



# TECHNICAL NOTE

422

## Activities of the NBS Spectrochemical Analysis Section

July 1966 through June 1967



U.S. DEPARTMENT OF COMMERCE  
National Bureau of Standards

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UNITED STATES DEPARTMENT OF COMMERCE  
Alexander B. Trowbridge, Secretary  
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# TECHNICAL NOTE 422

ISSUED JANUARY 1968

## Activities of the NBS Spectrochemical Analysis Section

July 1966 through June 1967

Edited by Bourdon F. Scribner

Spectrochemical Analysis Section  
Analytical Chemistry Division  
Institute for Materials Research

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

## FOREWORD

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

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

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

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1967 we plan to issue these summaries for all of our sections. The following is the third annual report on progress of the Spectrochemical Analysis Section.

W. Wayne Meinke, Chief  
Analytical Chemistry Division

## PREFACE

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

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

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

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

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

Bourdon F. Scribner, Chief  
Spectrochemical Analysis Section

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ACTIVITIES OF THE NBS SPECTROCHEMICAL  
ANALYSIS SECTION

July 1966 to June 1967

Edited by Bourdon F. Scribner

ABSTRACT

A summary is given of activities of the NBS Spectrochemical Analysis Section for the year July 1966 through June 1967. In optical spectrometry, studies were made of (1) the effectiveness of a liquid Q-switch for laser pulse control and (2) the applicability of the high-frequency plasma torch in atomic emission and absorption spectroscopy. Two papers on laser probe spectrochemical analysis were published. In electron probe microanalysis an alignment procedure was developed for the x-ray spectrometer, data on x-ray mass absorption coefficients were collected and critically evaluated, and a review of techniques for scanning microprobe analysis was published. The factors entering into quantitative electron probe analysis are being investigated. In x-ray spectrometry studies were made of interferences especially in the analysis of complex alloys. A combination of techniques involving enrichment by electro-deposition, stable isotope dilution, and determination by the spark source mass spectrometer has provided an accurate method for trace analysis. Improvements in the Section's equipment, including digital readout devices, and developments in computer applications are also discussed. Listings are given of 15 publications and 23 talks by members of the Section during the year.

Key words:

Computing, digital readout, electron probe, gold analysis, isotope dilution method, laser probe, liquid Q-switch, mass attenuation coefficients, microphotometer, optical spectrometry, plasma torch, platinum analysis, preconcentration, selenium analysis, spark source mass spectrometry, spectrochemical analysis, standard reference materials, sulfur analysis, time-shared computer, x-ray absorption coefficients, x-ray fluorescence analysis, vacuum spectrometer.

## 1. FACILITIES

In two earlier annual reports [1,2] we described the general programs of the Section, the basic equipment in the laboratories, and the facilities of our new laboratories at Gaithersburg, Maryland. During the past year, additions have been made to our major equipment, including digital readout units. The extension of our data handling system has been particularly significant for improved operation of our laboratory.

### A. Additions to Equipment

Major additions of equipment during the year include a vacuum spectrometer, to serve principally for the determination of carbon, sulfur, phosphorus, and other elements having spectral lines below 2000 Å; (2) a digital readout unit for use with optical and x-ray spectrometers; (3) a microphotometer with chart and digital readout; and (4) a vacuum deposition unit for preparation of thin films for electron probe analysis. These units and their applications are discussed in some detail in the appropriate sections of this report.

### B. Data Handling System

The new digital readout units are of particular interest at this point since they represent parts of an established plan to provide automatic digital readout for the various instruments in our laboratory wherever applicable.

Our experience with digital readout dates back to the year 1957 when an optical emission spectrometer was equipped with electronic readout to print and punch spectral line intensities on punched cards. The cards were subsequently batch loaded into the NBS digital computer to convert intensity ratios to concentrations and to perform statistical operations involved in studies of homogeneity of standard reference materials.

This application, which worked very well, was later extended to x-ray spectrometry by a unit which read out through a digital voltmeter to a typewriter with simultaneous punching of tape. New applications in our laboratory lagged somewhat after this because of the high cost of the readout units. Recently the situation has become more favorable -- the cost of readout units has decreased and their reliability has increased. Furthermore, new computing facilities such as remote terminals and time-sharing have become available. All of these developments point toward extended utilization of automatic data handling in the analytical laboratory of the future. The advantages to be realized may be summarized as follows: (1) elimination of personal errors in reading and transcription of data, (2) increased speed in handling the usual analytical calculations, (3) new capability of applying complex calculating operations, as in matrix corrections in x-ray spectrometry, and (4) obtaining the results of computations in convenient forms often suitable for issuance directly as a report.

The extent of our conversion to automatic data handling is summarized diagrammatically in Figure 1. Here are listed eleven major pieces of spectrometric equipment together with their corresponding recording units. Solid lines indicate direct coupling of units while dotted lines represent manual operations. Six teletypewriter units (T) serve for direct recording of data; these are also available for manual typing of data and of programs where necessary. The operations are indicated as terminating in a teletypewriter terminal (TT). This terminal is at the present time connected by telephone to a remote time-sharing computer. In some cases where the amount of data is too large to be handled conveniently on the time-sharing system it is batch loaded into the main NBS computer. In the near future we expect to have available in our area a terminal connected directly to the NBS main computer.

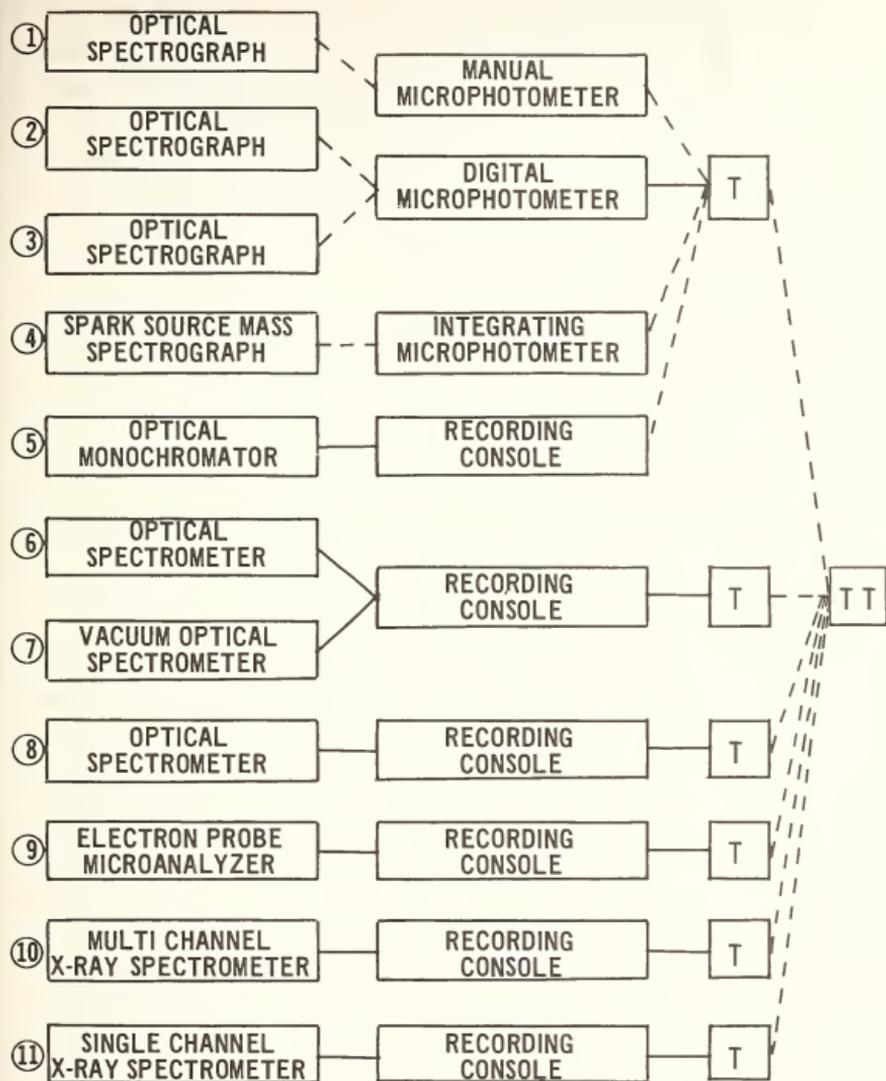


Figure 1. Diagram showing readout and computer systems in the Section.

Operations of the data handling system in conjunction with a time-sharing computer service are discussed in a separate report [3] which is available on request. Here we will briefly describe the operations of the data handling involved. The operations as outlined in Figure 1 generally increase in recording and computing complexity from top to bottom of the list. The first optical spectrograph (1) is employed almost exclusively for general survey analyses with spectrograms transferred to a manually operated microphotometer where visual comparisons of the spectra are made with standard spectra. However, transmittance measurements made here may be manually converted to punched tape on the teletypewriter and transferred to the teletypewriter terminal (TT) for computations.

The second and third optical spectrographs are used for research on excitation sources and for special applications such as trace analysis. To meet the greater demand for quantitative intensity measurements, the spectrograms are measured on the digital microphotometer which provides transmittance measurements printed and punched into paper tape on an attached teletypewriter. The tape may then be transferred to the teletypewriter terminal.

Some examples of computations performed include photographic plate calibrations from measurement of intensity patterns, conversion of transmittance to intensities, determination of functions relating intensities and concentrations, conversion of intensities to concentrations, statistical treatment of data, and computation of functions such as temperature in excitation sources from intensity measurements (Abel inversion).

Another instrument employing photographic recording is the spark source mass spectrograph (4). The spectrogram obtained here is measured on an integrating microphotometer in which the blackening under each line is integrated. The results are manually transferred to tape on the teletype-

writer and thence to the terminal for computations similar to those for the optical spectroscopy. (In view of the complexity of these measurements, automatic measurement and readout are being considered for the operations).

The optical monochromator (5) serves for single element measurements as in atomic emission and absorption flame photometry. Here the readout is to a chart recorder with manual transfer of data into the teletypewriter tape.

The next three instruments (6,7,8) are photoelectric optical spectrometers employed largely for homogeneity studies of proposed standard reference materials. The first two share the same recording console and teletypewriter readout. Intensity ratios of spectral lines for up to as many as 20 elements per sample are recorded digitally on the teletypewriter, the tape from which goes to the teletypewriter terminal or, in many cases, to the main NBS computer. The third spectrometer (8) records in the same manner through a separate console and teletypewriter. The computations include conversion of intensity measurements to concentrations and the statistical treatment of data, largely by analysis of variance, to extract information on homogeneity of samples.

The electron probe microanalyzer (9) has a readout from a non-dispersive x-ray detector through a pulse height analyzer to a teletypewriter unit. Soon to be added is the equipment to read out to the teletypewriter any scalar quantity such as x-ray signal or target current. Also incorporated will be a means to program a point-by-point scan over a selected grid of points and to readout the data in a prescribed array. Computations made with the time-shared computer include conversion of x-ray signals to element concentrations, application of correction functions, and statistical treatment of data.

The last two instruments (10,11) are x-ray spectrometers. For the multi-channel spectrometer (10), digital readout of x-ray spectral line intensity ratios is recorded and punched into tape on a teletypewriter unit identical with that for the optical spectrometers. Up to 10 elements may be measured simultaneously on this instrument which is used largely for homogeneity studies and service analyses. The last instrument is a single-channel vacuum x-ray spectrometer which serves mainly for research on x-ray methods; it reads x-ray intensities directly to an attached teletypewriter. The time-shared computer serves for correction of data for matrix effects and statistical analysis of data.

The mere listing of these operations does not really convey the marked gains in speed of operations and, what is most important, the enormous potential for mathematical treatment of data to study and apply statistical operations and complex correction systems. These applications are discussed to some extent in the reference cited [3] and will be recounted in separate papers in the future.

## 2. OPTICAL SPECTROMETRY

The year covered by this report has seen a continuation of our interest in the investigation of new spectroscopic sources. Two papers have been published on the laser probe [4,5], and a study is nearly completed of the effect on laser probe excitation of adding a saturable-absorber Q-switch to the laser head for improved control of the laser emission. A study of the properties of the plasma torch for emission and atomic absorption spectrometry has also been nearly completed.

The facilities for optical spectrometry have been improved by the addition of two major pieces of equipment as well as a new read-out device to serve both emission and x-ray spectrometers. One of the new items of equipment is a microphotometer equipped to provide readout in digital form for entry to a computer. This is, as far as we know, the first instrument of its type.

Application of the time-sharing computer system to our requirements has also progressed. A few new programs have been written, and some others have been improved. At this time, all of our routine calculations have been programmed for this computer system or for the larger NBS computer. A report describing our experience with a time-sharing computer system and listing a number of programs has been prepared [3] and should be available in the near future.

Homogeneity testing and analysis of Standard Reference Materials, and qualitative and quantitative analysis of a diversity of other samples are a continuing responsibility of this laboratory. Section 2E of this report describes some of these emission spectrochemical analyses done this year, and will give an indication of the variety of problems encountered in this work.

## A. New Equipment

### 1. Vacuum Spectrometer

A vacuum spectrometer has been installed for the determination of carbon, phosphorus, sulfur, arsenic, tin, and selenium in ferrous alloys. Table 1 lists the line array in the instrument, a photograph of which is shown in Figure 2. The vacuum spectrometer shares a spark power supply and a readout console with an air-path spectrometer in the same room. This arrangement saved money and space, although it does limit us to using only one of these spectrometers at a time.

Table 1. Line array of vacuum spectrometer.

<u>Element</u>	<u>Wavelength, Å</u>	<u>Element</u>	<u>Wavelength, Å</u>
Fe	2714.4	As	1972.6
C	1930.9	Sn	1899.9
P	1782.8	Se	2039.8
S	1807.3		

---

The vacuum spectrometer will be invaluable in homogeneity testing of standard reference materials and for other analytical requirements. It will also be employed in the development and improvement of analytical procedures, particularly for the determination of carbon, phosphorus, and sulfur in alloys. Only one internal standard line has been installed, for iron, so the instrument is presently limited to the analysis of ferrous alloys. There is room in the spectrometer for the addition of other internal standard and element lines as may be required in the future. In contrast, the two air-path spectrometers in this laboratory both have nearly the largest possible number of exit slits already installed, so addition of more lines would be quite difficult.



