.   Michaelis, R. E., Yakowitz, H., and Moore, G. A.
       Standard Reference Materials: Metallographic
       Characterization of an NBS Spectrometric Low-Alloy
       Steel Standard.
       NBS Misc. Publ. 260-3, October 22, 1964.

6.   Alvarez, R., and Flitsch, R.
       Standard Reference Materials: Accuracy of Solution
       X-Ray Spectrometric Analysis of Copper-Base Alloys.
       NBS Misc. Publ. 260-5, March 15, 1965.

7.   Scribner, B. F., Margoshes, M., and Rasberry, S. D.
       Laser Microprobe for Analysis of Very Small Samples,
       in "Research on Crystal Growth and Characterization
       at the National Bureau of Standards, July to December
       1964." NBS Technical Note 260, May 8, 1965,
       National Bureau of Standards, Washington, D. C.

8.   Scribner, B. F., and Margoshes, M.
       Emission Spectroscopy
       Chapter 64 of I. M. Kolthoff and P. J. Elving
       "Treatise on Analytical Chemistry", Part I, Vol. 6,
       pp. 3347-3461.
       New York - J. Wiley & Sons, 1965.

9. Dilworth, H. C.
    Spectrochemical Analysis of High-Temperature Alloys
    by Spark Excitation in Argon and Nitrogen.
    American Society Testing Materials Special Technical
    Publication, (In press).

10. Heinrich, K. F. J.
    X-Ray Absorption Uncertainty
    The Electron Probe Microanalyzer -- Proceedings of a
    Symposium on Electron Probe Analysis.
    Electrochemical Society, Washington, Oct. 1964
    New York, J. Wiley & Sons (In press).

11. Temple, A. K., Heinrich, K. F. J., and Ficca, J. F., Jr.
    Quantitative Electron Microprobe Analysis of
    Ilemite Ores.
    The Electron Probe Microanalyzer -- Proceedings of a
    Symposium on Electron Probe Analysis, Electrochemical
    Society, Washington, Oct. 1964
    New York, J. Wiley & Sons (In press).

12. Heinrich, K. F. J.
    Electron Probe Microanalysis
    "Lectures on Modern Techniques in Solid State Research"
    Garden & Breack, 150 Fifth Ave., New York, (In press).

13. Heinrich, K. F. J.
    X-Ray Optics and X-Ray Microanalysis.
    Book Review, American Scientist (In press).

14. Eick, J. D., Caul, H. J., Smith, D. L., and
    Rasberry, S. D.
    Analysis of Gold and Platinum Group Alloys by X-Ray
    Emission With Corrections for Interelement Effects.
    Anal. Chem., (Submitted).

15. Heinrich, K. F. J.
    Identification of Inclusions with the Electron Probe
    Microanalyzer.
    American Society for Testing and Materials, Special
    Technical Publication.
    (Submitted).

16. Heinrich, K. F. J.
    Problems in Excitation and Sampling in X-Ray
    Fluorescence Analysis.
    American Society for Testing and Materials, Special
    Technical Publication.
    (Submitted).

17. Margoshes, M.
    Recent Advances in Excitation of Atomic Spectra.
    Proceedings of the XIIth International Spectroscopy
    Symposium,
    Exeter, England (1965) (Submitted).

18. Rasberry, S. D., Scribner, B. F., and Margoshes, M.
    Characteristics of the Laser Probe for Spectro-
    chemical Analysis
    (A Summary)
    Proceedings of the XIIth International Spectroscopy
    Symposium,
    Exeter, England (1965) (Submitted).

19. Margoshes, M.
    Excitation and Ionization in Arc and Spark
    Excitation Sources.
    Appl. Spectry. (Submitted).

20. Scribner, B. F.
    Advances in Excitation Sources for Spectrochemical
    Analysis. XXth International Congress on Pure and
    Applied Chemistry, Moscow (1965).
    Pure and Applied Chemistry. (Submitted).

C.   Talks Given

1.   Margoshes, M., "Excitation of Spectra: Fact and Fancy",
     Society for Applied Spectroscopy, Third National
     Meeting, Cleveland, Ohio.
     October 2, 1964.

