NBS TECHNICAL NOTE

401

Activities of the NBS Spectrochemical Analysis Section

July 1965 through June 1966

Edited by Bourdon F. Scribner

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

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NBS TECHNICAL NOTE 401

ISSUED SEPTEMBER 30, 1966

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Spectrochemical Analysis Section
Analytical Chemistry Division
Institute for Materials Research

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FOREWORD

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

Formal publication in scientific periodicals is highl important. In addition, however, it has been our experienc that informal, annual summaries of progress describing efforts of the past year can be very valuable in dissemina ing information. At the National Bureau of Standards such publications fit logically into the category of a Technica Note. In 1966 we plan to issue these summaries for all of our sections. The following is the second annual report o progress of the Spectrochemical Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Divisio

PREFACE

This is the second annual progress report of the
ctrochemical Analysis Section of the Analytical Chemistry
ision. The Section, formerly known as Spectrochemistry,
established in 1948 as an outgrowth of an extensive
gram of spectrochemical analysis of uranium and related
erials and also in recognition of the growing importance
instrumental analysis. While the Section had been
marily concerned with optical emission spectrometry,
growing importance of related spectrometric fields in
mental analysis led to extension into x-ray spectrometry
1957, to the addition of electron probe microanalysis in
4, and to the inclusion of spark source mass spectrometry
1965.

The purpose of the Section is to develop measurement
hniques for determining the elemental composition of
erials through the use of optical, x-ray, and mass
ctra. Chemical elements are uniquely identified by the
racteristic frequency of emitted spectra, and amounts
sent can be determined by measurement of the intensity of
tted radiation. However, many factors enter into success-
spectral analysis and must be carefully controlled.
se include, in optical and x-ray spectrometry, the produc-
n of radiant energy by excitation, the dispersion of the
iant energy into a spectrum, and the measurement of
ctral wavelengths and intensities. In a similar way,
rk source mass spectrometry involves ion formation,
persion into a mass spectrum, and measurement of
ensities for recorded masses. Because of the complexity
the systems involved no way has yet been found to make
olute measurements of concentrations in analysis;
sequently, comparative methods are employed in which

spectra of unknowns are measured relative to those of reference materials of known composition.

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

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

In order to specify the procedures adequately, it has been necessary occasionally to identify commercial materia and equipment in this report. In no case does such identification imply recommendation or endorsement by the Nation Bureau of Standards, nor does it imply that the material o 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 1965 to June 1966

Edited by Bourdon F. Scribner

ABSTRACT

A summary is given of the activities of the NBS Spectrochemical Analysis Section for the period from July, 1965 through June, 1966, during which the move into the new facilities at Gaithersburg, Md. was made. Activities in optical spectrometry included development of programs for calculations on a time-sharing computer, measurement of arc temperatures, applications of the laser probe and the plasma jet, and studies on atomic absorption spectrometry. In x-ray spectroscopy, there have been some modifications of equipment, improvements in computation methods, and several applications. Improvements and additions were made to the electron probe analyzer, along with studies on measurement techniques, including non-dispersive analysis and computation procedures. The spark-source mass spectrometer has also been modified, and a new analog computer has been built and tested for reduction of photographic plate data; applications of this instrument to analyses of pure materials are described. Enrichment methods are being studied for the analysis of pure materials by emission spectroscopy, particularly with an electro-deposition technique. Homogeneity studies and analyses have been performed in the development of standard reference materials. Other activities included analyses of samples to assist other NBS groups and government agencies, and literature surveys. Listings are given of 20 publications and 26 talks by members of the Section during the year.

Key words:

Analysis, arc temperature, atomic absorption spectrometry, analog computer, bibliography, computer, electrodeposition, electron back scatter, electron prob microanalyzer, emission spectroscopy, laser probe, mass spectroscopy, photographic photometry, plasma jet, preconcentration, pulse height analyzer, spectrochemica analysis, spectroscopy, standard reference materials, time-shared computer, x-ray spectroscopy.

1. FACILITIES

. Space Facilities

This year marks a significant improvement in our eneral space facilities with the completion of the move f our laboratories to the new location at Gaithersburg, aryland. Detailed planning for the move began as long go as 1960 and attempts were made to anticipate the needs or the program as it would exist at the time of the move. he move itself required much detailed planning. We were articularly concerned about possible damage to several arge and costly instruments. For this phase of the move e enlisted the services of manufacturers' representatives o supervise the dismantling, move, re-assembly, and ealignment of the instruments. This proved to be effective nd permitted the laboratory to be in operation for the ost part within two weeks after the move. In general the ove was successful and the new space facilities offer many dvantages over those at the old location.

The new NBS site occupies 550 acres, some 20 miles orthwest of Washington, D. C. The scientific activities re largely accommodated in a series of interconnected general purpose laboratories", having three working floors nd an attic floor in which all service equipment, ncluding air-conditioning, is housed. Services are brought own from the attic in stacks to each module. The buildings re designed with two rows of laboratory rooms adjoining t the center axis of the building and, on each side, a orridor with office spaces at the outer wall. The rooms re of modular construction having removable steel artitions. The inner basic laboratory module is 11 feet ide by 22 feet long, and the outer office modules are 11 eet wide by 16 feet long.

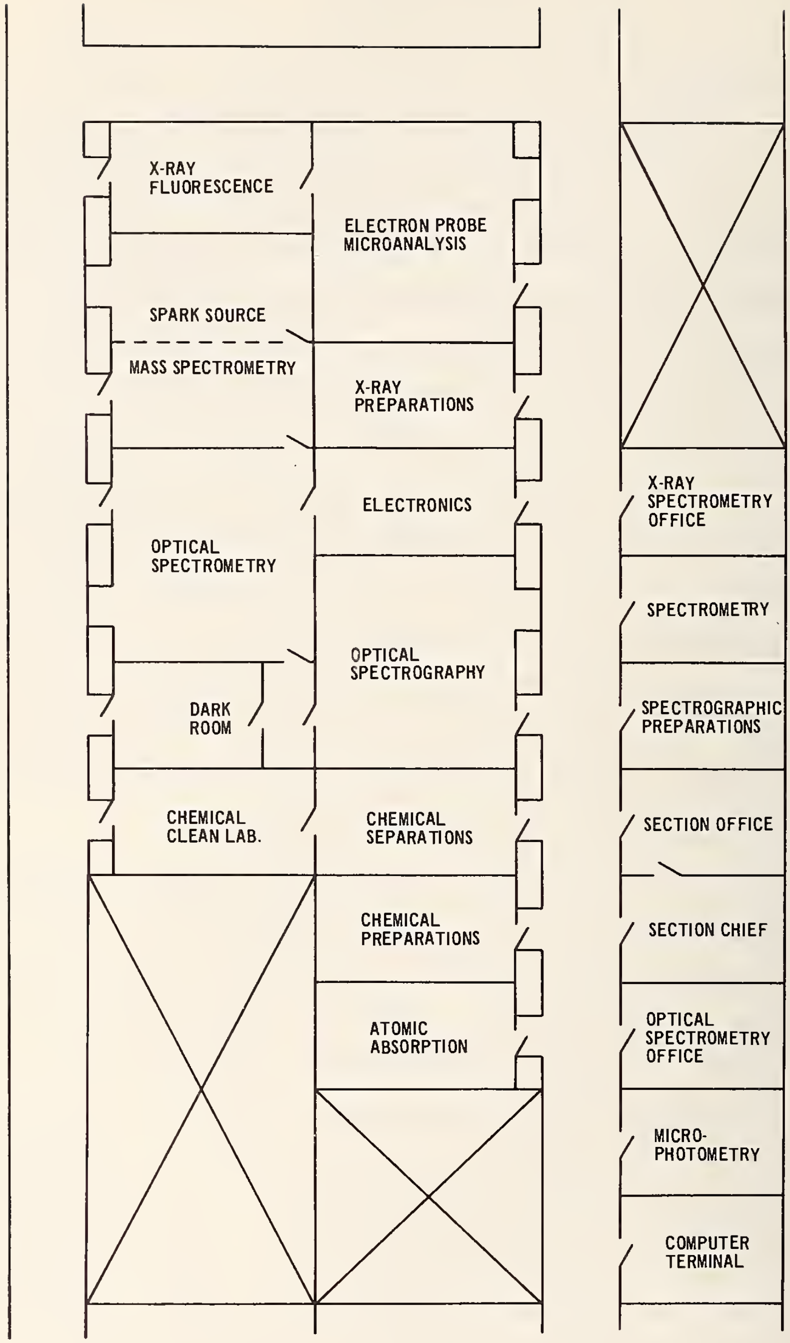

Figure 1. Floor plan of the Spectrochemical Analysis Section

The Spectrochemical Analysis Section occupies an area f 16 laboratory modules and 8 office modules located on he first floor of the Chemistry Building. Since the buildng has no basement the ground floor provides a firm support or our instruments. The floor plan of the laboratory is hown in figure 1.

The main instrument laboratories--for optical spectroraphs, optical spectrometers, the electron probe, and the ass spectrograph--each occupy a double module. An example f this type of room is the microprobe laboratory shown in igure 2.

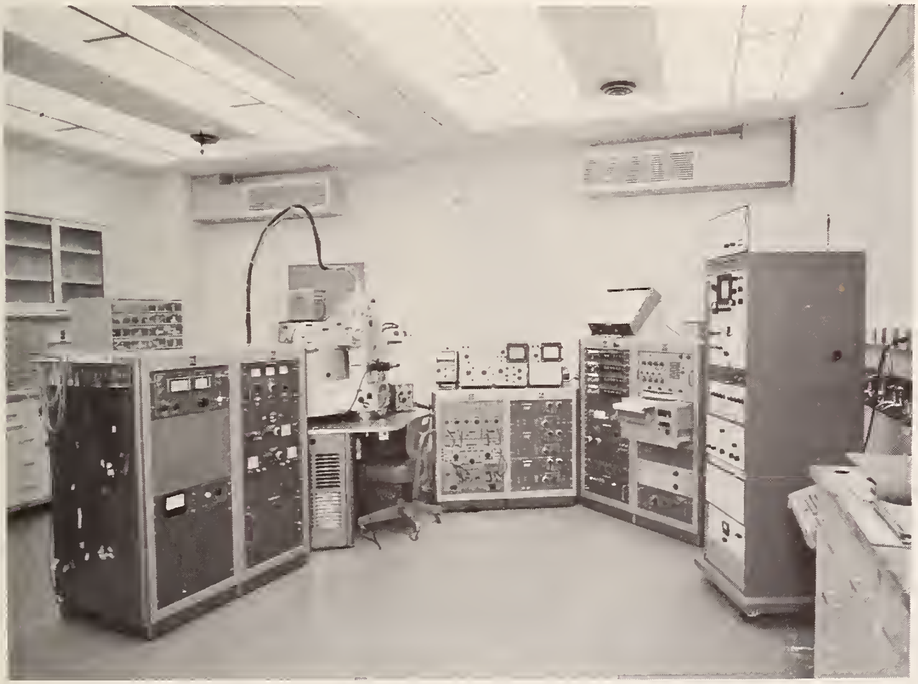

Figure 2. Electron probe microanalysis laboratory (double module).

Single laboratory modules are provided for x-ray fluorescence, atomic absorption, three chemical laboratories, and the supporting laboratories for x-ray preparations, electronics, and dark room. Some limited laboratory work is performed in smaller outer modules for spectrographic preparations and microphotometry. Two rooms for which we had no counterpart at the old location are a chemical clean laboratory (Figure 3) equipped with a special hood for work with radioactive materials, and a computer room where there is located a communication station with access to a time-shared, remote computer. The important role of the computer service in our work is described in Sections 2 and 3 of this report.

Figure 3. Chemical clean laboratory (single module).

Equipment

The major equipment of the laboratory was described d illustrated in 1965 progress reports [1,2]. This cludes the following:

3-meter Eagle mounting grating spectrograph
3.4-meter Ebert mounting grating spectrograph
21-foot Wadsworth mounting grating spectrograph
2-meter multi-channel optical spectrometer
3-meter multi-channel optical spectrometer
Multi-channel x-ray spectrometer
Single-channel x-ray spectrometer
Atomic absorption spectrometer
Electron probe microanalyzer with 3 spectrometers
  and associated read-out equipment
Spark-source mass spectrograph

Various accessory equipment including microphotometers, mple preparation devices, microscopes, etc., are available.

During the past year the major equipment of the boratory has been extended or improved to include (1) jor revamping of equipment for atomic absorption, (2) a cuum attachment for the single channel x-ray spectrometer, d (3) a multi-channel analyzer for the microprobe. In dition, several read-out devices were added or improved r use with the microprobe as described in Section 4 of is report.

With the completion of major phases of our equipment cessions and the final adjustments to our new space cilities, the laboratory is in an excellent position to rsue its program of research and service in spectro-emical analysis. On the following pages the progress the current program of the Section is reviewed in ch area.

2. OPTICAL SPECTROMETRY

In the period covered by this report, there have been no major changes in the emphasis in research on emission spectrometry. Our chief interests remain in developing new or improved excitation sources, studying the properties of such sources, and devising analytical methods to meet requirements which are common to many spectrochemical laboratories or which arise from NBS programs such as the preparation of standard reference materials.

Considerable progress has been made in some of the research activities described previously [1], including measurement of the temperature of the d-c arc in argon and a study of the applicability of a continuum source in atomic absorption spectrometry. Progress reports on these topics are given in the following pages. In several cases, earlier studies on excitation sources are now bearing fruit in difficult analytical applications. Examples are given below of the use of the laser probe and the plasma jet in the solution of specific problems which arose during the past year.

The studies of the properties of excitation sources have improved our knowledge of the physical theory of spectrochemical analysis. This knowledge can often contribute directly to the development of analytical methods. An example, described below, is the development and experimental testing of a method of selecting wavelengths for atomic absorption spectrometry on the basis of published tables of atomic properties.

For several years computers have been employed in our Section in reducing the extensive data recorded in homogeneity testing of spectrometric standards. The recent availability of time-sharing computers has enhanced our terest in the use of computers in emission spectrometry, well as in other areas of spectroscopy. During the past ar, programs have been written for several routine mputation tasks which were previously done graphically or a desk calculator. The time-sharing computer seems to be e ideal way of doing calculations which are smaller than e type of problem normally run on the computer, but which ill require considerable time by the older methods. The sk of preparing programs for the computer can, at times, ad to a new insight into the nature of the problem and to e development of more efficient solutions. The studies on libration of photographic emulsions with a computer present one such case.

Time-Sharing Computer

1. Description of the system

A time-sharing computer system similar to that developed Dartmouth College has been available to the Analytical emistry Division for more than a year, and the Spectroemical Analysis Section has made extensive use of this cility to improve the efficiency of its operations.

A teletype terminal in the laboratory, figure 4, allows e user to enter programs, data, and commands into the mputer and to receive printed output. This information carried over telephone lines to the computer system, veral miles away, which may serve as many as 40 terminals multaneously.

The central system consists of master and slave computers d a disk memory. Information transmitted from a terminal received by the master computer and is stored in the disk mory. When a user has entered all necessary programming structions and data, he types the command RUN. Each user o has typed RUN is assigned a turn of a few seconds on the ave computer. If one turn is not enough time to complete

Figure 4. Teletype terminal for communication with time-sharing computer.

the calculations, the master computer re-enters the program into the slave computer as often as is necessary.

The results of the calculations, as well as partially complete programs, are also stored in the disk memory. The master computer transmits the results from the memory to the user's terminal. Normally, only a few seconds pass after the command RUN is typed until the first output is received. If the program is written improperly so that the calculations cannot be made, or if the data format is wrong, specific diagnostic information will be received at the terminal. Programs may be permanently stored so that reentry with each use is not necessary.

The rapid response of time-shared computing has everal advantages. The process of preparing programs is peeded, since "bugs" can usually be removed in only a few minutes at the terminal. Similarly, the effects of changes n the program will be known quickly. Probably the most important advantage of this rapid response is that it makes the use of computers feasible for small jobs which require significant time by graphical methods or with a desk calculator, but which do not require enough time to justify a trip to the computer laboratory and the long wait until the results are available under the customary method of using computers. The cost of the time-sharing system is less than that of large computers for these small jobs.

This time-sharing system employs a programming language called BASIC, which was also developed at Dartmouth College [3]. Although BASIC lacks some of the capabilities of most other programming languages, it is exceptionally easy to learn and to use, and does permit the preparation of some quite complex programs. An advantage to the scientist of writing his own programs is that he will often develop a better understanding of his problems. In addition, having written the program himself, the scientist will be able to make modifications to alter the calculations or the form of the output.

An important feature of time-sharing computation is that there can exist an interaction between the scientist and the machine that is not normally available to computer users. Programs may be written so that the computer will present part of the results and pause for further instructions. Depending on how the program is written, such instructions may modify further calculations or control the form or amounts of the output. In this way, the educated judgment of the scientist can be brought to bear on the problem without requiring the difficult job of writing this judgment into a program.

The system does, of course, have some disadvantages. The most serious are the limited memory of the slave computer, which restricts the size of problems that can be handled, and the rate of data transmission over the teletype. Neither of these difficulties has proven to be serious in our applications. In a few cases, problems whic would otherwise require a larger computer have been divided into smaller segments. Some of the larger jobs are still taken to the computer laboratory, but these are generally ones for which speed of response is not important.

The limitation of the rate of data transmission is alleviated in two ways. The programs need not be transmitted each time they are run. They can be stored in the disk memory and called up when they are to be used. The stored programs can be modified, if desired. Thus, only the data must be transmitted. In addition, in many cases less output is required in this method of computer operatio than is commonly taken from a computer. Only the essential information is normally requested, and the programs can be modified to give more detailed information when needed.

2. Examples of applications

a. Emulsion calibration

When a linear relationship can be found between functions of the microphotometer readings and the relative exposures, a photographic emulsion calibration can be defined by the slope and intercept of this line. Since the exposure is stated only in relative terms, the intercept can be assigned any convenient value, and only the slope of the line must be known. In principle, the slope could be determined from one pair of microphotometer readings on lines of known relative intensity, but in practice a much more reliable value can be obtained by averaging the slopes obtained from several such pairs of readings.

A program, KAISER, has been developed for the calibration of photographic emulsions, employing the Kaiser transform [4] as the linearizing function. The Kaiser transform has the form

$$K = A \log(1/T) + (1-A)\log(1/T-1) = AD + (1-A)S,$$

where K is the Kaiser function, T is the transmittance, D is the optical density, and S is the Seidel function [4]. When an appropriate value is chosen for the parameter A, a plot of the Kaiser function vs. the logarithm of the relative exposure will usually be linear. Kaiser [4] has shown that an approximation to A can be found from the relation

$$-A = \frac{\Delta S_1 - \Delta S_2}{\Delta D_1 - \Delta D_2 - (\Delta S_1 - \Delta S_2)},$$

where S and D have the same meanings as above, Δ indicates the difference between the values for a pair of lines of known relative intensity, and the subscripts indicate two such pairs. A more reliable estimate of A can be obtained by averaging several such calculated values than from only two sets of pairs of readings.