Figure 2. Vacuum spectrometer for the determination of C, P, S, As, Sn and Se in ferrous metals and alloys.

## 2. Digital Readout

A new digital readout, shown in Figure 3, has been installed. It is used for both emission and x-ray spectrometers.

The readout measures the voltage on each of the capacitors in the spectrometer in turn. Four-digit numbers, representing voltages up to 10V, are formed by a voltage-to-frequency converter followed by a counting circuit. The numbers are then printed and punched into a paper tape by a teletypewriter, giving the data in tabular form for visual examination and in digital form for input to a computer. The readout rate is two seconds per capacitor. At the end of an individual capacitor reading, the readout transmits a pulse which causes the spectrometer to either step to the next capacitor or, after reading the last capacitor, to reset for the next exposure cycle.



Figure 3. Digital readout for use with emission and x-ray spectrometers.

Each set of data from an individual exposure includes the sample number, which is entered on a dial by the operator, and a serial number to permit editing of a block of data in the computer. The readout also records the integration time of the spectrometer; this information is helpful in detecting gradual or sudden changes in the conditions of excitation or measurement of the spectra.

Some options built into the readout extend its utility. The unit can be set to read any selected capacitor at two-second intervals during the exposure cycle, and it thus can be employed in time-of-wait studies and for instrument profiling. There is also some control of data format, which can be set to the requirements of the time-sharing computer or of the larger NBS computer. The data can be recorded on the tape in the ASCII or BCD codes, and the readout can be used to convert tapes in the ASCII code to BCD-coded tapes.

### 3. Digital Microphotometer

Figure 4 shows a microphotometer, installed this year, which is equipped to print out percent transmittance readings and to punch these readings into paper tape. This instrument was developed by the manufacturer to meet our specific needs for recording measurements in digitized format suitable for direct entry to a computer. The microphotometer is also equipped with a strip-chart recorder.

The instrument is semi-automatic, with the operator selecting and scanning lines in the normal way. During the scan of a line, a track-and-hold amplifier follows the percent transmittance signal and locks on the minimum reading. At the end of a scan, the minimum reading is shown on a digital voltmeter. When the operator presses a button, this reading is transferred to a teletypewriter equipped with a



Figure 4. Microphotometer equipped with digital readout for direct entry of data into a computer.

tape punch. Readings can be made on the background by moving the plate under the scanning head to the point to be measured and pressing a button.

The last annual report [2] described our use of a time-sharing computer system for emulsion calibration and conversion of microphotometer readings to relative intensities. With this computer system, the time required for transcription of microphotometer readings to machine-readable form became a significant fraction of the total calculation time. Transcription of the data can also introduce errors. The new microphotometer eliminates the need for data transcription prior to calculation. We have also found that there is substantially less operator fatigue with this microphotometer than when the operator must write galvanometer readings on a data form.

#### B. Experiments With a Liquid Q-Switch on the Laser Probe

Previous studies in this laboratory [4,5] have shown that the precision of analysis with the laser probe is directly related to the reproducibility of the light pulses from the laser. When the laser is adjusted for single-spike operation, the intensity of the laser beam has a coefficient of variation of about 10% and the spectral intensities have a similar precision. The intensity of the laser beam can be made higher by increasing the voltage to the flashlamp, and this increases the amount of material sampled and the spectral intensities. However, increasing the voltage to the flashlamp by more than about 150V above threshold causes the laser to emit a multiple-spike beam, and the reproducibilities of both the laser beam and the spectral intensities become very much poorer. High-power operation of the laser is preferable for all except the smallest samples because of the higher spectral intensities obtained, but this necessarily involves a serious degradation of quantitative capabilities.

The laser probe already contains a rotating-prism Q-switch to control the light flash to some extent. Additional Q-switching of the laser could improve the reproducibility of the laser. Of the several types of Q-switches available, the saturable absorber in the form of a solution of an appropriate dye (hereafter called the liquid Q-switch) is probably the simplest.

The liquid Q-switch is an optical cell, placed in the laser cavity, containing a solution of a dye. The dye must have an absorption band at the wavelength of the laser light, and the excited state of dye molecule must be transparent at that wavelength. When the laser rod is excited by the flashlamp, lasing is blocked by absorption of photons by the dye. As more photons are absorbed and more molecules are excited, the dye solution becomes progressively more transparent. Eventually, the dye solution becomes sufficiently transparent to permit lasing. In a short interval after the end of the laser pulse, the dye molecules will revert to the absorbing ground state, and will thus block successive spikes which are of too low energy to excite a sufficient number of dye molecules. The ability of the liquid Q-switch to restrict the laser output depends on the nature of the dye, the concentration of the dye in the cell, and the energies of the individual laser spikes. An additional requirement on the dye is that it should not be degraded by the intense laser light, or else the solution will have to be changed frequently.

Several dyes have been used in other laboratories for liquid Q-switching of ruby lasers, including cryptocyanine, phthalocyanine, and metal-phthalocyanines. We have tested several of these dyes in our laser, in a variety of solvents and at various flashlamp voltages.

## 1. Experimental Arrangement

The laser probe and the experimental arrangement for monitoring the laser emission have been described previously [4,5]. A holder was constructed to mount a 1-cm absorption cell between the ruby rod and the front reflector of the laser cavity.

Because of the low solubilities of most of the dyes, preparation of solutions by weighing the dye and dissolving in a known volume of solvent would have required either weighing very small amounts of the dye or using very large volumes of solvent. Solutions were prepared reproducibly by making saturated solutions of the dyes and diluting appropriately.

The dyes tested were cryptocyanine, the sodium, vanadium, beryllium, and chloroaluminum salts of phthalocyanine, and chloroaluminum chlorophthalocyanine. The solvents used were water, nitrobenzene, methanol, acetone, and xylene. These experiments showed that single-spike operation was more easily achieved with the phthalocyanines than with cryptocyanine. In particular, cryptocyanine was rapidly degraded by the laser. Little difference was found between the different phthalocyanine derivatives, but the solvent did affect the performance of the dye. The most detailed studies were made with sodium and vanadium phthalocyanines in nitrobenzene.

## 2. Results

Figure 5 shows the variation of energy in the first, second, and third spikes of the laser emission with flash-lamp voltage when there is no liquid Q-switch. There is only a narrow range of voltage giving single-spike operation, and the power of the laser beam changes rapidly with voltage within this range. By comparison, Figure 6

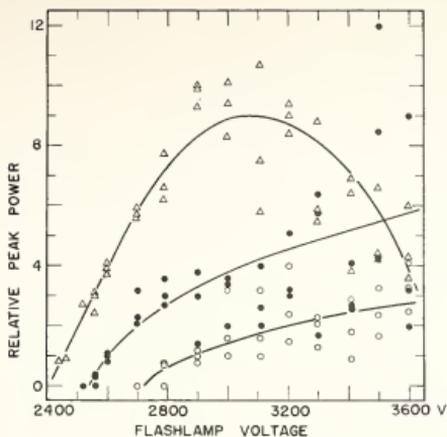


Figure 5. Variations of peak powers of first three spikes of laser output with flashlamp voltage.  
 $\Delta$  - 1st. spike,  $\bullet$  - 2nd spike,  $\circ$  - 3rd spike.

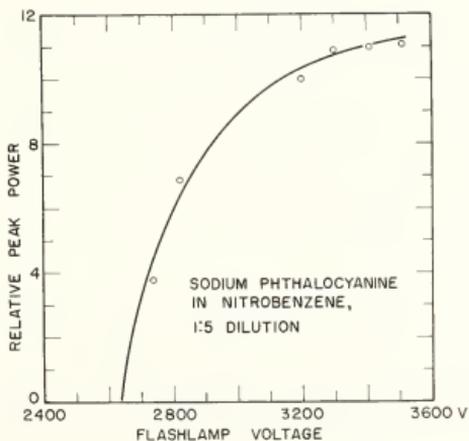


Figure 6. Variation of peak power of single-spike output of laser controlled by a saturable-absorber Q-switch.

shows similar measurements with a solution of sodium phthalocyanine in nitrobenzene as the liquid Q-switch. The solution used in this experiment was a 1:5 dilution of a saturated solution. In a series of experiments to determine the stability of this dye, single spikes were observed in the first 8 firings of the laser, a second spike starting with the ninth shot, and a third spike after 18 shots.

Figures 5 and 6 are drawn to the same scale. The liquid Q-switch makes it possible to obtain a single-spike output several times as energetic as the single-spike output available without the Q-switch.

Two experiments were conducted to determine the reproducibility of the single-spike, Q-switched pulses. In both experiments, the coefficients of variation of the peak power of the laser beam were about 10%, approximately the same as the reproducibility of the single-spike operation reported previously [5]. Thus, the liquid Q-switch should make it possible to retain the analytical precision of single-spike operation while obtaining the more intense spectra characteristic of high-energy laser operation.

It is planned to extend this experiment to observation of pit sizes and spectral intensities under various conditions, as has been done previously [5] for operation without the liquid Q-switch.

M. Margoshes, D. M. Marcellus, S. D. Rasberry

### C. Plasma Torch

A systematic investigation of an inductively-coupled, radio-frequency plasma torch is in progress. This plasma torch is used to convert analytical sample solution aerosols to atomic vapor, and thus permit atomic emission, absorption, and fluorescence measurements to be made. The torch configuration is essentially that described by Wendt and Fassel [6], except that the central tube has been omitted. Sample aerosol is conducted directly into the

central plasma tube. The torch is operated on argon, resulting in a low-intensity continuum background radiation, with only the most prominent argon spectral lines appearing on the continuum. Operation in an inert atmosphere tends to overcome one of the predominant limitations of the chemical flames, i.e., compound formation, most usually stable metal monoxides.

### 1. Description of Equipment

The electronics, optics, and radio-frequency generators have been described [2]. The plasma-torch, mentioned above, is placed in a two-turn, pancake-type, concentrator coil. Ignition is performed with an ungrounded graphite rod impregnated with a small quantity of a potassium salt.

To the electronics described elsewhere [2], a reference-generating circuit has been added (Figure 7). This circuit generates a modulation frequency signal of about 2V peak-to-peak, to be used in the signal demodulation section of the phase-sensitive amplifier. It is mounted on the synchronous mechanical chopper and therefore produces exactly the same frequency as the modulated source radiation

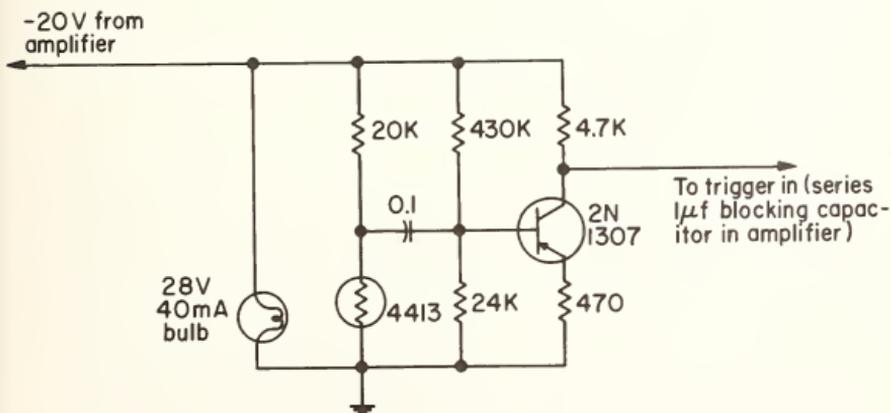


Figure 7. Reference signal generating circuit.

frequency. This device was found to be necessary when making emission measurements, and desirable when making absorption measurements.

The ultra-sonic nebulizer [6] was contemplated for the present research, as a means of sample solution introduction into the plasma. However, this was given up in favor of the more convenient and more efficient pneumatic nebulizer. This nebulizer produces very fine spray droplets and has a high solution-to-gas flow ratio. For example, at a pressure of 50 psi, 2.26 ml of water are aspirated by 1.71 liter of argon in one minute. The nebulizer sprays into a heated glass chamber of sufficiently high temperature to completely evaporate the solvent, and the effluent from this chamber is then fed into a chilled-water-cooled glass condenser, where most of the solvent vapor is condensed and drained away. The dry spray particles are then conducted into the plasma. The efficiency of the system is quite high. For example, under typical operating conditions, the overall efficiency of the system is about 30%, i.e., 30% of the metal sample element aspirated reaches the plasma.

## 2. Experimental Difficulties

Two major experimental difficulties were encountered in the operation of this atomic vapor source; namely, shielding and sample introduction. These are described below.

### a. Sample Introduction

The plasma discharge appears to have a low tolerance to molecular gases. One of the worst offenders in this respect is water vapor, causing the discharge to become quite unstable. This presents a significant problem when working with aqueous solutions. Organic solvents do not seem to be any better in this respect, and also destroy one of the advantages of the plasma torches, namely, low background radiation. However, the sample introduction system described previously reduces this effect to a tolerable level.

## b. Shielding

We are utilizing about 4 kW of radio-frequency power in operating the torch, and a significant amount of this energy is radiated from the coil and connecting leads. As the electronics are located in fairly close proximity to the coil and leads, considerable R-F noise was detected, leading to poor signal-to-noise ratios and consequently poorer limits of detection. Therefore, a brass-reinforced copper housing was constructed to contain the torch and coil. Attached to this is an enclosure of copper screening, shielding the leads from the R-F generator. The entire assembly is well grounded with copper tubing soldered to the housing. This enclosure serves several other functions: It provides suitable mounts for the accessory lenses; it provides shielding from the intense visible continuum produced by the plasma; it provides sound deadening from the audible noise produced by the torch (presumably 120 Hz ripple on the 4.8 MHz R-F); and it protects the operator from accidental contact with the coil, leads, or plasma flame.

