NBS TECHNICAL NOTE 505

Microchemical Analysis Section:

Summary of Activities July 1968 to June 1969

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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Office of Standard Reference Data—Clearinghouse for Federal Scientific and Technical Information [3]—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.
[2] Located at Boulder, Colorado 80302.
[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

UNITED STATES DEPARTMENT OF COMMERCE
Maurice H. Stans, Secretary
NATIONAL BUREAU OF STANDARDS • Lewis M. Branscomb, Director

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Microchemical Analysis Section:

Summary of Activities July 1968 to June 1969

Edited by John K. Taylor

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

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FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of nine sections and about 100 technical personnel encompassing some 57 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

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

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

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1969 we plan to issue these summaries for all of our sections. The following is the fifth annual report on progress of the Microchemical Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

This report summarizes the current program and recent activities of the Microchemical Analysis Section of the Analytical Chemistry Division. This Section has the primary mission to contribute to the science and technology of the analysis of small samples and its program includes both fundamental studies to improve the precision, accuracy and sensitivity of analytical techniques, and developmental research to provide new and improved methods applicable to wide areas of materials characterization. As a closely related activity, the Section provides analytical measurements for various research programs of the Bureau and develops and characterizes Standard Reference Materials.

Research projects are active in the following competence areas: gas analysis; polarography; coulometry; potentiometry; microscopy; conventional microchemical analysis; nuclear track technology; and ionic equilibria studies.

It has been found to be convenient to classify activities in this report either as research or analytical developments. Such classification must be considered to be arbitrary in many cases in that developmental aspects have been involved in virtually all work reported, resulting in improved procedures and techniques. Space limitations have dictated only a brief description of methods in most cases. It is hoped that such descriptions will be understandable to an experienced analyst. However, specific details of all work reported here will be made available to anyone interested in such matters.

A major effort of the Section during the year has been concerned with the analysis of standard reference materials. No effort has been spared to characterize these materials to a high degree of reliability. The use of such materials not only establishes benchmarks for industrial control but also provides a sound basis for inter-laboratory comparisons and for the intercomparison measurement techniques and methodology.

Such materials are regularly used in this laboratory to verify the accuracy of analytical procedures. They are referred to by an identification such as SRM #160b, for example. A catalog containing full descriptions of these materials may be obtained from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D. C. 20234.

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

John K. Taylor, Chief
Microchemical Analysis Section

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MICROCHEMICAL ANALYSIS SECTION: SUMMARY OF ACTIVITIES
JULY 1968 to JUNE 1969

Edited by John K. Taylor

ABSTRACT

This report describes the research activities and scientific programs of the Microchemical Analysis Section of the Analytical Chemistry Division of the NBS Institute for Materials Research during the period July 1968 to June 1969. General activities are reported in the areas of gas analysis, polarography, potentiometry, coulometry, chemical microscopy, and classical microchemical analysis. Research activities described in some detail include: gravimetric preparation of gas analysis standards; polarographic determination of trace elements in glass; fabrication and performance of a microfluorine electrode; elucidation of the boric acid-borate-mannitol system; investigation of the relation between the equilibrium point and inflection point in acidimetric titrimetry; coulometric determination of trace quantities of chromium; and determination of trace elements by nuclear track measurements. A number of procedures which have been developed for the analysis of a variety of materials, utilizing the techniques mentioned above, are also included.

Key words: Chemical analysis, Coulometric analysis, Gas analysis, Ionic equilibria, Ion-selective electrodes, Microchemical analysis, Microscopic analysis, Polarographic analysis.

1. GAS ANALYSIS

A. Research Activities

1. Trace Oxygen Analyses

Four electrochemical cells based on a modification of a design previously described [1] were constructed and incorporated into a system for the analysis of trace oxygen concentrations at levels below one part per million (ppm). The modification consisted primarily of eliminating all possible sources of leakage which might introduce minute quantities of oxygen to the system. Electrical connections were made through glass-to-tungsten joints and all gas connections are vacuum-tight ground joints. The operation of the cells was found to be superior to those previously used both in the higher and lower concentration ranges. Extensive experiments with the cells, however, merely indicated a cell theoretically sensitive but deficient in actual practice. This deficiency lies not within the cell, but rather can be attributed to the associated hardware. It was found that commercial valves and fittings, no matter how carefully used, were never entirely leak-free in terms of the detection of traces of oxygen between 1 ppb (part per billion) and 1 ppm.

Reluctantly this effort was shelved until such time is available to allow construction of a completely leak-free gas handling system. Therefore, further work on gas standards with very low concentrations of oxygen in nitrogen has been deferred.

2. Atmospheric Argon

A method for the accurate determination of argon in air was briefly described in a previous report [1]. More extensive details and initial results have been presented [2]. Briefly, these results indicate a value for the concentration of atmospheric argon lying closer to that of Shinya Oana [3] than that of Moissan [4]. The method depends on the careful pre-

paration of weighed mixtures of argon and nitrogen which are used to calibrate a mass spectrometer for subsequent determinations of the ratio of argon to nitrogen in atmospheric air samples from which the oxygen has been removed. Table 1 gives some of the results of the three investigations. Results are expressed as the mole percent of argon in the argon-nitrogen portion of the atmosphere.

Table 1. Results of three determinations of atmospheric argon.

	Argon in Mole Percent		
No.	Moissan (1903)	Shinya Oanu (1949)	This Investigation (1968)
1	1.183	1.16	1.133
2	1.181	1.16	1.176
3	1.183	1.16	1.154
4	1.184	1.18	1.167
5	1.187	1.16	1.159
6	1.179	1.16	1.164
7	1.184	1.16	1.164
8	1.183	1.14	1.158
9	1.182	1.16	
10	1.181	1.16	
11	1.179	1.16	
12	(1.201)	1.16	
Avg.	1.182	1.16	1.159
s	0.002	0.01	0.013

These preliminary results, while lacking the precision of Moisson's results, show a clear discrepancy. The method by which the results were obtained will be modified in accordance with the availability of new and better equipment for both the preparation of standards and the mass spectrometric comparison of the standards with atmospheric air. It is hoped that a minimum accuracy of about one part in 10,000 can

eventually be achieved. If this accuracy can be realized, a determination of the argon-to-nitrogen ratio of eighty atmospheric samples obtained from locations around the world will be attempted.

3. Atmospheric Carbon Dioxide

The National Bureau of Standards issues as standard reference materials three concentrations of carbon dioxide in nitrogen and are identified as SRM #1601, 1602, and 1603, respectively. These are intended to bracket atmospheric concentrations and to serve for the calibration of instruments used to determine these levels of carbon dioxide. While the accuracy of these standards (± 1 mole percent of the total carbon dioxide) is adequate for most routine monitoring problems, there exists the need for at least one ultimate and definitive sample with an accuracy of at least two orders of magnitude better than 1%. A preliminary investigation of the feasability of the preparation of such a mixture has been completed and the preparation of three primary standards has begun. Because of the cost, time, and degree of care necessary for the production of these standards, they are not intended for distribution but it is expected that not only will they serve as the primary standard for atmospheric carbon dioxide concentrations but will also be used to recertify the currently available standard reference materials to a value one order of magnitude better than at present.

The new samples are being prepared by successive dilution of higher concentrations of carbon dioxide in nitrogen. Formerly such standards were prepared in a similar manner and the final concentration was determined by calculations based on measured pressures. Methods for measuring pressures in the range through which the dilutions were made were adequate for producing mixtures with an accuracy of 0.1%.

Other factors such as temperature and compressibility added additional uncertainties which combined to result in an

overall accuracy of about 1%. Probably the largest and least easily determined sources of error are the compressibilities of the two gases involved and the unknown manner in which the compressibility varies in the composition of the mixture. Little or no data are available concerning the compressibility of gas mixtures. The final degree of uncertainty in the concentration of gas mixtures prepared by measurement of volume would necessarily remain high until such data are available. An alternative method, and one which has just recently found increased use in industry, is the preparation of gas mixtures by weight. In principle, it should be simple to prepare mixtures by such means but in practice numerous problems may arise. The very low density of gases as compared to the usual substances encountered in chemical gravimetry require large, relatively heavy containers whose total weight far exceeds the weight of the gases. Buoyancy corrections became quite significant and in relation to this any changes in shape of the gas container with changes of pressure must be known or be predictable.

The preparation of the carbon dioxide standards required a balance capable of weighing to at least one part in ten thousand. The total weight of the sample and the cylinder containing it was about 8 kg. A balance meeting such requirements is shown in Figure 1. The volume of the container is about 2ℓ; the contained gas has a total volume of about 60ℓ (S.T.P.) and weighs about 100 grams.

Buoyancy corrections were determined to be negligible both under conditions of varying barometric pressure and temperature when cylinders are weighed against a tare of similar volume. Possible buoyancy changes due to the distortion of the cylinder under full working pressure (500 psi) are considered negligible. It is impossible to measure changes arising from this source, unlike changes arising from barometric pressure and ambient temperature which can be determined by observing changes as these parameters change, and therefore

Figure 1. Preparation of standard gas mixtures by weighing.

it is necessary to measure the physical changes of a cylinder under conditions when it is empty and full. A cylinder was measured with a micrometer caliper at three points on its circumference at three points along its length for a total of nine points. The cylinder was then charged to full pressure and remeasured. No change in dimension was observed under these conditions, however, this single determination is not considered definitive and a further investigation is planned.

In practice, cylinders to be used for mixtures are weighed against two other cylinders which are carried through the mixing process without change. The order in which cylinders are weighed is such that abrupt shifts in the "zero" of the balance are readily observed and gradual "zero" shifts are compensated. At least ten separate weighings of each sample are made and the standard deviation of the average of each sample weight must be less than 1 part in 10,000. In Table 2 is an example of a single weighing in the process of making

a mixture. Cylinders 1 and 4 are references and remain unchanged through the procedure. Cylinders 2 and 3 contain a mixture of carbon dioxide and nitrogen. The weights shown are the differences between the weights of cylinder 1 through 4 and a tare consisting of a similar cylinder. The weight of the sample shown in Table 3 is determined from the difference in weight between cylinder 2 and 1 before and after filling and cylinder 3 and 4 under similar conditions.

Table 2. Typical weighings obtained at one step in mixing procedure.

	Weight in Grams			
No.	Cylinder 1	Cylinder 2	Cylinder 3	Cylinder 4
1	57.747	155.832	149.957	36.838
2	57.746	155.831	149.956	36.838
3	57.744	155.830	149.956	36.840
4	57.745	155.832	149.956	36.838
5	57.744	155.833	149.958	36.839
6	57.749	155.835	149.961	36.841
7	57.740	155.833	149.958	36.839
8	57.746	155.832	149.957	36.839
9	57.745	155.832	149.956	36.838
10	57.745	155.832	149.957	36.839

Table 3. Weight of sample calculated from weights in Table 2.

No.	Cylinder 2	Cylinder 3
1	104.534	104.369
2	104.534	104.368
3	104.535	104.366
4	104.536	104.368
5	104.538	104.369
6	104.535	104.370
7	104.535	104.369
8	104.535	104.368
9	104.536	104.368
10	104.536	104.368
Avg.	104.536	104.368
s	0.001	0.001

The weight differences are measured with brass weights and since no change in volume of the sample occurs the only buoyancy correction that must be applied is that represented

by the differences in the air volume of the brass weight difference occurring between weighings. Barometric pressure and temperature were noted at each weighing in order to allow this calculation.

The gases used to compound these mixtures were prepared and analyzed in such a way that the required accuracy could be maintained throughout the mixing procedure. The carbon dioxide was obtained from a cylinder of research grade material which was cooled to dry ice temperature and "blown off". It was subsequently blown off several times at room temperature. Both the carbon dioxide and nitrogen were analyzed mass spectrometrically. The nitrogen used in the dilution to the final concentration must either be carbon dioxide free (< 30 ppb) or the carbon dioxide content must be known with an accuracy within ± 30 ppb. The method of analysis will probably be an adaptation of the method described in section A.3., "Atmospheric Carbon Dioxide".

4. Oxygen in Air

Samples of atmospheric air were obtained during cruises of the research vessels, U.S.N.S. Oceanographer and U.S.N.S. Eltanin. The purpose of the sampling was to determine possible variations in oxygen content in the atmosphere over the oceans in areas of varying oxygen producing organisms. These samples, 46 from the Oceanographer and 32 from the Eltanin, were analyzed for oxygen content by comparison with NBS Standard Reference Material #1609, 20.95 mole percent oxygen. The method is described in detail in a previous report [1]. The results are shown in Tables 4 and 5. The limit shown on each value is the standard deviation of three values. Each value represents ten instrument readings. It is interesting to note that almost without exception the value for the oxygen content is 20.946 mole percent. The few exceptions are also those with the greatest standard deviations suggesting an experimental error rather than an actual variation in atmospheric oxygen content.

Table 4. Oxygen content of air obtained during the cruise of the Oceanographer.