2.   Heinrich, K. F. J., "X-Ray Absorption Uncertainty in
     Electron Probe Microanalysis," The Electrochemical
     Society, Washington, D. C.
     October 13, 1964.

3.   Heinrich, K. F. J., "Electron Probe Microanalysis,"
     School of Metallurgical Engineering, University of
     Pennsylvania, Philadelphia, Pennsylvania.
     October 27, 1964.

4.   Heinrich, K. F. J., "Analytical Applications of X-Ray
     Spectrometry," Analytical Chemistry Seminar, NBS,
     Washington, D. C., Nov. 6, 1964.

5.   Scribner, B. F., "The Role of Gaseous Atmospheres in
     Spark Excitation for Spectrochemical Analysis,"
     Joint Meeting, Society for Applied Spectroscopy,
     Delaware Valley Section, and American Chemical
     Society, Lehigh Valley Section, Reading, Pennsylvania.
     November 20, 1964.

6.   Heinrich, K. F. J., "The Determination of Trace
     Impurities and Light Elements by X-Ray Fluorescence
     Spectrometry," Society for Applied Spectroscopy,
     Pittsburgh Section, Pittsburgh, Pennsylvania.
     February 17, 1965.

7.   Rasberry, S. D., "Quantitative Aspects of Laser Probe
     Spectral Analysis," Spectroscopy Society of
     Pittsburgh, Pittsburgh Conference on Analytical
     Chemistry and Applied Spectroscopy, Pittsburgh,
     Pennsylvania. March 4, 1965.

8.   Scribner, B. F., Michaelis, R. E., and Darr, M. M.,
     "The Pittsburgh Conference on Analytical Chemistry
     and Applied Spectroscopy, held March 1-5."
     Discussion Meeting in Analytical Chemistry, NBS
     Washington, D. C., March 24, 1965.

9.   Scribner, B. F., "Metallurgical Applications of Laser
     Probe Analysis," American Chemical Society, Detroit,
     Mich., April 5, 1965.

10. Rasberry, S. D., "Spectrochemical Analysis by the Laser Probe," Joint Meeting of the Chemical Society of Washington and the Maryland Section, American Chemical Society, College Park, Md., May 7, 1965.

11. Scribner, B. F., "Accuracy in Spectrochemical Analysis," Panel Discussion on Accuracy, Analytical Chemistry Division, May 21, 1965.

12. Heinrich, K. F. J., "Electron Probe Microanalysis," Society of the Sigma Xi, Washington, D. C., May 10, 1965.

13. Heinrich, K. F. J., "Identification of Inclusions With the Electron Probe Microanalyzer," American Society for Testing and Materials, Purdue University, Lafayette, Ind., June 14, 1965.

14. Heinrich, K. F. J., "Problems of Excitation of X-Rays and Surface Effects of the Sample in X-Ray Fluorescence Spectrometry," American Society for Testing and Materials, Purdue University, Lafayette, Ind., June 14, 1965.

D.   Committee Activities

American Society for Testing and Materials,
ASTM Committee E-2 on Emission Spectroscopy.

   B. F. Scribner, member, attended a meeting in Pittsburgh,
      Pa., March 2, 1965.

   R. Alvarez, member, attended meetings in Lafayette, Ind.,
      June 15-18, 1965.

ASTM Committee E-4 on Metallography

   K. F. J. Heinrich, Chairman of Microprobe Task Group
      presided at meetings in Lafayette, Ind., June 15-18,
      1965.

ASTM Committee E-13 on Absorption Spectroscopy

   B. F. Scribner, member, attended meeting in Pittsburgh,
      Pa., March 1, 1965.

Chemical Society of Washington, Committee on Meetings

   B. F. Scribner, member, attended two meetings.
      November, 1964 and January, 1965.

XII Colloquium Spectroscopicum Internationale, Exeter, 1965.

   B. F. Scribner, member of Advisory Committee.

Eastern Analytical Symposium

   B. F. Scribner, Program Chairman, EAS 1965, attended
      meetings of the Planning Committee, February 12, and
      May 14, 1965.

   M. Margoshes, Publicity Chairman, EAS 1964, attended
      meetings of the Planning Committee, in September and
      December, 1964.

International Union of Pure and Applied Chemistry.