Input to the KAISER program includes the wavelength at which the plate is being calibrated and an identification code for the plate, the step factor, the low and high values of transmittance that should be accepted (e.g. 5 to 90% T), and pairs of transmittance readings through a step sector or filter. As a first step, as many values of A are calculated as there are pairs of transmittance readings, and from this list are calculated the average and standard deviation. The individual estimates of A are each compared with the average, and any of the individual values differing from the average by more than 3σ are rejected and a new average and standard deviation are found. With this value of A, the value of the Kaiser function corresponding to each transmittance is found, and the Kaiser values are taken in pairs to give individual slopes for the calibratio function. The average and standard deviation of the slope are calculated from this list, and individual slopes differing from the average by more than 3σ are rejected.

Table 1 shows the form of the output, which includes a summary of the input data followed by estimates of A and the slope, the standard deviation for each, and the number of data pairs rejected in each case as giving results outside the 3σ limits. The operator is then asked if he wants more detailed information. In this case he answered affirmatively, and the computer presented a summary of the data arranged according to the transmittance reading for the lighter step. (The notation "E-2" means "X 10^{-2}"). A glance at this summary indicates that there is no marked trend of the slope with transmittance readings, but that the calibration may not be reliable for transmittances above 90%. The operator is asked at this point if he wants still more output, and in this case he answered negatively.

The program is written to accept two or more sets of data at a time. These may, for example, be calibration data for the same plate at different wavelengths. The output "OUT OF DATA IN (LINE) 110" shows that there were no more such sets of data. The "TIME: 8 SECS." output shows the time taken by the slave computer to perform the calculations.

The values of A and the slope given by this program are part of the input to the program INTEN, along with

Table 1. Output from KAISER.

```
KAISER     10:15     CEIR     06/01/66

PLATE CALIBRATION BY FIT TO KAISER TRANSFORM
DATA FROM PLATE L-463
WAVELENGTH= 3300    ANGSTROMS
PCT. T LIMITS: 0   TO 100
NO. OF INPUT PAIRS= 19
NO. OF LIMIT REJECTS= 0

BEST A           COEFF. VAR.      NO. 3S REJ.     NO. PRS. USED
 .214858          217.548          0               19

AVE. SLOPE       COEFF. VAR.      NO. 3S REJ.     NO. PRS. USED
 .563404          4.85105          0               19

DO YOU WANT SUMMARY OF SLOPE VS. PCT. T, YES(1) OR NO(0)?1

RANGE OF LIGHT T VALUES
FROM             TO          AVE. SLOPE   NO. OF PRS.   PCT. DEV.
 30               40          .563782      1             6.72484E-2
 50               60          .555409      2            -1.41903
 60               70          .577085      5             2.42833
 70               80          .58326       4             3.5244
 80               90          .563742      6             6.00486E-2
 90               100         .528577      2            -6.18142

DO YOU WANT INDIVIDUAL SLOPES, YES(1) OR NO(0)?0

----------------------------------------------------

OUT OF DATA IN 110

TIME:   8 SECS.
```

transmittance readings to be converted to relative intensities. INTEN includes several options. For example, the readings may all be from one wavelength region, with a single plate calibration curve, or more than one plate calibration may be needed. The options are summarized in table 2. The input and output formats depend on which option is to be used. One output is shown in table 3.

Table 2. Options in INTEN program.

Option	More than one plate calibration	More than one step	Background correction
1	-	-	-
2	-	+	-
3	-	+	+
4	+	+	-
5	+	+	+

Table 3. Output from INTEN (Test data).

```
INTEN      10:20     CEIR     06/01/66

RELATIVE INTENSITIES OF SPECTRAL LINES

ANGSTROMS  PERCENT T  REL. INT.  BKGD. INT.  CORR. REL. INT
 2500         60        6.53197    3.26599     3.26599
 2500         20        8.         2.          6.
 2600         60        6.53197    3.26599     3.26599
 2600         20        8.         2.          6.

TIME:    3 SECS.
```

b. Fitting analytical curves

The programs CODEBC and CODEBD fit analytical curves to instrument readings of intensity ratios from standards of known composition and calculate analytical results from data on samples. To find the analytical curves, the computer makes least-square fits to polynomials, starting with the first degree and continuing through the eleventh degree if there are sufficient input data. The user studies output indicating the goodness of fit for each degree of polynomial, and then enters the degree of polynominal that he wants to have used in subsequent calculations. At his option, the user will then receive as output for each standard the calculated concentration and the absolute and percentage differences between the calculated and given element concentrations. If there is some standard which does not fit on the calibration curve, the user can stop the program, edit the data to remove the values for this standard, and start the program again.

The final output is the concentrations found for the samples. CODEBC provides output in terms of concentration ratios and concentrations. For each sample run in multiplicate, information is given on the individual runs as well as averages and standard deviations. CODEBD will not provide data on concentration ratios, and for each sample run in multiplicate only the average and standard deviation are given.

c. Other programs

Space does not permit listing all of the programs that have been written, but a few more examples will be cited briefly.

Several programs have been written for statistical calculations. CODEB, for example, computes the average, maximum, minimum, range, and standard deviation for any list of up to 100 numbers. Many other programs include statistical calculations.

TEMPER and PROFIL are used in the studies on arc temperature measurements. Both programs fit least-square lines to log $(I\lambda^3/gf)$ vs. E and, from the slope and standar deviation of the slope of this line, calculate the temperature and standard deviation of the temperature of th arc. The two programs differ only in the format of the output, that of TEMPER being more detailed.

The terminal is used by several Sections within the Analytical Chemistry Division, and a program, TIME, has been developed to keep records of the use and to compile this information periodically. Each user, when he has completed his operations, enters into the data section of the program his code number, the times he came on and is going off, and the day of the month. These data are stored in the disk memory of the computer. At the end of each month the program is run and the output lists the total usage (numbers of uses and total hours) and the total and percentage uses for each person. When the program is run before the end of the month, it will also provide a prediction of the total use to be expected during the month based on the rate of use to date.

Copies of these programs will be supplied on request.

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

B. Arc Temperature Measurements

The previous annual report [1, pp. 13-18] described the reason for and the basis of the measurements of the temperature distribution in a d-c arc in argon, and showed the first experimental results. During this year, the measurement methods have been improved by more extensive application of computers, particularly by the time-sharing system, to reduction of the data.

The applications of the time sharing computer in this tudy include the programs for photographic plate alibration and for conversion of microphotometer readings o relative intensities, described elsewhere in this eport. In the first set of measurements, a week was eeded to calculate the plasma temperatures at 19 radial ositions by making least-square fits to log ($I\lambda^3$/gf) vs. . With the time-sharing computer, the temperature and the tandard deviation of the temperature can be calculated for ll of the radial positions in about one-half day, ncluding the time required to prepare punched paper tapes f the data for entry into the computer.

Additional measurements have now been made under the ame experimental conditions as for the first set. All of he new measurements are in agreement among themselves, and hey show the same qualitative temperature distribution as n the first set. However, the temperatures found in the ew measurements, about 6500° K at the center of the arc, re somewhat higher than the results of the first easurements (5800° K).

(M. Margoshes and M. M. Darr)

. Laser Probe Excitation

The previous annual report [1, pp. 21-7] included a escription of studies of the properties of the laser probe or qualitative and quantitative analysis. On the basis of hese studies, we now feel confident in applying this xcitation source to the analysis of samples which might be ifficult to handle by other methods. A description of hese studies is being prepared for publication.

We are cooperating with the Laser Section of Committee E-2 of the American Society for Testing and Materials in a round-robin test. Several laboratories have agreed to make laser probe exposures with specific NBS Standard Reference

Materials, to return these samples for measurement of the pits formed, and to fill out a form with information on excitation and exposure conditions. The purpose of this round-robin test is to develop standards for terminology and procedures for laser probe excitation.

Among the unusual problems solved with laser probe excitation was the identification of inclusions in bottles made of a fluorinated polymer. These inclusions ranged downward in size from about 1 mm, and they were of various shapes and colors. Attempts to remove some of the inclusions for arc excitation failed because the particles would pop out and be lost when a cut was made into the plastic. Samples were prepared for laser probe excitation by excising pieces of the plastic containing one or more inclusions, removing some of the plastic if necessary to bring the inclusions near the surface, and mounting the plastic pieces on microscope slides with double-sided adhesive tape. The analyses showed that some of the particles, which looked dark red under the microscope, contained iron as the major metallic constituent and presumably were bits of rust. Other particles, which looked metallic, contained aluminum, copper, or zinc as major constituents. Several opaque particles contained large amounts of silicon and presumably were bits of glass or ceramic. It was concluded that bottles made of this material are not suitable for storage of pure solutions.

Microfilm which is stored for several years occasionally develops spots up to 100 or 200μ in diameter, which can affect the quality of the images. Localized impurities in the emulsion might be a cause of such spots. To analyze the spots, samples of the microfilm were taped to microscope slides and sampled with the laser probe. A total of 43 exposures were made. The pits were approximately cylindrical, about 100μ in diameter and 100μ deep. Some of the spots were found to contain metallic impurities which were not found in adjacent unaffected areas, but no consistent pattern of impurities was observed. Very often, no difference in metallic content was found between spots and unaffected areas.

A nickel printing plate, coated on one side with chromium, was submitted for the analysis of small corroded areas on the uncoated side. Laser probe analyses were made of unaffected areas on both sides of the plate, of the corroded areas, and of the printing ink. The corrosion spots were found to contain chromium in significant amounts, but only traces of iron, which was the major metallic constituent of the ink. It was concluded that the corrosion may have been caused during the chromium plating rather than by reaction of the plate with the ink.

Other applications of the laser probe included the identification of surface deposits on cathodes from an electrical discharge, and the sampling of the outside and cross-section of a small spring to determine whether or not it had been plated.

Our experience in these applications indicated that the laser probe is a useful addition to the other analytical capabilities of this laboratory. However, these applications have been restricted to cases where qualitative results are adequate, and we have not yet attempted to apply the laser probe to quantitative determinations.

(S. D. Rasberry, M. Margoshes, M. M. Darr)

D. Atomic Absorption Spectrometry

During the past year, a study of atomic absorption spectrometry with a high-pressure xenon lamp continuum source has been completed, and will be prepared for publication. The emphasis of experimental studies has now been shifted to non-flame methods of converting samples to an atomic vapor. In addition to this experimental work, as well as several analytical applications, a method has been developed for selecting wavelengths for atomic absorption spectrometry without tedious experimental measurements. This method has been tested, partly with published data and partly with new data obtained in this laboratory.

Towards the end of this year, the atomic absorption spectrometer has been rebuilt to provide significant improvements in ease, speed, and accuracy of measurement.

1. Modification of the instrument

The instrumentation for atomic absorption spectrometry has been modified and improved. The rebuilt instrument is shown in figure 5. Nearly the only part retained from the old instrument is the 3/4-m Fastie-Ebert monochromator, which is kinematically mounted on a sturdy base, to which a 1.25-m optical bench is rigidly attached. This arrangement allows considerable flexibility for the external optics. The major modification has been to replace most of the electronics. The electronics now consist of the following: stable d-c power supplies for hollow cathode and high-pressure xenon lamps; a highly-regulated (0.001%), high-stability (0.005%/hr) 0-2000 V d-c photomultiplier power supply; a variable-frequency, phase-sensitive amplifier with a remote high input-impedence pre-amplifier, adjustable time constant, and zero suppression; a 390-Hz synchronous mechanical chopper for modulating the radiation; and a 10-mV, 0.25-sec response strip chart recorder. All of the electronics, except for the pre-amplifier and the chopper, are mounted in an upright cabinet provided with casters for mobility.

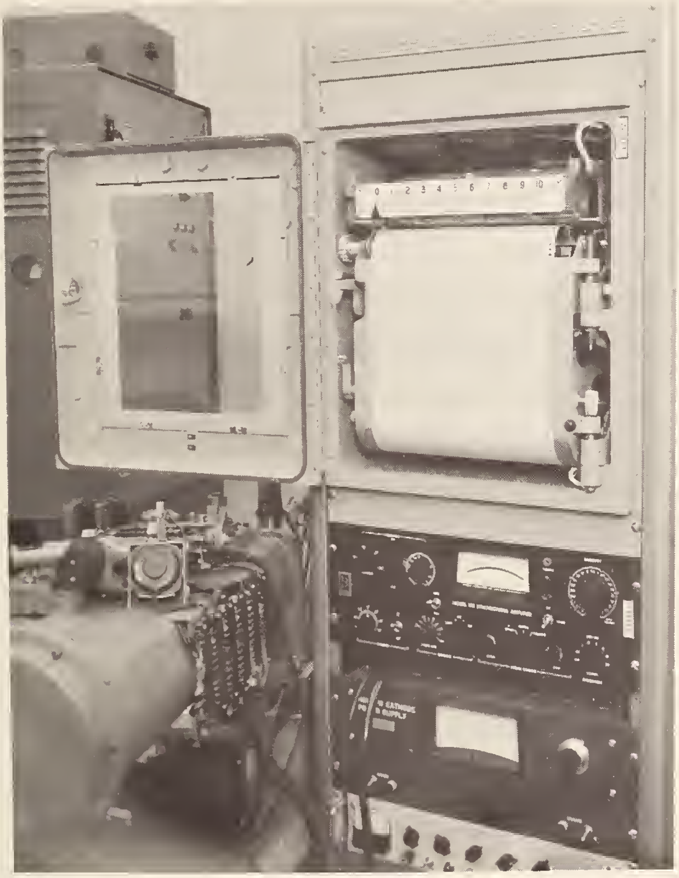

Figure 5. Newly modified atomic absorption spectrometer.

A 5-kW, 4.8 X 10^6-Hz radio-frequency power supply has recently been installed, to provide power for a plasma torch which will be studied as a means of vaporizing samples for atomic absorption spectrometry. Studies of atomic fluorescence with the plasma torch are also contemplated.

(C. Veillon and M. Margoshes)

2. Selection of wavelengths

The selection of a wavelength for measurement in atomic absorption spectrometry is ordinarily based on published data for suitable lines or on direct measurements on a number of lines of the analyte of either the concentration required to give an arbitrary absorbance or the absorbance at a fixed concentration. Direct measurements on many lines are time-consuming, and reliance on published data may not result in the selection of the best possible wavelength. Differences in instrumentation must be taken into account, and the necessary information may not be given in the literature. For example, the most sensitive line of the analyte may be in a wavelength region that was not accessible with the spectrometer employed in the original measurements. The particular filler gas in the hollow cathode lamp is an experimental variable which can affect the choice of wavelengths, since the gas may have emission lines nearly coincident with one or more lines of the analyte. When there are such adjacent interfering lines either from the filler gas or other lines of the analyte, the resolving power of the spectrometer becomes an important factor.

When two or more analytes are to be determined in the same solution, it will not always be possible to make use of the most sensitive line of each element, since only a limited concentration range can be covered with a particular absorption line. There has been little information published on wavelengths suitable for the determination of elements present at high concentrations.

Two relationships have been derived for the selection of analytical wavelengths in atomic absorption spectrometry from the gf-values tabulated in NBS Monograph 53 [5]. Both relationships have been tested experimentally and found to hold within the precision of the gf-values. However, the gf-values given in NBS Monograph 53 must be corrected for a wavelength-dependent error at wavelengths below 2450Å. Figure 6 shows the correction factor as a function of wavelength, according to Corliss [6]. Multiplying the listed gf-values by correction factors taken from this graph has been found to give reasonably accurate results in this application.

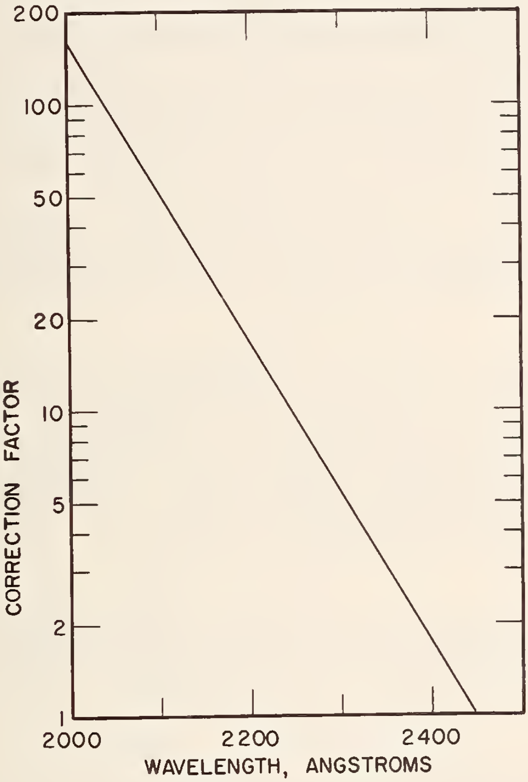

Figure 6. Wavelength-dependent correction factor to gf-values in NBS Monograph 53. Values from tables should be multiplied by factor taken from this chart.

For atomic absorption spectrometry with a narrow-line source, such as a hollow cathode lamp, the concentration of an element required to give a selected absorbance with a given experimental arrangement should be inversely proportional to gf exp(-E/kT), where E is the energy of the lower level of the transition, k is Boltzmann's constant, and T is the flame temperature. For resonance lines, where E=0, the exponential term is equal to unity. Similarly, the absorbances for a series of lines of the same element at a given concentration in the test solution will also be proportional to gf exp(-E/kT).

A somewhat different theory applies to atomic absorption spectrometry with a continuum source. In this case, either the reciprocal of the concentration of the analyte required to give a selected value for the percent absorption, or the percent absorption at a fixed analyte concentration, will be proportional to $gf\lambda\ e^{-(E/kT)}$ at low absorbances. Note that, in the case of the continuum source, it is the percent absorption that is to be measured rather than the absorbance.