Sample No.	Oxygen Content	Sample No.	Oxygen Content
S-1	20.946 ± .001	S-26	20.945 ± .001
S-2	20.946 ± .001	S-27	20.945 ± .001
S-3	20.945 ± .001	S-28	20.945 ± .006
S-4	20.945 ± .002	S-29	20.948 ± .002
S-5	20.946 ± .002	S-30	20.947 ± .001
S-6	20.945 ± .002	S-31	20.946 ± .001
S-7	20.946 ± .001	S-32	20.946 ± .001
S-8	20.946 ± .001	S-33	20.946 ± .001
S-9	20.946 ± .001	S-34	20.946 ± .001
S-10	20.945 ± .001	S-35	20.945 ± .001
S-11	20.946 ± .001	S-36	20.946 ± .001
S-12	20.946 ± .001	S-37	20.946 ± .001
S-13	20.946 ± .001	S-38	20.945 ± .001
S-14	20.946 ± .001	S-39	20.946 ± .001
S-15	20.946 ± .001	S-40	20.945 ± .001
S-16	20.946 ± .001	S-41	20.949 ± .006
S-17	20.946 ± .001	S-42	20.949 ± .004
S-18	20.946 ± .001	S-43	- -
S-19	20.946 ± .001	S-44	20.945 ± .003
S-20	20.946 ± .001	S-45	- -
S-21	20.945 ± .002	S-46	- -
S-22	- -	S-47	20.942 ± .002
S-23	20.947 ± .001	S-48	20.949 ± .001
S-24	20.947 ± .001	S-49	20.944 ± .001
S-25	20.949 ± .001	S-50	20.946 ± .001

Table 5. Oxygen content of air obtained during the cruise of the Eltanin.

Sample No.	Oxygen Content	Sample No.	Oxygen Content
1	20.946 ± .001	17	20.944 ± .001
2	20.946 ± .001	18	20.947 ± .002
3	20.946 ± .001	19	20.942 ± .003
4	20.946 ± .001	20	20.946 ± .001
5	20.946 ± .001	21	20.943 ± .002
6	20.946 ± .001	22	20.953 ± .008
7	20.946 ± .001	23	20.947 ± .002
8	20.945 ± .001	24	20.945 ± .001
9	20.945 ± .001	25	20.945 ± .001
10	20.945 ± .001	26	20.946 ± .001
11	20.946 ± .001	27	20.941 ± .004
12	20.946 ± .001	28	20.943 ± .002
13	20.946 ± .001	29	20.947 ± .002
14	20.946 ± .001	30	20.947 ± .001
15	20.946 ± .001	31	20.945 ± .001
16	20.946 ± .001	32	20.946 ± .001

B. Standard Reference Materials

1. Sulfur Dioxide in Air

It had previously been determined that ordinary mild steel and stainless steel containers, while satisfactory for high concentrations, were not suitable for storage of mixtures of dilute concentrations of sulfur dioxide in air. Before a comprehensive investigation of other methods of preparing sulfur dioxide mixtures was attempted, a single high concentration (0.2 mole percent) was prepared in a large (1A) cylinder. The mixture was then transferred to 20 small (2ℓ) cylinders.

A mass spectrometric comparison was made between the gas in the small cylinders and the gas in the large cylinder. The comparison was made by admitting a sufficiently high pressure of the mixture into the inlet system so that the mass 64 due to SO_2 was easily read to better than 1%. The ion current due to nitrogen in air at mass 28 was brought within readable limits by adjustment of the input resistor of the preamplifier and by scanning the mass 28 at a lower sensitivity than for the 64. Thus differences of 1 part in 40 thousand could be easily determined. Using this method it was possible to obtain a comparison between the contents of the large cylinder and the contents of the small cylinders with rapidity and ease compared to other methods for determining sulfur dioxide in this concentration range.

The results obtained in the above study and with a later duplicate study using a new mixture indicates that little or no reaction (less than 1%) occurs in the small cylinders after transfer from the large cylinder. Analytical results obtained after refilling cylinders previously exposed to 0.2 mole percent sulfur dioxide in air indicates that no residual sulfur dioxide remains in the cylinders.

The mass spectrometric method described above is adequate for comparison of one concentration of sulfur dioxide with

another but is not considered to be sufficiently absolute for certification of the final concentration. This value must depend on careful analysis of the individual components and accurate measurement of the pressures of each component. The value obtained mass spectrometrically must agree within limits with this value but will not be used in the final certification.

Some preliminary work has been done on a method for producing low concentrations of sulfur dioxide in an air stream. The device is that described by O'Keefe et al. [5] and depends on the effusion of sulfur dioxide at a fixed rate from a porous plastic tube containing liquid sulfur dioxide. A specimen tube was obtained and the constancy of the effusion rate was ascertained by measurement of the weight loss versus time. Subsequent use of such a tube would depend on the constancy of this weight loss. In order to determine whether an independent check of effusion rates might be possible a simple titrimetric procedure was evolved.

The tube was placed in a container filled with a dilute hydrogen-peroxide solution. This was immersed in a thermostated water bath and the interval during which the tube was immersed was measured. At the end of the interval the sulfuric acid formed was titrated with dilute sodium hydroxide and the total evolved sulfur dioxide could be calculated. The values obtained by weighing and by titration of the sulfur dioxide evolved by a single tube are as follows.

0.069 mg/min by weight at 25 °C
0.067 mg/min by titration at 25 °C

The agreement is quite good and the possibility of measuring effusion by titration will be pursued. The advantages are that the time interval between weighings can be much more easily defined and errors in weighing are eliminated. Once equipment is set up and solutions standardized, determinations can be performed quite rapidly. Using suitable techniques it

is possible to obtain a good value of the effusion rate in about 15 minutes after immersing the tube in solution.

2. Hydrocarbon in Air Standards

A series of methane in air standards containing approximately 1, 10, 100 and 1000 ppm methane was prepared and analyzed. Preparation of certificates of analysis is now in progress. The analyses of the standards were performed by using a flame ionization instrument to compare the response from the standard to the response from two calibration standards. The two calibration standards were prepared as follows. A calibration standard in the hundred ppm range was compounded by stepwise dilution of methane with air of known low hydrocarbon content, concentrations being determined from the weights of the components with a precision analytical balance. With this standard and air containing no hydrocarbon, obtained by passing air through cupric oxide at 1050 °C, a calibration standard containing about 2 ppm hydrocarbon was analyzed accurately using the flame ionization instrument:

The concentrations of the standard reference gases obtained from the pressures of the components during compounding and the concentration determined with the flame ionization instrument agree within 1%.

Difficulty in finding a suitable prepared container was experienced with mixtures containing 1 and 10 ppm hydrocarbon. Certain containers using a resin sealant between the valve and the body of the cylinder were found to contribute markedly to the hydrocarbon content of a mixture therein. Cleaning the sealant from these containers and resealing with teflon tape alleviated the problem. However, each container of standard reference gas at the 1 and 10 ppm levels of hydrocarbon has been analyzed to make certain that the concentration is the same as that in the bulk mixture.

3. Carbon Dioxide in Air

As mentioned earlier in this report, standard reference materials consisting of carbon dioxide in nitrogen will probably be recertified to a higher degree of absolute accuracy. In addition, work has begun on a method for the determination of atmospheric carbon monoxide and carbon dioxide based on the catalytic conversion of these compounds to methane with subsequent determination of the methane using a flame ionization detector. The method was first described by Stevens [5].

Preliminary results indicate that the method has promise but many technical details must be evaluated. A promising feature of the method is its applicability to the absolute determination of low concentrations of carbon dioxide. Heretofore, these determinations could only be performed on rather specialized infrared apparatus which is not available in this laboratory. It is hoped, as previously mentioned, to adapt the method for the determination of the "zero" level of carbon dioxide in the gases used in the preparation of the standard mixture of carbon dioxide.

C. Research Materials Service Analysis

1. General

Service analyses and compounding of gas mixtures are a regular function of this laboratory. Mass spectrometry is the most frequently used analytical technique, however electrochemical cells, gas chromatography, infrared, and other methods are used when the need arises. Table 6 summarizes analytical and mixture compounding services.

Table 6. Summary of gas analytical services.

A. Mass Spectrometric Analysis

Material	Number of Samples	Sample Size	Determined
		Organic Materials	
Gases evolved from plastics	3	10 ml	C_2Cl_4
Pyrolysis products	3	small ampoules	∿ 30 different organic and inorganic components in each sample

Table 6. (Continued)

Material	Number of Samples	Sample Size	Determined
		Inorganic Materials	
Air samples from various geographic locations	82	1ℓ STP	O_2
"Anomalous" water	1	small capillary	O_2, CO_2, H_2O
Gas mixtures	3	∿ 200 ml STP	H_2
Gas mixtures	3	cylinder	H_2
Sample from airplane cabin	1	1 gallon STP	composition
NH_3	1	cylinder	H_2O
Reactor products	1	500 ml flask	N_2, O_2, NO, N_2O, CO_2
Hydrogen	1	cylinder	purity
Power plant stack gas	3	∿ 200 ml STP	H_2O, N_2, CO, O_2, Ar, CO_2, SO_2
Air sample	1	large yellow cylinder	CCl_2H_2
ClF_5	1	glass ampoule	impurities
Combustion products	1	glass ampoule	H_2, He, N_2, NO, Ar, CO_2
Mixture of organic and inorganic gases in O_2	1	cylinder	approximate composition

Table 6. (Continued)

Material	Number of Samples	Sample Size	Determined
		Inorganic Materials (Continued)	
Mixture of organic and inorganic gases in N_2	1	cylinder	approximate composition
Helium from Reactor	3	1ℓ STP	He, N_2, O_2, Ar, D_2
		Isotopically Altered Materials	
N_2O	2	large ampoules	$N^{15}N^{15}O$, $N^{14}N^{15}O$, $N^{14}N^{14}O$
Neon	3	cylinders	impurities and Neon isotope composition
Gas mixtures	2	500 ml flask	CH_3D, CH_4, impurities
Gas mixture	1	cylinder	CH_3D, CH_4, impurities
Helium-3	2	30 ml ampoules	He^{-3}, He^{-4}, H_2O, N_2, O_2, Ar, CO_2
Helium-3	10	30 ml ampoules	He^{-3}, He^{-4}
Oxygen evolved from irradiated solids	6	small ampoules	oxygen-18, oxygen-16

B. Compounding of Gas Mixtures

Mixture	Concentration of Minor Component
CO in air	0.102 mole %
Co in air	90 ppm
SO_2 in air	215 ppm

Table 6. (Continued)

B. Compounding of Gas Mixtures (Continued)

Mixture	Concentration of Minor Component
O_2 in N_2	21.508 mole %
O_2 in N_2	20.627 mole %
CH_4 in air	119.1 ppm
CH_4 in air	11.1 ppm
H_2 in air (2 cylinders)	1.39 mole %
H_2 in He	2.15 mole %
CO_2 and O_2 in He	1.09 mole % CO_2, 2.08 mole % O_2
O_2 in He	5.18 mole %

C. Electrochemical Determination of Oxygen

Material	Number of Samples	Sample Size	Determined
Ar	1	cylinder	O_2
Mixture of organic and inorganic gases in N_2	1	cylinder	O_2

2. Miscellaneous Analyses

In addition to the relatively routine analyses listed in Table 6, the work of this laboratory often involves either the modification of existing techniques or the origination of new methods of treating or handling samples in order to accomodate urgent or unusual conditions. Identification of possible incendiary fluids, determination of unusual atmo-

Figure 2. Analysis of "submicro" gas sample.

spheric components, and determination of contamination in ultraclean systems are but a few. The operation shown in Figure 2 involved the analysis of a "microscopic" gas sample contained in a short length (approx. 1 cm) of quartz tubing so thin that it was almost invisible to the unaided eye. The sample was of such small volume that the inlet system of the mass spectrometer used for the analysis had to be completely closed and the sample was contained in a small "L" attached to the leak line. The sample was crushed by manipulating an internal magnet with an external magnet. By means of this technique it was possible to identify two components whose total volumes at N.T.P. were only 1×10^{-10} and 2×10^{-9} liter.

(E. E. Hughes and J. M. Ives)

2. POLAROGRAPHIC ANALYSIS

A. Introduction

Experience gained in this laboratory over a period of years and particularly in the last few years has established polarography as a prime technique for both trace and major constituent analysis. Accordingly, such measurements have been utilized for solution of a number of important analytical problems involving standard reference materials as well as material related to several areas of NBS research. During the course of this work, a number of methods have been developed or modified to provide improved analytical utility. Some of these developments during the past year are outlined in the following sections.

B. Major Constituent Analysis

The improved precision obtained by the comparative polarographic method [6] has continued to be applicable to other analytical problems during the past year, particularly those concerned with SRMs. A few of these will be discussed below.