## 3. Results -- Absorption and Emission

Data, as of this writing, are incomplete, but indicate that the R-F plasma torch is not a "cure-all" for the ills of the chemical flame. Detection limits, both by atomic emission and atomic absorption, are not spectacularly greater, except for the so-called "refractory" elements, which have very poor detection limits in flames. For most of the elements investigated thus far, the detection limits by atomic emission appear to be considerably lower, in general, than those obtained by atomic absorption. This is believed due to a high plasma "temperature," use of an atomic support gas and coolant gas (i.e., a neutral, non-quenching atmosphere), and a low background continuum radiation in the plasma region studied. In connection with the latter, the region of the discharge studied was found to be approx-

imately optimum for absorption and emission, and agreed with the results of Wendt and Fassel [6,7]. Also, the sample introduction system apparently removes most of the water vapor, as a spectrum of the plasma region studied shows no OH band structure around  $3100\text{\AA}$ .

Detection limits for atomic absorption are in the low parts-per-million level for most of the elements studied, and below one part-per-million by atomic emission.

Atomic fluorescence measurements may be made in the near future, and should provide an interesting comparison. Studies of cation and anion interference effects are in progress.

C. Veillon and M. Margoshes

#### D. Computer Applications

The last annual report [2] included a brief description of the time-sharing computer system in use in this laboratory and gave some examples of its applications in spectrochemical analysis. We have now prepared a more detailed report on this subject [3], with separate listings, instructions for use, and sample input and output for several programs and subroutines. Table 2 lists the programs and subroutines outlined in the report; they are all in the BASIC language. Copies of this report and listings of programs are available without charge on request to this laboratory.

Table 2. Programs outlined in the report on time-sharing computer system.

---

<u>Program name</u>	<u>Purpose</u>
CODEBC	Fitting of analytical curves and conversion of instrument readings to element concentrations.
CFIT2	Similar to CODEBC, but with shorter output format.
PLATE1	Calibrates plating thickness as a function of x-ray fluorescent intensity.

Table 2. (Continued)

Program Name	Purpose
PLATE2	Compute plating thicknesses from measurements on unknown specimens given calibration equation from PLATE1.
KAISER	Calibration of photographic emulsions.
INTEN2	Conversion of microphotometer readings to relative intensities. (See text for details).
TEMPER, PROFIL	Calculate plasma temperature from relative intensities of spectral lines. The programs differ in output format.
XRAY1	Data analysis for proposed analytical methods, where all data is from standards and the calibration is presumed linear.
XRAY2	Computation of statistics for intensities measured on unknown specimens.
STAT	Computation of following statistics for each of 1 to 8 columns: average, maximum, minimum, range, standard deviation, 95% confidence limits for the standard deviation, percent coefficient of variation, and 95% confidence interval for the lot mean.
TABLE	Generates a table of X as a function of Y for a selected function and range and increment of Y arguments.
COLS8	Subroutine which may be added to the end of a program where tabular output is desired for 6 to 8 columns instead of the maximum of five normally provided by the computer system.
WRITE1, WRITE2, WRITE4	Subroutines for having lists of one to four variables punched onto paper tape for reentry as input data to another program.
TIME	Program for computer terminal usage accounting.

During this year, we have written several new programs for the computer system and revised some others. A few of the new or revised programs are included in the report mentioned above. One of the revised programs and one new program (not in the report) are described here.

1. Program INTEN2

The program INTEN, described in the last annual report [2] has been rewritten to extend the available options and to simplify data input. INTEN2, like INTEN, is intended for the conversion of microphotometer readings to relative intensities, employing the emulsion calibration constants computed with the program KAISER. INTEN2 includes the following options:

1. From one to ten sets of emulsion calibration constants may be entered. If more than one set of constants is entered, the wavelength range for each set is also entered and the program will select the proper set of constants for a particular line.
  2. The program assumes a step sector or filter with a step ratio of 1:2 was used, unless a different step ratio is entered. In either case, up to six steps are accommodated.
  3. Background correction may or may not be required.
  4. Step correction may or may not be required.
  5. Both background and step correction may be required.
  6. Options 1 through 5 may be used in any combination.
- A single block of input data may include sets for different lines requiring different combinations of options 3, 4, and 5.

The operator need not state explicitly which combination of options is required. The computer will make this decision from inspection of the input data, using information inherent in the data. For example, when both line and background transmittance values are given to provide for background correction, there will be twice as many input values as when only line transmittances are given; any number larger than 1000 must be a wavelength; a number

below ten may be a step number but it cannot be the transmittance of the background.

The input data are inspected for some possible errors, such as failure to specify the plate calibration constants at the wavelength of a line.

## 2. Program PRESTO

The last annual report [2] contained a brief description of the programs CODEBC, CODEBD, and CODFIT (called CFIT2 in Table 2) which are used to fit analytical curves to data obtained with standards and to convert instrument readings on unknowns to concentrations. When analytical curves are plotted in the normal way, the scientist decides what shape of curve to draw (straight line, simple curve, S-shaped curve) and whether or not to leave out one or more of the points in fitting the curve. These decisions could be made by the computer on a statistical basis if there are a sufficient number of standards. Normally, however, the number of standards available is too small to apply the usual statistical tests.

In the program CODEBC and its variants, advantage was taken of the capabilities of the time-sharing computer system to permit the scientist to work with the machine. The computer fits a series of least-square polynomial equations, representing curves of various shapes, and gives as output two statistical parameters for each polynomial equation. The operator then decides which polynomial to use. The next output shows the agreement between the input and computed concentrations for each standard, and the operator can decide from this if the input data should be edited to remove one or more of the standards.

This use of the time-sharing computer system is not entirely satisfactory in all respects. The computer cannot accept very large blocks of data, and when many multi-element runs are made on the emission or x-ray spectrometers the

data must first be sorted by element before being entered into the computer for computation. The sorting can be done by the computer, using a program SORT, but this is a somewhat time-consuming process. Use could be made of the larger machine in the NBS computer center for this purpose, but only if the decisions being made by the operator were programmed. The time-sharing computer system has been used to arrive at a method of computation which makes these decisions and to test the method. The computation process is now being programmed in FORTRAN for a larger computer.

The BASIC program for this purpose is called PRESTO. The computer first fits a first-degree least-squares polynomial to the data for all of the standards and computes a parameter  $P_{10}$ ,

$$P_{10} = ((\Sigma(\Delta/c)^2)/(N-1))^{1/2}$$

where  $\Delta$  is the difference between the concentrations given and found for a standard,  $c$  is the concentration given, and  $N$  is the number of standards. A fit is again made for all the standards except the first, a factor  $P_{11}$  found, and the process is repeated by successively making trial rejections of each of the standards. A test is then made for permanent rejection of the standard. If rejection of any of the standards reduces the factor  $P_{1n}$  to one-third or less the value of  $P_{10}$ , the output instructs the operator to edit the input data to remove the standard.

A second series of calculations is then made with first-degree polynomial fits, rejecting each of the remaining standards in turn on a trial basis.

When no standards are to be rejected for a first-degree polynomial, a fit is made to all standards for a second-degree polynomial, and  $P_{20}$  is calculated. If the value of  $P_{20}$  is less than the value of  $P_{10}$  by one-fourth, the decision is made that the fit is significantly better for the second-degree equation. A test is then made for rejection

of the individual standards, as in the first-degree polynomial fit. If a standard is rejected at this point, the calculations return to the first-degree polynomial. Otherwise, a third-degree equation is tried. In any case, the degree of polynomial is restricted so that the number of terms in the equation is not more than half the number of standards: six standards or more for a second-degree polynomial, and eight standards or more for a third-degree polynomial.

When the proper equation has been found, the computer will, at the option of the operator, print a coarse graph of the curve, adequate for the operator to judge the general shape. After this, the readings for the samples are converted to concentrations, and the output includes the individual readings and concentrations, and the average standard deviation for a single determination, and standard deviation of the mean for each sample.

The program has been tested with about 50 sets of data. In all tests except two, the computer made reasonable decisions concerning the points to be rejected and the shapes of the curves, and these were such poor sets of data that even the most experienced scientist would have difficulty in deciding what curve should be drawn. Even though these early results are encouraging, much more testing is needed before the results of the computer calculations can be accepted routinely.

One advantage of the computer fitting of analytical curves is that the parameter  $P$  for the curve finally used gives some indication of the goodness of fit of the data to the curve. In time, it should be possible to know what range of values of  $P$  corresponds to a satisfactory fit, and to program the computer to print a warning whenever the maximum acceptable value of  $P$  is exceeded. Further statistical treatment of the data may also be added in the future.

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

## E. Applications to Analysis

The facilities of this Section for spectrochemical analysis are, of course, employed for analytical work as well as for the research activities outlined above. For the Section as a whole, the analytical work in the period June 1966 through May 1967 included 684 samples, with 23,523 determinations, and 176 reports written. Of the totals, emission spectroscopy accounted for 425 samples, 16,618 determinations, and 134 reports.

### 1. Analyses of Standard Reference Materials

This Section has an important part in the production and certification of Standard Reference Materials, starting with the preliminary evaluation of the material and carrying through to the final quantitative analyses.

Most of the materials, even when they are not intended to be certified for composition, are submitted for semi-quantitative analysis for 50 or more chemical elements as a step in the preliminary evaluation. This screening process, largely by emission spectrographic analysis, will show whether or not the material is pure enough for the intended purpose or, in the case of materials such as alloys, whether it has approximately the desired composition. In addition, the extensive preliminary analysis of a proposed reference material permits proper planning of the subsequent analytical procedures for certification of composition. Among the samples carried through the semi-quantitative analysis procedure for this purpose were fluorspar, solder, ductile iron, isotopic lead, rubidium chloride, steel, metallo-organic compounds, and plant leaves.

A second step in production of a Standard Reference Material is to procure a large quantity of the material and determine its homogeneity. A common procedure is to select samples from chosen points in the bulk of material and to make analyses at each of these points for the elements of

interest. The choice of sampling points, of the elements to be measured, and the number of replicate determinations to be done is made in such a way as to provide the necessary information with a minimum effort. In this laboratory, emission spectrometric methods are frequently employed for the homogeneity testing. Data from the emission spectrometer are recorded directly in digital form and entered into a computer for statistical analysis. X-ray fluorescence methods may also be applied, depending on the particular analytical requirements. Among the materials carried through this procedure this year were high-temperature alloys, ductile irons, beryllium-copper alloys, and electronic nickel alloys.

Finally, we are also involved in the quantitative determination of the compositions of the Standard Reference Materials. These analyses are always done by two or more independent methods, and one of these methods is frequently spectrometric. Each method must be chosen and developed to yield the best possible accuracy and precision. Each determination must be done a sufficient number of times to give meaningful information on the precision of analysis and to give an average value which is significantly more precise than an individual determination. Also, the method of analysis must be absolute. Generally, the samples must be converted to some form which will permit the accurate preparation of standards.

The extensive analyses performed on beryllium-copper alloy Standard Reference Materials will illustrate this point. Beryllium, cobalt, and aluminum were determined on an emission spectrometer with rotating disk -- spark excitation; 141 individual determinations were made. Chromium, lead, nickel, tin, and zinc were determined by arc excitation of powders prepared by dissolution and drying of the samples; 108 determinations were made. Finally, cobalt, iron, manganese, nickel, and zinc were determined by atomic absorption spectrometry, and 120 individual determinations

were made by this method. The determinations by each procedure were made only after studies designed to optimize the methods.

## 2. Other analyses

This Section performs numerous analyses for other groups within NBS and for other government agencies. The diversity of materials analyzed keeps this work from becoming routine in any sense. Depending on the purpose of the analyses, a general emission spectrographic semi-quantitative analysis may be made, or specific elements may be determined quantitatively.

Quantitative analyses are frequently performed to determine whether or not a part of a machine is the alloy specified by the designer. Such analyses are usually a part of a detailed failure study performed at the Bureau of Standards. One source of such samples is aircraft parts which have failed in service, sometimes resulting in a crash. These machine parts usually do not have a suitable shape for spectrometric analysis, and considerable ingenuity is required to mount the samples.

In a single study of this type, 32 samples of aluminum alloy from a single aircraft were submitted for alloy identification. Multiplicate determinations were made for each of 10 elements in each of the samples. Samples analyzed from other aircraft included 4 samples of high-temperature alloys from a jet engine and a torque piston and cylinder.

Another aluminum alloy analyzed was a part of a bridge rail which had failed under impact forces which it was intended to withstand. The sample was found to be the alloy specified, showing that either another alloy or another design would have to be used for the railing. One sample analyzed was a steel part from a crane boom which had broken. It was found not to be the specified alloy.

Fortunately, specification testing does not always require a quantitative analysis. One case in point was a

primer paint which had been used on a government building and which had not given satisfactory service. A qualitative analysis showed that this red material contained iron, presumably as the oxide, as the major metallic constituent, and was not the red lead paint that had been specified.

Qualitative or semi-quantitative analyses are often made to help solve particular problems. We are occasionally asked to identify corrosion deposits found in a machine or a part of a laboratory apparatus. Qualitative analysis of the deposit may make possible identification of the source of the deposit, which may be remote from the place where the material builds up. A similar case was the analysis of an ion-exchange resin which had been depleted much more rapidly than had been expected. The analysis showed that the major element picked up by the resin was copper. This information served as a guide to the examination of the total system to pinpoint the source of the copper.

This brief discussion includes only a small fraction of the "service" analyses performed this year. It should, however, show why this aspect of our work never becomes routine. Analyses may be performed by any member of the group depending on the degree of complexity. Much of the emission spectrochemical analysis described here was ably performed by Mrs. E. K. Hubbard, Mrs. J. Darr, and Mr. D. M. Bouchette.