   B. F. Scribner, Titular member, Commission on Spectro-
      chemical and Other Optical Procedures for Analysis.

Society for Applied Spectroscopy

M. Margoshes, Delegate, attended a meeting of the
Governing Board in October, 1964.

M. Margoshes, Chairman, Conference Committee, 1965.

B. F. Scribner, Chairman of the SAS Advisory Committee,
presided at a meeting of the Committee in Pittsburgh,
Pa., March 2, 1965.

Spectrochimica Acta, Editorial Advisory Board

B. F. Scribner, member, attended a meeting of the
Editorial Advisory Board, at Pittsburgh, Pa.,
March 3, 1965.

Washington Academy of Sciences

B. F. Scribner, Chairman, Auditing Committee, attended
meeting, December, 1964.

Members of the Section also serve on Division Committees,
for which several meetings were held during the year, and
on other assignments.

These are listed as follows:

NBS Analytical Chemistry Division,

Committee on Analytical Chemical Information.

B. F. Scribner (Chairman), K. F. J. Heinrich, and
M. Margoshes

Committee on Analytical Services

B. F. Scribner, and M. Margoshes

Committee on Standard Reference Materials

B. F. Scribner

Division Newsletter

E. K. Hubbard

8. ACKNOWLEDGMENTS

The Spectrochemical Analysis Section has received assistance from groups and individuals at NBS which has aided our work in marked degree. While it is not feasible to mention the many individuals involved we wish to express our appreciation to all concerned for their contribution.

The NBS Procurement, Plant, and Shops Divisions have been especially helpful in the purchase, installation, and modification of new equipment, including the Electron Probe Microanalyzer. The Electronic Instrumentation Section (of the Measurement Engineering Division) through Louis Marzetta has provided excellent service in the construction of electronic devices.

In the Analytical Chemistry Division, the Radiochemical Analysis Section through James R. DeVoe has provided advice and assistance on electronic readout and computer applications.