For the first case, atomic absorption spectrometry with a hollow cathode source, a test of the theory could be made on the basis of data from the literature. Figure 7 shows a

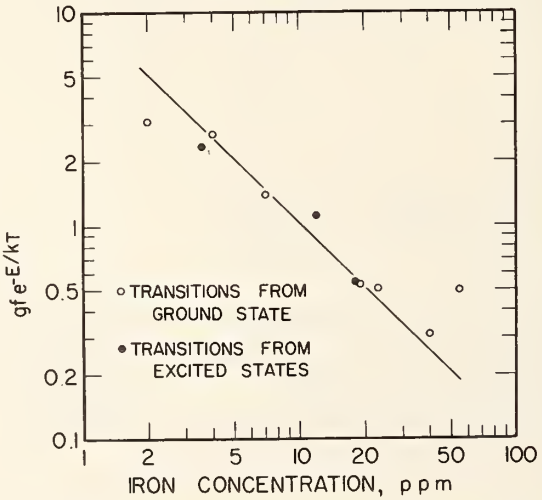

Figure 7. Test of theory for atomic absorption with a hollow cathode light source. The straight line has a unit slope as required by the theory.

comparison of theory with experiment with data on iron given by Allan [7], who measured the concentration of iron in solution which would give an absorbance of 0.1 for a number of lines. A flame temperature of 2000° K was assumed. The points lie on a straight line within the precision of the gf-values, indicating that the theory can predict relative sensitivities of detection.

No similar sets of data could be found in the literature for atomic absorption spectrometry with a continuum source. To test the theory, a set of measurements was made for manganese with a high-pressure xenon lamp as the source. Figure 8 shows the results of these measurements.

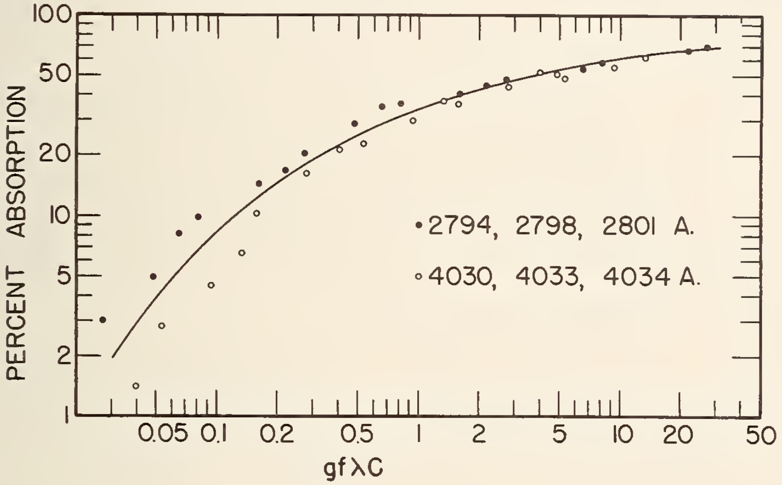

Figure 8. Test of theory for atomic absorption with a continuum source.

Measurements for six lines at several different concentrations were combined by plotting gfλC vs the percent absorption, where λ is the wavelength and C is the concentration in parts per million. As expected, the curve is asymptotic to a line of unit slope at low absorption values, but approaches a lower slope at higher percent absorption readings. All of the data fit the curve within the accuracy of the gf-values, but there is discrepancy between the data for the lines at 2794-2801 Å and for the lines at 4030-4034 Å. When the same data are plotted with the gf-values of Ostrovskiĭ and Penkin [8], a similar discrepancy is observed, but in the reverse direction in that the curve for the group of lines at shorter wavelength then falls to right of the curve for the longer-wavelength lines. However, either set of gf-values will lead to the prediction that the manganese line at 2794 A will give the best sensitivity of detection, in agreement with the measurements

This method cannot predict relative sensitivities of detection for different elements or for different experimental arrangements. The proportionality between the analyte concentration in solution and the number of atoms in the flame depends on the element, on the construction of the atomizer, on the temperature of the flame, and on many other factors. No attempt has been made to correlate sensitivities of detection with atom and ion lines of the same element, though this would be possible if the degree of ionization in the flame were known.

It should be recognized that, in applying this method of selecting lines, the criterion of sensitivity of detection is in terms of the absorbance or percent absorption. This is less meaningful than a definition of sensitivity in terms of signal-to-noise ratios. In many cases, however, either criterion will lead to selection of the same line. In addition, if the most sensitive line is too strong, the treatment described here will satisfactorily predict the less sensitive line which must be used.

(M. Margoshes)

3. Use of a Continuum Source

Studies have continued on the use of a high-pressure xenon lamp as a continuum source in atomic absorption spectrometry. In particular, the precision of analysis by this technique has been measured for both pure solutions and actual samples. Only the data on actual samples will be discussed here, as these should be representative of the type of results which could be obtained in routine applications.

It was not possible, in this study, to utilize the stepping capabilities of the spectrometer to determine several elements in rapid succession. The recorder then on the spectrometer had too slow a response to accurately follow the line intensity as each line was quickly scanned. However, the instrument has now been modified (see above), and such measurements should be possible in the future. In the work described below, the wavelength was adjusted manually for each line, and data were taken by reading the recorder pen deflection for a 20-second period.

The samples chosen for this study were NBS Standard Reference Materials 1011, 1013, 1014, 1015, and 1016, which are portland cements. Solutions were prepared by dissolving weighed samples in dilute HCl, filtering off the insoluble silica, and diluting to volume with water. It was found to be possible to determine Fe, Mg, and Na in a single solution; Ca was too concentrated in this solution to be determined without dilution and the concentrations of other elements were too low. Each solution was run 4 times over a 3-day period to establish analytical curves, and the solution from NBS 1014 was run 20 times to determine the precision of analysis.

Fe gave a linear analytical curve over the range of concentrations (145 to 259 ppm) in the solutions, the curve for Na (6 to 41 ppm) was nearly linear, while that for Mg (25 to 256 ppm) had a pronounced curvature. Table 4 lists the results of the precision studies, including statistical analyses in terms of the absorbance and the concentration. These data indicate that reasonably precise and accurate results can be obtained in the determination of several elements in the same solution by atomic absorption with a continuum source. This study has also defined some limitations of the method. The sensitivity of detection is somewhat poorer than with hollow-cathode lamps, and the analytical curves are linear only over a restricted range of concentrations. These limitations arise from the fact that the band width of the spectrometer is much larger than the width of the absorption lines. Better results could be obtained with a spectrometer of higher resolving power,

Table 4. Precision of determination of Fe, Mg, and Na in Portland cement by atomic absorption spectrometry with a continuum source.

Element	Fe	Mg	Na
ppm in solution	175	169	18
ave. absorbance	0.0426	0.518	0.0969
std. dev. of absorbance	0.0021	0.016	0.0034
coeff. var. of absorbance (%)	4.9	3.1	3.5
slope of anal. curve (ppm/absorbance unit)	3110	606	202
std. dev. of concentration (ppm)	6.4	9.8	0.69
coeff. var. of concentration (%)	3.7	5.8	3.8

but data equivalent to what can be obtained with hollow-cathode sources would be possible only with an instrument with a band width of hundredths or thousandths of an angstrom.

(M. Margoshes, M. M. Darr, C. Veillon)

E. Plasma Jet Excitation of Solutions of Cast Iron

In the course of analyzing proposed standard reference materials of cast iron, it was necessary to determine zirconium by another analytical method. The powder d-c arc method, for determining the minor elements, had yielded unreliable results for this element. A solution method was desirable despite two immediate and obvious disadvantages.

1. Some cast irons dissolve with great difficulty -- large amounts of carbide residue being present.
2. Zirconium has poor spectral sensitivity and in general, solution methods do not provide high sensitivities.

The sealed-tube procedure of Gordon et al. [9] has been used to dissolve difficultly-soluble materials. The high temperature and pressure which is developed dehydrates most of the silica, facilitating its removal by centrifuging. This convenient silica removal step makes it feasible to use plasma jet excitation since satisfactory atomization of the solution will now occur. Details of the procedure are described below.

One gram of the cast iron sample is weighed into a heavy-walled Pyrex tube. Ten ml conc. HCl and 0.6 ml conc. $HClO_4$ are added and the top of the reaction tube sealed by melting with an oxy-gas torch. The tube and a weighed quantity of solid CO_2 are inserted into a heavy-walled steel tube. A threaded, copper gasketed steel cap seals the open end. The tube is heated for 15 hrs at 300° C developing a pressure of approximately 3500 psi in the glass tube. The CO_2 gas generated provides pressure compensation.

After cooling and opening the tube, the contents are transferred to a centrifuge tube. After centrifuging, the residue is washed with distilled water and the washings added to the centrifugate in a 15-ml volumetric flask. The residue, in a platinum crucible, is treated with HF and a few drops of H_2SO_4. The crucible is heated to vaporize SiF_4 and the resulting sulfates added to the solution and made up to volume.

Synthetic standards were prepared by dissolving high-purity metals to approximate the composition of the cast iron matrix and then incorporating known amounts of the zirconium as a solution. The plasma jet was used to vaporize and excite solutions of samples and synthetics. Analytical curves were prepared from which the zirconium concentration could be determined.

For NBS 1183, the individual determinations were: 0.118%, 0.126% and 0.120%, compared to an average photometric value of 0.125%.

If zirconium silicate is present, it will not be dissolved by this treatment. The procedure would be complicated by a required fusion of the residue.

Determinations of cobalt and titanium in NBS 1175 and NBS 1181 were also made. The results compared to the certificate value are shown in table 5.

Table 5. Results of the determination of Co and Ti in NBS 1175 and 1181

	Percent	
	Co	Ti
NBS 1175	0.120	0.358
	.118	.340
Average	.119	.349
Certified value	.11	.35
NBS 1181	0.0120	0.0419
	.0105	.0414
Average	.0113	.041
Certified value	.012	(.04)

(R. Alvarez)

3. X-RAY SPECTROMETRY

A. Basic Considerations

The application of x-ray spectrometry to chemical analysis is one of the fastest growing areas of instrumental analysis. It is thus necessary to maintain, and further develop, a laboratory equipped and prepared to perform analyses, provide consultation, and undertake research in this important field.

The theory of x-ray generation, absorption, and measurement was developed several decades ago and is well understood. The technological development in this area has, however, been considerable in the last two decades, particularly in the low energy (long wavelength) range, and in the measurement of low intensity levels. Thus, phenomena which were of theoretical interest only, such as line and band shifts as a function of chemical binding energy or the distribution in depth of x-ray emission, have acquired great practical importance. This, in turn, requires the re-measurement of certain related parameters, such as electron back-scatter coefficients, x-ray mass attenuation coefficients, and x-ray fluorescence yields. The development of the theory of quantitative x-ray spectrochemical analysis (x-ray fluorescence and microprobe analysis) has been adversely affected by the lack of reliable data of this kind. Although increasing efforts are made to fill this gap, the work done is still insufficient and poorly coordinated. This laboratory will increase its efforts to experimentally determine, collect, interpolate, and publish data of this nature.

As the physical foundations of x-ray spectrometry are more quantitatively understood, the sources of error in existing methods can be investigated in more detail. Since this branch of spectrometry is based upon the measurement of relative intensities, the problem of choice, evaluation, and use of standard materials must also be critically considered. Efforts in this direction are hoped to produce correction systems for x-ray fluorescence matrix effects which require a smaller number of reference standards, and to achieve some progress in the selection and testing of standard materials for quantitative microprobe analysis.

As in the previous year, analytical capabilities in both x-ray fluorescence and in microprobe analysis were utilized for various problems. It is planned to intensify in the next fiscal year the use of the microprobe for homogeneity studies, particularly of existing NBS standard reference materials. It is desirable to develop for this purpose methods of fast automatic or semiautomatic collection and evaluation of data for many points on the specimen. Several promising approaches to this problem are presently being investigated.

Coincidently with the move to the new facilities at Gaithersburg, the auxiliary services needed for an x-ray spectrochemical laboratory are being expanded. Rooms for the preparation of specimens and for electronics repair and development were installed. It is hoped that by the end of next fiscal year the section will be practically self-sufficient in these auxiliary activities.

B. 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]. The x-ray fluorescence equipment in the Spectrochemical Analysis Section is described in the same reference, with special emphasis being given to modifications which were being made at that time to update the equipment and extend its range of applicability.

In the past year techniques for automatic logging and processing of x-ray data have been under critical study in an effort to reduce the number of manhours required in the manual reduction of x-ray data. This work has been especially important in view of the increased time that would be required for manual computation of x-ray data using the more complex mathematical treatments which recently have been developed.

One of the mathematical treatments that we [10] have successfully applied to resolve matrix interelement intensity interferences is the technique of Lucas-Tooth and Price [11]. In this method the concentration of each element is treated as a function of line intensity plus a summation of intensity contributions from every other element in the matrix. To linearize the function each summation term is multiplied by an empirically determined coefficient. One of the difficulties of this procedure is the large number of standard specimens of known composition which are required; at least N+2 standards are required to form the set of N+2 simultaneous equations needed to empirically determine the linearizing coefficients. N is the number of elements present. One of the goals of our future research effort is to investigate the possibility of a theoretical or semi-theoretical approach to the interelement correction problem which would yield an improved physical model.

1. Modification of Equipment

The Spectrochemical Analysis Section is equipped with a single-channel x-ray fluorescence spectrometer (the Norelco Four Specimen Position 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].

During the past year several modifications to the single-channel spectrometer were completed. A new specimen changer and spectrometer housing were installed to permit the x-ray optics to be operated in vacuo, helium atmosphere, or in air. In the new arrangement alternative or simultaneous use can be made of a gas flow proportional counter and a scintillation detector. Revisions to the electronic read-out unit, which are now complete, include an improved single-channel pulse height analyzer and a fully electronic timer.

At the end of the last fiscal year the multi-channel spectrometer was reprogrammed for the analysis of heavier elements. Checking out these modifications, revising the mounting of the primary slit chamber, and re-aligning the monochromators was complete early in September. During September a test of sensitivity and precision for each of the 18 fixed monochromators and 2 scanning monochromators was completed with the finding that the new monochromators were properly aligned.

2. Computation Techniques in Data Reduction

In recent years improvements in x-ray fluorescence technology and equipment have effected an increase in the speed with which x-ray line intensities can be measured for routine spectrochemical analysis. On the other hand the physical models which have been developed and which are required to make these intensities useful as measures of element concentration have progressed toward increased complexity and thereby slower analysis, so long as manual computation methods are used.

We have written several computer programs to automate certain types of computations, using established physical models and mathematical techniques which we wished to apply to routine analytical problems. A clear distinction must be made here between: (a) the development of new physical models to relate x-ray intensities to element concentration, and (b) the application of existing techniques (with their current inherent limitations) to the automatic computation of element concentrations and associated statistical data. In consideration of the practical analyses we are called upon to make, our early efforts have been directed toward programs which fit into category (b). In the next year we wish to shift the emphasis of our work to a search for improved models for relating x-ray intensities to the composition of a sample.

The computation facilities available to us include an IBM 7094, a CDC 3100, and a remote terminal for a GE-265 time-shared computer system. The GE-265 system and terminal are described in Section 2 of this report.

The GE-265 system has sufficient memory and computation capacity to be useful in many of our analytical problems. It provides easy access to the computer and quick processing of the data; so we have written several programs for use on it. A brief description of four of these programs is given here; full texts and punched paper tape copies of these programs are available.

XRAY 1 is a program for processing data from known analytical standards, when the relationship between x-ray intensity and element concentration is known to be linear. Sets of intensities from repeated measurements on a set of standards are input to the computer. The intensities are averaged for each element and the average is equated to the known concentration. The concentrations for individual runs are computed and then ordinary statistical parameters, including maximum, minimum, standard deviation, and coefficient of variation are computed and printed out. A sample output is shown in table 6.

Table 6. Computer output from XRAY 1 program.

```
XRAY1      16:07    CEIR    06/01/66

ANALYSIS FOR 4 ELEMENTS FOR 4    RUNS ON SPECIMEN 14

ITEM            AG          CU            ZN CH.1         ZN CH.2
-------         -------     -------       -------         -------

PCT              73.6241     1.5002        .1088           .102805
PCT              73.888      1.505         .1344           .096345
PCT              75.0164     1.589         .0768           .092945
PCT              75.4714     1.6058        .08             .107905

STATISTICAL ANALYSIS
----------- --------
AVE PCT          74.5        1.55          .1              .1
STD DEV PCT      .885442     5.51957 E-2   2.70742 E-2     6.67056 E-3
AVE INTEN        3462.25     2822.5        86.5            450.5
STD DEV INTEN    97.3015     45.9964       16.9214         39.2386
PCT COEF VAR     1.18851     3.56101       27.0742         6.67056

MAX PCT          75.4714     1.6058        .1344           .107905
MIN PCT          73.6241     1.5002        .0768           .092945
RANGE PCT        1.8473      .1056         .0576           .01496
```

XRAY 2 is analogous to XRAY 1 with the exception that it is for processing data from unknown specimens. The statistics in this case are computed only for intensities.

STAT is a program which computes analysis of variance and a confidence interval for the lot mean (T test) for any sets of numbers, either concentrations or intensities. These statistics are particularly useful in making decisions about the homogeneity of specimens. A sample output of this program is shown in table 7.

CODFIT is a program similar to CODEBC AND CODEBD, which are described in section 2 of this report; it differs from them primarily in that the format of data input and result output is altered to especially fit x-ray fluorescence spectrochemical analysis. Input data are intensities from

Table 7. Computer output from STAT program.

```
STAT        16:19   CEIR   06/01/66

STATISTICAL ANALYSIS FOR SETS OF 16   RUNS ON 4 ELEMENTS•••

ITEM               SI            AL           FE              TI
----               ----          ----         ----            ----

AVERAGE             43•125        38•4813      •541875         2•09063
MAXIMUM             43•8          39•3         •58             2•25
MINIMUM             42•3          37•6         •48             1•96
RANGE               1•5           1•7          •1              •29

ANALYSIS OF VARIANCE

STD• DEV•           •452415       •547992      3•63719 E-2     8•42592 E-2
95 CONF U LIM       1•44004       1•74426      •115772         •268197
95 CONF L LIM       •234261       •28375       1•88334 E-2     4•36294 E-2
PCT COEF VAR        1•04908       1•42405      6•71224         4•03034

T TEST•••95 PCT• CONFIDENCE
INTERVAL FOR THE LOT MEAN•

AVERAGE             43•125        38•4813      •541875         2•09063
95 CONF U LIM       43•4967       38•9315      •571758         2•15985
95 CONF L LIM       42•7533       38•031       •511992         2•0214
```

standards and unknowns. The assumption of XRAY 1 that concentration is a linear function of intensity is not required in CODFIT. Instead, a least-squares fit to a polynomial equation of degree less than 12 is made for the average intensities for each standard. The analyst selects the proper degree equation on the basis of fitting data which is presented by the computer. Then the program computes the concentration of each unknown by solving the equation with the intensity of the unknown.