Marvin Margoshes

### 3. ELECTRON PROBE MICROANALYSIS

#### A. Basic Considerations

Our efforts in the past year were centered on a plan to increase the precision of quantitative analysis. For this purpose, the effects of errors in the preparation and measurement of the specimen and the reference standard were systematically studied, and the preparation of reliable standards, which are necessary for the testing of analytical procedures, was investigated. The correction procedures to be applied to the results of measurement were critically analyzed and a system of procedures was established incorporating the selection and modification of techniques proposed by various investigators.

This line of work will be continued in the near future. At the same time, greater attention will be directed to the practical problems of efficient data collection, and to problems arising with diverse types of specimens, such as non-conducting materials, organic specimens, and small particles. Thus, a proper balance should be achieved between more basic issues and the requirement for applying electron probe microanalysis to a wide variety of materials. Both aspects are expected to benefit the development of standard reference materials and the service activities which will continue to be applied on specimens of many kinds submitted by Divisions of NBS and other government agencies.

#### B. Instrument Development

Since the last report we have obtained the following instrumentation.

(1) A new optical plate was installed on the electron probe microanalyzer. This plate improves considerably the beam resolution and it also has an interchangeable low magnification microscope objective so that a wider area of the specimen can be seen in the optical microscope.

(2) A device for scanning pulse height analysis for qualitative wavelength scans was designed and constructed in this laboratory. The schematics of the device are shown in Figure 8. The method consists in varying the pulse amplification during the scan in synchronization with the setting of the x-ray spectrometers so that the first order reflections of all lines of a scan are within the channel of the pulse height analyzer, while higher order reflections fall outside the channel. In order also to make visible the higher orders, a device has been installed which switches at intervals of approximately one second from the integral mode (in which all orders of pulses are registered) to the differential mode (which only registers the first order lines) of the pulse height analyzer. The higher order lines will be seen in interrupted traces while the first order lines are registered in the usual fashion (see Figure 9). This device can operate concurrently for the three pulse height analyzers and spectrometers of the electron probe.

(3) A new non-dispersive detector for soft radiation was installed. Since earlier experiments with non-dispersive detectors for a quick preliminary qualitative analysis [2] were encouraging, an additional non-dispersive detector system has been installed. The first detector is a sealed neon proportional detector and the one added is an argon-methane flow proportional counter with a very thin Formvar window. The distribution of energies which is efficiently detected by the first detector is restricted to a wavelength range of approximately 5 to 15 Å while the second detector has a much wider range, from about 1 to 90 Å. The purpose of this dual system is to obtain a simple spectrum in the most important region by means of the first detector and to get further information of complementary nature in the second detector. A spectrum of several lines in the very soft region, obtained with the new detector, is

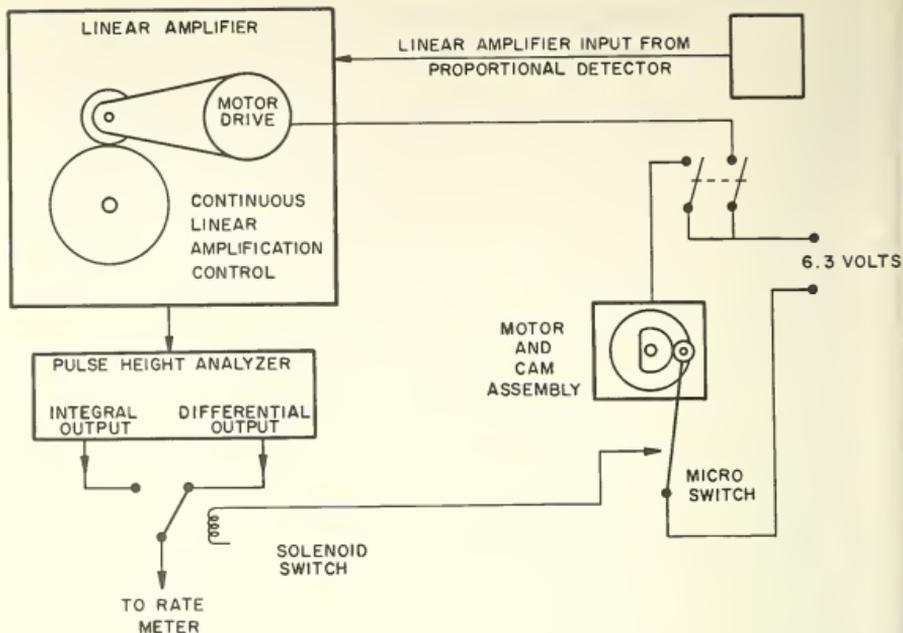


Figure 8. Schematics of a device for scanning pulse height analysis, with alternating presentation of integral and differential pulse height analyzer output.

shown in Figure 10. Several spectra obtained with the first non-dispersive detector have been illustrated previously [2, p 60].

(4) Vacuum evaporator for metallic and carbon coating. A vacuum evaporator has been installed in the electron probe microanalysis laboratory. For non-conductive specimens it is necessary to provide a thin film of carbon, aluminum, or other metals which conduct both electricity and heat. The evaporator acquired this year has been successfully tested for this use. The second possible application is to produce thin films for the determination of the depth distribution of x-ray emission from targets. For this the instrument will be provided with devices for measuring the

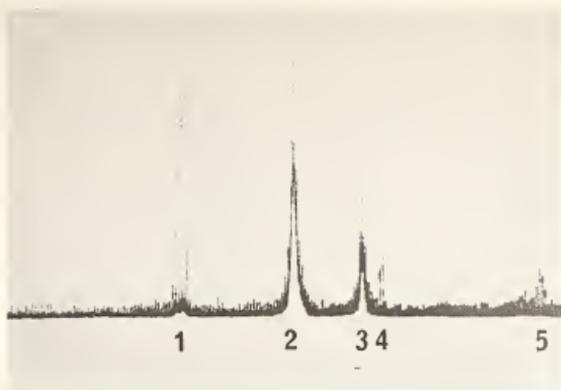


Figure 9. Section of a wavelength scan performed with the device shown in Figure 8.  
 (1)  ${}^4\text{CuK}\alpha$ , (2)  ${}^1\text{AuM}\alpha$ , (3)  ${}^1\text{AuM}\beta$ ,  
 (4)  ${}^4\text{CuK}\beta$ , (5)  ${}^4\text{AuL}\alpha$ .

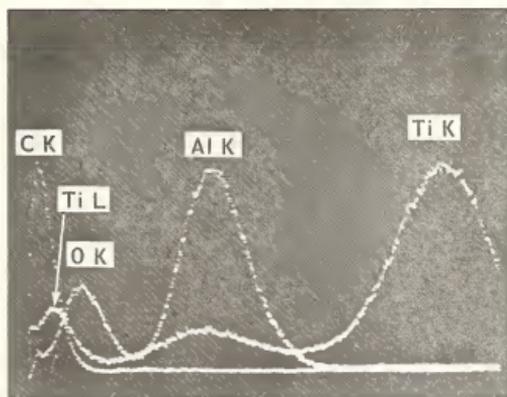


Figure 10. Nondispersive spectra obtained with an argon-methane flow proportional detector, showing the K lines of carbon, oxygen, aluminum and titanium, and the L line of titanium.

coating thickness. A third possible application is to produce thin films supported on Mylar or other materials of high x-ray transparency, which we plan to utilize in the determination of mass attenuation coefficients, as discussed further on.

The following additions are planned for the next fiscal year.

(5) An interfacing system for automatic grid scans with electronic and mechanical scanning. This device is shown schematically in Figure 11. It will provide an automatically programmed scanning operation in which the point of analysis on a specimen is advanced in a line or grid fashion with predetermined distance between points. Up to four x-ray signals and current signals will be counted and the results of the measurements automatically registered on a punched paper tape. After registration the device automatically advances to the next point. The purpose of this operation is to obtain in the fastest possible manner analytical information over a great number of points on a specimen. This is necessary to study homogeneity of alloys such as the NBS standard reference materials or other alloys proposed as standards for micro-analytical techniques. Since many measurements are necessary to obtain the needed statistical information, a hand operation for this type of investigation would be extremely tedious. It is hoped that with this device a great number of materials can be investigated with a reasonable operating efficiency.

(6) A device for multiple exposures on color film. Multiple exposures of scans combining x-ray and electron signals are extremely useful for the rapid transmission of information. Such color representations have been published by us [8] as well as by other investigators [9, 10]. The possibility of replacing expensive color television systems, sometimes used for this purpose, by a simple device using

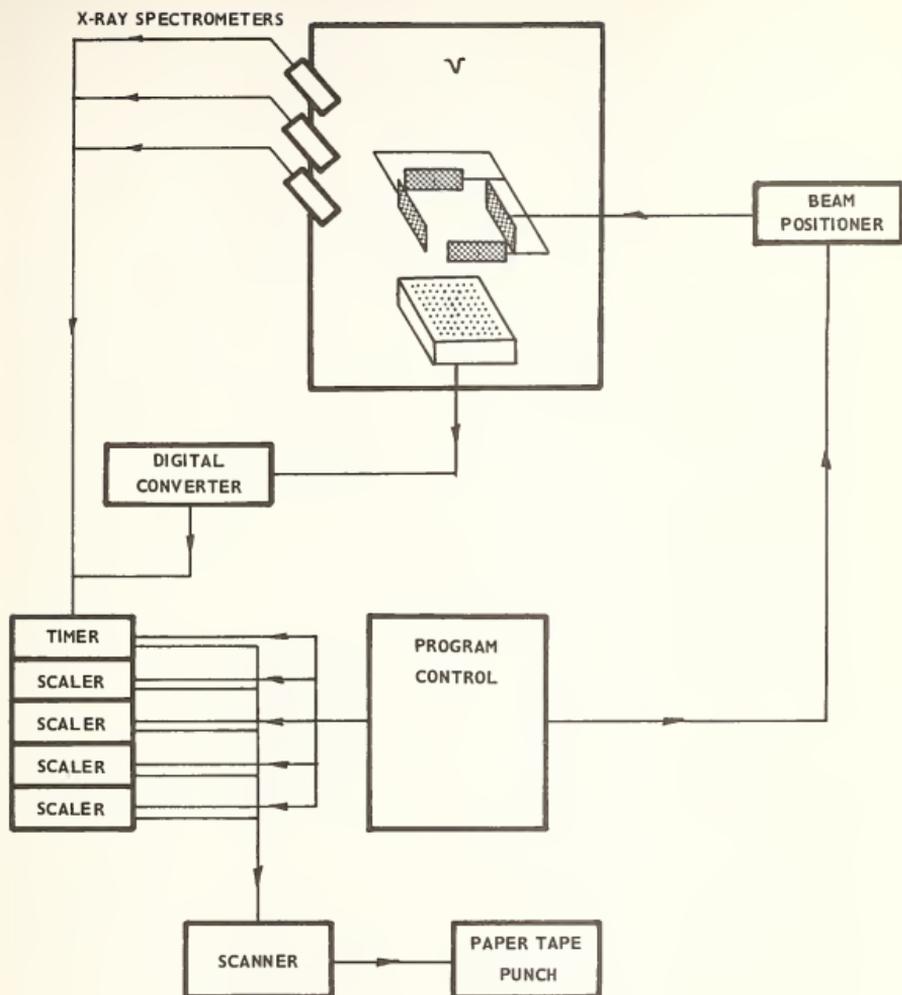


Figure 11. Schematics for the electron microprobe interfacing system.

Polaroid color film is presently being investigated. The method consists of placing colored filters in front of the oscilloscope screen so that the result of each individual scan is registered on a Polaroid film in a different color. If the difficulty of relatively low sensitivity of the color film can be overcome this will be considerably cheaper than the television technique and much less tedious than producing synthetic color diagrams by super-position of black and white exposures.

(7) Device for rapid quenching of alloy standards. (Figures 12, 13). Studies in this laboratory have shown [11] that the present knowledge of correction techniques in quantitative microanalysis is severely limited by the scarcity of metallic standards of known composition, homogeneous on a microscopic scale. It has been shown [12] that such standards can be fabricated by a method originally proposed by Duwez [13]. The device described by Goldstein, et al. [12] has been tested by the authors on various alloys. A modified design which is expected to give thicker specimens and to make them more practical for quantitative microprobe analysis than those obtained with the method [12] is presently under construction.

(8) A double pulse generator will be purchased. This equipment is extremely useful in the critical testing of the pulse handling electronics of the microprobe. It will be used for trouble shooting as well as for the determination of coincidence losses in pulse counting operations. The instrument can also be used for x-ray fluorescence spectrometers.

(9) A monitor and measuring device for the operating voltage (0-50 keV) is presently under construction. This device will permit detecting high voltage fluctuations which might affect the stability of microprobe operations of long duration.



Figure 12. Photograph of the device for rapid quenching of standard reference alloys.