1. Analysis of Bis(1-phenyl-1,3-butanediono) Copper(II) (SRM #1080a)

The copper metallo-organic standard, which is used for blending with lubricating oils to prepare standards for monitoring wear of engine parts, was checked for homogeneity and analyzed by the following procedure:

After drying for 2 hrs at 110 °C, 0.6-g samples were slowly ignited to destroy organic material. The residues were dissolved in 20 ml of 50% hydrochloric acid (V/V), 20 ml of pyridine was added and the solutions were diluted to one liter. Copper was then measured polarographically at about -0.4V vs. a mercury pool anode in comparison with reference solutions prepared in the same manner from melting point copper, SRM #45d. Results for six samples taken from different parts of the same lot are shown in Table 7 along with results obtained by the NBS Activation Analysis Section.

Table 7. Copper in SRM #1080a.

Sample designation	Copper, percent	
	Polarography	Activation analysis[a]
1	16.355	16.43
2	16.375	16.32
3	16.360	
4	16.365	
5	16.385	
6	16.360	
Avg.	16.367	16.37
s	0.011	

[a]by S. S. Nargolwalla, Activation Analysis Section.

2. Copper and Lead in Microstandard Particles

Comparative polarography has proved useful in the analysis of microstandard ion-exchange beads [7], a new standard reference material being issued by NBS. Accuracies of 1% or better are required and often the amount of sample available is limited.

Two different lots of the copper microstandard were submitted for analysis. Copper was eluted from 0.15-g duplicate samples of Sample I-11-1 using concentrated hydrochloric acid. The acidity was adjusted to be equivalent to 4 ml of 50% HCl (V/V), 4 ml of pyridine was added, the solutions were diluted to 200 ml, and copper was measured polarographically at about -0.4V vs. a mercury pool anode in comparison with reference solutions prepared in the same manner from melting point copper, SRM #45d.

For the determination of copper in Sample R17-0015, duplicate 0.3-g samples were slowly ignited to about 700 °C. The residues were dissolved in 10 ml of 50% HCl (V/V), 10 ml of pyridine was added, the solutions diluted to 500 ml and

measured polarographically as described above. The results are shown in Table 8. Sample 1-11-1 contained an appreciable amount of sodium which accounts for its copper content being lower than that of Sample R17-0015.

Table 8. Copper in microstandard particles.

Sample		Copper, percent
I-11-1 (Cu)		11.96
		11.94
	Avg.	11.95
R 17 0015		13.35
		13.36
	Avg.	13.36

The first attempts to determine lead after elution with nitric acid were unsuccessful owing to the oxidation of the ion-exchange resin to sulfate by nitric acid and consequent precipitation of lead sulfate. Duplicate 0.2-g samples were then eluted with warm dilute hydrochloric acid and diluted to 500 ml with approximately 3M hydrochloric acid. Lead was measured polarographically at about -0.5V vs. a mercury pool anode using reference solutions prepared as before from melting point lead, SRM #49d. The results, as well as those obtained by atomic absorption on a sample of the same material, are given in Table 9.

Table 9. Lead in microstandard particles.

	Copper, percent	
Sample	Polarography	Atomic Absorption[a]
I-11-1 (Pb)	33.09	
	32.87	
Avg	32.98	32.99

[a]By T. C. Rains, Analytical Coordination Chemistry Section.

Some isotopic lead (equal-atom, ^{206}Pb-^{208}Pb) microstandard particles were prepared in very limited amounts. Only about 300 mg total of material was available for analysis and for issuance as a standard. There was no difficulty in determining the lead polarographically using duplicate 30-mg samples, leaving sufficient material for issuance. The lead was eluted and determined essentially as described above, except the dilution volume was 100 ml. As only 1 to 5 ml of this solution is necessary for the final polarographic measurement, it is seen that samples as small as 1 mg could be used without difficulty. The results, calculated on the basis of an average atomic weight of lead in the samples as 207, are given in Table 10.

Table 10. Lead in isotopic microstandard particles.

Sample Designation		Lead, percent
Run 16		34.47
		34.73
	Avg	34.60

The bead residues remaining after elution were examined spectrochemically. No lead was detected. The limit of detection of about 20 ng confirms virtually complete elution of lead under the experimental conditions.

3. Copper and Nickel in Service Samples

Methods similar to those described above have proved useful in the analysis of a number of samples received through the NBS Service Analysis Program. For example, it was possible to determine copper at the 12% level in 25-mg samples of a metal-organic compound in a similar pyridine-pyridinum chloride supporting electrolyte after destruction of organic material Results agreeing within 0.8% of the theoretical composition were obtained by the single cell mode of operation.

A series of 8 Cu-Ni alloys ranging from less than 0.1 to 50% Ni were also analyzed polarographically in a pyridine-pyridinum chloride supporting electrolyte at about -0.9V vs. a mercury pool anode. If necessary, copper could have been determined simultaneously.

4. EDTA (Disodium Salt, Dihydrate)

Methods for the analysis of EDTA were investigated in anticipation of its adoption as a standard reference material. The use of an indirect polarographic method appeared most feasible. For example, a known excess of a metal ion which forms a complex with EDTA could be added and the excess measured polarographically, allowing the concentration of the EDTA to be determined. More accurate possibilities include adding either a deficiency or an excess of the metal ion, then titrating with a dilute solution of the metal ion or back titrating with a dilute solution of EDTA. In either case the polarograph would be used as an end point detector. In the first situation, the end point would be at the appearance of a peak of the uncomplexed metal ion at high polarographic sensitivity; in the second, the end point would be at the disappearance of the peak of the metal ion.

Several systems were investigated. One of the most favorable was the Cd-Cd EDTA complex in an ammonium hydroxide-ammonium chloride buffer solution. Both the metal ion titration and EDTA back titration were investigated. In the first case, an accurately weighed amount of a commercial lot of EDTA and a slightly deficient amount of high purity cadmium in 50 ml of the buffer solution were titrated with a dilute solution of the high purity cadmium to the appearance of a cadmium peak at about -0.7V vs. a mercury pool anode. The apparatus used is shown in Figure 3. A 100-ml beaker suffices for a titration cell together with a one-ml beaker to contain the mercury pool anode.

Figure 3. Apparatus used for EDTA determination.

In the second case, a slight excess of cadmium was present in the same system as discussed and the solution was titrated with a dilute solution of EDTA to the disappearance of the cadmium peak. The results are shown in Table 11 along with those obtained by coulometry for the same material. Further work on this procedure has been postponed until receipt of a lot of EDTA for use as an SRM. The precision and accuracy of the method should be comparable to that obtained by coulometry, provided larger samples and weight burets were used.

Table 11. Analysis of EDTA (disodium salt, dihydrate).

Na_2 EDTA·2H O_2, percent

Cd titration	EDTA back titration	Coulometry[a]
100.05	100.00	100.036

[a]By George Marinenko, Microchemical Analysis Section.

C. Minor Constituent Analysis

1. Meso-bilirubin

Work at NBS to issue bilirubin sufficiently pure for use as a clinical standard led to the investigation of polarographic determination of a possible impurity, namely meso-bilirubin. Polarographic waves have been reported for each of the materials in a sodium hydroxide supporting electrolyte [8]; however, the separation of half-wave potentials is not sufficient to permit small amounts of meso-bilirubin to be determined in the presence of an excess of bilirubin by using direct polarographic procedures. Since both constituents dissolve readily in dimethylsulfoxide, the use of this solvent was investigated. Lithium chloride was added as a supporting electrolyte. Bilirubin was reduced at about -1.1V and meso-bilirubin at about -1.25V vs. a mercury pool anode. Both peaks were drawn out and ill defined on the cathode-ray polarograph so that slightly less than 30% of meso-bilirubin could be detected in the presence of about 70% bilirubin. By the use of sufficiently pure meso- or bilirubin for calibration solutions in differential polarography, the determination of either would be no problem as the effect of an excess of either one could be eliminated by adding a similar amount to the supporting electrolyte in the second cell. The use of another type of high sensitivity polarographic technique such as pulse polarography, might lead to better peak resolution and lower limits of detection. Also, it is possible that other supporting electrolytes would provide better resolution of the peaks.

D. Small Sample Analysis

1. Antimony and Bismuth in Thin Film and Source Material

The program started several years ago on the analysis of very small quantities of thin films has continued with the analysis of a number of antimony-bismuth films with total weights of several hundred micrograms. The bismuth/antimony

ratios in the samples analyzed recently ranged from about 20/80 to 90/10. Antimony(III) is measured at about -0.1V and bismuth at about -0.2V vs. a mercury pool anode in a supporting electrolyte of dilute sulfuric and hydrochloric acids.

E. Trace Analysis

1. Lead in Fish Protein Concentrate

Samples of a fish protein concentrate produced by the Bureau of Commercial Fisheries for use as a high protein source were submitted for determination of lead. Similar samples were analyzed here earlier [9] by an improved and shortened procedure over the AOAC method. The present samples were produced from fish from a different source and the possibility existed of the presence of large amounts of interfering metals; hence a separation seemed advisable.

The fish protein concentrates, which had been dry-ashed by the Bureau of Commercial Fisheries were received in Vycor crucibles. The samples were moistened with water and nitric acid and evaporated and ignited over a Bunsen burner to oxidize residual organic material. The residues were dissolved in one ml of hydrochloric acid and a few ml of water and again taken to dryness at a low temperature. The residues were then dissolved in 10 drops of hydrochloric acid and 15 ml of water and iron was reduced by heating with a few mg of hydrazine dihydrochloride. The solutions were transferred to a separatory funnel and lead was extracted with sodium diethyldithiocarbamate and chloroform. After evaporation and destruction of organic material, the residues were dissolved in 0.1N hydrochloric acid and measured on the cathode-ray polarograph in the subtractive mode of operation using a background blank carried through the entire procedure. Solutions for the construction of a calibration curve were also carried through the procedure. The peaks measured were extremely well defined and the lead concentration found ranged from 0.5 to 0.7 ppm. Bismuth could have been measured in the same solution if de-

sired. The procedure is more sensitive and quicker than the AOAC spectrophotometric method and the peaks, being better defined, may be measured with greater accuracy than by the earlier polarographic procedure.

2. Lead and Bismuth in Ductile Irons and Stainless Steels

Polarography is very useful in the analysis of low levels of lead and bismuth in a number of SRMs. Not only is the sensitivity and selectivity greater than that obtained by other techniques, but both elements in the ductile irons can be determined simultaneously in a supporting electrolyte containing nitric acid and sodium tartrate after separation of the iron with isobutyl acetate and the lead and bismuth with sodium diethyldithiocarbamate. For the stainless steels, volitalization of the chromium as chromyl chloride is necessary. The results are shown in Table 12.

Table 12. Lead and bismuth in ductile irons and stainless steels.

SRM Number	n	Lead, percent		Bismuth, percent	
		Avg.	s	Avg.	s
		Ductile Iron			
1140	3	0.0052	0.0003	0.0015	0.0001
1140a	3	.0128	.0014	.0031	.0001
1141	4	.00092	.00003	.00008	.00001
1141a	4	.00035	.00001	.00006	.00001
1142	4	.00048	.00008	.00002	.00001
1142a	4	.00028	.00001	.00002	.00001
		Stainless Steel			
160b	2	0.00097	0.00001	< 0.0005	0.00005
1155	2	.00096	.00001	< .0005	.00005

A value of 0.001% lead was obtained for SRM #160a which was carried through the procedure as a control. This agrees with the certified value of lead; bismuth was not certified in SRM #160a.

3. Lead, Bismuth and Tellurium in Special Iron and Low-Alloy Steel Standards

The polarographic methods described above for lead and bismuth are applicable for analysis of a new series of spectrographic iron and low-alloy steel standard reference materials (SRM #1261-1265). Since some of the levels are in the sub-ppm range, the magnitude of the blank encountered is a problem, particularly for lead, as it is a common contaminant of many reagents.

Work to the present time has been confined to acceptance testing and has proved the utility of the method, but blanks of more than 0.5 µg of lead were obtained. One-gram samples were used for SRM #1265, which contained the least lead and bismuth and the concentrations found were approximately 0.3 and 0.1 ppm, respectively. Spark Source Mass Spectrometry (SSMS) found 0.3 ppm of lead, but no bismuth or tellurium was detected. Larger samples will probably be used when the final melts are submitted for certification analysis. Results obtained for the acceptance testing of SRM #1261 and #1263 are shown in Table 13 along with values obtained for SRM #1180 which is provisionally certified to contain 0.0043% lead and 0.0025% bismuth, respectively.

Table 13. Lead and bismuth in steels.

	Polarography		SSMS[a]	
Sample	Pb, %	Bi, %	Pb,%	Bi, %
1261	< 0.0001	0.001	0.00001	0.0003
1263	.002	.001	.001	.002
1180	.004	.002		

[a]By C. W. Mueller and P. J. Paulsen, Spectrochemical Analysis Section.

A method developed in this laboratory for the determination of tellurium in brasses and cast irons [10] was applied to its determination in SRM #1261, 1263, and 1265. The method has proved to be extremely sensitive. Results are shown in Table 14. SRM #1178 has not been certified for tellurium but a value of 0.004% has been obtained by another cooperating laboratory. One-gram samples were taken for SRM #1265. For the certification analysis, larger samples will probably be used and the bulk of the iron will be removed prior to the tellurium separation.