3. Examples of Applications

X-ray fluorescence spectrometry has been applied to make more than 8000 quantitative determinations in the past year. A wide variety of materials have been analyzed including dental gold alloys, dental silver alloys, tungsten on rhodium mirrors, selenium in steel, tin-bismuth binaries, and refractory clay specimens.

In the analysis of 300 dental gold alloy specimens the previously mentioned mathematical technique of Lucas-Tooth and Price was applied, yielding linear and singular calibration curves. An earlier test of this technique for the dental gold system had been made by Eick, Caul, Smith, and Rasberry with a similar finding [10].

The analysis of 32 clay specimens provided experience in another form of matrix correction; here the particle structure was reduced by subjecting the samples to a fusion with $Li_2B_4O_7$ at 2200°F, following the fusion technique outlined by Rose, Adler, and Flanagan [12]. In this technique the interelement effects are reduced by physical dilution of the specimen to the point of having a light element matrix.

Last year, a preliminary study of nickel plating thickness measurement by x-ray fluorescence was performed using a single-channel spectrometer [1, p 45]. During this year the study was successfully concluded and satisfactory thickness calibration curves were prepared.

(S. D. Rasberry)

4. ELECTRON PROBE MICROANALYSIS

A. Instrumental Developments

The development and installation of modifications and equipment accessory to the Applied Research Laboratories EMX electron probe microanalyzer was continued in the past year. Some of these accessories will now be described in detail.

1. X-ray Spectrometer for Long Wavelengths

A spectrometer for the detection of x-rays of wavelength up to 90 angstroms was purchased from and installed by the manufacturer. Each spectrometer now carries two crystals which can be exchanged from outside the vacuum chamber. The present arrangement of crystals and detectors, which is thought to be very satisfactory, is shown in table 8.

The long wavelength spectrometer not only adds to the capabilities of the instrument the detection of elements of atomic numbers 5-11; it also permits the use of emission lines of long wavelength emitted by elements of higher atomic numbers. These lines can be used to advantage when high resolution in depth is required, or when studies of wavelength shifts or changes of band shapes are performed.

2. Detector Slits of Variable Width

Detector slits of externally adjustable width were installed in the spectrometers I and II. Although the characteristics of this slit device have not been systematically investigated as yet, its use to increase line resolution was demonstrated in one practical case of line interference.

3. Solid State Target Current Preamplifier

A solid state operational amplifier (figure 9) was installed to permit an initial amplification of the target

Table 8. Spectrometer characteristics of the electron probe microanalyzer.

Spectrometer:	I	II	III	Non-dispersive
Crystals and wavelength ranges:	LiF(1-3.75Å) ADP(2.65-10Å)	LiF(1-3.75Å) EDDT(2.2-8.2Å)	KAP(7.9-24.8Å) Pb-stearate (29.9-93.4Å)	--- 1.5 - 13Å
Detector:	Ar sealed	Ar sealed	Ar flow	Ne sealed
Externally adjustable slits:	yes	yes	no	no
Main range of atomic numbers	19-35,(K)	22-35,(K)	8-13,(K)	> 11
	50-88,(L)	50-88,(L)	5-8, (K)	
	12-22,(K)	13-23,(K)		
	34-56,(L)	35-58,(L)		
	78-92,(M)	78-92,(M)		

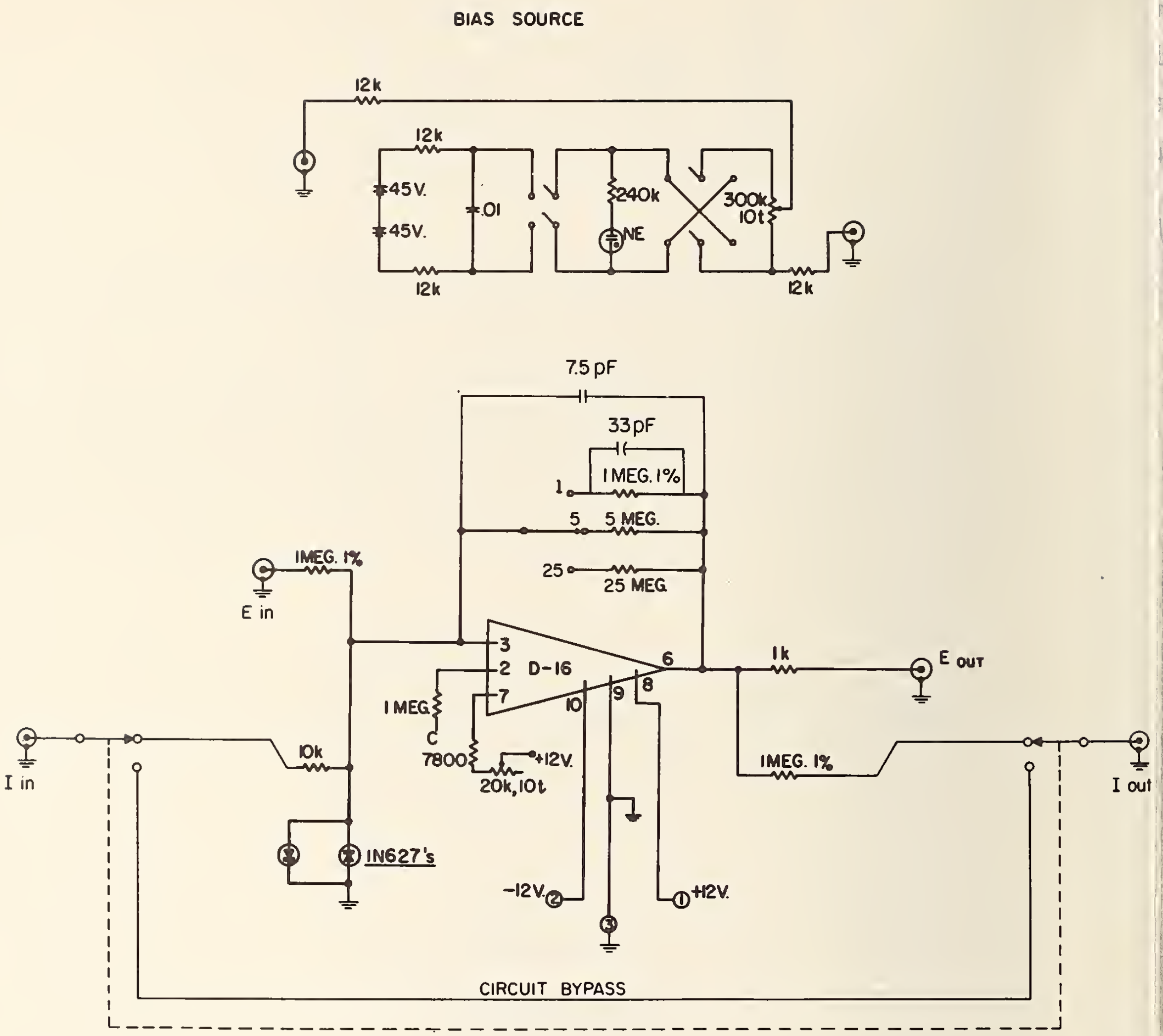

Figure 9. Target current preamplifier with selectable gain, and dual-polarity specimen-biasing battery.

current by factors of 5 and 25. The device contains two floating batteries which can be used to bias specimens positively or negatively [13]; it can be by-passed if so desired. The main purpose of this device is to achieve stronger contrast in target current scanning images, as illustrated in figure 10. For this purpose the bias range of the ARL d-c amplifiers was enlarged. Images obtained by using the target current amplified with this device exhibit a contrast superior to that of conventional backscatter detectors, for both atomic number differences and topographic features of the specimen surface.

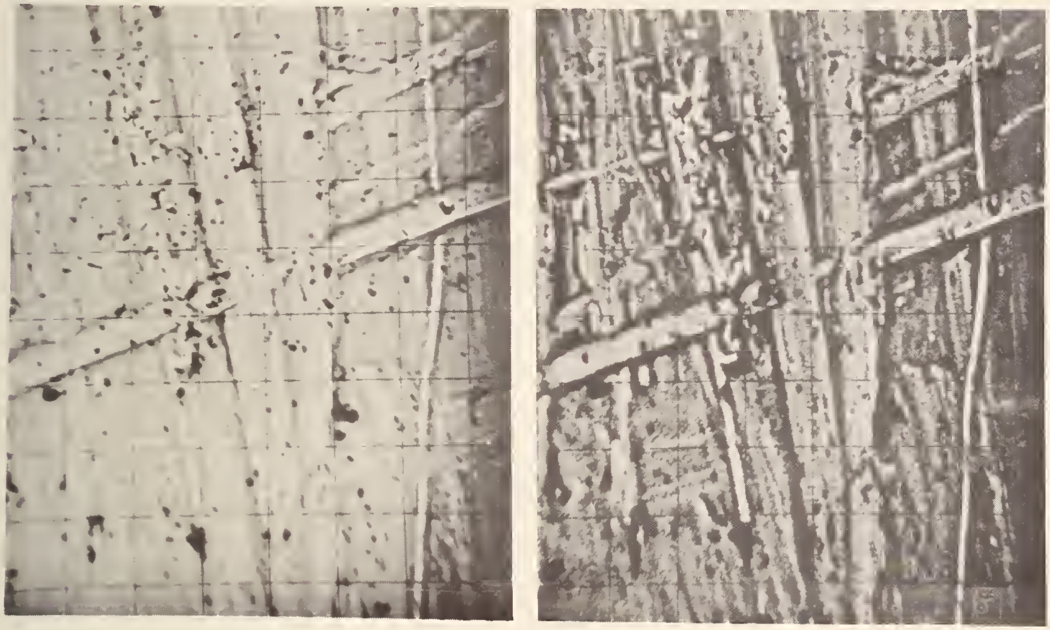

Figure 10. Aluminum surface with scratches, 30 keV, 5×10^{-8} amps., 300μ x 380μ. Target current images formed without (left) and with (right) target current preamplifier.

4. Solid State Concentration Mapping Device

The use of this type of device has been described previously [14, 15] (figure 11). The concentration mapper is a d-c amplifier the output voltage of which varies

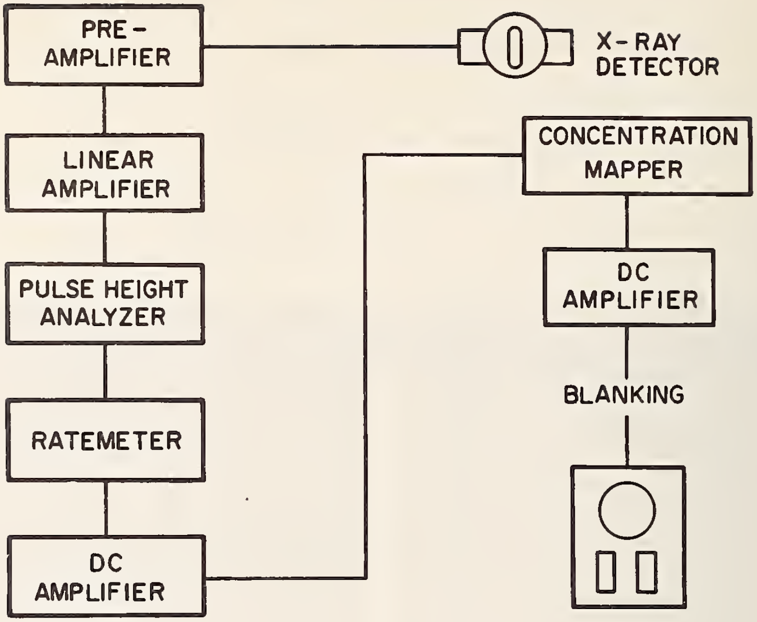

Figure 11. Interconnecting system for the use of the concentration mapper with x-ray signals.

discontinuously as a function of input voltage. The range of the input signal is divided into a limited number of adjustable input zones. Within each zone, the output is constant, stepping to a different level when the input signal crosses the limit between zones. This output is used, through a d-c amplifier, to modulate the brightness of a scanning image. Specimen areas corresponding to an input signal within one zone appear in uniform brightness on the image. The output of an x-ray pulse ratemeter is usually connected to the input of the concentration mapping device, so that each brightness level of the image corresponds to a range of x-ray signal intensity. If a unique calibration curve of intensity vs. concentration of the emitting element can be established, the zone limits can be set to represent chosen concentration levels of this element. X-ray concentration maps are thus obtained. Similar mapping operations can be performed using the amplified target current as an input signal. Such techniques are useful to map the abundance and distribution of a phase within a multi-phase specimen; and these maps can be evaluated using the methods of quantitative metallography.

A simple solid state device capable of mapping four ranges simultaneously was constructed at NBS by Mr. L. Marzetta, NBS Electrical Shops. The level triggering characteristics are indicated in figure 12. The circuit is shown in figure 13. The output voltage (vertical) as a function of input (horizontal) is shown schematically, for

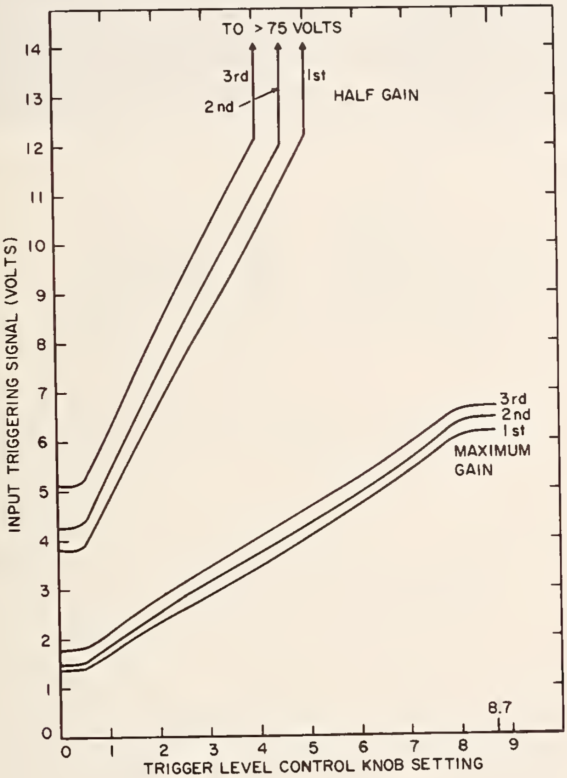

Figure 12. Calibration curves for level control of the concentration mapper.

the two operating modes available, in the upper right corner of figure 13. The subtract mode is used to emphasize

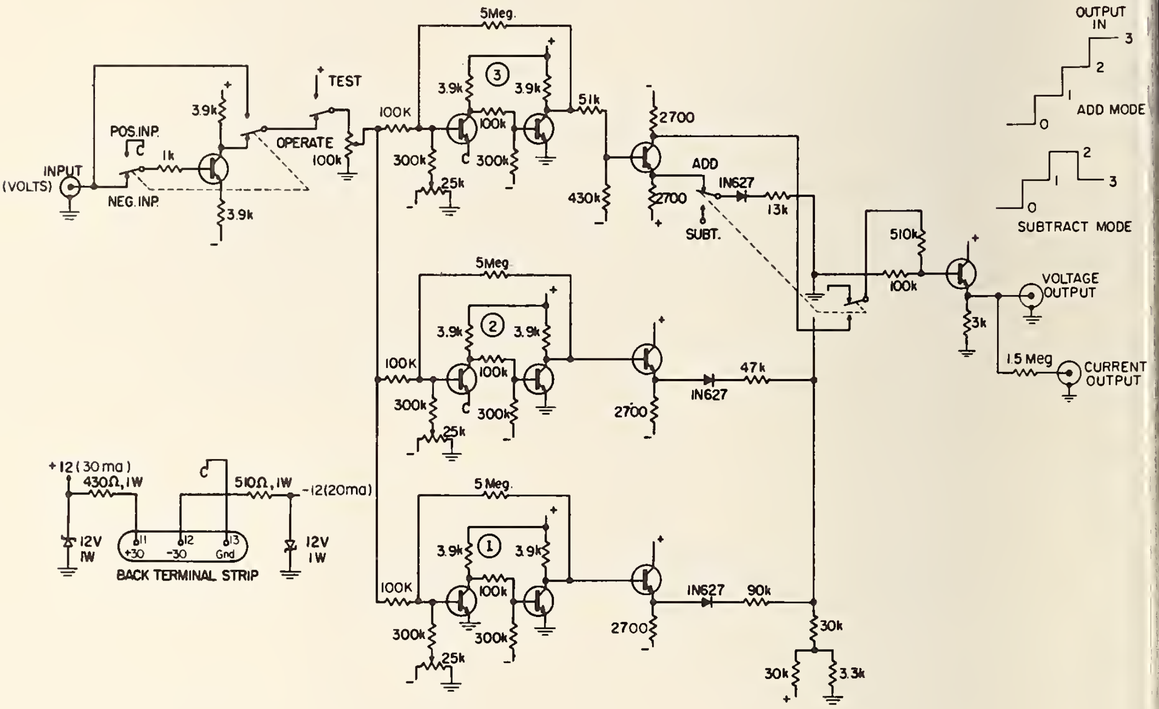

Figure 13. Four-level solid state concentration mapper.

a phase of intermediate input level, which can be shown black or white (depending upon the polarity of the second d-c amplifier) on the resulting concentration map.

Concentration maps obtained with this instrument in the "add" mode are reproduced in figure 14.

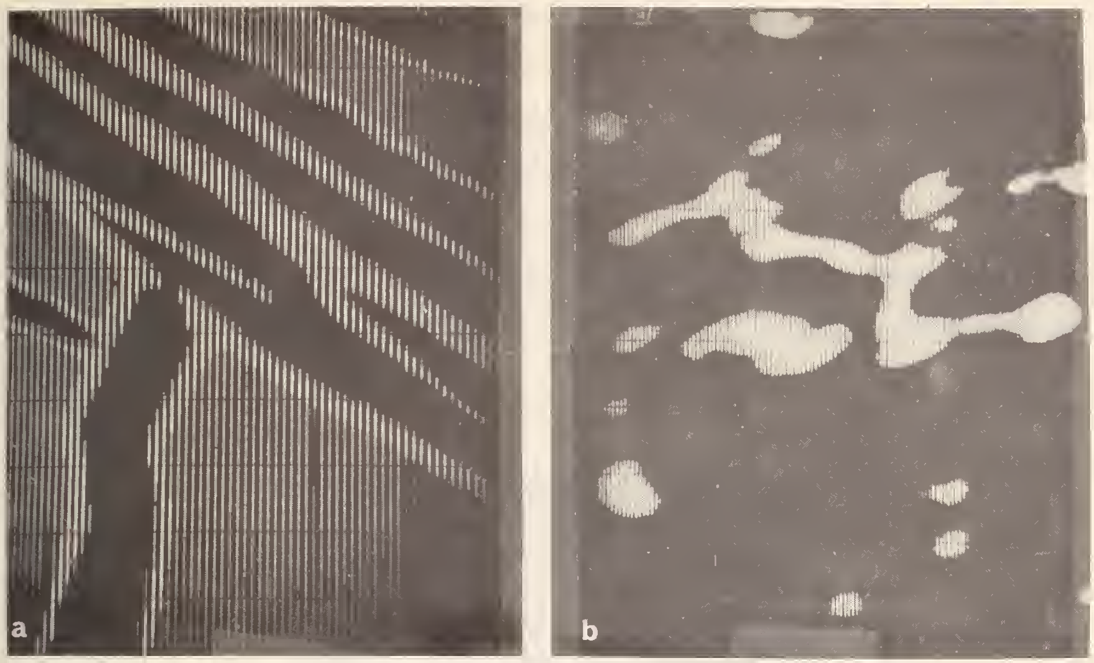

Figure 14. Concentration maps. (a) X-ray concentration map of Ni in Tazewell meteorite. 20 keV, .15 x 10^{-8} Amps. 240μ x 300μ. (b) Target current concentration map, lead inclusions in brass, 20 keV, .05 x 10^{-8} Amps. 40μ x 50μ.