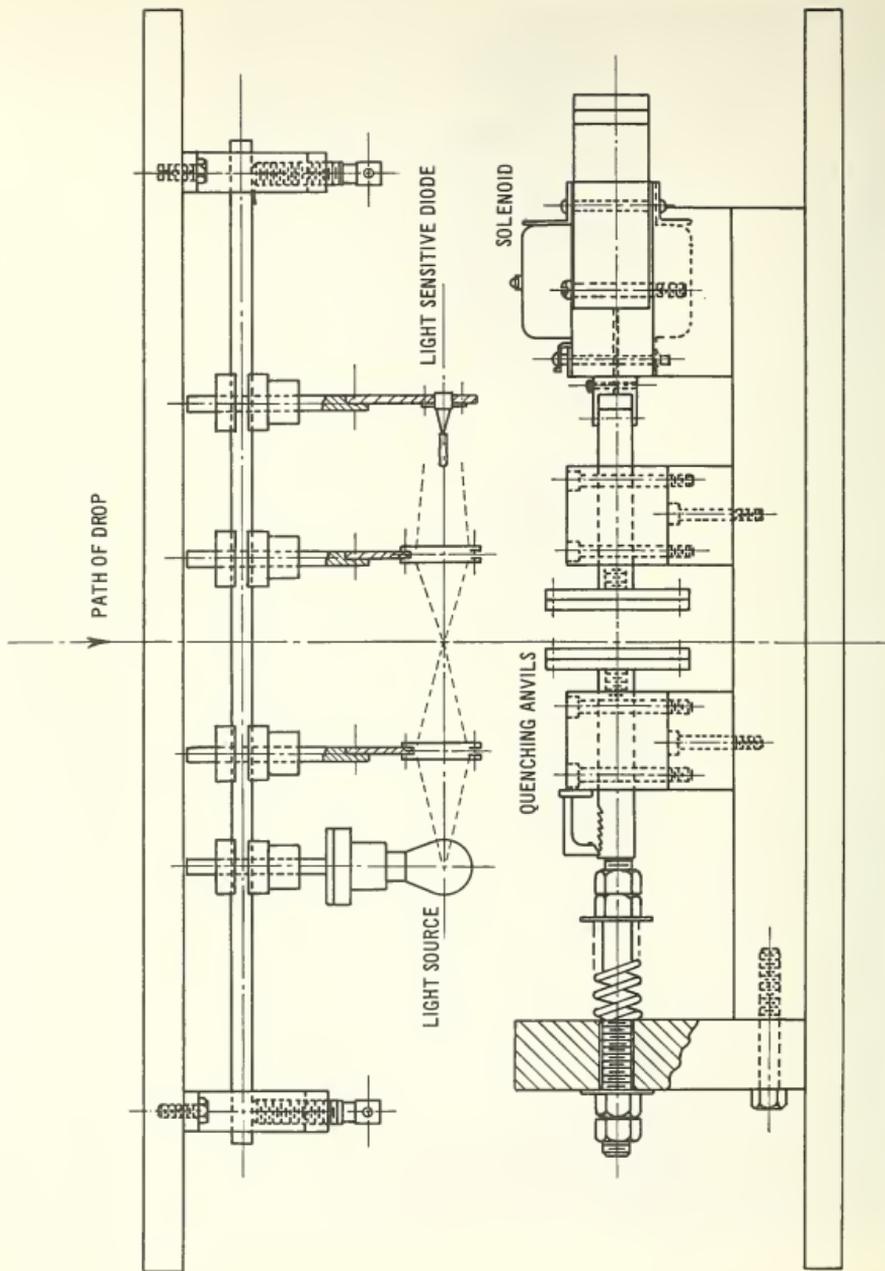


Figure 13. Diagram of the quenching section of the device shown in Figure 12.

## C. Research Activities

### 1. Techniques of Measurements

An alinement procedure for the x-ray spectrometer was developed. The curved crystal spectrometer has two adjustments which must be used for alinement: The focal circle alinement which regulates the passing of the focal circle through the point of impact of the electron beam on the specimen, and the crystal alinement which permits rocking the crystal with respect to the Rowland circle. There is a unique position of both the crystal and the focal circle adjustments which will give the maximum intensity over the spectral range of the spectrometer. In order to obtain these parameters the following procedure is recommended. A line close to the higher extremity of the spectrometer is selected, for instance, antimony La for the LiF crystal. One starts with a given focal circle setting and increases the crystal setting stepwise (on our instrument the crystal setting is changed 10 units each time). Each time that the crystal position is set the wavelength setting of the spectrometer is adjusted for maximum intensity and both the counting and the spectrometer reading are recorded. Then one proceeds to the next focal circle setting and repeats the operation. On a plot of focal circle settings vs crystal settings a line is obtained which indicates the maximum readings for the line used. The same procedure is then repeated for a line on the other extreme of the spectrometer and a similar line of maximum readings is obtained. The intersection of these two lines (see Figure 14) marks the optimum settings of both focal circle and crystal adjustment for the entire range of the spectrometer. This procedure must be repeated for each crystal and spectrometer.

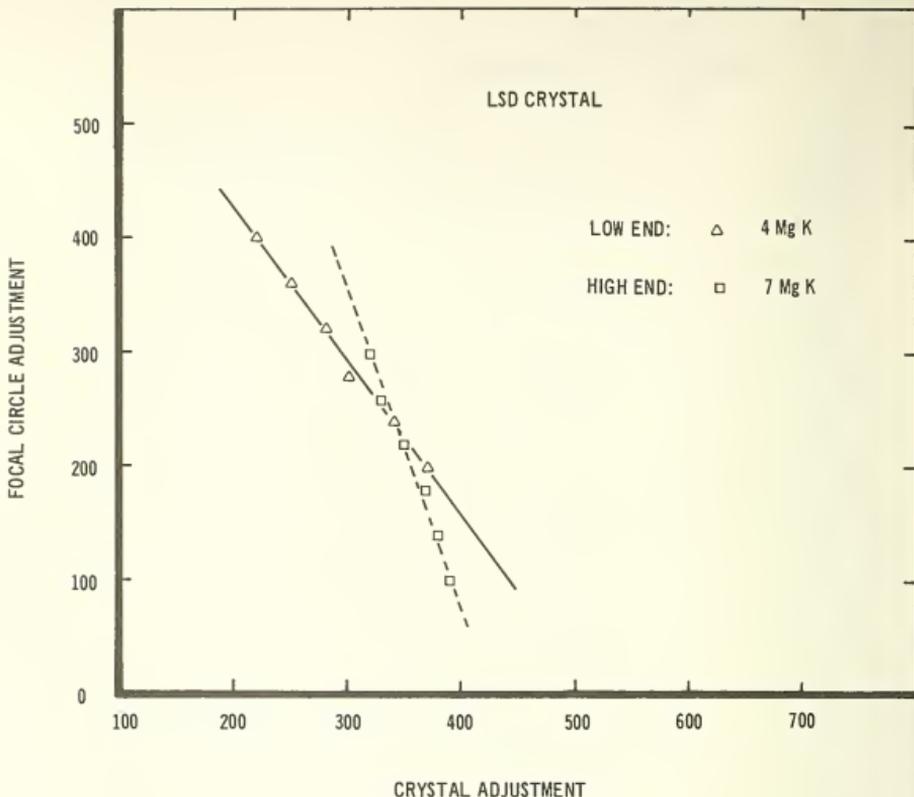


Figure 14. Graph illustrating the spectrometer alinement technique.

## 2. Mass Attenuation Coefficients

We have continued to collect the recently published data of mass absorption coefficients and we are presently investigating interpolation procedures. A program of measurements of mass absorption coefficients in critical areas has also started. These measurements are being performed on an x-ray fluorescence spectrometer using solid absorbers. We have also encouraged other Sections within the Bureau to perform such measurements and the results will

eventually provide a new table of recommended mass absorption coefficients for electron probe microanalysis. The x-ray fluorescence equipment is presently being modified for the insertion of absorbers in the path. At a later time it is planned to further modify the instrument so that the measurements can be obtained by attenuation of continuous radiation, making the operator independent of the position of the x-ray emission lines which have been used by most investigators in this field.

### 3. Scanning Electron Probe Microanalysis

A review of techniques of scanning electron probe microanalysis (NBS technical Note No. 278) has been issued in the last year. Further investigation of scanning techniques will be performed as needed.

### 4. Quantitative Electron Probe Analysis

The propagation of errors in the input parameters of correction models for absorption and fluorescence has been investigated [14]. These investigations showed that the most important source of errors in microprobe analysis is probably the absorption correction. In order to minimize these errors it is necessary to operate under conditions such that the correction itself is minimized. This means that one should work at high x-ray emergence angles and at the lowest voltages compatible with the necessary x-ray output intensity. It has been shown that there is no contraindication to these prescriptions concerning the fluorescence correction [15]. These studies will be pursued further in the next year, with particular attention to the quality of existing models for the correction calculation. We believe that in this area the theoretical considerations must be supplemented by adequate experimental data. At the present there are two main difficulties in the test of quality of existing models: the lack of reliable standards

of known composition having acceptable homogeneity on a microscopic scale and the relative scarcity of data concerning the depth distribution of x-ray generation. In order to overcome the first hurdle we propose to build an instrument for producing small quantities of alloys which are homogeneous on a microscopic scale following the rapid quenching methods proposed by Duwez (See Section A-7). On the basis of experience with this device it will be decided which materials are the best candidates for standard reference materials for electron probe microanalysis. It is also planned to prepare special targets by different techniques to investigate the depth distribution of x-ray generation by the tracer method and the production of secondary or fluorescent radiation under varying operating conditions. It is hoped that these investigations will permit establishing an improved algebraic correction model and also provide a check of more complex calculation procedures presently being investigated by several laboratories. Computer programs for the use of these correction models are also being produced, particularly for the time-shared computing system which has the particular advantage of immediate accessibility for analytical work with the electron probe microanalyzer.

In order to facilitate a better coordination of individual research efforts in quantitative microprobe analysis, a Seminar on this subject was held at the Gaithersburg facilities of NBS, on June 12 and 13. The Seminar was attended by 26 scientists, including 12 visitors from foreign countries. The Seminar consisted of an informal discussion of all important aspects of quantitative microprobe analysis. Several participants prepared reports on the subjects of their particular interest. It is planned to publish these reports, after revision by the authors and editing, as an NBS publication.

## 5. Literature Research

An extensive literature research has been performed in order to up-date the bibliography which we have issued on a previous occasion [16]. This work is now in an advanced stage and a new bibliography of microprobe analysis and related subjects will be issued within the next fiscal year. We are also investigating techniques to record this material, probably on a magnetic tape, so that future revised issues can be produced with a minimum of effort.

## 6. Wavelength Read-out Tables

Our microprobe has three spectrometers, each of which is provided with a crystal changing device so that a total of six crystals is available. Since each wavelength indicator scale is shared by two crystals of different spacings, it is not always possible to directly read the wavelength in angstroms of an x-ray line found in qualitative wavelength scans. The frequent appearance of higher order lines mentioned above further complicates qualitative analysis. In order to simplify this operation, a table was constructed which contains all the lines and orders of practical importance, in the order of elements, with the readings corresponding to our particular indicator scales. The numerical values in this table are extracted from the extensive compilation published by E. W. White et al. [17]. The table is complemented by a set of graphs showing the indicator readings for all crystals, lines, and orders.

## D. Analytical Applications

Analyses were performed for several divisions of NBS as well as for other agencies. Specimens analyzed include diffusion couples, alloys studied for homogeneity, failures in diverse alloys, blemishes in microfilm, and bonding interfaces of ceramic-coated alloys.

#### E. Contributions of Project Personnel

The service work with the electron probe microanalyzer was performed by Mrs. Mary Ann M. Giles and by Donald L. Vieth. The technical design of the pulse height analyzer device was developed by G. Wolfson and D. Vieth. S. D. Raspberry made valuable contributions to the planning of the interfacing system for the electron microprobe output. D. L. Vieth designed the cassette for multiple probe scan exposures and the device for the rapid quenching of alloy standards. Mr. A. M. McDermott and Mr. L. Marzetta (146.01) designed the high voltage monitor for the electron probe and gave valuable assistance in the maintenance and modifications of the microprobe electronics. Dr. Ping-Kay Hon performs the theoretical and experimental work on mass attenuation coefficients. Progress in the formulation of programs for the shared-time computer is due to the efforts of S. D. Raspberry and M. A. M. Giles. Mrs. Giles is also mainly responsible for the progress in the preparation of the bibliographic compilation to be issued shortly, as well as for the preparation of the spectrometer setting table for qualitative analysis.

K. F. J. Heinrich

#### 4. X-RAY FLUORESCENCE SPECTROMETRY

A brief description of the capabilities of x-ray fluorescence spectrometry for elemental analysis has been given by Heinrich [1, pp 28-30]. Due to the complexity of the underlying physical phenomena, this technique has been based primarily on empirical procedures which require an inordinate number of standards of composition close in analyses to those of the specimens to be analyzed. With the greater availability of high speed computing facilities, the application of mathematical correction techniques becomes more practical. This offers the possibility of a considerable reduction in the number of standards required.

In the past year, a thorough review of techniques proposed for this purpose was performed, as well as a study of available standard reference materials which will be employed in the experimental part of this study. In order to perform high precision measurements, the x-ray fluorescence equipment, which was to a great extent obsolete, had to be brought up to date. Much of our effort was directed to this goal and to providing the instrument with read-out facilities directly compatible with computer input. These improvements, which are now close to completion, will not only permit the performance of the basic research program mentioned above, but will also increase the speed with which analytical service can be performed. The preparation of the corresponding computer programs is also in an advanced stage.

The Spectrochemical Analysis Section is equipped with a single-channel x-ray fluorescence spectrometer (the Norelco Four Specimen Vacuum Spectrometer) and a multi-channel x-ray fluorescence spectrometer (the Applied Research Laboratories, Inc., PXQ). These instruments are described in an earlier NBS Technical Note [1, pp 30-34]. The single-channel instrumentation is of modular design; this has been

advantageous in upgrading the counting electronics and adding a teletype printer and paper tape readout.

The single-channel spectrograph is currently the primary instrument for research and measurement in three different projects: resolution of matrix interelement effects, redetermination of selected x-ray mass absorption coefficients, and measurement of plating thickness. Both instruments have been used in satisfying the requests for x-ray fluorescence analyses for the NBS, especially the Standard Reference Materials Program.

#### A. Modification of Equipment

The multi-channel spectrometer data readout unit, described in Section 2 of this report, was designed to be compatible with the multi-channel x-ray spectrometer. This readout unit has been checked out and applied several times with the multi-channel x-ray spectrometer.

More extensive changes have been made on the single-channel x-ray spectrometer. During the past year, the following instrumentation has been added to improve the precision of x-ray counting:

- (a) Solid state 6-decade printing preset scaler.
- (b) Solid state 6-decade printing preset timer.
- (c) Solid state linear count ratemeter.
- (d) Replacement of x-ray detector high voltage DC power supply.