Table 14. Tellurium in steels.

	Tellurium, percent	
Sample	Polarography	SSMS[a]
1261	0.0004	-
1263	.002	0.001
1265	< .0001	not detected
•1178	.004	

[a]By C. W. Mueller and P. J. Paulsen, Spectrochemical Analysis Section.

4. Reagent Analysis

To evaluate blanks in a number of trace analyses, including some discussed above, it was necessary to analyze a number of the reagents used. Whenever available, commercially prepared high-purity reagents or regular commercial reagents which have been found to have low metal contents are used for all trace determinations. In some cases the regular commercial reagents were of sufficient purity and occasionally were even better than the high-purity reagents.

Prior to the analysis of SRM #1265, several reagents and the distilled water used were checked for lead. At the same time, beakers made of two different types of materials, pyrex

and quartz, were used. Both types had been subjected to repeated cleanings and had been used exclusively for trace lead determinations for a long period of time prior to this experiment.

One-hundred ml samples of the reagents in question were evaporated to dryness in the respective beakers. The residues were dissolved in 0.1N hydrochloric acid and lead was measured subtractively with the cathode-ray polarograph at about -0.5V vs. a mercury pool anode. No difference was found in the lead that could be attributed to beaker composition. The results are given in Table 15.

Table 15. Lead in reagents.

	Lead found, ppb (W/W)	
Sample	Evap. in Pyrex	Evap. in Quartz
HCl, commercially purified, bottle A	22 18 18	20 20
HCl, commercially purified, bottle B	18	
HNO_3, commercially purified	1	1
HCl, commercial grade		2
Distilled H_2O		0.1 .1

An unexpected high concentration of lead was found in the purified hydrochloric acid. Accordingly, a second sample was taken from bottle B to eliminate the possibility of an accidental contamination of bottle A, which might have accounted for its high value.

Several different commercially purified acids were also analyzed for iron and titanium to determine their suitability for use in analysis of some new standard reference glasses

(section E.5.). One-hundred ml samples were evaporated to dryness at a low temperature in teflon beakers. The residues were dissolved in 0.1N hydrochloric acid and solutions of oxalic acid and ammonium hydroxide were added. Iron and titanium were then measured subtractively with the cathode-ray polarograph at about -0.2V and -0.5V vs. a mercury pool anode, respectively. The results are shown in Table 16.

Table 16. Iron and titanium in acids.

	ppb (W/W)	
Sample	Iron	Titanium
HCl, commercially purified	11	6
HNO_3, commercially purified	6	< 1
HF, commercially purified	9	2

5. Trace Elements in Glass-Simulated Lunar Standard Reference Materials

As a result of wide-spread need for new glass and rock-type standard reference materials certified for a number of elements in trace concentrations, NBS is now concerned with the issuance of 5 new glass standards, designated as simulated lunar materials. The melts for the standards were prepared at Corning Glass Works and the aim composition is shown in Table 17.

Table 17. Trace elements in glass.

Glass designation	Composition
95GCA	Base glass
95GCC	Base glass + 0.02 ppm of 61 elements
95GCD	Base glass + 1 ppm of 61 elements
95GCE	Base glass + 50 ppm of 61 elements
95GCG	Base glass + 500 ppm of 61 elements

The soda-lime base glass has the approximate composition 72% SiO_2, 12% CaO, 14% Na_2O, and 2% Al_2O_3. This was chosen as the base partially because it can dissolve a wide concentration range of many elements. The 61 different elements added are shown in Figure 4 by the crosshatched portions of the periodic table.

In the preparation of the glass, each melt was withdrawn from the crucible as rods in 6-foot lengths and each length numbered consecutively. It was necessary first to establish the homogeneity of a given lot. The homogeneity checking and analyses of these materials obviously present new problems for many analytical methods. Cathode-ray polarography is a very advantageous technique to use for many of these determinations because of its sensitivity and resolution, however in the presence of the large number of possible interferences, some separations will be necessary for certain elements.

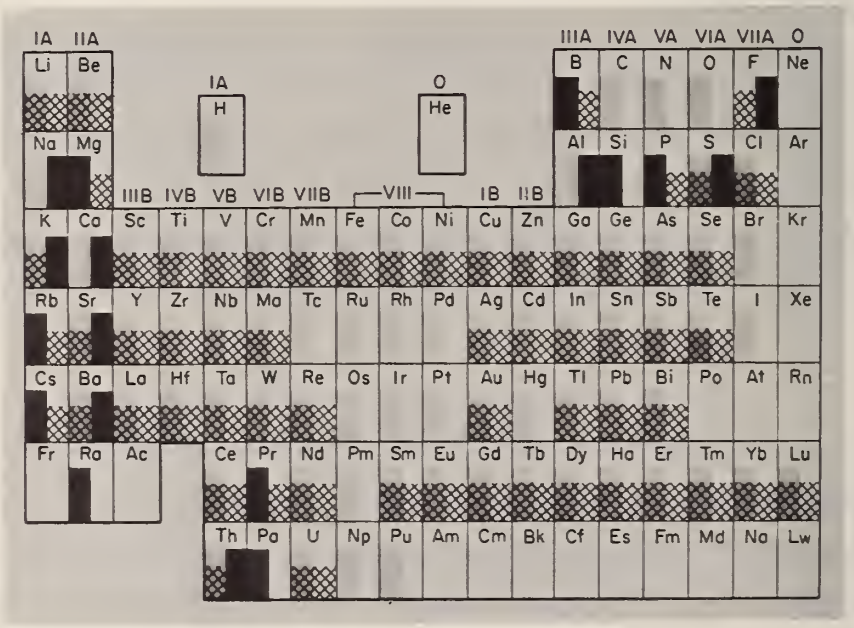

Figure 4. Elements added to glass standard reference materials.

The 500-ppm glass was the first to be ready for analysis. The development of polarographic methods and the determination of Fe, Ti, Ni, and Zn was requested as well as homogeneity testing for nickel at 8 different portions along the glass rods.

It was first necessary to find the optimum supporting electrolytes. It seemed probable that both iron and titanium could be determined simultaneously, as an EDTA-sodium acetate supporting electrolyte had been used previously here with good results for titanium and tables of half wave potentials showed the iron reduction peak to be far enough away from titanium to allow both to be measured with the cathode-ray polarograph. A similar separation of reduction peaks was reported for a sodium pyrophosphate-sulfuric acid supporting electrolyte.

Standard curves for the 1-10 ppm concentration range showed the EDTA media to have better linearity than the pyrophosphate; however either are suitable for this concentration range. Interferences in the doped glasses can be removed by ammonium hydroxide and cupferron separations.

The methods were tested by determination of iron and titanium in SRM #80, a soda lime glass which is presently out of stock. The results are shown in Table 18. Procedure A used the EDTA supporting electrolyte and B, pyrophosphate. The results, particularly for A, show good agreement with the recommended value. This glass was issued in 1927. The earlier certified value for iron was found to be high owing to an inaccurate iron blank correction in the gravimetric procedure used.

The results for titanium in SRM #80 which were obtained at the same time as those for iron are shown in Table 19. Here, also, the results show good agreement for Ti with either supporting electrolyte. Although the TiO_2 value had only been certified to one significant figure, the values reported by cooperating analysts had been rounded off and actually were

known to two significant figures from which an average of 0.023% TiO_2 or 0.014% Ti could be computed.

Table 18. Iron in soda lime glass, SRM #80.

	Iron, percent	
Recommended value	Procedure A	Procedure B
0.056% Fe_2O_3	0.0378	0.0367
	.0382	.0367
(0.039% Fe)[a]	.0382	.0360
	.0382	.0366
Average	0.0381	0.0365
s =	.0002	.0003

[a]Revised 8/30/57 from earlier value of 0.065% Fe_2O_3 (.045% Fe).

Table 19. Titanium in soda lime glass, SRM #80.

	Titanium, percent	
Certified value	Procedure A	Procedure B
0.02% TiO_2	0.0140	0.0141
	.0136	.0139
(0.014% Ti)	.0138	.0137
	.0140	.0133
Average	0.0138	0.0138
s =	.0002	.0003

Methods were then developed for the determination of nickel and zinc in these glasses. Previous experience with nickel has shown it to be best determined in pyridine and either pyridinium chloride or pyridinium sulfate supporting electrolyte, with few interferences. Zinc also gives a very well defined peak in these supporting electrolytes, but is subject to more interferences. In an ammonium oxalate supporting electrolyte, zinc also gives a well defined peak with no interference from Ni, Co, or Mn. Aluminum and a number of other ions present, however, form a colloidal hydroxide precipitate under some of these conditions, possibly occluding some Ni and Zn, making separations from the glass advisable for most accurate results.

Dimethylglyoxime appears to be the most suitable extractant for nickel, and dithizone for zinc. The extraction procedure was checked by spiking 1-g portions of SRM #80 with 0 to 500-µg portions of nickel and zinc. The unspiked glass was used as a blank in the second cell when the final polarographic measurement was made and was also measured against a reagent blank on the second cell and subtracted from the spiked values. Solutions containing 0 to 500 µg of nickel and zinc alone were also taken through the extraction procedure and the results are shown in Table 20.

Table 20. Nickel recovery.

	Ni recovered, µg	
Ni added, µg	Ni alone	Ni + SRM glass
50	48.5	49.8
100	100.6	101.0
200	202.9	201.1
500	512.2	505.6

The nickel recovery from the spiked soda lime glass was calculated by subtraction of that found in the soda lime glass which had not been spiked. The average error in the nickel recovery from the glasses is about a percent which is within the measuring error of direct polarography.

The zinc recovery from the spiked glass was calculated in the same manner as that for nickel. With the exception of the 100-µg spike sample, the recoveries were also within the expected measurement error. The results for zinc are shown in Table 21.

Table 21. Zinc recovery.

	Zn found, µg	
Zn added, µg	Zn alone	Zn + SRM #80
50	49.8	49.4
100	sample lost	96.4
200	197.2	199.0
500	503.6	498.2

The 500-ppm glasses were analyzed for nickel homogeneity using the above method. The glass rods which were 1/2 in. in diameter were cut with a silicon carbide wheel into wafers weighing about 0.7 to 1 g. The use of an entire wafer for analysis provided results representative of the entire cross section.

Samples were taken through the procedure in 6 different sets with 3 to 7 separate determinations being made for each sample position. No differences between different portions of the rods were found greater than that found between sets, thus indicating nickel homogeneity. A total average of 450 ppm of nickel was obtained with a standard deviation of 7 ppm. This uncertainty is about 1.6% of the amount present and is well within the measurement error expected from a direct cathode-ray polarographic measurement.

Preliminary results for zinc show a similar precision. Work now in progress for the determination of iron and titanium in the 500-ppm samples indicates an equally favorable performance.

The methods described should also be applicable to the remaining standards; however, preliminary work on iron and titanium in the blank and 0.02-ppm glass has shown the precision to be much lower and that blank corrections are a major problem.

6. Analysis of Air Pollutants

Among the increasing problems accompanying atmospheric pollution studies has been the lack of reliable and sensitive methods for determination of many of the particulate contaminants. Although the newer polarographic techniques now available should be especially useful for these problems, they do not seem to have been utilized significantly.

In order to check the applicability of polarographic techniques to some of these problems, as well as to obtain information on possible atmospheric contributions to blanks

encountered in trace analyses, a number of air particulate samples were collected and analyzed polarographically. This work was done in collaboration with R. A. Paulson, also of the Microchemical Analysis Section.

An open-type metallic filter holder was used for all samples except for several collected with a glass filter holder ordinarily used for liquids. The latter was used to eliminate the question of contamination from the metal filter holder. Although the glass filter can be cleaned more rigorously, it is not convenient to assemble for air sampling.

It was necessary also to check the blank arising from the filter materials used to collect the sample. A number of types of filters were analyzed and were found to contain appreciable amounts of several elements particularly iron and copper. By simply washing the filters prior to use, however, the blank could be lowered considerably.

A number of samples were taken, both in the laboratory and in two outdoor sampling locations using acid-washed, 47 mm, 0.8- membrane filters.

For the samples taken in the laboratory, the house vacuum line was connected to the sampler and a 10 l/min limiting orifice was placed in the outlet connector of the filter holder. The sampler was placed about 2 feet above the laboratory bench and the amount of air sampled varied from 28 to 80 cubic meters. The samples were then ashed in a low temperature asher, dissolved in hydrochloric acid and measured in an oxalic acid-ammonium hydroxide supporting electrolyte. Iron, copper, lead, and cadmium can all be measured concurrently. Cadmium was not looked for in the first samples as it was assumed that the amounts present would be too low to be detected without resorting to prolonged preconcentration and anodic stripping. It was found, however, that a ten-second pre-electrolysis time was sufficient to obtain a measurable cadmium peak by the stripping technique. The results are shown in Table 22.

Table 22. Analysis of particulates.

	μg/m^3			
	Fe	Cu	Pb	Cd
Room B309, avg	0.22	0.019	0.35	0.002
Room B325, avg	.15	.036	.45	-[a]

[a]Not determined.