5. Pulse Height Analyzer Monitor

Monitoring on an oscilloscope of the pulses produced by a proportional x-ray detector is current practice in x-ray spectrometry. It is advantageous to display simultaneously the range of acceptance of the single channel pulse height analyzer normally used with proportional detector equipment. This can be done very simply by implementing the conventional pulse display with a modulation of the brightness of the oscilloscope by the output of the pulse height analyzer. Using a delay line the analyzer is made to mark an appropriate sector of the displayed pulses. The position of the accepted pulse height range is marked as a black sector. Pulses not accepted by the pulse height analyzer are shown as uninterrupted traces. The monitoring of the pulse height setting is particularly advantageous when x-ray wavelength scans are performed, since the mean pulse height varies progressively with the wavelength setting.

The arrangement used in our laboratory is shown in figure 15. The instrumental components are as follows:

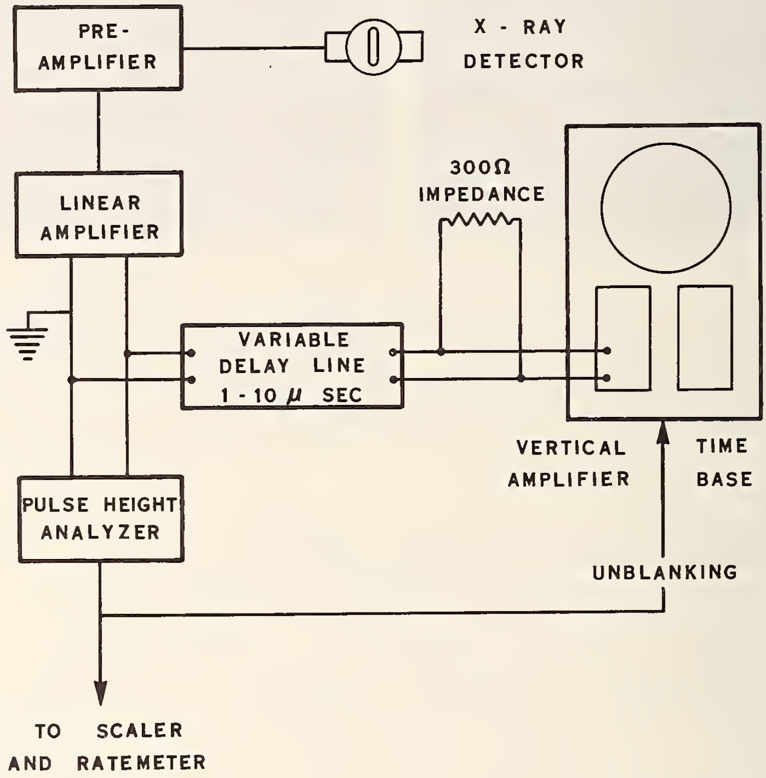

Figure 15. Pulse height monitoring by use of a variable delay line and oscilloscope blanking.

Detectors: Applied Research Laboratories proportional detectors, as specified in Table 8.

Preamplifiers: Applied Research Laboratories preamplifiers.

Linear Amplifier and Pulse Height Analyzer: Hamner Model Nr. N-302

Oscilloscope: 564 Tektronix storage oscilloscope, used with the memory device inactive. Vertical amplifier 3A6, time base 3B4.

Figures 16 to 18 illustrate the effects of different pulse height analyzer settings on the unblanking patterns on the monitor scope.

Figure 16. Oscilloscope representation of the amplified pulse output of a gas proportional detector. The pulse height region accepted by the pulse height analyzer, operating in differential mode with a narrow window, is represented by the black wedge.

Figure 17. Representation of the distribution shown in figure 16, with the pulse height analyzer in integral mode. Pulses falling below the base line of the analyzer are represented by uninterrupted traces.

Figure 18. Same pulse height distribution as in figure 17. The base line setting of the pulse height analyzer is lowered, so that all pulses are accepted.

6. Multi-channel Pulse Height Analyzer

A Victoreen SCIPP 1600 channel pulse height analyzer was purchased and installed this fiscal year (figure 19).

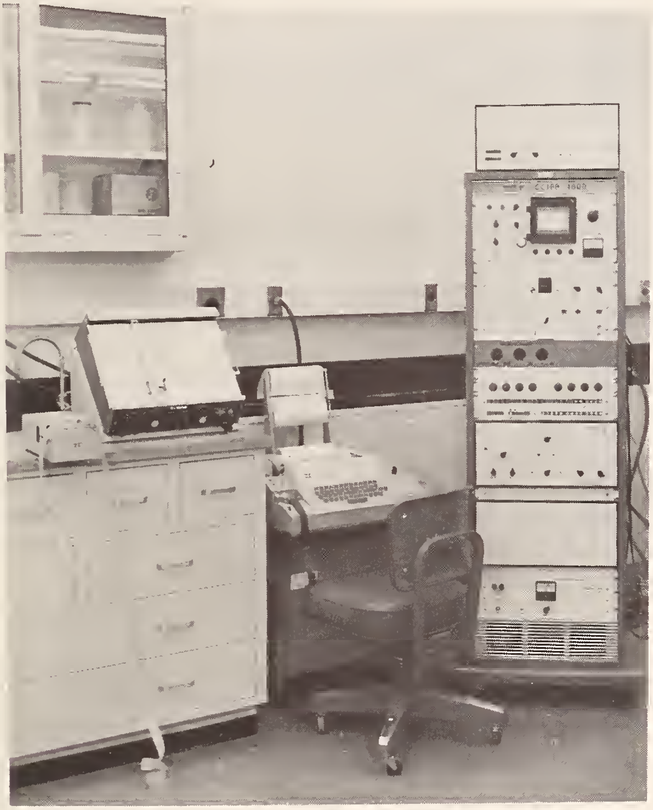

Figure 19. SCIPP 1600-channel pulse height analyzer and associated read-out equipment.

This instrument contains the following basic sections:

a. An analog-to-digital converter which sorts incoming pulses according to their height into a number of channels up to 1600.

b. A magnetic core memory containing 1600 "slots" for storage of digital information. Each slot can store the number of pulses assigned to the corresponding channel by the analog-to-digital converter. Digital information generated by sources other than the converter can also be stored. The capacity of each slot is 10^6-1 pulses.

c. A timer which can be used to switch slots when externally generated pulses are fed into the memory.

d. Devices for transfer of information from one part to another of the memory; for division by powers of 10; addition, subtraction, and erasure of partial or total memory contents.

e. Read-out devices for display of the memory contents on an oscilloscope screen or on a digital scaler, for their recording by means of an X-Y recorder, print-out by a Teletype unit, or punching of a paper tape.

f. A tape reader for transferring digital information from punched paper tape into the memory of the SCIPP.

In connection with the electron probe microanalyzer, this unit has been used in two ways:

a. To analyze, store, and display the energy distribution of pulses generated by proportional detectors.

b. To direct the beam of the analyzer to scan in a grid array over the specimen surface, and to store in succesive slots the number of x-ray signal pulses generated at each spot of the grid (figures 20 and 21).

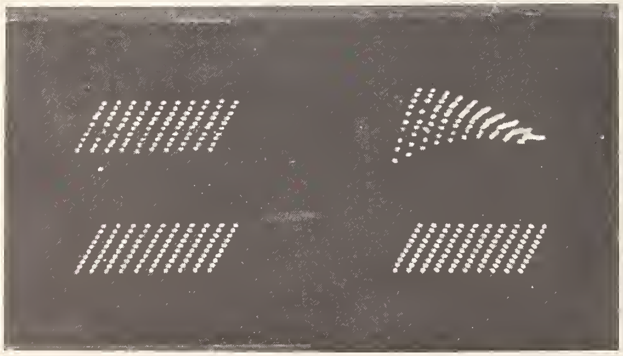

Figure 20. Oscilloscope representation of counts accumulated in two grid scans over an area of 400μ x 400μ. Left: SiKα non-dispersive. Right: SiKα dispersive

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02117 102115 101831 102126 101124 102530 101816 102556 102764 102174
02115 101999 102103 102526 102036 102379 102319 102736 102329 102270
102508 102439 100937 102187 102322 102443 102129 103046 102761 102947
102650 078020 101825 102662 102241 102196 102718 102703 102518 102252
101831 101167 102340 102547 102366 102331 102834 103344 103035 102061
102385 102375 101782 102758 103171 102748 102727 102730 102302 102876
103607 102953 102168 102742 102482 102203 102676 102758 103012 102792
102765 102601 102647 102903 102701 102286 102745 102600 102762 102931
102696 102651 102808 102480 102604 102244 102048 102989 103207 103153
102373 102954 103107 102251 102697 102856 102668 103206 103676 102807
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094284 098539 103568 107038 109170 110896 111801 111433 109625 108160
098813 102339 105687 108304 110750 111873 111557 109634 108285 104288
101954 105991 108330 110090 111972 111265 110965 107946 106794 103555
105641 107199 109732 111846 111917 111326 109218 107137 104060 101064
107280 107776 111291 112450 111889 110154 108062 103661 100626 097027
109632 111236 112343 111666 110311 108580 104514 101418 097423 093459
110817 094976 110887 111209 108367 106194 102592 097966 094162 089300
111650 111787 111352 109403 107401 104149 100184 095021 089841 085550
111868 111232 110437 108561 105191 100826 096394 091295 086146 081395
111894 111426 109420 106272 103378 098560 093780 088802 083378 078169
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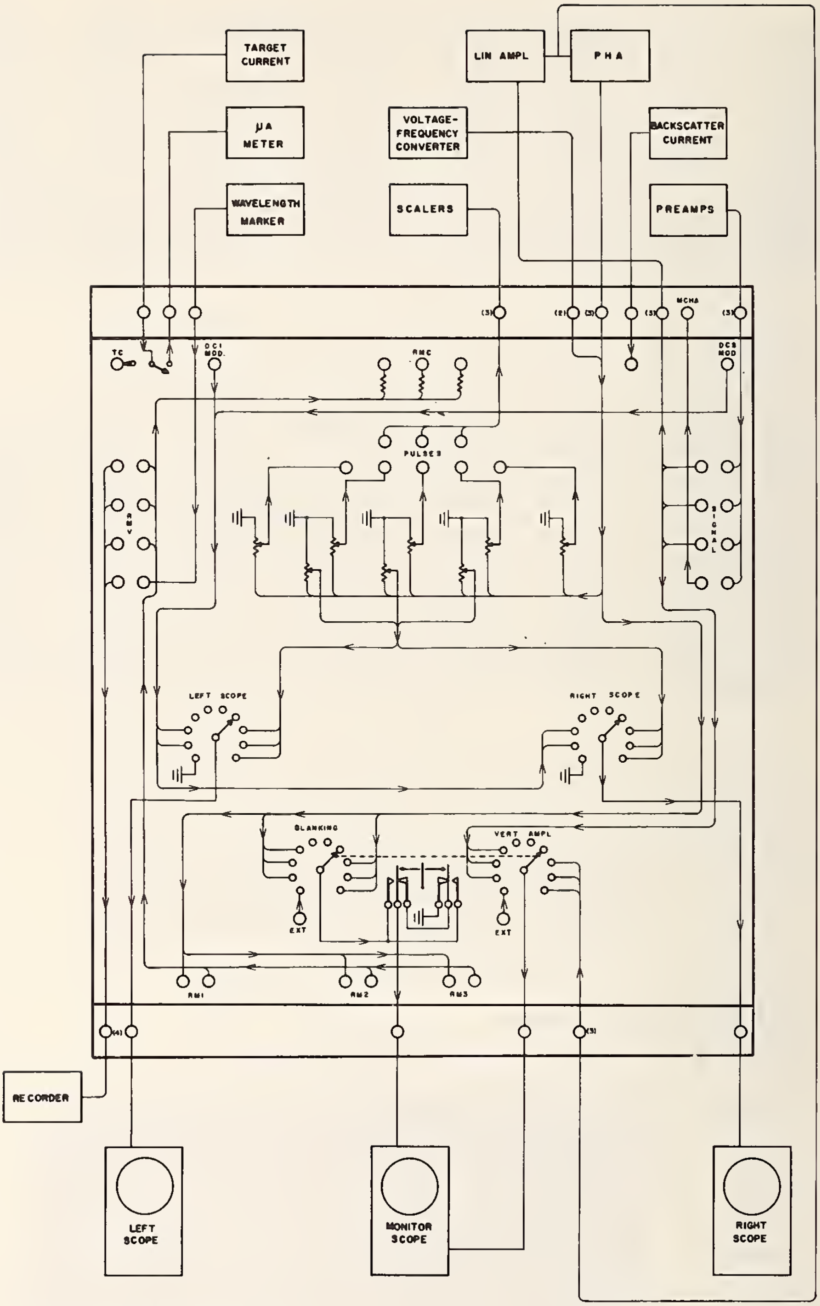
Figure 21. Print-out of grid scans as on figure 20. Silicon dispersive (top); Silicon non-dispersive (bottom).

7. Other Additions

Further additions to the equipment include a second voltage-to-frequency converter [1, p. 51] a wavelength marker for stripchart recordings, an automatic gate valve which isolates the diffusion pump in case of vacuum failure, and a new switch board panel which permits selecting among the diverse operating modes of the instrument (figure 22).

8. Plans for Future Additions

Plans for further instrumental developments include the following:



NOTES: ( ) INDICATES NUMBER OF BNC CONNECTORS.
ALL VARIABLE RESISTORS ARE 5K OHMS.
ALL FIXED RESISTORS ARE 1 MEG OHM.

Figure 22. Readout distribution system including wiring diagram of the main control panel.

a. Interfacing of components for increased flexibility of operation, and simpler transfer of the data output to the time shared computer used by the Section.

b. Use of a color oscilloscope read-out for simultaneous recording of several signal channels in line and area scans.

c. Installing a second non-dispersive x-ray detector of different efficiency characteristics.

d. The purchase of a double pulse generator for instrumental service and development.

e. The purchase of a vacuum evaporator for the metallizing and carbon coating of microprobe specimens.

We include here a schematic drawing of the cathodoluminescence detector (figure 23) mentioned in a previous report [1, p 50].

Mr. G. Wolfson is in charge of the electronic maintenance of the x-ray equipment and he has been active in most of the aforementioned modifications and additions to the microprobe electronics.

B. Research Activities

The research activities concerning microprobe analysis were mainly directed towards the following objectives: study of sources of error in quantitative analysis, exploratory study of non-dispersive x-ray detection, area scanning techniques, and literature research.

1. Techniques of Measurement

X-ray intensity measurements with the microprobe can be affected by several sources of error; the technical difficulties have been underestimated even by experienced operators. It was therefore deemed necessary to investigate the effects of spectrometer alignment, of defocusing of x-ray optics, of poor electrical conductivity of the specimen, and

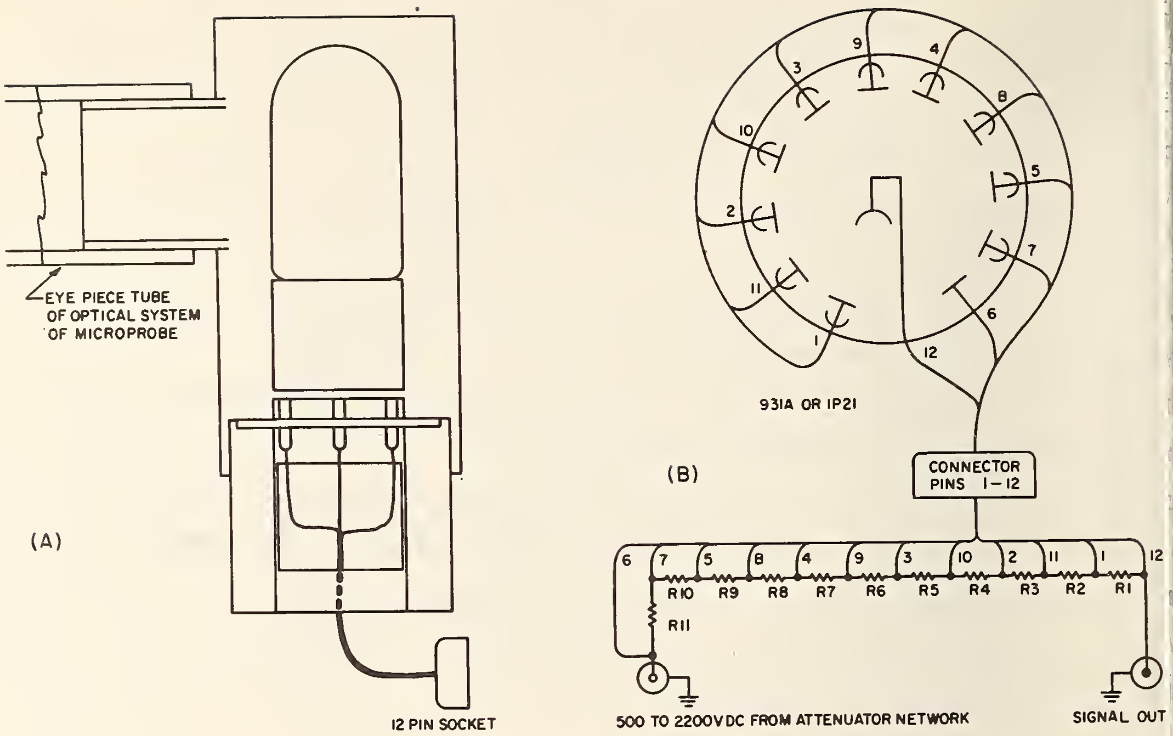


Figure 23. Cathodoluminescence detector (A) Physical layout of photomultiplier tube for cathodoluminescence. (B) Wiring diagram of photomultiplier tube connected to external voltage divider network. (R1 = 200 kohms, 1/2 W, 1%; R2 thru R11 = 100 kohms, 1/2 W, 1%).

of similar factors of disturbance. The discussion within the Washington Probe Users Group of such sources of error has been most helpful. A source of concern was the experimental determination of coincidence losses in the x-ray detector systems. The conventional techniques using double sources or multiple absorbers cannot be employed for instruments in which the x-ray spectrometers are enclosed in the vacuum chamber. Two techniques for the determination of coincidence losses in such instruments were developed in cooperation with H. Yakowitz and D. Vieth, [16], Metallurgy Division, NBS. These techniques are based upon the simultaneous measurement of intensities from two spectrometers, or from one spectrometer and target or monitor current.