As a part of upgrading the single-channel spectrometer, the following will be added during the next year:

- (a) Interface unit to link the scaler and timer to a teletype printer and tape punch.
- (b) Oscilloscope to monitor x-ray pulses and to assist in routine electronic check out.

Figure 15 shows how the electronic components mentioned above will ultimately be linked together for x-ray monitoring, counting, and recording. The only element shown

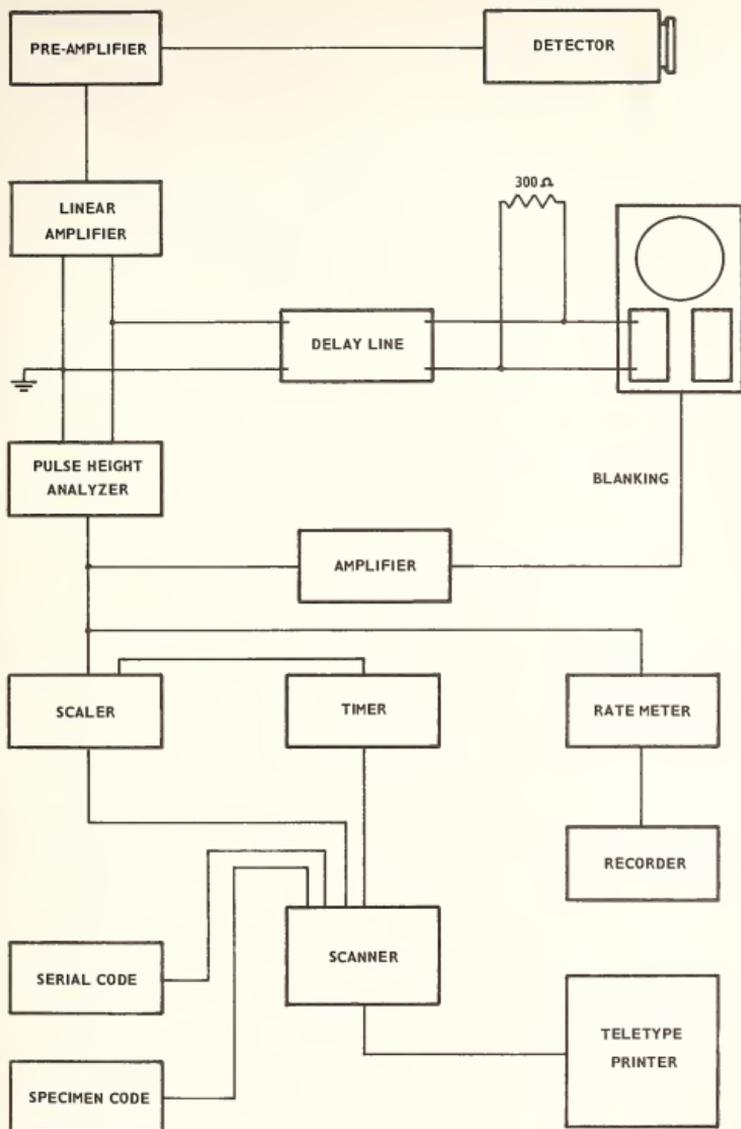


Figure 15. Interconnection diagram of the x-ray fluorescence readout electronics.

in this figure yet to be installed is the teletypewriter interface. The oscilloscope shown here is a Tektronix 581; it is on loan from another project until a permanent unit is obtained. It is connected according to the procedure given by Heinrich [2, p. 47] for analog display of the pulse height analyzer baseline and window. To achieve blanking, it was necessary to add a one-stage, inverting amplifier, with 5X gain, into the blanking circuit.

## B. Research Activities

In an earlier Technical Note [1] investigations into the x-ray analysis of silver alloys were described. A manuscript, "X-Ray Fluorescence Analysis of Silver Dental Alloys with Correction for a Line Interference," has been prepared and submitted to Spectrochimica Acta as a conclusion to this research.

Our current research efforts center around investigations into the interelement interference problems in x-ray fluorescence analysis [18]. Extensive time has been spent in evaluation of spectrometer alignment and counting techniques preparatory to data accumulation for this study. This evaluation is at an advanced stage and has already resulted in the instrument changes mentioned above. X-ray data are now being accumulated on high alloy steel systems where high and varying concentrations of Ni, Cr, and Fe produce substantial absorption and enhancement effects.

In another study, research has continued in measuring the thickness of electroplated Ni on steel and Au on brass. In this work, Fielding Ogburn and William Metzger have provided the technology on plating while Stanley Rasberry has been responsible for the x-ray instrumentation and data analysis.

Two data reduction computer programs were written to assist the plating thickness study. These are included in a compilation of our programs prepared this year [3]. In the compilation several other programs useful to x-ray fluorescence analysis are described.

### C. Examples of Application

X-ray fluorescence spectrometry has been applied to several thousand quantitative determinations and plating thickness measurements in the past year. A wide variety of materials have been analyzed including low alloy steel, high alloy steel, aluminum alloys, tin-bismuth alloys, dental gold alloys, and dental silver alloys.

In concluding work previously mentioned [1, p. 39] on the analysis of dental gold alloys, forty-six specimens of wrought gold wires were quantitatively analyzed for gold, silver, copper, palladium, platinum, zinc, and nickel, according to the method of Eick, Caul, Smith, and Rasberry [19].

X-ray fluorescence has been applied in the past year to the positive identification of standard reference materials as a check on the correctness of specimen labeling. The techniques used are nondestructive and do not alter the finished specimen surface, so the procedure of label checking can be used as a final step of quality assurance. For most specimen types that we have checked, the procedure has required approximately 45 seconds per specimen.

S. D. Rasberry

## 5. SPARK SOURCE MASS SPECTROMETRY

Recent work with the spark source mass spectrograph has been directed toward improving analytical accuracy and precision as well as instrument design to speed analysis and lower specific line background. An accurate method of sub ppm analysis, which is independent of external standards, has been developed. This involves stable isotopic dilution analysis combined with preconcentration of impurities. A computer program has been established which permits an "ion sensitive" plate response curve to be computed in the presence of plate background. The mass spectrometer has been improved in several respects, including the addition of a high speed pump to the spark source region which not only lowers specific background from source gases but also decreases the time required to pump down. In addition, a number of high purity materials have been analyzed for homogeneity; several of these show promise as possible spark source mass spectrographic standards. As an example, results on the analysis of platinum wire are described.

Plans for future work include an extension of present activity in improving analytical accuracy for the established methods and seeking new techniques, a continued effort to lower specific source interferences (C, O, N, etc.) through improved source vacuum, and an increased effort to develop standard reference materials for this field.

### A. Instrumental Improvements

#### 1. Increased Ion Beam Current

The modification kit reported installed at the end of the period covered by last years progress report [2] has now been fully evaluated. Increased accelerator voltage (from 15 to 24 kV) and wider slits throughout the instrument have increased the average ion beam current about 20 fold. Thus under comparable sparking conditions less time and sample are now required to make a  $1 \times 10^{-6}$  coulomb exposure (10 ppb

detection limits) than were previously required to make a  $1 \times 10^{-7}$  exposure (100 ppb detection limits). The increased ion current however, has resulted in a marked increase in matrix line widths due to charge broadening. In addition this charge broadening changes considerably for the matrix lines from one exposure to another when very short ( $1 \times 10^{-12}$  -  $1 \times 10^{-13}$  coulomb) exposures are made to determine the plate sensitivity to the matrix element. The increased line widths for the matrix lines have two major effects:

a. A decreased sensitivity for elements a few mass units away from the matrix line because of higher background.

b. Due to differences in line widths between the matrix and impurity elements, peak intensities must be corrected for variations in line width in order to compare data. Since all our computations are based on peak intensity-areas obtained from an analog computer (described in reference 2), correction for these width variations are made automatically.

## 2. Line Mask

A new mask has been fabricated for the exit of the magnet sector to produce shorter lines on the plate. With this mask approximately 25 exposures per plate will be possible as compared to the 15 presently available. The larger number of exposures should allow better comparison among samples run on the same plate.

## 3. Reduction of Plate Background

During a discussion held at the 1966 E-14 Mass Spectrometry Conference the use of a magnetic shim stock behind the photographic plate was reported to reduce certain major types of general plate background. A 0.003-inch thick iron shim has been tested and a marked decrease in plate background has been observed. All plate holders now have

shim stock spot-welded in place since losses of the shim in the magnetic sector have occurred on several occasions when the shim became accidentally displaced in the plate holder.

#### 4. Reduction of Source Background

The present detection capability of the spark source mass spectrograph is about 10 ppb atomic for all elements except those where instrument background interferes. There are two major sources of background: metal ions from the material of which certain critical source parts are manufactured and from gases in the vacuum system and gases released from the sample surfaces and source parts under sparking conditions. The former problem can be circumvented by using source parts made from two different materials and comparing spectra run with both. The normal practice is to use tantalum parts since few materials are expected to contain tantalum and therefore it seldom is necessary to replace the tantalum parts in order to detect tantalum in a sample. The gas background causes interferences at the ppm level at C, O, N, CO, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O and hydrocarbon masses. These lines can be minimized by the following procedures which yield the lowest pressures both before and during the sparking of a sample.

a. Overnight pumping -- for our instrument with an oil diffusion pump this yields pressures of  $1 \times 10^{-7}$  torr (measured in the source chamber, and not the pump).

b. Overnight pumping with baking -- pressures of  $1 \times 10^{-8}$  torr.

c. Liquid nitrogen cold finger in source -- pressure drops varying inversely with initial pressure -- causes significant decrease in all hydrocarbon lines.

d. Presparking of sample before analysis -- even with starting pressures of  $1 \times 10^{-8}$  torr, initial sparking causes the pressure to rise as high as  $1 \times 10^{-5}$  on some samples when using the sparking rates necessary for obtaining maximum exposures in 1-2 hours. Adequate presparking results

in operating (sparking) pressures in the low  $10^{-6}$  or high  $10^{-7}$  range depending on sample type. The presparking does reduce "gas" background as well as surface contamination. A comparison of the prespark exposure with a later exposure allows identification of both surface contaminants and gas background.

Harrington, Skogerboe, and Morrison [20] reported the development of a cryosorption pump placed inside the source chamber to maintain low pressures during analysis. The 4 1/2 x 5-in. liquid nitrogen cooled surface of charcoal was only inches away from the spark and maintained a pressure of  $2-3 \times 10^{-7}$  torr while sparking. A significant decrease in gas background was observed with this pump. The source configuration on our instrument does not allow a cryosorption panel of this size to be added, therefore we decided to add external source pumping of a much higher speed than the oil diffusion pump in the original equipment. A combination titanium sublimation -- ion pump system was selected for two reasons; first, ion pumped systems are reputed to have lower hydrocarbon content than oil diffusion pumped systems and second, we were well satisfied with a previously built sublimation ion pump system. The oil diffusion pump connection to the source was cut off and a 4-in. diameter connection now replaces it in the same relative position. Figure 16 shows a photograph of the new pumping system.

The computed conductance between the source and the sublimation chamber is about 400 liters per second or more than 20 times the estimated speed of the oil diffusion pumped system. The area coated by titanium in the sublimation chamber is adequate to give sufficient capacity so that it is not necessary to sublime Ti during an analysis. The 100 liters-per-second ion pump is closed off by a 6-in. gate valve during venting of the source to maintain its high vacuum. This procedure allows a much faster pump

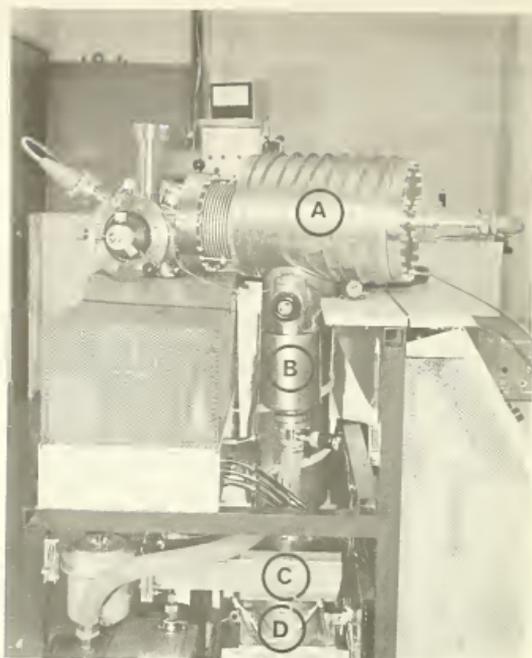


Figure 16. Photograph of source pumping system showing (A) Sublimation chamber, (B) Liquid nitrogen trap valve, (C) 6-in. gate valve, and (D) 100-liter/sec ion pump.

down cycle. The system is roughed by a mechanical pump through a combination liquid nitrogen cold trap and 1 1/2-in. high vacuum valve. At the time the pumping system was added, a nude ion gauge was mounted in a 1 1/2-in. diameter tube directly on the source chamber. This gauge should be reading true source pressures. A typical pump down schedule is as follows:

1. The system is roughed through the cold trap-valve to a pressure of about $1 \times 10^{-4}$ torr	TIME 15 min
2. The titanium sublimator is turned on -- a pressure of $2 \times 10^{-5}$ torr is obtained	1 min

3. The trap-valve is closed and the gate valve to the ion pump opened -- a pressure of  $2 \times 10^{-7}$  torr is obtained.