For the outside sampling, a pump was used which provided an average flow of about 25 l/min which was checked by attaching a rotometer flow meter to the filter holder. Flow measurements were taken at the beginning and end of a run and an average value was used for calculations. The Station I sampling location is in a suburban residential section, Silver Spring, Md., where all homes are heated with gas. The Station II sampling location is in a heavily wooded country area in Potomac, Md., approximately 5 miles from the nearest town and on a dead end road. The heating in this area is by fuel oil, gas, and electricity. The samples collected were ashed, treated and measured polarographically in the same manner as those just described. The results are shown in Table 23.

Table 23. Analysis of particulates.

	μg/m^3			
	Fe	Cu	Pb	Cd
Station I, avg	1.17	0.040	0.75	0.002
Station II, avg	0.65	.006	.51	.0003

The results represent the average of about 12 determinations of samples collected during the period of November 1968 to February 1969. They are generally in keeping with those obtained for similar sites in different localities showing that polarography is very suitable for determination of certain metallic contaminants of the atmosphere.

(E. J. Maienthal)

3. COULOMETRIC ANALYSIS

A. Introduction

The coulometric analysis laboratory has been engaged in several closely related activities. The major portion of the research effort was devoted to a continuing study and development of precise and accurate methods for major constituent analysis. In general, this effort is dovetailed with the anticipated needs of the Standard Reference Material program. The output of this phase of research (the resulting methods) serves as the basis for evaluation and certification of chemical properties (stoichiometry, oxidizing power, hydrogen ion content, chloride content, etc.) of a large number of SRMs which are disseminated throughout the United States and abroad. It is significant to stress that the evaluation of materials by coulometric methods is conducted on the absolute basis. Thus, the use of coulometry for assay purposes unifies the measured properties through a common set of standards (volt, ohm, gram and second), directly traceable to the four fundamental units, which in turn form the basis of the International System of Units (SI).

To meet the existing need for precise determination of chromium in laser materials a significant effort was devoted to the development of a micro method, which enables determination of total chromium in the material as well as the Cr^{+6}/Cr^{+3} ratio.

As an outcome of NBS research it was possible to recalculate the atomic weight of potassium using a combining weight ratio, which has not been previously used for this purpose.

On the basis of extensive research in the area of analytical chemistry of boric acid, described in a previous report [1] it was possible to verify experimentally the validity of the Roller equation, which predicts the difference between the inflection point and the equivalence point of acid-base titrations.

Through the combined effort of this laboratory and the Mass Spectrometry Section, the atomic weight of naturally occurring boron was redetermined. Also, a number of SRMs and other research materials were characterized coulometrically in the course of the year.

Details of some of the more significant aspects of these activities are given in the following sections.

B. Research Activities

1. Verification of the Roller Equation

It has been known for many years that as acids become progressively weaker, the hydrolysis of their salts is more pronounced and the inflection point of a potentiometric acid-base titration curve occurs prior to the stoichiometric equivalence point. The subject has been treated theoretically in great detail in the early part of this century. However, very little attention has been given to this potential source of significant systematic error in practical analyses. This indifference to a source of error was not an oversight on the part of eminent experimentalists but rather the error was insignificant for their purposes. Moreover, most of the work in chemistry was done by comparative methods in which systematic sources of error are totally or to a large extent compensated, provided an accurately known appropriate standard is used. This characteristic of comparative methods is in fact their forte. On the other hand, the necessity of "an accurately known appropriate" standard is perhaps their weak point.

In the case of absolute methods of analysis such as coulometry, no compensation is encountered and as a result all sources of systematic error (such as equivalence point error) must be evaluated and appropriate corrections need to be applied To this end, it was necessary to establish experimentally the magnitude of this source of error.

According to Roller [11] the difference between the pH at the equivalence point (ep) and the pH at the inflection point

(ip) can be represented by the following equation:

$$(pH)_{ep} - (pH)_{ip} = 0.65 \sqrt{K_w/cK_a}$$

where K_w is the ion-product constant for water ($K_w = 10^{-14}$ at 25 °C), c is the concentration of the salt of the weak acid at the equivalence point (moles/liter) and K_a is the dissociation constant of the weak acid. It is apparent from this equation that $(pH)_{ep} - (pH)_{ip}$ in an "unsymmetrical" titration of weak acid with strong base becomes larger as the concentration of salt at the equivalence point is decreased and as the acid becomes weaker.

Converting the above equation to reflect the error in the titer as a function of cK_a, Roller arrived at essentially the following relationship:

$$\Delta = -3x10^{-12}(cK_a)^{-1}$$

where Δ is the percentage error in the titer due to the $[(pH)_{ep} - (pH)_{ip}]$ difference. Several methods have been used to study, experimentally, the dependence of the inflection point on cK_a.

Valik, in collaboration with MacInnes, conducted differential potentiometric titrations of the dibasic aspartic acid, in which $K_{a_1} = 1.5x10^{-4}$ and $K_{a_2} = 2.5x10^{-10}$. However, these investigators did not find any difference between the titer to the first inflection point and that from the first to the second inflection point. MacInnes pointed out that the difference between the stoichiometric and potentiometric end points increased as the acid or base became weaker, but the difficulty of locating the end point also increased. He stated that "it may be safely concluded that within the accuracy to which the potentiometric end point of a titration can be established, it is identical with the stoichiometric end point" [12].

Bates and Wichers [13], in their precise intercomparison of acids by differential potentiometric titration with a hydrogen electrode, were also concerned about the difference between the inflection point and the equivalence point. They pointed out that a study of the course of titration curves adjacent to and on both sides of the inflection point was made by Bates and Canham. In every case, the inflection point determined experimentally appeared at a pH lower than the equivalence point computed from the dissociation constant of the acid and the ion-product constant for water. Moreover, the differences were somewhat greater than the uncertainties in the calculations and larger than those estimated by the Roller equation.

In the course of a coulometric investigation of the boric acid-mannitol system in our laboratory, pK_a of boric acid was measured in media containing different amounts of mannitol. The results of this study indicate that by merely varying the concentration of mannitol one can have a whole spectrum of acids, varying smoothly in pK_a. The continuum of acids thus produced offers a unique possibility for the study of the relationship between the inflection point and the equivalence point.

a. Experimental. The measurements were conducted using previously-described instrumentation and apparatus [14]. Since, in coulometric acidimetry, it is advantageous to employ 1M KCl as the supporting electrolyte, all measurements reported here were made in aqueous 1M KCl at 25 °C. No attempt was made to control the temperature but on the basis of other measurements in this laboratory, it is known that the temperature of the environment does not ordinarily differ from 25 °C by more than a degree.

In the determination of pK_a of boric acid as a function of mannitol concentration, two concentrations of boric acid solutions were used. They were prepared by weighing appropriate

amounts of borax (NBS pH standard, SRM #187a), addition of a precalculated weight of mannitol to produce the desired final concentration of mannitol, and dilution to volume with 1M KCl. Nitrogen was passed through the solutions to remove CO_2, after which the pH was measured.

Since this borax is very close to stoichiometric $Na_2B_4O_7 \cdot 10H_2O$, or in the resulting solution $[H_2BO_3^-]/[H_3BO_3]$ is close to 1, the value of the pH measured, was considered to be equal to pK_a, where pK_a is the apparent dissociation constant of the boric acid.

A plot of the dependence of pK_a of boric acid in media containing different amounts of mannitol is shown in Figure 5. The effect of mannitol on the ionic equilibria of

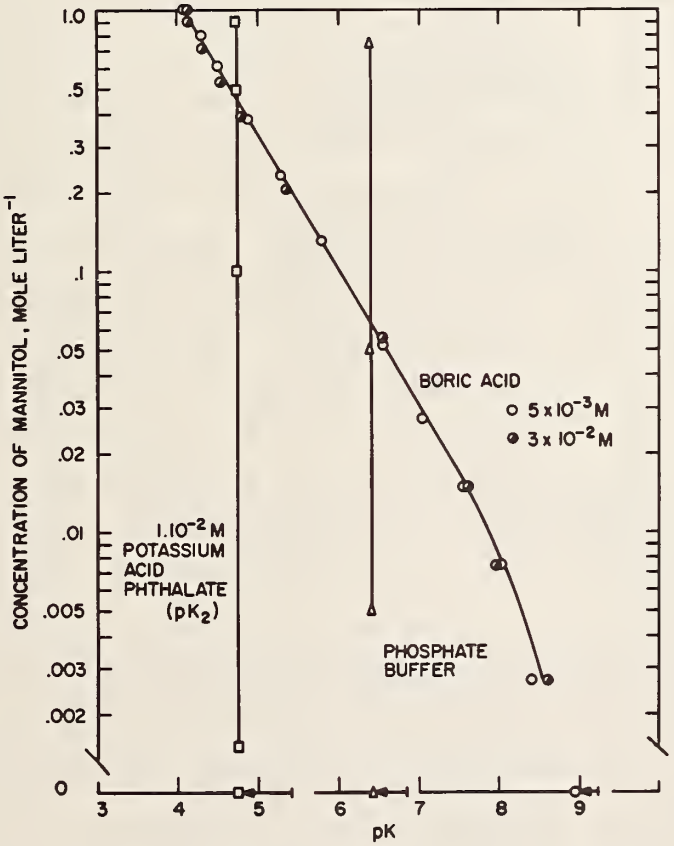

Figure 5. Effect of mannitol concentration on the apparent ionization constant of boric acid in 1M KCl at 25 °C.

phthalate and phosphate buffers was also measured. These two buffers were used in the role of controls and the appropriate curves for them are also plotted on the same figure.

The values of pK_a (or pH) plotted on the abscissa axis were obtained by measurements of the same parameters in the absence of mannitol and the horizontal arrows indicate the apparent change of these parameters caused by the presence of 1M KCl.

A number of different sized samples of virtually stoichiometric boric acid were titrated coulometrically to a differential potentiometric inflection point in 1M KCl containing various amounts of mannitol. Figure 6 shows data for two such titrations. Both the upper and the lower curves show titration of approximately the same size sample of boric acid. The upper titration (A) was carried out in 1M KCl while the lower curve (B) corresponds to a titration carried out in 1M KCl and 0.25M mannitol. The parameters calculated for the systems are shown in the legend of the figure. The presentation of these titration curves is somewhat unconventional and for that reason it merits some explanation. It is well known that a relatively smooth potentiometric titration curve, when plotted as a first derivative, may show a significantly large amount of scatter. Accordingly, while the potentiometric curve itself may appear to be very precisely reproduced under a given set of conditions, the random scatter of points in the differential plot would impair precise determination of the inflection point. When the acid is as strong as B, in the lower part of Figure 6, the pH difference measured for a reaction increment is sufficiently large that the uncertainty of the measurement itself does not affect significantly the differential titration curve. On the other hand, for boric acid titrated in noncomplexed form in 1M KCl, shown in the upper part of Figure 6, the pH differences measured per microequivalent of hydrogen ion reduced the amount to only a few hundredths of a pH unit and therefore the random errors of measurement affect significantly the

differential plot. For this reason, the multiple retitration method was used in order to identify more precisely, the pH of the inflection point. After the sample is titrated beyond the inflection point, a few hundredths of a ml of strong acid such as hydrochloric acid are delivered into the titration cell thus regenerating some of the boric acid, after which a differential potentiometric titration is carried out. The composite curve resulting from 3 such repetitive titrations is shown as A of Figure 6. It is seen that for titration A, where the cK_a value is $7.27 \cdot 10^{-13}$, the potentiometric inflection point occurs approximately 3% prior to the calculated equivalence point, whereas for cK_a value of $2.4 \cdot 10^{-9}$ in B, it is practically coincident with the equivalence point.

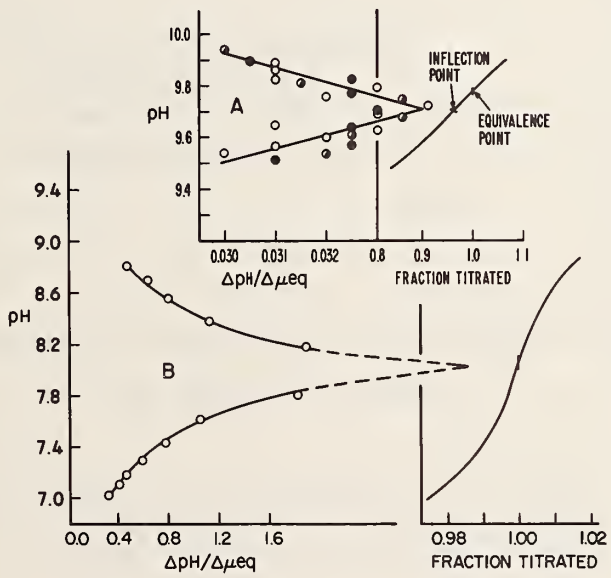

Figure 6. End points of titrations of 0.06 meq samples of H_3BO_3 at different apparent values of K_a.