2. Parameters Employed in Correction Calculations

Experimental data on x-ray mass attenuation coefficients reported recently by G. O. Hughes and J. B. Woodhouse [17] showed good agreement with previous predictions, on the basis of interpolation, by Heinrich [18]. However, in many areas further experimental data are sorely needed, particularly in the long wavelength region. Therefore, this laboratory has started action to collect experimental data, to encourage cooperative effort among laboratories [19], and to prepare for a revision of the tables issued previously [18], including new experimental data, using improved interpolation procedures, and extending the range of wavelength. If more personnel becomes available, this should be complemented by experimental measurement of mass attenuation coefficients in selected regions of absorbers and wavelengths. It is not expected that this work will produce a tabulation during the next fiscal year.

Studies of the factors contributing to target current formation, initiated at a previous location [13], were brought to a conclusion and reported at the Fourth International Conference on X-ray Optics and Microanalysis, Orsay (France) [20] September 1965. It was shown that the measurement of electron backscattering coefficients with the aid of the electron probe is feasible if the measurements are corrected for the effects of low energy electrons. The back-scatter coefficients of 23 elements were measured at 10, 20, 30, 40, and 49 keV. Data presented at the same conference by Bishop [21] are in good agreement with those obtained at NBS (figures 24, 25). Reasonable agreement exists also with data found recently by two other authors [22, 23].

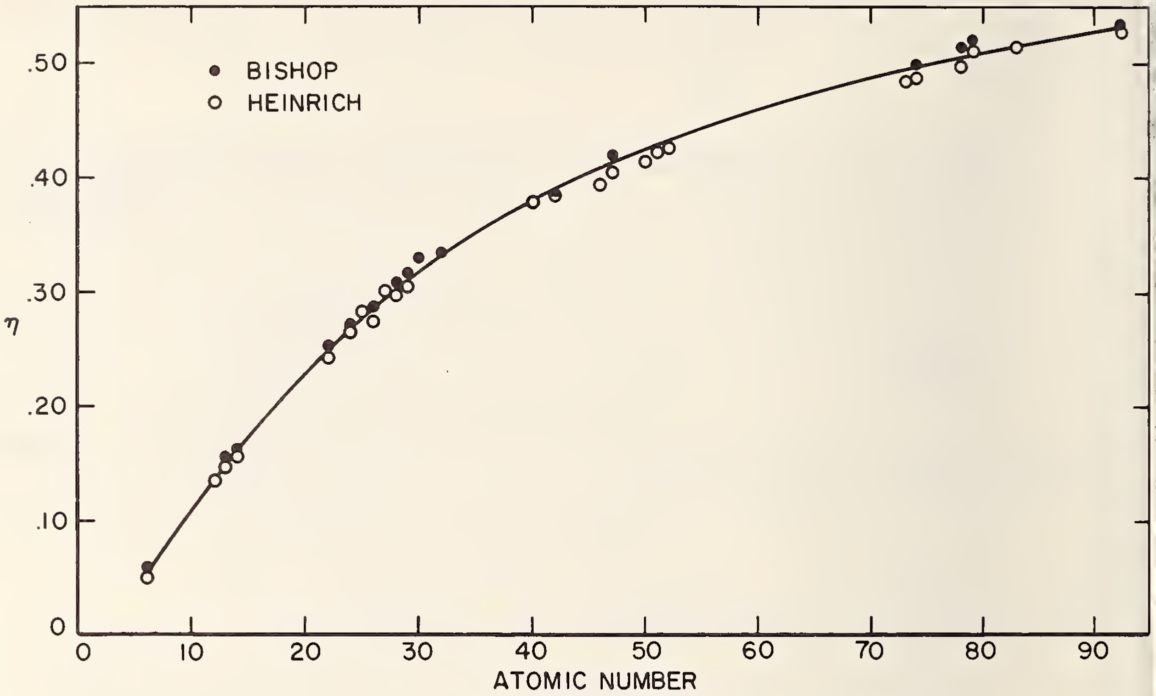


Figure 24. Electron backscattering coefficients obtained by Heinrich [20] and by Bishop [21].

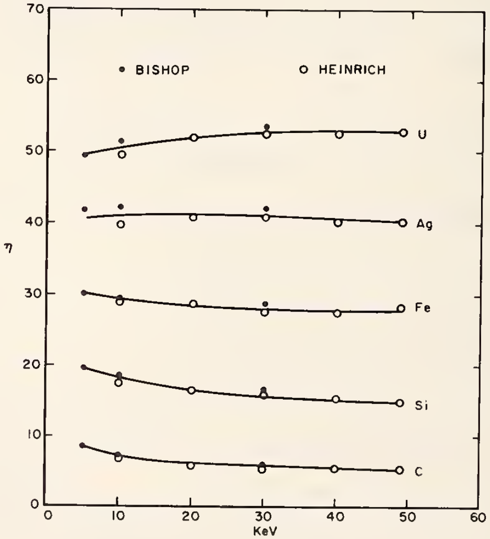


Figure 25. Variation of electron backscattering coefficients as a function of electron energy.

Consequently, the backscatter coefficients within the energy range of microprobe analysis can now be considered well known. It would be of great interest to proceed to measure the energy distribution of back-scattered electrons in an instrument such as used at the Cavendish Laboratory, in Cambridge, England by Green [24] and by Bishop [21].

The errors in the calculation of the absorption correction were investigated in cooperation with H. Yakowitz, Metallurgy Div., NBS [25]. Such errors arise due to errors in the input data used in the calculation (mass attenuation coefficients, x-ray emergence angles, and electron accelerating voltages) and to the imperfection of the models of the function f (χ) used in the calculation. The results of this investigation can be summarized as follows:

a. Experimental data concerning the absorption losses of radiation emergent from the target show mutual agreement where measurements by more than one author are available. However, the quantity of available experimental data is insufficient.

b. Of the generalized models tested, that proposed by Philibert and modified by Duncumb and Shields [26] is the most satisfactory. None of the models, however, is free of significant systematic errors.

c. The extent to which errors in input data can affect the absorption correction has not been fully recognized in the past. It is improbable that significant improvement of the accuracy of quantitative microprobe analysis will be achieved -- particularly at longer wavelengths -- until our knowledge of data such as the mass attenuation coefficients is significantly increased. This is particularly true when low x-ray emergence angles are used. Some effects that have been attributed to the "atomic number effect" can be explained entirely by uncertainty in the absorption correction.

3. Non-dispersive Analysis

The use of the non-dispersive detector in microprobe analysis has been demonstrated by Dolby [27] and by Birks [28]. Its application in combination with multichannel pulse height analysis is particularly attractive. As a starting point, a neon filled proportional detector was employed. This yields very simple spectra due to the absence of significant escape peaks. Shifts by one unit of atomic number produce appreciable changes in the spectra (figure 26).

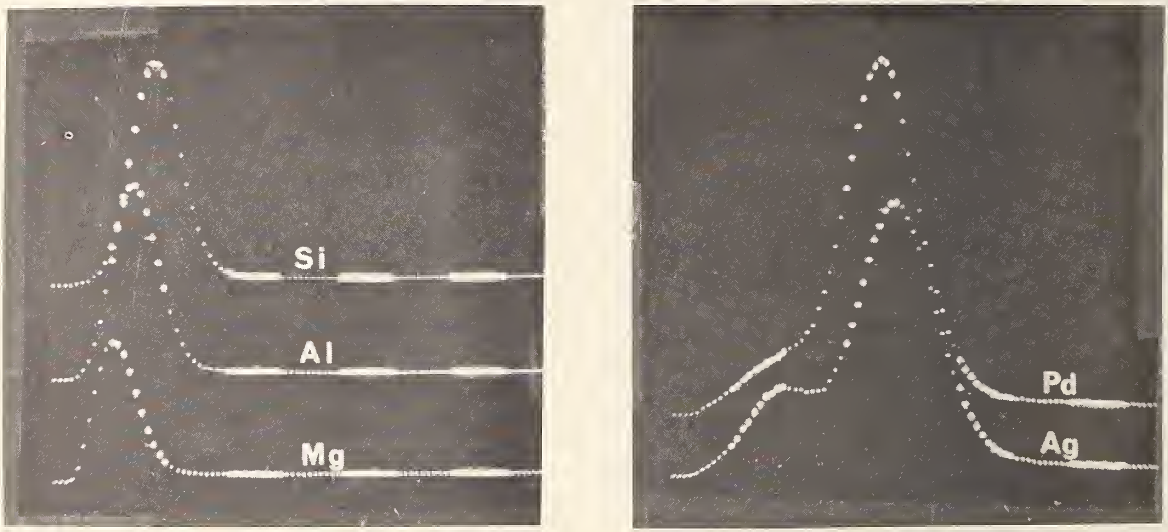


Figure 26. Pulse-height spectra obtained with a sealed neon-proportional detector.

However, the sensitivity of this detector for radiation of wavelength shorter than 2Å is very low. Further studies with detectors covering a wider wavelength range are planned.

One obvious application of such detector systems is the rapid qualitative comparison of different points on a specimen. This technique should also be useful for electron beam scanning procedures where the defocusing effect of curved cyrstal spectrometers is objectionable.

4. Progress in Scanning Techniques

A study of the limits of quantitative evaluation of electron beam area scans has been started. It greatly expedites the analysis of specimens requiring measurements at many points, if the speed of the area scanning technique can be combined with a quantitative evaluation of the signal received, as proposed in the concentration mapping [14, 15] method. A similar procedure is the aforementioned grid step-wise scan of the beam with storage in the memory of the multichannel analyzer of the counts obtained at each point (figure 18). The accuracy of these procedures is limited by the statistics of random pulse arrival, by defocusing of the x-ray optics, and by difficulties of calibration of systems containing more than two components. While a general solution of the problem might be difficult to obtain, there are possibilities of applications under restrictive conditions.

The limitations of the general case are presently under investigation. Special techniques designed to overcome some of these limitations will be investigated soon.

5. Literature Research

An index of literature on x-ray spectrometry and electron probe microanalysis, issued privately for several years, has been published in the Proceedings of the Microprobe Symposium held in Washington, in October 1964, by the Electrochemical Society [29]. Material for a supplement to this bibliography, to be issued by the NBS in the next fiscal year, is being collected and indexed. This task, as well as a great part of the recent experimental work, was performed by Mrs. M. A. Morris Giles.

(K.F.J. Heinrich)

5. SPARK SOURCE MASS SPECTROMETRY

The spark source mass spectrograph is established as a tool for the analysis of solids for elements present at the parts-per-billion (ppb) level. Without standards, semi-quantitative analyses good to within a factor of three can usually be obtained; with analytical standards accuracies as good as ± 20% are obtainable. The only major inherent interferences of the instrument are from the gases in the source (C, O_2, N_2, CO, etc.) at about 1 to 10 ppm. However, it should be possible to lower the pressure of these gases by use of special source pumping and sample treatment. The interferences that are associated with the sample itself are caused by multiply charged ions of the matrix material obscuring lower mass elements. Most of the high purity metals examined by the spark source mass spectrograph have also been examined by the optical emission spectrograph. Since the two techniques do not normally have the same interferences, the emission spectrograph can often supply results for the elements which have interferences on the spark source mass spectrograph. Between the two methods a complete analysis can be obtained for almost all samples.

Work with the spark source mass spectrograph during the period covered by this report included an extensive investigation in the area of data computations, the analysis of a number of high purity metals, and instrument modifications aimed toward increasing detection sensitivities. A recent progress report of our group [2] contains detailed equipment descriptions of the equipment modifications made up to this year.

A. Electronic Analog Computer for Measuring Intensity-Areas of Peaks

The need to correct for variations in peak widths on mass spectrographic plates is a generally recognized problem

[30, 31]. Basically the information needed is the total number of ions which produce a given mass line. Due to variations in line widths and shapes between the matrix lines and impurity lines, plus variations of these across the photographic plate, the maximum peak intensities are not a valid measure of the number of ions producing the different peaks. In addition to line width variations with mass there will be changes upon repairing and refocussing of an instrument, and there will certainly be differences in line widths between two instruments. Because of these variations in widths, maximum peak intensity measurements cannot be used to undertake any long term study of elemental sensitivity factors in various matrices or to compare these data among laboratories. The intensity-area of a peak is a valid measure of the number of ions causing a line and would be unaffected by variations in both line width and shape.

An intensity-peak area can be measured in several ways: peak width at one-half intensity multiplied by maximum intensity, a point by point replotting of the percent transmittance (%T) peak as an intensity peak followed by graphical integration, collection of many %T values for each peak combined with the digital computer computation of peak area, or the use of an analog computer system. Based upon consideration of speed, accuracy, and cost, the analog computer system was selected. A commercial instrument using an analog system is available. However, we were unable to determine if it would perform exactly as required by our needs. It was therefore decided to build an analog computer to our own specifications. Basically the unit is simple; a slave slide wire on the microphotometer recorder to retransmit the % absorption signal, a function generator with an input of % absorption and an output of intensity, a means of subtracting the plate background signal after it has been converted to intensity, and an integrator to measure the area of the intensity peak. The detailed wiring diagram of the finished equipment is shown in figures 27 and 28.

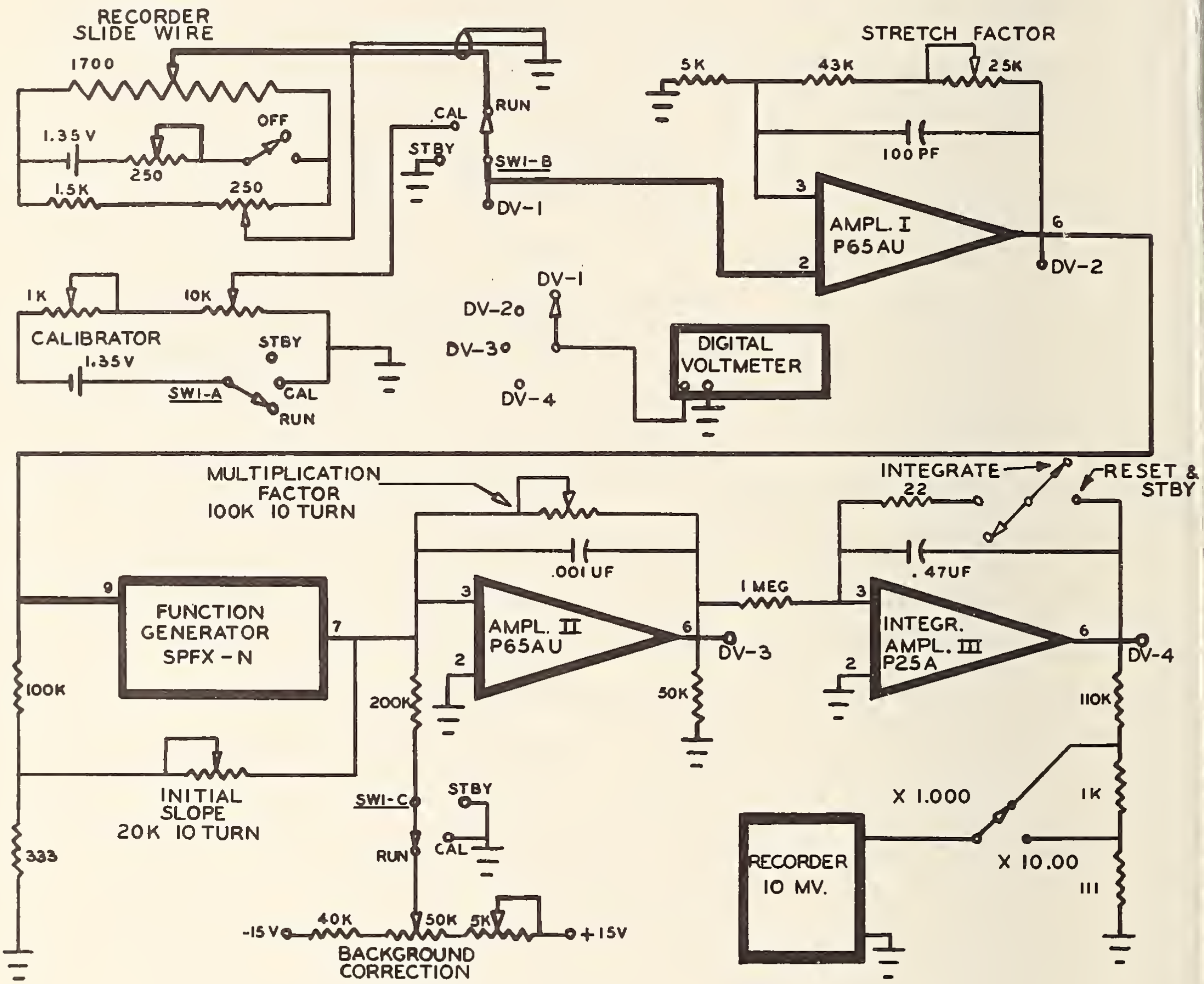


Figure 27. Wiring diagram for analog computer.

The most critical component of the system is the fucntion generator which must electronically reproduce the response curve of the photographic plate.