Robert E. Michaelis, formerly with our Section and now with the NBS Office of Standard Reference Materials, has been very helpful in consultation on the standards work of the Section.
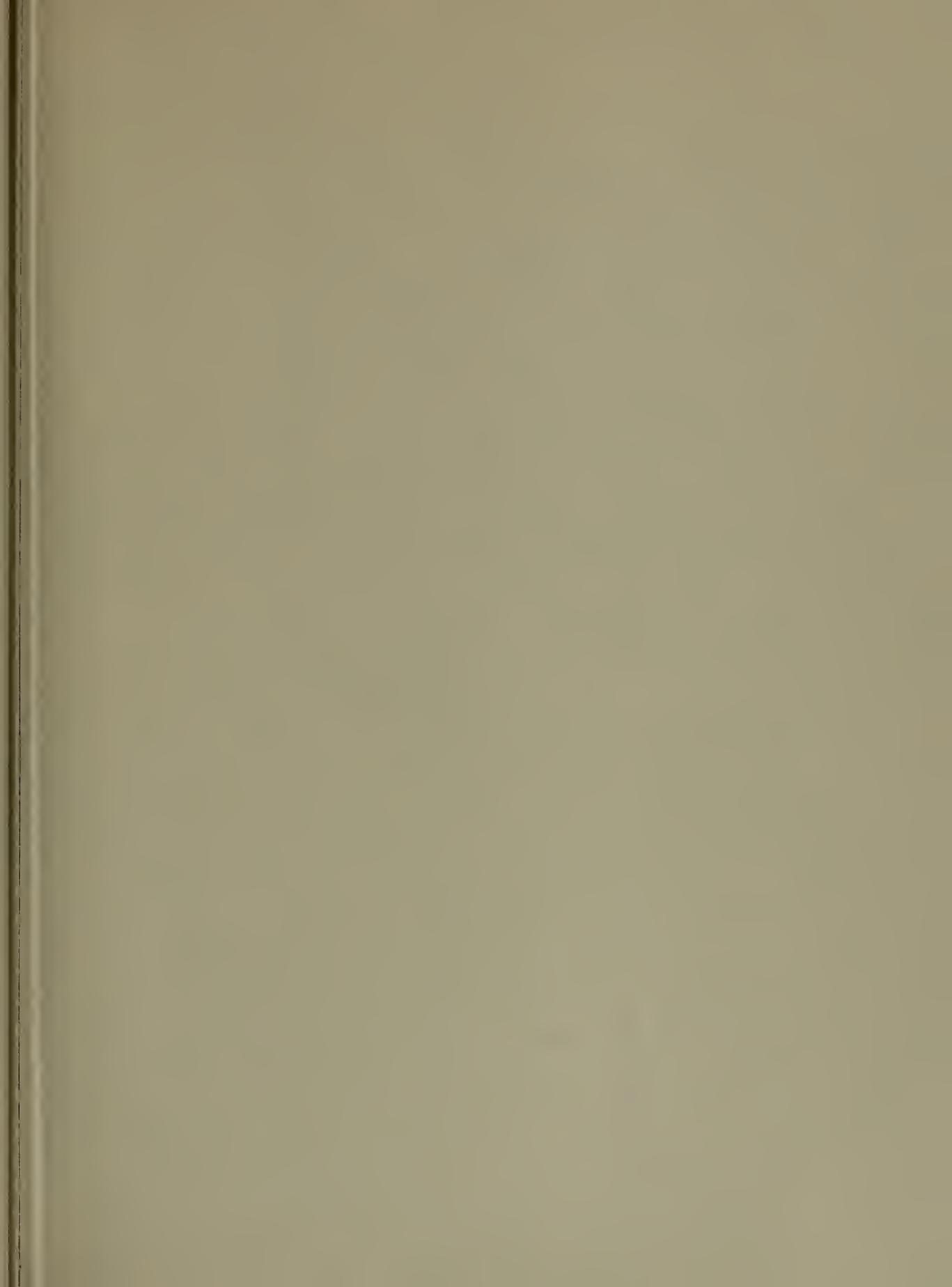
Two members of the Metallurgy Division, Harvey Yakowitz and Donald L. Vieth have aided in providing metallurgical services and in making measurements of mutual interest with the Microprobe.
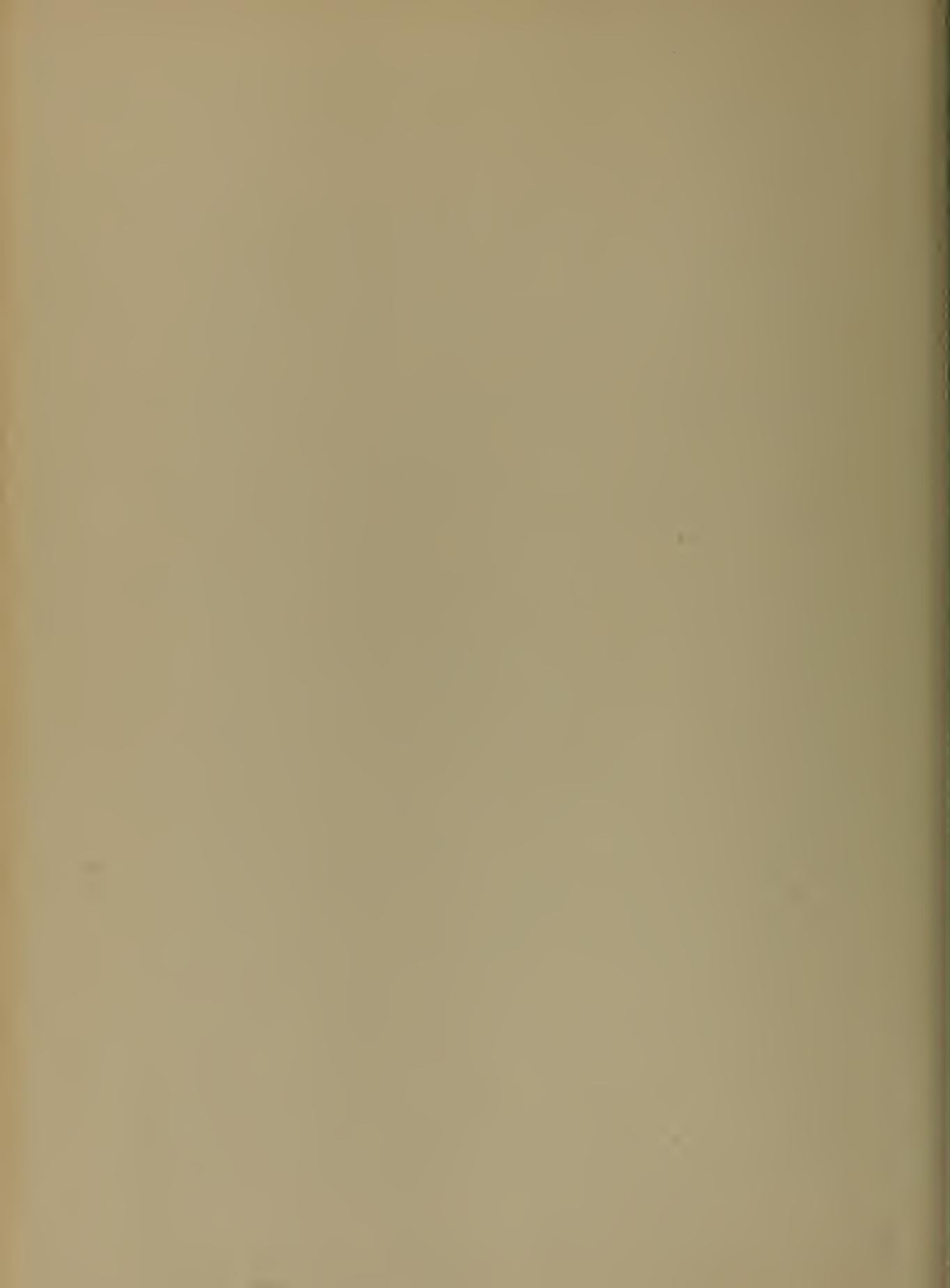
Our Section secretary, Mrs. Frances L. Hilten, performs a wide variety of essential duties. It is a pleasure to acknowledge her contributions to the work of the Section and especially her assistance in preparing this and other reports and in meeting critical typing deadlines.