A. $C = 6.32 \times 10^{-4}$ M H_3BO_3;
$K_a = 1.5 \times 10^{-9}$; $cK_a = 7.27 \times 10^{-13}$

B. $C = 6.02 \times 10^{-4}$ M H_3BO_3;
$K_a = 3.98 \times 10^{-6}$; $cK_a = 2.40 \times 10^{-9}$

The calculated values of the fraction titrated are based on the assumption that assay of the same material in an electrolyte containing higher concentrations of mannitol and boric acid is accurate. The validity of this assumption is substantiated by titration of a number of large samples in three relatively high concentrations of mannitol. These data are summarized in Figure 7.

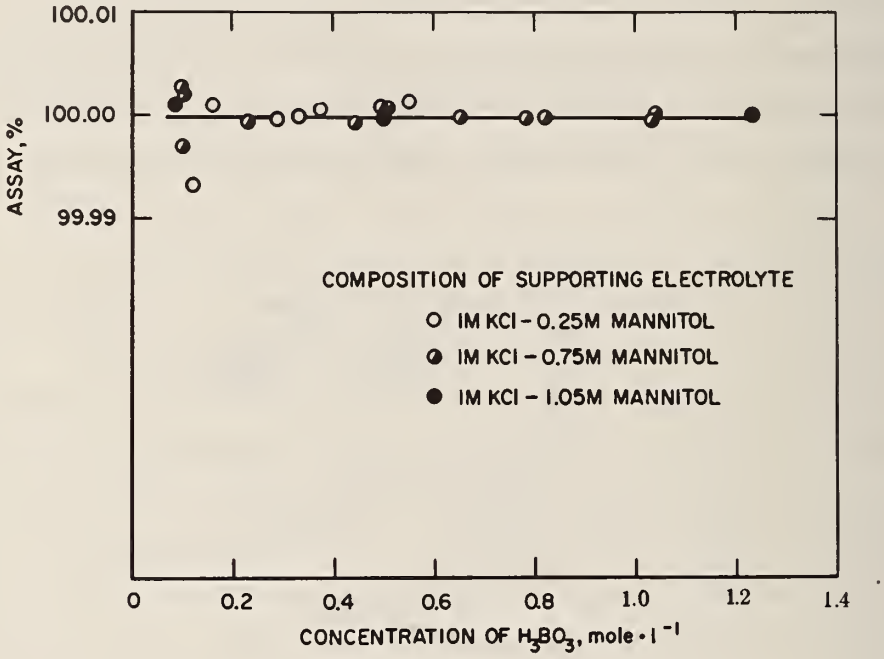

Figure 7. Assay of boric acid as a function of the composition of electrolyte and the concentration of boric acid.

b. Results and discussion. On the basis of data shown in Figure 7, it is evident that in the mannitol concentration range from 2×10^{-2} to 1M, pK_a of boric acid is a linear function of the log C_m, where C_m designates the molar concentration of mannitol. In this range

$$-\frac{dpK_a}{dpC_m} = 2.$$

Since neither the phthalate nor phosphate hydrolytic equilibria are affected by the concentrations of mannitol used in this investigation, as evidenced by the constancy of pH of these two buffers on such addition, it seems reasonable to conclude that the changes in pK_a of boric acid result from the mannitol-borate interaction (complexation). The elucidation of the hydrolytic equilibria in this system is under investigation in our laboratories and will be described elsewhere.

The data obtained in titrations of boric acid for several values of cK_a are summarized in Figure 8. In the figure, experimental points for the error in the assay of boric acid titrated in different media are plotted against the appropriate cK_a. For $cK_a = 2.5 \times 10^{-9}$, the point on the graph represents an average value since some of the individual titration results were greater than 100% and the error function for these results could not be represented on the log graph. The experimental value of the error of this point is 0.002 ± 0.010 absolute percent, where the uncertainty represents the standard deviation of the mean based on 6 degrees of freedom. The solid line represents the titration error predicted by the Roller equation. It can be seen that the errors encountered due to the difference between the inflection point and the equivalence point, determined in these titrations, are in excellent agreement with the errors predicted by the Roller equation over 5 orders of magnitude of the cK_a values.

The use of mannitoboric acid in media of different mannitol concentrations has provided the first test of the Roller equation under conditions where both parameters, c and K_a, can be varied for a single acid of known stoichiometry. Moreover, the applicability of the Roller equation to hydrolytic equilibria involving a complex acid in a medium which is not simply water has been verified, a fact which was not known until the present investigation.

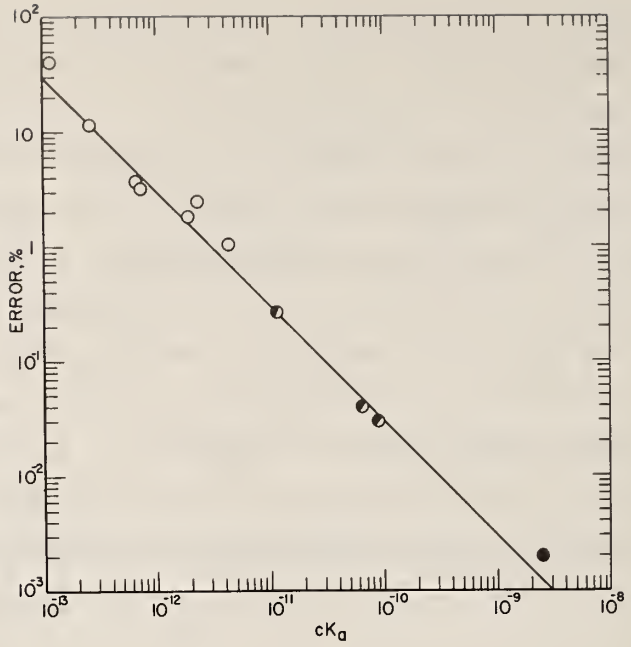

Figure 8. Error encountered in coulometric titrations of mannitoboric acid at different cK_a values due to the difference between potentiometric inflection point and the equivalence point.

Titrations conducted in:

- 0 1M KCl ($K_a = 1.2 \times 10^{-9}$)
- ◐ 1M KCl + 0.047M mannitol ($K_a = 2.4 \times 10^{-7}$)
- ● 1M KCl + 0.25M mannitol ($K_a = 4.0 \times 10^{-6}$)

Solid line represents the error calculated by Roller equation.

The study of pK_a of boric acid in media of different mannitol concentrations opens up an interesting possibility of producing variable pH buffers. In examining Figure 8 one can see that the pH of a borax buffer can be changed 5 pH units (from 9 to 4) by varying the mannitol concentration from 0 to 1M. In the lower mannitol concentration region it would be difficult to accurately prepare buffers because the pH is a log function of mannitol concentration. However, at the two

extremes (0 concentration of mannitol and in the 0.15-1.0M mannitol range) the pH of a buffer can be adjusted with a high degree of precision. The pH of such buffers of a given borax concentration will be a function of mannitol concentration and can be changed by varying the buffer but they would have the same buffer capacity.

2. Recalculation of the Atomic Weight of Potassium

Absolute analytical methods (such as coulometry or absolute gravimetry) may now be carried out with precision comparable and sometimes better (0.001%) than the uncertainty in the atomic weights, so that accurate knowledge of the latter is a prime requisite.

For many years chemical methods for determination of combining weight ratios have been used with reasonable success for the evaluation of atomic weights. Recently, there has been a tendency to determine atomic weights through the use of mass spectrometric measurements of the isotopic abundances and values of nuclidic masses [15]. Denying the mass spectrometric methods no due credit, it should be kept in mind that reliable values of atomic weights can still be obtained by other methods, including accurate analytical methods. It is, therefore, surprising that when one examines the 1961 report of the International Commission on Atomic Weights [16], one discovers that the atomic weight of potassium was apparently based on a single set of measurements of the abundance of ^{39}K, ^{40}K, and ^{41}K isotopes by Nier [17] and the values of the nuclidic masses from the table of Everling, Konig, Mattauch, and Wapstra [18]. (No changes in the atomic weight of K have been made since that time.) The atomic weight value for potassium thus arrived at is 39.102 which is significantly different from 39.098, the value obtained by converting the 1959 chemical atomic weight value (O = 16) 39.100 to the ^{12}C unified atomic weight scale.

Nier's measurements were made on the relative basis since the mass spectrometer was not calibrated on the "absolute" basis with isotope mixtures prepared from the separated isotopes of the element in question. Instead, the mass spectrometer was calibrated with argon. Since argon and potassium have significantly different physical properties it appears that the accuracy of such measurements is contingent on the proof that volatilization of potassium does not alter the isotopic ratios. Such proof was not offered. Nier's measurements show the abundances of ^{41}K, ^{40}K, and ^{39}K to be 6.91 ± 0.04, 0.0119 ± 0.0001 and 93.08 ± 0.04 percent, respectively. The combined uncertainties of the isotopic abundances represent an overall uncertainty of 0.002 AMU in the atomic weight of potassium.

Data obtained in earlier work at the National Bureau of Standards in differential potentiometric titrations of acids by Bates and Wichers [13] may be used for the evaluation of the atomic weight of potassium. Their comparison of the single crystal benzoic acid and potassium hydrogen phthalate to the same lot of Na_2CO_3 produced the following ratios:

$$\frac{C_7H_6O_2}{Na_2CO_3} = 2.304075 \pm 0.00051$$

$$\frac{C_8H_5O_4K}{Na_2CO_3} = 3.853045 \pm 0.000031$$

where the uncertainties represent standard deviations. Using these values, one can readily arrive at the ratio of potassium acid phthalate to benzoic acid

$$\frac{C_8H_5O_4K}{C_7H_6O_2} = 1.672274 \pm 0.000050$$

The atomic weight of potassium, then, may be expressed in terms of the atomic weights of C, H and O as follows:

$$K = 3.705918[C]+5.033644[H]-0.655452[O]$$

where symbols in the brackets represent atomic weights of the indicated elements. Using 12.01115, 1.00797, and 15.9994, for the atomic weights of C, H, and O, respectively, one arrives at 39.099 (± 0.001) as the value for the atomic weight of potassium.

It can be seen that this value is in much closer agreement with 39.098, the atomic weight of potassium adopted in 1959 (normalized to ^{12}C scale), than with the presently accepted value. Since the discrepancy between the presently accepted value and those obtained by other techniques can not be reconciled with the uncertainties ascribed to each, it is hoped that more work will be stimulated to verify the accuracy of the atomic weight of potassium by other independent means.

3. Coulometric Determination of Microgram Amounts of Chromium

Research programs elsewhere at NBS required data on the total amount of chromium in ruby laser material. The concentration of chromium in ruby is approximately at the 0.03% level. The material available for analysis is often in limited amount. In the present instance, a 30-mg sample appeared to be the maximum amount available for analysis. Thus it was necessary to develop a precise and accurate method for determination of 10 μg of Cr with precision and accuracy of a few tenths of a relative percent. In other words it became necessary to develop a method which would enable the determination of 300 ppm of Cr within a few ppm.

A further objective was to develop a method sensitive enough to establish the Cr^{III}/Cr^{VI} ratio. Such a determination is based on the determination of hexavalent chromium originally present in the sample, followed by an oxidation procedure and the determination of total chromium. Small differences encountered in such indirect analyses require precise analytical methods at the submicrogram level.

Earlier studies [19] showed that coulometric generation of ferrous ion at the Pt-cathode can be achieved with one hundred percent current efficiency from an electrolyte two tenths molar or more with respect to ferric ion in two molar sulfuric acid, provided the current density never exceeded four milliamps per square centimeter. The end point in this investigation was determined amperometrically using a polarized Pt-indicator anode and a saturated calomel electrode as the nonpolarizable reference cathode.

A special coulometric titration cell assembly was designed for this determination and is shown in Figure 9. The cell consists of three separate compartments each with a maximum volume of 10 cm^3, separated horizontally by intermediate compartments, in which two fine porosity sintered glass frits are sealed. The two intermediate compartments have stopcocks

Figure 9. Coulometric determination of chromium at nanogram levels.

sealed to the top to allow application of suction or pressure to fill or empty the compartments. The cathode compartment has two 1-cm^2 platinum electrodes sealed in each side of the compartment. The two electrodes serve as the generator cathode and the indicator electrode. Such a cell construction has several advantages: 1) increases the sensitivity of the detection system, 2) eliminates losses of sample into liquid junction by diffusion, 3) minimizes IR drop across the indicator circuit, and 4) allows indicator currents to be measured concurrently with generation.

The separation of the titration cell compartment (cathode) from the reference electrode and the auxiliary anode with small intermediate compartments is essential to eliminate loss of sample into the liquid junction by diffusion. The small amount of sample which diffuses into the two intermediate compartments can be returned to the titration cell by applying nitrogen pressure or vacuum as needed through the stopcocks that are sealed to the top. The auxiliary Pt anode and the SCE reference electrode are further separated from the titration cell with porous vycor rods. This separation minimizes the interference effects which one would encounter if the species formed at the auxiliary anode or the KCl at the SCE electrode were able to diffuse into the small intermediate compartments and later forced into the titration cell. The technique was evaluated with standard hexavalent chromium solutions prepared from SRM #136b Potassium Dichromate. The preparation sample was weighed to the nearest 0.003 mg in a platinum boat using the substitution method.