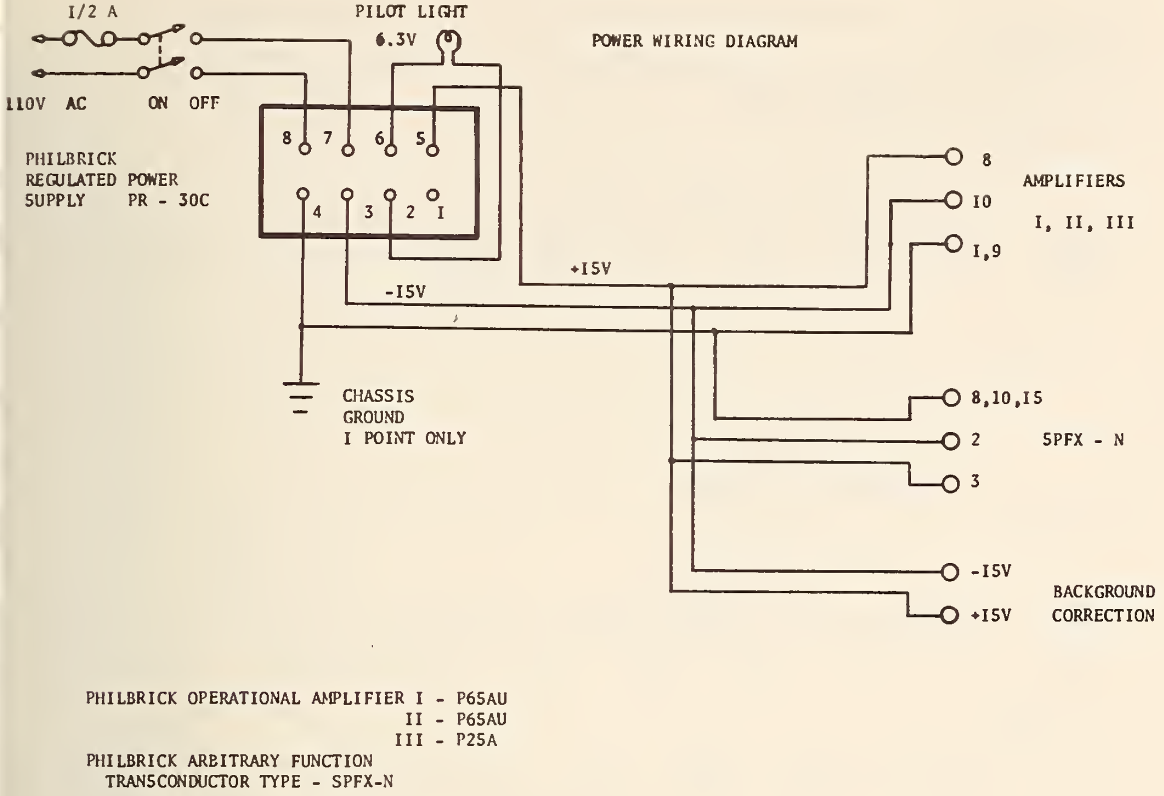


Figure 28. Power supply wiring for analog computer.

We were able to obtain the loan of a prototype transistorized function generator from Philbrick Researches, Inc. This unit is considerably simpler and more amenable to our specific requirements than the older tube-type function generators previously available.

Figure 29 illustrates the ability of the function generator to reproduce the desired photographic plate response curve. The error in the output of the function generator is plotted vs the % absorption input. The upper curve is the original curve with the triangular points being the set points used to introduce the curve into the function generator.

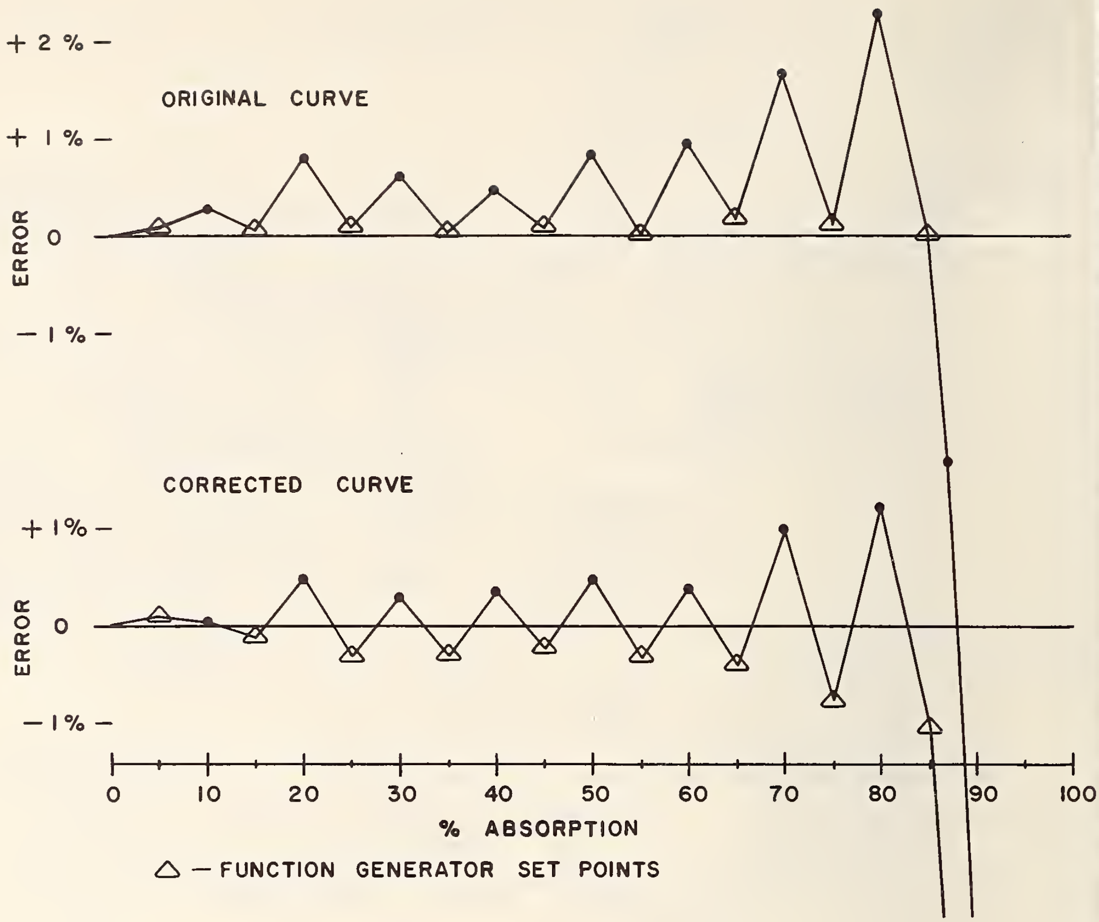


Figure 29. Error in the output of the function generator versus the % absorption input.

A positive bias was thus introduced which gave an average bias of +1% at 80% absorption. The set points were re-adjusted low by one-half the error found previously to give the lower graph. This plot shows no net bias, with errors less than 1% at any input. At approximately 87% absorption the function generator is no longer capable of reproducing the function as is indicated by the upper graph.

Area measurements were made on the isotopes of tin from a "six nines" pure sample. The results are shown in figure 30. There is a linear relationship between the area measured and the abundance of the tin isotope. In general, the deviations from the straight line response corresponded to less than a 5% error. The areas were measured from peaks ranging from 6 to 80% absorption.

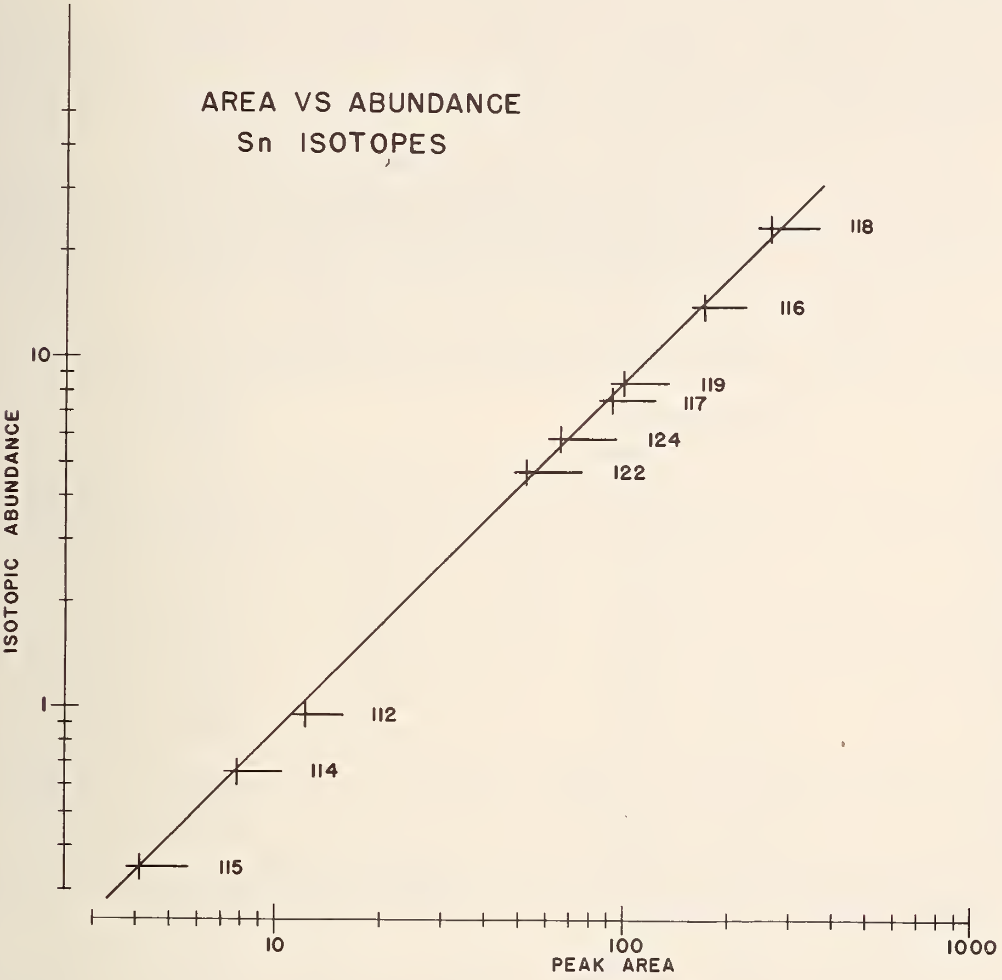


Figure 30. Area measured for isotopes of tin versus their isotopic abundance.

In order to prove the ability of area measurements to compensate for changes in peak widths, the instrument was deliberately defocused to change the widths. Fourteen equal exposures were made on a doped platinum sample, seven with the instrument focused, seven with it defocused. Both maximum peak intensities and area measurements were made on the focused and defocused exposures using the same photographic plate exposure curve. The results of these measurements are shown in table 9. Listed in the first column are the ratios of the average peak intensity of the focused lines divided by the average peak intensity of the defocused lines. The deviations from a value of 1.00 indicate how much the changes in peak width brought about by defocusing have affected the maximum peak intensity readings. The second column was computed from the same peaks except that the peak areas were measured instead of peak intensities. All of the data were within the 2 limits of the ratio of 1.00 indicating that the area measurements have completely compensated for changes in peak widths.

Table 9. Area measurement compensation for changes in peak widths.

	(14 equal exposures -- of doped Pt- 7 focused, 7 defocused)	
	Ratio of focused to unfocused values	
	Intensity	Area
Pb 208	1.43 ± 18%*	1.00 ± 16%*
Pt 190	1.40 ± 10%	.91 ± 5.9%
Ag 107	1.74 ± 24%	1.00 ± 18%
Pd 106	1.85 ± 14%	.99 ± 13%
Zr 90	2.17 ± 19%	1.10 ± 21%
Cu 63	1.88 ± 14%	1.08 ± 13%
Fe 56	1.66 ± 17%	1.07 ± 10%
Al 27	1.64 ± 9.6%	1.16 ± 8.7%
Mg 26	1.46 ± 13%	1.11 ± 11%

*% Standard deviation.

The cost of the parts necessary to build this analog omputer is approximately $500 excluding the recorder and igital voltmeter. The unit can be built in about one week y a person with some practical experience with electronics. etailed operating instructions for the unit plus other undry information will be made available upon request to ny persons interested in building a similar unit.

. Analysis of High Purity Materials

Within the past year multiple samples of "six nines" inc, copper, gold, tungsten and tin have been analyzed. s an example, the results for one of six zinc samples are iven in table 10.

Table 10. Analysis of zinc bar.

(A) Impurities found -- ppm by weight.

W	Cd	Ni	Fe	Cr	Ca*	K*
0.3	0.05	0.06	0.05	0.01	0.006	0.03
Cl	Al*	Na*				
0.1	0.004	0.01				

*These elements are probably surface contamination.

(B) Limits of detection for elements with interference -- ppm by weight.
(These elements were not detected in the sample)

Au	Pt	Ta	Nb	Se	Ga	Cu	Co
7	0.2	200	0.1	0.1	0.6	13	0.03
S	Si	Mg	O	N	C		
13	0.05	0.001	6	15	1		

From table 10A it is seen that the total detected mpurities come to less than 1 ppm; it is therefore ossible for the sample to be six nines pure. The nformation in table 10B tells what is not known about he sample. It should be mentioned here that this sample was also analyzed by optical emission spectrometry and activation analysis. From these techniques lower values for Au, Cu, and Ta were reported which superseded the values listed in table 10B. However, the mass spectrographic numbers on C, O, N, and S were the only ones available. The combined total of the detection limits of these four elements is 35 ppm. This points up the fact that improvement in technique to lower the detection limits for the common gaseous elements is needed for more definitive measurement of total impurity.

C. Instrument Modifications

A manufacturer's modification kit to increase the instrument detection sensitivity was being installed and adjusted at the end of this year. The kit consists of a unit to provide a higher accelerating voltage (24 kV to replace the old 15 kV), wider slits throughout the analyzer section, plus other auxiliary equipment made necessary by the use of 24 kV in the source.

Based on the manufacturer's claim of a 10-fold increas in detection sensitivity with the conversion kit and our present detection limits of about 100 parts per billion (ppb), we should now be able to detect elements as low as 10 ppb.

Unfortunately the increased sensitivity will apply not only to specific mass lines which are of interest, but also to many of the sources of plate background. One of these backgrounds is a general darkening across the photographic plate caused by gas scattering and charge exchange collisions within the magnetic sector. This background is directly related to the pressure in the magnetic sector. Since this background has been observed on photographic plates obtained at 15 kV (100 ppb detection limits), it was oncluded that it would partially degrade the 10-fold ncrease in sensitivity unless the pressure in the magnetic ector could be lowered. It should be noted that this ackground doesn't cover the entire mass range, but only a imited range determined by the mass of the major onstituent of each sample. Because of the very low gas onductance between the magnetic sector and its source of umping at the electric sector (5A and 5B of figure 31),

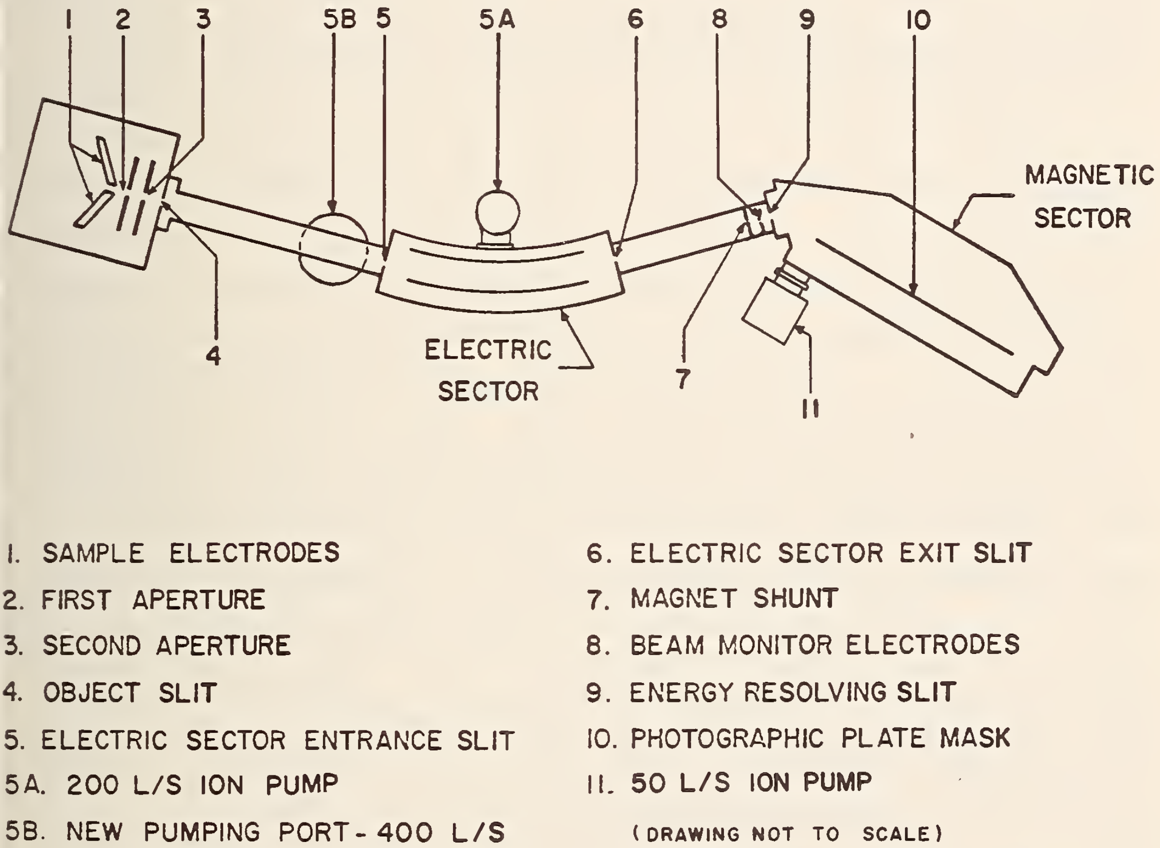


Figure 31. Diagram showing position of major components of mass spectrograph.

it has been assumed that the pressure in the magnetic sector could be as much as 100 times higher than the 4×10^{-9} torr registered at the 200-liter per second ion pump at position 5A of figure 28. A 50-liter per second ion pump has just been added at position 11 of figure 28 to provide high conductance pumping to the magnetic sector. During the time the system has been pumping down the currents drawn by the ion pumps have indicated pressures 20 times higher at the magnetic sector (position 11) than at the electric sector (position 5A). With the pressure still lowering at this time, the magnetic sector reads 8×10^{-8} torr as compared to 4×10^{-9} torr at the electric sector.