9. LIST OF REFERENCES

[1] Margoshes, M., Excitation and Ionization in Arc and Spark Spectroscopic Sources, Appl. Spectry. (Submitted).

[2] Margoshes, M., and Scribner, B. F., Appl. Spectry. 18, 154-5 (1964).

[3] Compilation of Chemical Compositions and Rupture Strengths of Super-Strength Alloys, Am. Soc. Testing Matls., Spec. Tech. Publ. 170-C (1964).

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[6] Brech, F., and Cross, L., Xth Colloquium Spectroscopicum Internationale, College Park, Md., 1962, Paper No. 80; Appl. Spectry. 16, 59 (1962) (Abstract).

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[8] Scribner, B. F., Margoshes, M., and Rasberry, S. D., Laser Microprobe for Analysis of Very Small Samples, in "Research on Crystal Growth and Characterization at the National Bureau of Standards, January to June, 1964," NBS Technical Note 251, October, 1964, p. 28.

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[10] Moseley, H. G. J., Phil. Mag. 6 26, 1034 (1913); 27, 703 (1914).

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[12] Von Hevesy, G., Chemical Analysis by X-Rays and Its Applications, McGraw-Hill Book Co., Inc., New York, 1932

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        323 (1948).

[14]   Henke, B. L., Adv. in X-Ray Analysis 7, Plenum Press,
        New York, 1963, p. 460.

[15]   Alvarez, R., and Flitsch, R., NBS Misc. Publ. 260-5,
        National Bureau of Standards, Washington, D. C.,
        1965.

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        Scribner, B. F., J. Res. Nat. Bureau of Standards
        68A, 5 (1964).

[17]   Lucas-Tooth, H. J., and Price, B. J., Metallurgia 64,
        149 (1961).

[18]   Eick, J. D., Caul, H. J., Smith, D. S., and Rasberry,
        S. D., "Analysis of Gold and Platinum Group Alloys
        by X-Ray Emission with Corrections for Interelement
        Effects" (Submitted for publication).

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        Press, New York, 1963, p. 382.

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        (1964).

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        Literature on Spectrochemical Analysis, Part IV,
        1951-1955, Philadelphia, American Society for
        Testing and Materials, 1959.

[22]   Scribner, B. F., and Margoshes, M., Anal. Chem. 36,
        329R (1964),

[23]   Margoshes, M., Anal. Chem. 34, 221R (1962).