With this system, pressures of less than  $1 \times 10^{-8}$  torr are obtained overnight without baking. Under sparking conditions this pump maintains pressures more than 10-fold lower than the old system (low  $10^{-7}$  to high  $10^{-8}$  vs low  $10^{-6}$  to high  $10^{-7}$  torr). An example in the improvement of an analysis is illustrated by the problems involved in determining lead in a platinum matrix. In this particular Pt sample,  $PtN^+$ ,  $PtC^+$ , and  $PtO^+$  lines formed overlapping spectra with the  $Pb^+$  isotopes at 204, 206, 207, and 208. A determination of lead is possible since only  $^{194}PtN^+$  interfered with the  $^{208}Pb^+$  line and the magnitude of this interference could be computed \* by measuring the 209 mass line which was due only to  $^{195}PtN^+$  (Bi being absent in the sample). A comparison of the magnitude of the  $PtN^+$  interference showed that the new pumping system lowered the level of  $PtN^+$  by 16 fold over that produced in the oil diffusion pumped system.

#### B. Analysis of High Purity Materials Using Preconcentration and Stable Isotopic Dilution

Thermal ion source mass spectrometers have been applied to isotopic dilution analysis for some time with considerable success and precision, but there are many elements which are not detectable with these instruments. The SSMS on the other hand detects all elements with essentially equal sensitivity with detection limits in the ppb range. However, the "photographic" plate detection system limits the precision to roughly 5%. Thus the SSMS can extend the range of elements analyzed by stable isotope dilution to their fullest, but it

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\* The ratio of line intensities is the same as the known ratio of the two Pt isotopes.

cannot compete in precision with thermal ion source instruments for the elements that can be determined by the latter.

The aim in the work to be described was to develop in our laboratory the ability to apply the techniques of stable isotope dilution, with SSMS measurements of isotope ratios, to the analysis of high purity materials. We have several potential applications for this technique; first, for the analysis of materials where suitable standards are not available (and the need for accurate results justifies the extra effort involved) and second, for the analysis and certification of materials to be used for SSMS standards. A direct technique such as stable isotope dilution is the only way the SSMS, with its low detection limits, can be used to help certify its standards as to composition without the recourse of referring the analysis to yet another "standard sample."

For our study we chose an intermediate purity sample of zinc for several reasons:

1. The material contains impurities over a range of concentrations from 10 ppm to ppb level.
2. An electrochemical preconcentration technique appeared promising for use on this material to increase the effective sensitivity of the SSMS.
3. This zinc is currently being characterized at the Bureau and therefore we could compare our results to those obtained by other techniques.

The preconcentration and spiking procedures are described by R. Alvarez in Section 6 of this report.

<u>Spikes used</u>	<u>Ratios measured</u>
Pb 206	208/206
Tl 203	205/203
Cd 111	112/111

The results of these analyses are given in table 3.

Table 3. Impurities in zinc (ppm by wt)

	<u>Lead</u>	<u>Cadmium</u>	<u>Thallium</u>
Lot 1 a	10.7	1.13	0.16
b	10.7	1.23	.15
c	10.6	1.09	.16
Lot 2	10.2	1.09	.17
Lot 3	10.3	1.16	.17

From these data it was concluded that all three lots were of the same composition. A comparison of these results to those obtained on Pb and Cd by polarographic analysis shows agreement well within the experimental error. Details of this work will be included in a manuscript being prepared for publication.

#### C. Computer Program for Obtaining Response Curves from Plates With Background

The present system of computing data from plates assumes a linear response when the log of intensity is plotted against the probability value of the percent absorption. That is, the plate response follows the equation:

$$\log I \text{ (intensity)} = kx + 1.575 \quad (1)$$

where  $k$  = slope,  $x$  = probability value  
of % absorption reading of a peak.

With the spark source mass spectrograph isotope ratios can be measured 3 to 5 times more accurately than absolute intensities. Therefore, the known ratios of isotopes of elements and the percent absorption values of their lines are generally used to compute the slope  $k$  of the response curve.

The equation applied is:

$$k = \frac{\log y - \log z}{x_y - x_z} \quad (2)$$

where y and z = abundance of isotopes  
y and z

and  $x_y$  and  $x_z$  = probability values of the  
maximum % abs. of peaks y and  
z

Unfortunately most mass spectrographic plates contain varying background for which correction must be made when computing the plate response. The above equations and in fact most methods of plate calibration do not work in the presence of background.

A computer program has been written in cooperation with the computer division to correct for background and to compute the slope k in the following manner.

1. For computation purposes an initial value of k is assumed -  $k_1$
2. Peak intensity and background reading are taken for all peaks.
3. Using equation I and  $k_1$ , intensity values are computed for the peak and background from their % absorption reading.
4. The background is subtracted from the peak intensity to give a net intensity and again using eq 1 and  $k_1$  a value of x is computed. This corresponds to the probability value of the peak maximum value that would occur if the background were at 0% abs.
5. The corrected x values for two isotopes are combined with their abundances in eq 2 to compute a slope  $k_2$  representing the plate response.
6. The above is repeated for all the exposures on each element making up a group of data and on the groups of data arising from different elements.

7. All  $k_2$  values are averaged.

8. If  $|k_1 - k_2 \text{ ave}| > .002$  then the value of  $k_2$  average is substituted for  $k_1$  in step 1 and all the above procedure is repeated.

9. The above procedure is repeated until the  $k_2$  value computed differs by less than .002 from the value computed in the previous cycle. This value of  $k_2$  is the slope of the plate response curve.

10. The computer lists:

(1)  $k_2$  and  $|k_1 - k_2|$  for each cycle

(2) for the last cycle

individual  $k_2$  values

average  $k_2$  values for each group

This was applied to computing a slope  $k_2$  from data on spectra of a Pt sample on a plate with varying background. Assuming an initial value of  $k_1 = .650$ , each successive cycle of computation produced these results:

Cycle	$k_2$	Coefficient of Variation	$ k_2 - k_1 $
1	-0.605	$\pm 4.5\%$	.045
2	-0.585	$\pm 5.1\%$	.019
3	-0.579	$\pm 5.2\%$	.0062
4	-0.576	$\pm 5.3\%$	.0027
5	-0.575	$\pm 5.4\%$	.0012

The final value of  $k_2 = -.575$

Broken into groups according to elements the slopes computed in the last cycle were:

	$k_2$
$\text{Pd}^{+1}_{110-108}$	$-0.571 \pm 4.3$
$\text{Zr}^{+1}_{90-91}$	$-0.558 \pm 1.8$
$\text{Pt}^{+3}_{196-198}$	$-0.582 \pm 2.4$
$\text{Pt}^{+4}_{196-198}$	$-0.575 \pm 2.1$

The differences in the listed slopes are small in terms of their effect on data computation. It is somewhat gratifying to find that the slope computed from  $Pt^{+4}$  agrees so well with those from plus one ions of other elements.

#### D. Investigation of Homogeneity of Platinum Wire

Homogeneity studies were performed on a sample of platinum wire to which impurities had been intentionally added. The mass spectrographic comparison of ends 1 and 2 of the wire are given in Table 4. Two separate runs were made on

Table 4. Homogeneity tests on platinum wire.

	<u>Relative peak areas</u>			
	<u>End 1</u>		<u>End 2</u>	
Mg	9.8	12.1	11.7	12.0
Al	8.9	13.6	23.6	12.0
P	1.24	1.54	1.88	2.0
Ca	23	25	36	28
Fe	5.5	4.8	5.8	6.1
Cu	7.0	7.3	6.8	6.9
Zr	1.79	1.38	1.67	2.01
Rh	4.1	4.1	4.0	4.1
Pd <sup>a</sup>	1.00	1.00	1.00	1.00
Ag	1.4	2.0	1.5	1.3
Pb	4.3	4.0	3.8	2.9

<sup>a</sup>All numbers based on Pd = 1.00

each end. The values listed have been normalized by assigning Pd a value of 1.00 in each sample. This normalization assumes that the Pd content is the same in all samples. The numbers listed for each element are not concentrations, but they are related to concentrations by elemental sensitivity factors which must be experimentally determined from standards. The significance in these values is in the variation from sample to sample and from end to end. From these

results it appears that Rh, Cu, Fe, Mg and possibly Pd are homogeneously distributed in the sample. But as of yet it is not known whether the variations in Al, P, Ca, Zr, and Ag represent local inhomogeneities as well as inhomogeneities end to end or problems in controlling instrument operating parameters during analysis.

P. J. Paulsen

## 6. PRECONCENTRATION IN THE ANALYSIS OF HIGH PURITY MATERIALS

### A. Enrichment by Electrodeposition

As a preconcentration method for spectrochemical analysis, electroseparating and depositing certain trace elements onto high purity graphite electrodes from a solution of a sample has many advantages as discussed previously [2, pp 74 to 77]. The electrodeposited trace elements provide a sample form particularly well-suited for excitation by the high-voltage spark. Employing a minimum number of highly purified reagents and chemical manipulations, this method is less subject to contamination errors than chemical preconcentration techniques, furthermore, by housing the cells in a limited-size clean environment, airborne contamination is reduced to a low value.

For many elements, contamination problems would appear to limit the application of stable isotope dilution techniques to the determination of trace elements by spark source mass spectrometry. The possibility of electrodepositing trace elements directly onto a material suitable as a substrate for sparking would afford a minimum of contamination. Consequently, a joint investigation with P. J. Paulsen (see Section 5 on Spark Source Mass Spectrometry) was initiated. Gold was selected as the electrode material upon which the trace elements and isotope additions would be deposited for subsequent analysis on the mass spectrometer. It was chosen because it is obtainable in high purity (the concentration of common metallic impurities being less than one ppm), it is mononuclidic and produces a simple spectrum when sparked, and it does not react with the solution being electrolyzed. After determining the conditions for depositing trace elements on the gold wire cathodes, an isotopic dilution

method was developed for determining Pb, Cd, and Tl in high purity zinc. The essentials of the method consist of: (1) dissolution of the sample, (2) addition of the stable isotope, (3) electrodeposition of the trace elements upon the ends of high-purity gold wires and (4) sparking of the electrodeposit and measurement of the isotopic ratios.

Isotope dilution methods have the following advantages:

1. Once the isotopic addition, in suitable chemical form has been made to a solution of the sample, the results are unaffected by "sorption" and mechanical losses.

2. For chemical operations involving separation of the trace elements, it is unnecessary to determine the recovery or yield of the trace and because of the high detection sensitivity of the spark source mass spectrometer, a near-quantitative recovery of the trace elements is not required.

3. Multi-element determinations can be made simultaneously.

A technical paper on this work entitled, "Spark Source Mass Spectrographic Analysis of High-Purity Materials by Isotope Dilution and Electrodeposition of the Trace Elements" was presented at the Fifteenth Annual Conference on Mass Spectrometry and Allied Topics. A manuscript is being prepared for publication.

## B. Enrichment by Matrix Volatilization

### 1. Impurities in Sulfur

To evaluate the relative purity of sulfur samples with respect to metallic trace impurities by conventional, emission-spectrochemical procedures presents several difficulties. First, spectral line intensities cannot be related to concentrations, without standards, and second,

the high volatility of sulfur in the arc results in poor limits of detection for the impurity elements. Therefore, a method was developed employing a preliminary chemical concentration procedure and a "collector" into which the impurity elements are incorporated.

The sulfur sample was oxidized to sulfuric acid and then evaporated in the presence of high-purity gallium nitrate as a "collector." The residue was placed in a quartz boat and ignited in a tube furnace equipped with a quartz tube as a liner. The evaporation of the sulfuric acid was performed in a quartz crucible housed in a crystallizing dish modified by the addition of a tube through which filtered nitrogen was introduced. The analysis was completed by exciting the oxide residues in a direct current arc, photographing the spectra, and comparing them to synthetic standards. Recoveries for several trace elements were determined using high specific activity radioisotopes. It was felt that fewer trace elements would be lost by vaporizing sulfuric acid than by vaporizing the sulfur sample directly.

## 2. Impurities in Selenium

The direct arc spectrochemical determination of trace elements in selenium has several disadvantages:

1. Dense fumes are produced which absorb the incident radiation thus adversely affecting the detection limits.
2. The fumes are more toxic than those of HCN.
3. Standards of selenium to relate spectral intensities to concentrations are not available.

These considerations made it desirable to remove the matrix and incorporate the trace elements into a small amount of a collector which could then be compared to synthesized standards. Two procedures for removing selenium were examined. In the first procedure, selenium was

dissolved in nitric acid and volatilized by heating with a minimum amount of sulfuric acid. This evaporation was done in quartz using the apparatus described under section 1 above. Gallium nitrate was used as the "collector", and after igniting, the ignited residue was compared to standards of gallium oxide. In the second procedure, HBr was employed to volatilize the selenium as the bromide. Teflon crucibles were employed in addition to the quartz crucibles.

### 3. Impurities in gold

Several portions of a lot of 60-mil gold wire intended for spark source mass spectrometry were examined by an optical spectrographic technique involving selective volatilization of the matrix. The samples were arced continuously using a 15-amp direct current arc while the camera was being racked at 20 sec intervals. The spectra were recorded photographically. Ag, Fe, and Si were estimated as being 0.2 ppm and Cu, Mg, and Ca as being 0.1 ppm.