In a previous progress report [2] we reported the replacement of the stainless steel sample holders, the first aperture (No. 2 in figure 5), and the second aperture (No. 3 in figure 28) with parts made of tantalum in order to remove a source background of iron, chromium, and nickel. In the period since these parts were replaced with tantalum a number of "six-nines" pure materials have been run and in all cases from 0.1 to 0.05 ppm of iron has been found. Most of these same samples have also been analyzed with an emission spectrograph and the results either indicated the presence of iron or reported minimum detection limits higher than the amount of iron found by the spark source mass spectrograph. For the latter case it is not known whether the iron found by the mass spectrograph represents a true impurity content or a small residual background from other stainless steel source parts. In order to further elucidate this question of source background a series of exposures was made of a high purity gold sample containing very little tin. These exposures were made with a source which had been thoroughly coated with tin from a previous analysis. The parts already known to be sources of background (all the Ta parts listed reviously) were first replaced with clean parts, a aximum exposure was made on the gold sample, and then the emaining source parts were replaced stepwise with cleaned arts (with subsequent exposures of the gold) until all the ource had been cleaned. By observing the apparent tin ontent of the gold for the various exposures, probable ources of background were pinpointed. From these and revious experiments the following general and to some xtent obvious rules governing the sources of stainless teel background can be drawn.

1. Background comes from parts in-line-of-sight from he sample spark, or to be more exact from parts bombarded y ions from the spark.
2. The closer a part is to the spark, the more the ackground.
3. Parts at ground potential are a much larger source f background than parts sitting at the accelerating voltage i.e., the potential of the sample electrode).

It was found that the object slit (No. 4 of figure 28), he supports holding the Ta sample jaws, and the grounded arts behind the sample were probable background sources. arts at the accelerating voltage more than 1 in. from the park supplied no background.

A tantalum object slit and tantalum pieces to shield ll parts behind the sample jaws have been fabricated for the ew source coming with the 24 kV conversion kit. They will e evaluated as soon as the conversion kit is made perational. What is actually needed is a sample, inde-endently certified to contain less than 10 ppb of iron, hich can be used either to prove a lack of iron background n the instrument or to track down all the sources of ackground.

(P. J. Paulsen, P. E. Branch)

6. ANALYSIS OF HIGH PURITY MATERIALS: ENRICHMENT BY ELECTRODEPOSITION

High purity materials are being produced with a total impurity content of less than one ppm. Technologically important in such diverse fields as metallurgy, nuclear engineering, and semiconductor physics, these materials contain trace elements that significantly affect their properties. To determine these elements and evaluate their individual and collective effects on physical properties requires reliable analytical methods and standards.

For trace constituents at the sub-ppm level, the development of standard reference materials is a formidable problem. The production of materials with a homogeneous distribution of the desired trace elements is an essential requirement. The degree of homogeneity attained will determine the minimum sample size and the analytical techniques for which the sample is useful.

A. Analysis Problems

To analyze proposed Standard Reference Materials, analytical methods are selected for suitability as primary standardization procedures. Since almost all trace analytical methods are comparative methods, the errors inherent in preparing the synthetic or comparison standards must be evaluated.

Although many elements at concentrations of less than one ppm are below their spectrographic limits of detection, they can be determined by using preliminary chemical concentration procedures. The reliability of the enrichment procedure and the synthetic standards determine whether the combined preconcentration-spectrochemical method can serve as a basic standardization procedure. In most of these methods, the separated trace elements have been incorporated into a small amount of another high purity substance acting s a "collector" or "gatherer" and then excited with the irect current arc. However, since this excitation source as poor precision, the copper [32] and graphite spark [33] echniques, which do have both high precision and high bsolute sensitivity, would be particularly attractive for xciting trace elements obtained from preconcentration rocedures. However, if the selected procedure produces n appreciable amount of residue to be transferred to the lectrode surface, the electrical discharge dislodges the esidue. Consequently for these spark techniques, it is ot advisable to use a collector matrix for bulk. If a ollector is not used and the trace constituents are resent alone as an extremely dilute solution, serious osses can occur by any of several mechanisms grouped under he generic term "sorption losses." This is particularly rue if the solution is to be evaporated to a small volume nd transferred to the electrodes. The evaporation step lso increases the possibility of contamination.

3. Electrodeposition as an Enrichment Method

A preconcentration process by electrodeposition would e expected to minimize errors of this type since elements aving suitable electrodeposition potentials are deposited irectly on the cathode from a concentrated solution of the atrix. The cathode can serve as the electrode for pectroscopic excitation.

In comparison to most preconcentration procedures, electrodeposition would appear to be less subject to contamination errors. A minimum number of reagents are employed, sometimes only an acid to dissolve the material and an electric current as a reducing agent. Since the process is conducted in a small cell and extensive manipulations are not involved, a clean environment of limited size is easily provided. Other merits of the electrodeposition process are: its capability of multi-element separation from the matrix permitting multi-element determinations by spectrochemical techniques and its general applicability to diverse analytical problems.

Mark and Berlandi [34] demonstrated the usefulness of controlled potential electrodeposition using pyrolytic graphite in neutron activation analysis. In a later article Vassos, et al [35] described some of the conditions for quantitatively depositing microgram to milligram amounts of gold, silver, cobalt and copper. The authors wrote, "Unfortunately because little is known about the principles of electrodeposition on graphite, the pretreatment procedure arrived in this study may seem like witchcraft ..."

C. Current Research

In our laboratory the feasibility of electrodeposition as a preconcentration technique for spectrochemical analysis is under investigation. It was considered necessary to study the extent of deposition at the submicrogram level, the adherence of the deposit and whether its distribution on the electrode surface was sufficiently uniform. By the use of high-specific activity radioisotopes, it was found that for submicrogram amounts of silver, from solutions containing macro-amounts of zinc, 99% of the total silver could be electrodeposited onto the surface of 1/4 inch spectroscopic, graphite electrodes. The deposit was sufficiently adherent to allow removal of the matrix solution by washing, and the deposit was distributed sufficiently uniformly on the electrode surface to permit proper sampling by the high voltage spark.

Using the same zinc solution, submicrogram amounts of cadmium did not deposit on graphite. However, since other electrode materials can be employed in high-voltage spark procedures, cadmium was deposited on the surface of mercury-plated copper electrodes. The deposition was not as quantitative as for silver. A combination of electrode material and controlled potential makes this a rather versatile method for separations.

A technical paper on this subject entitled, "Electrodeposition of Trace Constituents as an Enrichment Method for Spectrochemical Analysis" was presented at the Fifth National Meeting of the Society for Applied Spectroscopy. A written paper describing experimental details and data is planned to be submitted for publication.

(R. Alvarez)

7. STANDARDS, ANALYSIS, AND LITERATURE ACTIVITIES

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

A. Standard Reference Materials

1. Standards Program

The program of standard reference materials and calibration in spectrochemical analysis has been a major activity of the Section. The output of this program has consisted of standard reference samples with certified composition, and the determination of information on applying the reference samples, including methods of analysis. In cooperation with the NBS Office of Standard Reference Materials and the other Sections of the Analytical Chemistry Division, the Section continues its activity on the analysis of proposed reference materials.

The analysis of reference materials consists of two phases, first, a study of homogeneity of the material, and second, accurate analysis by two or more cooperators or techniques. Homogeneity of the intended standard is essential to its use, since each user should receive a specimen corresponding in analysis to the certificate provided. In spectrochemical analysis the amount of specimen consumed in an analysis may be of the order of a milligram or less and the analysis may be affected by the physical state of the material. Consequently, much effort has been devoted in our Section to the design of optimum procedures for study of homogeneity. For spectrochemical analysis, experiments have been designed to obtain the maximum of information from the minimum of testing, using photoelectric spectrometers for high precision. The information is read out in the form of punched cards or tape and submitted to a computer for statistical analysis of the data. Analysis of variance serves appropriately for determining that part of variation in concentration attributable to segregation in the sample. Two large photoelectric spectrometers are installed in our laboratory primarily for homogeneity testing, although they are also used for general analytical service and research work. These were described and illustrated in our 1965 progress report [1].

The addition of the spark source mass spectrometer [2] to our facilities provides a powerful tool for the analysis of high purity materials.

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

2. Analyses Made of Standard Reference Materials

Analyses of standard reference materials during the 12-month period from June, 1965 through May, 1966 included

204 samples, with 911 qualitative determinations and 3892 quantitative determinations, and 43 reports written.

A large part of this work was concerned with homogeneity studies, especially of ferrous alloys, with analyses made on the photoelectric spectrometers. Studies were performed on 13 steels: a Se steel, four basic open hearth steels (11h, 13g, 15g; and 16e), a Cr-V steel 30f, and a test of added supplies of boron steel 827 and stainless steels 845-850. In addition, survey semi-quantitative analyses were made of these materials to ensure that all significant elements were detected before final analyses were made. Other studies made of ferrous alloys include analyses of three cast irons for phosphorus relative to well established standard cast irons, the determination of Mn in a Ni-Cr cast iron by atomic absorption, and the determination of Se in a steel by x-ray fluorescence. These analyses were performed largely by D. M. Bouchette.

In the past the homogeneity studies were limited to the metallic elements because of the lack of a vacuum optical spectrometer for determinations in the wavelength region below 2000Å. Carbon, phosphorus, and sulfur lines fall in this region.

With the cooperation of outside laboratories, Roanoke Electric Steel Co., the Jarrell-Ash Co., and the Applied Research Laboratory of the U. S. Steel Co.,we were able to use vacuum equipment for homogeneity studies for C, P, and S. Analyses were made of B.O.H. steels 11h and 16e, and Cr-V steel 30f for these elements. A vacuum spectrometer, now on order, will enable our laboratory to perform these analyses in the future.

X-ray fluorescence analysis is also employed in homogeneity studies for metallic elements in alloys. In his year the studies were applied to the analysis of non-etallic materials, a flint clay 97a and a plastic clay 8a, as described in section 3 of this report.

Homogeneity studies were made of three beryllium-opper alloys; these were found to be acceptable and ccurate determination of the impurities present are now nder way by several laboratories. The elements to be etermined include Be, Co, Ni, Fe, Zn, Pb, Al, Sn, Si, Cr, n and Ag. Procedures are being applied to determine all f these by emission spectrometric analysis relative to standards synthesized from pure metals.

A large part of our efforts on standard reference materials are now being applied to the analysis of materials of high purity ("6 nines") or of intermediate purity. Optical and mass spectrometric analysis were made of high purity copper, gold, tungsten, tin, and zinc. As pointed out in section 5 of this report, these two methods complement one another especially on the serious problems of identifying contamination.

For optical emission, a fractional distillation technique involving the direct excitation of the sample as the camera is being racked provides high spectral line-to-background ratios. Many trace metallic elements most likely to be found as impurities have excellent detectabilities by this method.

The analysis of high-purity materials is a difficult problem and may involve special sample handling and the separation of impurities where possible. Enrichment procedures are under study as described in section 6 of this report. Electrodeposition was applied as an enrichment procedure in conjunction with the spectrographic determination of copper and silver in zinc. An enrichment procedure also was applied to the analysis of selenium, a reference material of intermediate purity. Details of this procedure are being worked out and will be reported later.

(B. F. Scribner, R. Alvarez,
M. Margoshes, M. M. Darr)

B. General Spectrochemical Analyses

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

1. Types of Analyses

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

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

Quantitative analyses are made by both optical and x-ray fluorescence spectrometric methods using equipment described earlier. The problem is relatively simple for the analysis of metals and alloys when a solid sample with a diameter of 1 to 2 cm is provided, and when adequate reference samples are available. However, many samples are in the form of powders, solutions, thin wires, or thin films. In these cases the samples may be analyzed in the orm of dry powders or solutions, relative to standard amples synthesized from pure elements or salts.

For the analysis of high purity materials, the spark ource mass spectrograph offers the advantage of detection imits in the parts per billion range and is now being pplied in analysis.

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

2. General Analyses Made

Spectrochemical analyses, other than those made of tandard reference materials, during the 12-month period rom June, 1965 through May, 1966 included 269 samples, ith 7837 qualitative determinations and 437 quantitative eterminations, and 102 reports written.

(E. K. Hubbard, R. Alvarez,
M. M. Darr, D. M. Bouchette)

C. Literature Surveys

The problem of keeping up with the extensive literature in spectrochemical analysis is being met by maintaining reference files on the literature in the several fields. These are optical emission, including flame photometry, atomic absorption, x-ray fluorescence, electron probe microanalysis, and spark source mass spectrometry. To collect information on the literature, systematic surveys are made using Chemical Abstracts, Chemical Titles, and similar sources. Final checking is made against selected journals. Card files are maintained with the abstract typed or pasted on 5 x 8 in. cards.

The references serve for the preparation of bibliographies and reviews. During this year a biennial review of emission spectrometry was prepared by Margoshes and Scribner [36]. An extension of a bibliography on emission spectrometry and a bibliography on electron probe microanalysis are in preparation. The reference file serves very well in planning programs of research, in reviewing manuscripts, and answering inquiries.

(V. C. Stewart, M. Margoshes,
M. A. Giles, B. F. Scribner)

8. PERSONNEL AND ACTIVITIES

. Personnel Listing

pectrochemical Analysis Section

Bourdon F. Scribner, Section Chief
Frances L. Hilten, Administrative Aid

Group I. Optical Spectroscopy

Marvin Margoshes, Chemist
Claude Veillon, NBS-NRC Post Doctoral Research Chemist
Martha M. Darr, Chemist
Elizabeth K. Hubbard, Physicist
Stanley D. Rasberry, Physicist
Daniel Marcellus, Chemist (Summer Student 1966)
Doward M. Bouchette, Physical Science Technician

Group II. X-Ray Spectrometry and Electron Probe Microanalysis

Kurt F. J. Heinrich, Chemist
Mary Ann Giles, Chemist
Detlef F. Gerlach, Chemist (Summer Student 1965)
Gerald A. Wolfson, Electronic Technician

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

Group III. Spark Source Mass Spectrometry

Paul J. Paulsen, Chemist
Paul E. Branch, Physical Science Technician

Group IV. Enrichment Techniques

Robert Alvarez, Chemist

Group V. Literature Survey

Virginia C. Stewart, Chemist

B. Publications

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   X-Ray Optics and X-Ray Microanalysis.
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Margoshes, M., "Recent Advances in Excitation of Atomic Spectra," XII International Spectroscopy Colloquium, Exeter, England, July 12, 1965.

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Scribner, B. F., "Advances in Excitation Sources for Spectrochemical Analysis," Plenary Lecture, XXth International Congress of Pure and Applied Chemistry, Moscow, July 14, 1965.

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Rasberry, S. D., "Application of the Laser Probe in Spectrochemical Analysis," Fourth National Meeting, Society for Applied Spectroscopy, Denver, Colorado, August 31, 1965.

Margoshes, M., "Selection of Wavelengths for Atomic Absorption Spectrometry," Fourth National Meeting, Society for Applied Spectroscopy, Denver, Colo., Aug. 31, 1965.

Scribner, B. F., "Atomic Emission Spectroscopy: Arc Spark and Plasma Jet," 150th National Meeting, American Chemical Society, Atlantic City, N. J., Sept. 14, 1965.

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13. Rasberry, S. D., "Aspects of Laser Probe Excitation for Quantitative Spectrochemical Analysis," Eastern Analytical Symposium, New York City, November 18, 1965.

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15. Heinrich, Kurt F. J., "Advances in Electron Microprobe Analysis," Baltimore-Washington Section, Society for Applied Spectroscopy, Baltimore, Md., Feb. 15, 1966.

16. Rasberry, S. D., "Applications of Time-Shared Computers in Spectrochemical Analysis." Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb. 23, 1966.

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3. Margoshes, M., "Temperature Profile of a Direct-Current Arc in Argon," Fifth National Meeting, Society for Applied Spectroscopy, Chicago, Ill., June 17, 1966.

4. Margoshes, M., "Computer Calibration of Photographic Emulsions in Spectrochemical Analysis," Fifth National Meeting, Society for Applied Spectroscopy, Chicago, Ill., June 17, 1966.

5. Alvarez, R., "Electrodeposition of Trace Constituents--An Enrichment Method Prior to Spectrochemical Analysis," Fifth National Meeting, Society for Applied Spectroscopy, Chicago, Ill., June 17, 1966.

26. Heinrich, Kurt F. J., "Scanning Electron Probe Microanalysis," American Society for Testing and Materials, Atlantic City, N. J., June 30, 1966.

D. Committee Activities

B. F. Scribner

Member, ASTM Committee E-2 on Emission Spectroscopy
Member, ASTM Committee E-13 on Absorption Spectroscopy
Program Chairman, Eastern Analytical Symposium, 1965
Delegate to Governing Board, EAS, 1966.
Titular member, Commission on Spectrochemical and othe 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, Advisory Committee, Society for Applied Spectroscopy, 1965
Chairman-Elect, Baltimore-Washington Section, SAS, 1966
Member, Wavelength Tables Committee, University of Michigan
Technical Program Chairman, NBS Symposium on Trace Characterization, 1966
Member, Analytical Standards Committee NBS

M. Margoshes

Delegate to Governing Board, Society for Applied Spectroscopy, 1965-66
Chairman, Conference Committee, SAS, 1965
Member, Publications Committee, SAS, 1966
Member, Program Committee, and Chairman, Publicity Committee, NBS Symposium on Trace Characterization, 1966

K. F. J. Heinrich

Chairman, Microprobe Task Group, ASTM Committee E-4 on Metallography
Member, Advisory Board, Mikrochimica Acta

R. Alvarez

Member, ASTM Committee E-2 on Emission Spectroscopy

S. D. Rasberry

Member, Laser Task Group, ASTM Committee E-2

E. K. Hubbard

Analytical Chemistry Division Newsletter

9. ACKNOWLEDGMENTS

It is a pleasure to recognize the assistance from roups and individuals who have aided our work in several ays. Assistance has been received from outside aboratories as well as those in the NBS.

For the optical spectrometric determination of carbon, hosphorus, and sulfur in homogeneity studies of steels, we eceived the generous cooperation of Mr. J. C. Staton of he Roanoke Electric Steel Co., Mr. S. Smith of the Jarrell-sh Company, and Dr. J. K. Hurwitz of the Applied Research Laboratory, United States Steel Corp.

We are indebted to the U. S. Geological Survey, through Mr. Harry J. Rose, for helpful advice and the use of their facilities in the x-ray fluorescence analysis of clay samples.

Two members of the Metallurgy Division, Mr. Harvey Yakowitz and Mr. Donald L. Vieth, have continued to aid in providing metallurgical services and in making measurements of mutual interest with the microprobe. Mr. Louis Marzetta of the Electronic Instrumentation group has contributed effectively to the design and construction of read-out devices for the microprobe. Mr. Ronald W. Shideler, electronic consultant in the Analytical Chemistry Division, provided excellent suggestions for problems connected with the multichannel analyzer.

Mr. George Marinenko, of the Microchemical Analysis Section was very helpful on problems in electrodeposition.

Mrs. Frances L. Hilten, Administrative Aid in our Section, performs a wide variety of duties essential to the smooth working of the Section. Her assistance in preparing this and other reports is deeply appreciated. Our thanks also are extended to Miss Sandra Beall who assisted in the preparation of this manuscript.

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