When required, the persulfate oxidation process was used to oxidize chromium to the hexavalent state. The weights of all solutions were determined by the substitution method.

Two procedures were used to obtain a satisfactory end point. The first technique, applicable to sample sizes of 1 microgram or more is as follows.

A small amount of chromium(VI) is added to the supporting electrolyte in the cell containing 0.5M ferric ion in 2M sulfuric acid. This amount is required in order to oxidize any reducing impurities in the electrolyte and to establish a pretitration curve. Along the linear portion (poised with ferrous ion) of the amperometric curve, the diffusion current is extrapolated to zero current to determine the excess ferrous ion which is formed in pretitration.

Subsequently about 95% of the precalculated amount of ferrous ion is generated, and the weighed hexavalent chromium solution is delivered into the cell. The remaining portion of hexavalent chromium is used to establish a titration curve which has a slope identical to the pretitration curve. The sensitivity (slope) for both curves is about 40 μamp/μeq Fe^{++}. It is apparent that in view of comparable slopes, reliable zero current intercepts for the pretitration and the titration curves can be established to make possible precise and accurate titrations. This procedure of extrapolation to a fixed current value (zero) is essential for samples in the microgram range because the uncertainty in establishing the residual current (0.01 μeq Cr) approaches the working sample size (0.05 μeq or 1 μg Cr). An investigation of the Cr(VI)-Fe(II) amperometric titration curve shows that this uncertainty is primarily due to the reaction rate of the system and to the instability of the indicator currents in the region of the equivalence point.

The second technique (direct reading amperometry) employs a measurement of the change in indicator current along the coulometrically calibrated amperometric curve after the addition of the unknown Cr^{+6} sample. It is used for determining from 200 ng down to 10 ng of chromium. The pretitration is conducted until the indicator current becomes a linear function of $[Fe^{++}]$. Subsequently the indicator current is displaced down scale and then expanded to the maximum sensitivity of the polarograph. Then in this sensitive region the amperometric

curve is calibrated by coulometric generation of small amounts of ferrous ion. The weighed sample is delivered to the titration cell and the indicator current decrease is observed after the reaction is completed. The linear change in iron(II) concentration is evaluated graphically along a normalized indicator current and its intercept is taken as the end point.

Sample solutions (prepared from SRM #136b Potassium Dichromate) ranging in size from approximately 15 nanograms to 30 micrograms of chromium were titrated by the above-described method and the results were studied for precision and accuracy. A summary of the results is shown in Table 24. The average assay value and the standard deviation are given for each sample size. Within the experimental uncertainty, the assay value for any sample size is in good agreement with the certified oxidizing power (99.977 percent). The accuracy of the results for any sample size set is determined by the random errors of measurement. Examination of data shows that this random uncertainty represents virtually a constant amount of chromium, independent of sample size. This error is really the random error of the titration system (i.e., end point sensitivity, volume of electrolyte, stirring rate, etc.). Further improvement is anticipated by appropriate changes of these parameters.

4. Determination of Cr^{+6}/Cr^{+3} Ratio

Future characterization of laser materials will require an accurate knowledge of Cr^{+6}/Cr^{+3} ratio. To this end an investigation of the feasibility of determination of Cr^{+6}/Cr^{+3} ratio was conducted at the microgram sample size level.

Three standard solutions containing known amounts of Cr^{+6} and Cr^{+3} at approximate ratios of 9:1, 1:1, and 1:9 were prepared from $K_2Cr_2O_7$, SRM #136b, the same material as used in the previous section.

Aliquots of these solutions were titrated directly to determine the concentration of Cr^{+6}. Subsequently a procedure

was developed for aliquoting the samples, conducting micro-scale oxidations of Cr^{+3} to Cr^{+6} with persulfate and delivering the resulting oxidized samples into the titration cell without any significant loss.

Table 24. Analysis of $K_2Cr_2O_7$ solution, SRM #136b, assay percent 99.977.

Sample No.	μeq calc	μeq found	% assay
I. Sample size approximately 30 μg of Cr			
1	1.1447	1.1443	99.97
2	1.3678	1.3671	99.95
3	1.4252	1.4245	99.95
4	1.7361	1.7351	99.94
		Average	99.95
		s =	0.02
II. Sample size approximately 2 μg of Cr			
1	0.13005	0.12940	99.50
2	.11219	.1117	99.56
3	.11216	.1119	99.77
4	.11997	.1204	100.36
5	.11095	.11070	99.77
6	.1255	.1253	99.84
		Average	99.80
		s =	0.3_1
III. Sample size approximately 150 ng of Cr			
1	0.00949	0.00950	100.1
2	.00944	.00952	100.9
3	.00940	.0092	97.9
4	.00692	.0070	101.2
		Average	100.0
		s =	1.5
IV. Sample size approximately 15 ng of Cr			
1	0.00089	0.00095	107
2	.00094	.00087	93
3	.00120	.00110	93
4	.00072	.00076	105
		Average	99
		s =	7

Additional aliquots of the above three solutions were analyzed by this new technique. The results of analysis of the above three solutions for Cr^{+6} and total chromium are shown in Table 25.

Table 25. Analysis of synthetic solutions with 9:1, 1:1, and 1:9 ratios of chromium(III) and chromium(VI).

Solution 1. [9:1 ratio of Cr(III) and Cr(VI)]

Sample No.	μeq Cr(VI) calc	μeq Cr(VI) found	% Recovery
1	0.1109	0.1108	99.9
2	.1255	.1253	99.8
3	.1200	.1204	100.3
4	.1122	.1119	99.7
5	.1122	.1117	99.6
		Average	99.9
		s =	0.3

Sample No.	μeq Cr(VI) calc	μeq Cr(III) calc	μeq Cr found	μeq Cr(III)	% Recovery
1	0.1292	1.1262	1.2550	1.1258	99.97
2	.1195	1.0408	1.1598	1.0403	99.96
3	.1233	1.0736	1.1968	1.0735	99.99
4	.1466	1.2763	1.4223	1.2757	99.96
Average	0.1297	1.1292	1.2585	1.1288	99.97
				s =	0.02

Average ratio $\left(\frac{Cr(III)}{Cr(VI)}\right)_{calc} = 8.7062$

$\left(\frac{Cr(III)}{Cr(VI)}\right)_{found} = 8.7032$

Solution 2. [1:1 ratio of Cr(III) and Cr(VI)]

Sample No.	μeq Cr(VI) calc	μeq Cr(VI) found	% Recovery
1	1.0830	1.0826	99.96
2	1.0497	1.0496	99.99
3	1.1203	1.1198	99.96
4	1.0400	1.0397	99.97
		Average	99.97
		s =	0.02

Table 25. (Continued)

Solution 2. (Continued)

Sample No.*	μeq Cr(VI) calc	μeq Cr(III) calc	μeq Cr found	μeq Cr(III)	% Recovery
1	1.1231	1.1440	2.2664	1.1433	99.97
2	0.6626	0.6751	1.3376	0.6750	99.99
3	.8792	.8957	1.7743	.8951	99.96
4	1.0906	1.1110	2.2010	1.1104	99.97
Average	0.9389	0.9565	1.8949	0.9560	99.97
					s = 0.02

Average ratio $\frac{Cr(III)}{Cr(VI)}_{calc} = 1.0187$

$\frac{Cr(III)}{Cr(VI)}_{found} = 1.0182$

Solution 3. [1:9 ratio Cr(III) and Cr(VI)]

Sample No.	μeq Cr(VI) calc	μeq Cr(VI) found	% Recovery
1	1.3432	1.3430	99.98
2	1.5442	1.5436	99.96
3	1.2692	1.2690	99.98
4	1.6833	1.6827	99.96
		Average	99.97
		s =	0.02

Sample No.	μeq Cr(VI) calc	μeq Cr(III) calc	μeq Cr found	μeq Cr(III)	% Recovery
1	1.2339	0.1336	1.3671	0.1332	99.97
2	1.2857	.1392	1.4245	.1388	99.97
3	1.5661	.1696	1.7350	.1689	99.95
4	1.6832	.1823	1.8653	.1821	99.99
Average	1.4422	0.1562	1.5980	0.1558	99.97
					s = 0.02

Average ratio $\frac{Cr(III)}{Cr(VI)}_{calc} = 0.1083$

$\frac{Cr(III)}{Cr(VI)}_{found} = 0.1081$

It is evident that the precision of titrations of these solutions is comparable to the precision of pure dichromate samples of corresponding size. Thus it is possible to determine Cr^{+6}/Cr^{+3} ratio by an indirect method based on the determination of Cr^{+6} followed by oxidation with persulfate and subsequent determination of total chromium as Cr^{+6}. The amount of Cr^{+3} can then be calculated as the difference between the latter and the former titrations.

5. Coulometric Method for Determination of Oxygen in Elemental Boron

In conjunction with other research activities of the National Bureau of Standards, two samples of elemental boron, one sintered in a furnace in the presence of oxygen and the other unsintered powder, were submitted for oxygen determination. It occurred to us that B_2O_3 could be easily converted to boric acid and titrated coulometrically in the presence of mannitol as already described [1]. Each mole of titrated H_3BO_3 would correspond to 0.75 moles of oxygen in the original oxide.

The submitted samples were analyzed by vacuum fusion as well as coulometrically. In the coulometric method, samples were crushed in a steel mortar and delivered into the solution containing mannitol (1M KCl-0.75M mannitol). The results of analysis for the two materials are summarized in Table 26.

It is interesting to note that the results obtained by titration are about a factor of 2-4 lower than those obtained by vacuum fusion.

Several possibilities exist for this apparent discrepancy. In view of the precision of the measurements one has to rule out the possibility of random errors. One must therefore consider possible differences in the two distinctly different measurements.

Vacuum fusion measures the oxygen in the total volume of sample. On the other hand, in the coulometric procedure, though the sample is very finely crushed (i.e., large surface

to volume ratio) there still exists a considerable amount of the sample which is not exposed to the solution. Thus a possibility exists that one measures only the surface oxide by titration. One would however expect that significant leaching of B_2O_3 from the interior would occur and thus the precision of measurement would be greatly affected by the leaching time. This was not indicated by the coulometric measurements.

It is also clear that oxygen in boron in any other form than B_2O_3 (such as iterstitial oxygen, adsorbed, combined with other elements as oxide) would not be detected coulometrically yet would be found in the vacuum fusion determination. Further work is in progress to elucidate the causes of this difference since they can, perhaps, be utilized to an advantage of discrimination between oxygen in the form of B_2O_3 and other possible forms.

Table 26. Determination of oxygen in boron.

Material	Coulometrically determined oxygen, wt %	Vacuum fusion[a]
Unprocessed boron		
Sample 1	0.005	
2	.003	
3	.002	
Average	0.004	0.01_8%
s =	.002	
Sintered boron		
Sample 1	0.306	
	.281	
	.292	
Average	0.298	0.4_5%
s =	.020	

[a]Vacuum fusion analyses were performed by J. T. Sterling Analytical Coordination Chemistry Section.

C. Analysis of Standard Reference Materials

In the course of the past year a number of standard reference materials were analyzed for the purpose of selection, acceptance, and certification. The highlights of this work are presented in the following sections.

1. Analysis of Separated Boron Isotopes

The method described in a previous report [1] was successfully used for standardization of separated boron isotope solutions which were subsequently used by the Analytical Mass Spectrometry Section to prepare known B^{10}/B^{11} ratio blends for calibration of mass spectrometer bias. On the basis of this work, the atomic weight of the reference boric acid sample was calculated (SRM #951, at. wt. 10.811756 ± 0.000053). The same work led to the certification of isotopic composition of SRM #952 Boric Acid. The atomic weight of this material is 10.063267 ± 0.000029.

2. Analysis of Potassium Dichromate

A new lot of potassium dichromate was selected on the basis of coulometric titration of hexavalent chromium with electrogenerated ferrous ion. The material will be reissued as SRM $K_2Cr_2O_7$ oxidimetric standard.

The method employed for the evaluation of this material was developed a few years ago in this laboratory [19]. The results of analysis of triplicate samples from three randomly selected bottles are shown in Table 27.

Table 27. Results of analysis of $K_2Cr_2O_7$, Lot 3608.

Sample No.	Assay, % (3608-1)	Assay, % (3608-12)	Assay, % (3608-26)
1	99.973	99.975	99.980
2	99.976	99.975	99.977
3	99.980	99.981	99.978
	Average	99.977	
	s =	0.003	

3. Calcium Carbonate

The most expedient evaluation of SRM #915, $CaCO_3$ appeared to be via acidimetric reaction. An excess of coulometrically standardized HCl was added to a preweighed sample of $CaCO_3$. The resulting solution was permitted to sit until reaction was complete. Subsequently the contents of the reaction flask were quantitatively transferred into a coulometric cell and the excess acid was back-titrated. The results of analysis of the material "as received" are shown in Table 28.