R. Alvarez

## 7. PERSONNEL AND ACTIVITIES

### A. Personnel Listing

#### Spectrochemical Analysis Section

Bourdon F. Scribner, Section Chief  
Arthur J. Ahearn, Research Physicist  
Frances L. Hilten, Administrative Aid

#### Group I. Optical Spectroscopy

Marvin Margoshes, Chemist  
Claude Veillon, Post Doctoral Research Chemist  
Joseph L. Weber, Physicist  
Martha M. Darr, Chemist  
Elizabeth K. Hubbard, Physicist (Terminated)  
Virginia C. Stewart, Chemist  
Doward M. Bouchette, Physical Science Technician  
Daniel Marcellus, Chemist (Summer Student 1966)

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

Kurt F. J. Heinrich, Chemist  
Ping-Kay Hon, Chemist  
Donald L. Vieth, Physical Metallurgist  
Stanley D. Rasberry, Physicist  
Mary Ann Giles, Chemist  
Chong K. Kim, Chemist (Summer 1967)  
Gerald A. Wolfson, Electronic Technician  
(Terminated)

#### Part Time Guest Workers:

Harvey Yakowitz, Metallurgist, NBS Metallurgy  
Division  
John D. Eick, Chemist, Dental Research Group  
H. John Caul, Chemist, Dental Research Group  
Fielding Ogburn, Chemist, NBS Metallurgy Division  
Ann R. Fritz, NBS Metallurgy Division  
Michael Duke, Chemist, Geological Survey

#### Group III. Spark Source Mass Spectrometry

Paul J. Paulsen, Chemist  
Paul E. Branch, Technician (Terminated)  
Daniel E. Kelleher, Chemist

#### Group IV. Enrichment Techniques

Robert Alvarez, Chemist

B. Publications

1. Scribner, B. F.  
Advances in Excitation Sources for Spectrochemical Analysis. XXth IUPAC Congress Moscow. Pure and Applied Chemistry 10, No. 4, 579-594 (1965).
2. Heinrich, K. F. J., Vieth, D. L., and Yakowitz, H.  
Correction for Non-Linearity of Proportional Counter Systems in Electron Probe X-Ray Microanalysis, Advances in X-Ray Analysis, 9, 208-220 (1965), New York, Plenum Press.
3. Margoshes, M.  
Recent Advances in Excitation of Atomic Spectra. Proceedings of the XIIth Colloquium Spectroscopicum Internationale, Exeter, England, Hilger & Watts, London (1966) pp. 26-42.
4. Rasberry, S. D., Scribner, B. F., and Margoshes, M.  
Characteristics of the Laser Probe for Spectrochemical Analysis (A summary). Proceedings of the XIIth Colloquium Spectroscopicum Internationale, Exeter, England. Hilger & Watts, London (1966) pp. 336-9.
5. Margoshes, M., and Scribner, B. F.  
Eastern Analytical Symposium 1966. (Meeting Report). Appl. Optics 5, No. 7, 1190 (1966).
6. Scribner, B. F. (Editor)  
Activities of the NBS Spectrochemical Analysis Section, July 1965 through June 1966. NBS Technical Note 401, September 1966.
7. Rasberry, S. D., Scribner, B. F., and Margoshes, M.  
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8. Rasberry, S. D., Scribner, B. F., and Margoshes, M.  
Laser Probe Excitation in Spectrochemical Analysis. II. Investigation of Quantitative Aspects. Appl. Optics 6, No. 1, 87-94 (1967).
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Scanning Electron Probe Microanalysis, NBS Technical Note 278. National Bureau of Standards, Washington, D. C., February 3, 1967.

10. Margoshes, M.  
Excitation and Ionization in Arc and Spark  
Excitation Sources. Appl. Spectry. 21, No. 2,  
92-99 (1967).
11. Heinrich, K. F. J.  
Electron Probe Microanalysis. "Experimental Methods  
of Materials Research. Advances in Materials  
Research, Vol. 1," Ed. H. Herman. John Wiley &  
Sons, New York, 1967, p. 145-162.
12. Meinke, W. W., and Scribner, B. F. (Editors)  
Trace Characterization, Chemical and Physical,  
National Bureau of Standards, U. S. Government  
Printing Office, Washington, D. C., April 1967.
13. Heinrich, K. F. J.  
Electron Probe Microanalysis by Specimen Current  
Measurement. Proceedings of the Fourth International  
Congress of X-Ray Optics and Microanalysis. Orsay,  
France 1965 (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.  
Appl. Spectry. 21, No. 5, 324-328 (1967).
15. Margoshes, M.  
Selection of Wavelengths for Atomic Absorption  
Spectrometry, Anal. Chem. 39, No. 10, 1093-1096  
(1967).

C. Talks Given

(The first three papers listed were contributions to the  
First Materials Research Symposium: Trace  
Characterization, Chemical and Physical, National  
Bureau of Standards, Gaithersburg, Md., October 3-7,  
1966).

1. Paulsen, P. J., "Electronic Analog Computer for  
Measuring Intensity Areas on Mass Spectrographic  
Plates," Symposium on Trace Characterization, NBS  
October 6, 1966.
2. Alvarez, R., "Electrodeposition of Trace Constituents as  
a Preconcentration Technique for Optical Emission  
Spectroscopy: Deposition of Silver from Zinc Solution,  
Symposium on Trace Characterization, NBS October  
7, 1966.

3. Heinrich, K. F. J., "Electron Probe Microanalysis and the Determination of Traces," Symposium on Trace Characterization, NBS October 7, 1966.
4. Heinrich, K. F. J., "Microscopic Analytical Techniques," University of Maryland, College Park, Md., October 18, 20, 25, and 27, 1966.
5. Margoshes, M., "Data Acquisition and Reduction in Spectrochemical Analysis," Canadian Symposium on Applied Spectroscopy, Montreal, Canada, Oct. 24, 1966.
6. Heinrich, K. F. J., "Instrumental Analysis in Situ," Conference on Characterization of Materials, Pennsylvania State University, University Park, Pa., November 17, 1966.
7. Rasberry, S. D., "A Review of New Techniques of Data Logging and Data Processing in X-Ray Spectrometry," Cleveland Section, Society for Applied Spectroscopy, Cleveland, Ohio, January 25, 1967.
8. Margoshes, M., "Spectrochemical Analysis with a Laser Probe," Niagara Frontier Section, Society for Applied Spectroscopy, Buffalo, New York, February 1, 1967.
9. Margoshes, M. "Laser Probe Microanalysis," New York Section, Society for Applied Spectroscopy, New York, N. Y., February 14, 1967.
10. Rasberry, S. D., "Development in Spectrochemical Computation with a Time-Shared Computer," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 10, 1967.
11. Heinrich, K. F. J., "Quantitative Electron Probe Microanalysis," Thomas J. Watson Research Center, IBM, Yorktown Heights, New York, N. Y., April 12, 1967.
12. Margoshes, M., "What Computers are Doing to Analytical Chemistry," Xavier University, Cincinnati, Ohio, April 19, 1967.
13. Margoshes, M., "Data Acquisition and Calculation in Spectrochemical Analysis," Society for Applied Spectroscopy, National Speakers Tour: Ohio Valley Section Society for Applied Spectroscopy, Dayton, Ohio, April 17, 1967; Cincinnati Section, SAS, Cincinnati, Ohio, April 18, 1967; Kansas City Section, SAS, Kansas City, Mo., April 19, 1967.

14. Paulsen, P. J., "Spark Source Mass Spectrographic Analysis of High Purity Materials by Isotope Dilution and Electrodeposition of Trace Elements," E-14 Conference on Mass Spectrometry and Allied Topics, Denver, Colo., May 16, 1967.

15. Heinrich, K. F. J., "Electron Probe Microanalysis," National Institutes of Health, Bethesda, Md., June 6, 1967.

(Following are three papers given at the Second National Conference on Electron Microprobe Analysis, (2nd NCMA) Boston, Mass., June 14-16, 1967.)

16. Heinrich, K. F. J., "Quantitative Electron Probe Microanalysis: The X-Ray Absorption Correction," 2nd NCMA, June 14, 1967.

17. Giles, M. A. M., "Pulse Height Programmed X-Ray Wavelength Scanning," 2nd NCMA, June 16, 1967.

18. Vieth, D. L., "Novel Design of a Kossel Pattern Generator," 2nd NCMA, June 14, 1967.

(Following are five papers given at the XIII Colloquium Spectroscopicum Internationale (CSI), Carleton University, Ottawa, Ontario, Canada, June 19-23, 1967).

19. Scribner, B. F., "Impact of Computer Techniques on Atomic Spectroscopy," XIII CSI, June 19, 1967.

20. Margoshes, M., "Properties of the Laser Probe with Rotating Prism and Liquid Q-Switches," XIII CSI, June 19, 1967.

21. Veillon, C., "Atomic Absorption and Atomic Fluorescence Spectrometry with an RF Plasma Torch," XIII CSI June 20, 1967.

22. Heinrich, K. F. J., "Inhomogeneity Studies of Alloys with the Electron Microprobe," XIII CSI, June 22, 1967.

23. Alvarez, R., "The Spectrochemical Determination of Ultra-Trace Elements in High Purity Metals by Preconcentration Using Matrix Volatilization," XIII CSI, June 23, 1967.

D. Committee Activities

B. F. Scribner

Member, ASTM Committee E-2 on Emission Spectroscopy  
Member, ASTM Committee E-13 on Absorption Spectroscopy  
Member, Program Committee, Eastern Analytical  
Symposium, 1967  
Delegate to Governing Board, EAS, 1966  
Titular member, Commission on Spectrochemical and Other  
Optical Methods of Analysis, International Union of  
Pure and Applied Chemistry  
Member, Advisory Board, Spectrochimica Acta  
Member, International Advisory Board, XIII Colloquium  
Spectroscopicum Internationale, 1967  
Chairman-Elect, Baltimore-Washington Section, SAS,  
1966-67  
Member, Wavelength Tables Committee, University of  
Michigan  
Technical Program Chairman, NBS Symposium on Trace  
Characterization, 1966  
Member, Analytical Standards Committee NBS  
Member, Analytical Services Committee NBS

M. Margoshes

Chairman, Conference Committee, SAS, 1966  
Member, Publications Committee, SAS, 1966  
Member, Program Committee, and Chairman, Publicity  
Committee, NBS Symposium on Trace Characterization,  
1966  
Editor, Spectrochimica Acta, Atomic Section  
Member, Professional Development Committee,  
Baltimore-Washington Section, SAS, 1967  
Liaison representative, Society for Applied Spectroscopy  
and XIII Colloquium Spectroscopicum Internationale,  
1967

K. F. J. Heinrich

Member, ASTM Committee E-4 on Metallography  
Assistant Editor, Mikrochimica Acta  
Member, Planning Committee, Symposium on  
Characterization, Pennsylvania State University, 1966  
Chairman, Seminar on Quantitative Microprobe Analysis,  
NBS, June 1967

A. J. Ahearn

Vice-Chairman, Subcommittee VII, ASTM Committee E-14  
on Mass Spectrometry and Allied Subjects

P. J. Paulsen

Member, Subcommittee VII, ASTM Committee E-14 on  
Mass Spectrometry and Allied Subjects

R. Alvarez

Member, ASTM Committee E-2 on Emission Spectroscopy

J. L. Weber

Member, ASTM Committee E-2 on Emission Spectroscopy,  
Subcommittees IV, VII, and IX

S. D. Raspberry

Member, Laser Task Group, ASTM Committee E-2

E. K. Hubbard

Analytical Chemistry Division Newsletter

## 8. ACKNOWLEDGMENTS

During the year we have had considerable assistance from groups and individuals for which we express our sincere appreciation.

Mr. Joseph M. Cameron, Applied Mathematics Division and Dr. Robert J. Arms of the Computer Services Division have been very helpful on problems of statistical analysis and computer programs.

Mr. Harvey Yakowitz of the Metallurgy Division has worked closely with our group on problems of quantitative microprobe analysis. The Electronic Instrumentation Section headed by Mr. Robert J. Carpenter has provided assistance in circuit designs.

Mrs. Rosemary Maddock has been very helpful to our group especially in arranging for slides and illustrations for papers.

It is a pleasure again to acknowledge the invaluable assistance of Mrs. Frances L. Hilten, Administrative Aid in our Section who performed a wide variety of duties essential to the Section's activity. Her assistance in preparing this and other reports is deeply appreciated.

- [1] Scribner, B. F., ed., "Spectrochemical Analysis: Optical Spectrometry, X-Ray Fluorescence Spectrometry, and Electron Probe Microanalysis Techniques, July 1964 to June 1965," NBS Technical Note 272, Oct., 1965.
- [2] Scribner, B. F., ed., "Activities of the NBS Spectrochemical Analysis Section, July 1965 through June 1966," NBS Technical Note 401, Sept., 1966.
- [3] Raspberry, S. D., Margoshes, M., and Scribner, B. F., "Applications of a Time-Sharing Computer in a Spectrochemistry Laboratory: Optical Emission and X-Ray Fluorescence," NBS Technical Note 407 (1967).
- [4] Raspberry, S. D., Scribner, B. F., and Margoshes, M., *Appl. Optics* 6, 81 (1967).
- [5] *Ibid.*, p. 87.
- [6] Wendt, R. H., and Fassel, V. A., *Anal. Chem.* 37, 920 (1965).
- [7] *Ibid.*, p. 337.
- [8] Heinrich, K. F. J., *Advances in X-Ray Analysis*, 7, 382 (1964).
- [9] Theisen, R., *Mem. Sci. Rev. Met.* 50, 189 (1963).
- [10] Lennartz, G., de Laffolie, H., *DEW-Techn. Ber.*, 6, 201 (1966).
- [11] Heinrich, K. F. J., "Common Errors in Electron Probe Microanalysis," submitted to *Advances in X-Ray Analysis*.
- [12] Goldstein, J. I., Majeske, F. J., and Yakowitz, H., *Advances in X-Ray Analysis*, 10, 217 (1967).
- [13] Duwez, P., Willens, R. H., and Klement, W., Jr., *J. Appl. Phys.* 31, 1136 (1960).
- [14] Yakowitz, H., and Heinrich, K. F. J., "Quantitative Electron Probe Microanalysis: Absorption Correction Uncertainty," Submitted to *Mikrochim. Acta*.
- [15] Heinrich, K. F. J., and Yakowitz, H., to be published.
- [16] Heinrich, K. F. J., Obtainable from the author.
- [17] White, E. W., et al., "X-Ray Wavelength and Crystal Interchange Settings for Wavelength Geared Curved Crystal Spectrometers," 2nd Ed., The Pennsylvania State University, University Park, Pa., 1965.
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- [19] Eick, J. D., Caul, H. J., Smith, D. L., and Raspberry, S. D., *Appl. Spectry.* 21, No. 5, 324-328 (1967).
- [20] Harrington, W. L., Skogerboe, R. K., and Morrison, G. H., *Anal. Chem.* 37, 1480 (1965).

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