Table 28. Results of analysis of calcium carbonate.

Sample No.	Assay, %
1	100.000
2	99.993
3	99.984
	99.992

The purpose of the second stage of investigation was to determine the effect of the environment on the assay of $CaCO_3$. Can $CaCO_3$, when exposed to high humidities, be returned to the original state by some physical treatment?

One portion of the material was exposed to 90% relative humidity for one week, then placed in a drying oven at 210 °C for 6 hrs, followed by storage in a desiccator over P_2O_5 until weighing and coulometrically analyzed after each step. A second portion was placed in a 75% RH environment for one week (with occasional stirring of the crystals). A third portion was placed in a 90% RH environment for one week. In each case, five hundred-milligram samples were weighed out, reacted with excess coulometrically standardized HCl, and the excess of HCl was back-titrated coulometrically. The results are summarized in Table 29.

Table 29. Effect of environment on the assay of $CaCO_3$.

Sample No.	Treatment		Assay
1	90% humidity;		99.993
2	210 °C for 6 hrs		100.000
3	P_2O_5 desiccator		99.996
		Average	99.996
4	75% RH		99.986
5	75% RH		99.992
6	75% RH		99.990
		Average	99.989
7	90% RH		99.979
8	90% RH		99.981
		Average	99.980

The value reported for the material "as received" was 99.992%. Since the humidity in the laboratory was about 30%, this value of humidity can be assigned to the assay on an "as received" basis.

It is apparent that the material is only slightly susceptible to moisture (0.02% at 90% RH; perhaps via physical adsorption) and can be returned to the virtually stoichiometric state by placing it in a drying oven.

4. Analysis of Gold-Silver Alloys

In the course of issuance of SRM gold-silver alloys for microprobe standards, it became necessary to have an accurate evaluation of the compositions of these alloys. Coulometry was called upon to do the determination of silver. However, it was found that alloys containing more than 40 percent gold gave difficulties due to problems of solution and required gravimetric determination. The results of both procedures are summarized in the following.

Preliminary studies have shown that an 80% Ag alloy can be parted by successively higher concentrations of nitric acid (starting with 1:4 = HNO_3:H_2O and finishing with essentially concentrated nitric). Similar parting of 60% Ag was not complete as evidenced by the formation of AgCl precipitate when the residual gold is dissolved in aqua regia. Alloys containing higher concentrations of gold (40% Ag-60% Au and 20% Ag-80% Au) could not be parted in nitric acid, nor could they be dissolved in aqua regia, because of encapsulation in the AgCl precipitate. Since the object of these determinations was Ag, the inquartation method was obviously discarded because it would require addition of several times the amount of the element in question. Au-Ag alloys containing less than 10% Ag can be easily dissolved in aqua regia.

The unfortunate situation is that the aqua regia dissolution product (AgCl) is not easily applicable to coulometric analysis.

Thus, the 80% Ag alloy was parted in nitric acid, a small excess of coulometrically standardized NaCl solution was added and the excess NaCl was back-titrated coulometrically with electrogenerated Ag^+. The two results obtained by this method are represented by samples Nos. 1 and 2 in Table 30 under Alloy 1707. The same alloy was also analyzed gravimetrically by parting it in nitric as above, then adding HCl to form aqua regia (thus dissolution of gold and precipitation of AgCl takes place), filtering and weighing AgCl. The results of this determination are shown as sample Nos. 3 and 4 under the same alloy. It is clear that the agreement of the two results is unbiased. The fifth sample was analyzed by first alloying the weighed sample with a sufficient amount of high purity gold to make it an approximately 10 Ag-90 Au alloy, dissolution of this alloy in aqua regia and gravimetric determination of AgCl. This was necessary to establish the accuracy of analysis when fusion of alloy with more gold is performed. Since result

No. 5 is concordant with the other four, the third method is demonstrated to be bias free. Accordingly, all results can be combined into one set and the data treated as homogeneous.

Table 30. Results of analysis of Ag-Au alloys.

	Sample No.		Ag, wt %
Alloy 1707	1		77.58_3
	2		77.52_2
	3		77.52_7
	4		77.58_1
	5		77.58_4
		Average	77.55_9
		s =	0.03_2
Alloy 1706	1		59.95_2
	2		59.96_0
		Average	59.95_6
		s =	0.00_6
Alloy 1705	1		39.98_3
	2		39.98_8
		Average	39.98_5
		s =	0.00_5
Alloy 1704	1		19.90_3
	2		19.94_8
		Average	19.92_6
		s =	0.02_3

The other three alloys (60, 40 and 20% Ag) were additionally alloyed with high purity gold to reduce Ag concentration below 10%, dissolved in aqua regia and the resulting AgCl was

determined gravimetrically. The above coulometrically analyzed 80% Ag Alloy, appropriately alloyed with Au was used as the control. Thus, the analysis of the three higher Au alloys are directly compared to the coulometric assay. The results of analysis are summarized in Table 31.

Table 31. Mass balance for Au-Ag alloys.

20 Au-80 Ag	
Ag determined in this lab	77.56%
Au (mean of 3 labs)	22.43
Total	99.99%
40 Au-60 Ag	
Ag determined in this lab	59.96%
Au (mean of 3 labs)	40.03%
Total	99.99%
60 Au-40 Ag	
Ag determined in this lab	39.98%
Au (mean of 3 labs)	60.05%
Total	100.03%
80 Au-20 Ag	
Ag determined in this lab	19.93%
Au (mean of 3 labs)	80.05%
Total	99.98%

5. Analysis of Potassium Chloride

A preliminary screening of various lots of KCl to permit the selection of the most suitable material for issuance as a SRM was accomplished by coulometric assay. The material will be issued as a halide composition standard as well as a standard for preparation of solutions for conductivity measurements.

Analyses of halides are now conducted in our laboratory by titration with electrogenerated mercurous ion. This appears

to be preferable to argentimetry in the precipitation of chloride since the solubility product of the former is about 8 orders of magnitude lower than that of AgCl. Thus the precipitation reaction is more complete.

The preliminary analysis of two composites from the selected lot under varying pretreatment conditions are shown in Table 32. The results show that a drying procedure is necessary to obtain material of satisfactory assay. Drying at 130 °C removes most of the water but the higher temperature of 200 °C is required to remove water presumed to be in interstices of the polycrystalline material.

Table 32. Results of analysis of SRM KCl.

Sample set		% Assay	Average	Remarks
		Composite 1-6		
I	1	99.915		As received
	2	99.901	99.908	
II	1	99.980		Crushed and dried at 130 °C for 18 hrs.
	2	99.981	99.980_5	
III	1	99.997		Crushed and dried at 200 °C for 18 hrs.
	2	99.996	99.996_5	
		Composite 7-12		
IV	1	99.912	99.912	As received
V	1	99.982		Crushed and dried at 130 °C for 18 hrs.
	2	99.975	99.978_5	
VI	1	99.994_8		Crushed and dried at 200 °C for 18 hrs.
	2	99.995_1	99.995	

6. Analysis of Sodium Chloride

Selection of a desirable lot of NaCl to be issued as a SRM presented similar problems as noted in the case of potassium chloride.

Two lots of sodium chloride (one fine and one coarse) were analyzed for their chloride ion content by titration with coulometrically generated mercury(I). The end point was determined potentiometrically with a mercury-mercurous chloride indicating electrode and a glass reference electrode. All samples were weighed by the substitution method and their masses were corrected for the effects of air buoyancy.

Both lots were analyzed on the "as received" basis and after drying at 130 °C for 18 hrs. Analyses were also carried out on samples from the coarse lot which were ground in an agate mortar and then oven dried at 200 °C for 18 hrs. The results of analysis are summarized in Table 33.

Table 33. Results of analysis of SRM NaCl.

Sample set		% Assay	Average	Remarks
		Fine material		
I	1	99.957	99.957	As received
II	1	99.998_7		Dried at 130 °C for 18 hrs.
	2	100.004_1		
	3	99.998_5	100.000_4	
		Coarse material		
III	1	99.929		As received
	2	99.919	99.924	
IV	1	99.942		Dried at 130 °C for 18 hrs.
	2	99.933	99.938	
V	1	99.996_6		Crushed and dried at 200 °C for 18 hrs.
	2	99.998_0	99.997_3	

It is apparent from sample sets I and III that both lots of "as received" material have a significant amount of moisture. The results for sample set II indicate that drying at 130 °C for 18 hrs is sufficient to remove all the moisture from the

fine lot of NaCl. The results for sample set IV show that the above treatment is not effective in removing all the moisture from coarse NaCl. For example, a comparison of the assay values for sample sets III and IV shows only about 0.01% loss in moisture. However, when this sample is crushed and dried (130 °C for 18 hrs) the assay value indicates that the material is virtually stoichiometric.

Both lots of NaCl appear to be of high purity; but the fine lot can be made stoichiometric somewhat easier than the coarse because it requires no crushing. However, it is evident that both of these materials would require a specification for drying if they are to meet the requirements for primary standard reference materials.

7. Stainless Steel Analysis

The coulometric determination of chromium in stainless steel is very advantageous since the method does not require the additional load of carrying control samples or preparation of standard solutions.

Six bottles of SRM stainless steel samples were received for chromium determination: SRM #160b - 2, SRM #160b - 12, SRM #160b - 15A, SRM #160b - 25, SRM #160b - 28, and SRM #1155.

The samples were weighed, dissolved and oxidized using the same procedure as described earlier for the analysis of chromium in SRM stainless steels #101F and #101G. The chromium(VI) was titrated coulometrically with electrogenerated iron(II). The results of analysis for 500 mg samples are summarized in Table 34. No correction was made for vanadium which was also titrated as chromium. Therefore, in the final calculations, a correction factor corresponding to %V x 0.34 must be subtracted from the weight percent obtained for chromium, based on an independent vanadium determination.

The uncertainty for the analytical process is on the order of 0.03%.

Table 34. Analysis of SRM stainless steel for chromium.

Preparation No.	Bottle No.	Wt %, Cr[a]
1	160b - 2	18.430
2	160b - 2	18.463
1	160b - 12	18.486
2	160b - 12	18.430
1	160b - 15A	18.473
2	160b - 15A	18.442
1	160b - 25	18.484[b]
		18.504[b]
2	160b - 25	18.504
	Average	18.461
	s =	0.028
1	1155	18.492
2	1155	18.460
3	1155	18.442
	Average	18.465
	s =	0.026

[a] Uncorrected for vanadium
[b] Results for same preparation

8. Potassium Dihydrogen Citrate

Assays of several lots of potassium dihydrogen citrate have been made in studies of feasibility as a pH standard. The laboratory scale purification of this material, done at NBS, was very gratifying. The resulting material, analyzed coulometrically, appeared to be virtually stoichiometric.

Coulometric acidimetric evaluation of commercial preparations to serve the same purpose have thus far been discouraging. Two commercial preparations of KH_2 citrate appear to be highly nonstoichiometric. The results of analysis of these two lots of commercial material are shown in Table 35.

Table 35. Analysis of KH_2 citrate.

Sample No.	Titration No.		Assay, %
7124	1		100.141
	2		100.135
		Average	100.138
7125	1		100.358
	2		100.364
		Average	100.361

It appears that these preparations are contaminated with some acid of lower equivalent weight than potassium dihydrogen citrate. Further investigation of possible SRM candidates is in progress.

D. Analysis of Research Materials

In addition to conducting research and analyzing standard reference materials, the coulometry laboratory analyzes at special request various research materials related to other NBS programs which require accurate assay (0.01% or better). A few typical examples which illustrate the nature of this phase of our work are cited.

The titration method described in section 3.B.4. has been successfully used to determine chromium in ruby laser. The results of analysis are summarized in Table 36. The weight percent, calculated as Cr_2O_3 is 0.0346. The standard deviation of the mean, 0.0001 wt %, is somewhat larger than the precision of the method tested with solutions of pure dichromate. Analytical manipulations including dissolution of the material in a pressure bomb, subsequent handling, dilution to volume, aliquoting and oxidation all contribute to the overall error. It is therefore not surprising that the precision of the results with real samples is about a factor of three lower.

Table 36. Determination of chromium in ruby laser.

Sample size - 30 milligrams

Sample No.	Wt % Cr_2O_3
1	0.0348
2	.0344
3	.0345
4	.0348
Average	0.0345

The laboratory continues to study HCl-HF mixtures, resulting from calorimetric experiments, involving combination of halogenated hydrocarbons. The analyses entail determination of hydrogen ion concentration and chloride concentration. Acidimetric analyses of DCl solutions which are needed in conjunction with the establishment of pD scale have also been continued.

Research in the area of conductance standards requires accurate analysis of potassium chloride solutions. A sample set of results in this area is illustrated by the following. Two KCl solutions (labelled #9 and #10) were aliquoted by weight, corrected to true mass and the Cl^- in each aliquot was titrated with electrogenerated Hg(I). The end point of titrations was determined potentiometrically. These analyses are summarized in Table 37. On the basis of these analyses, the #9/#10 ratio is 1.00041_0.

Table 37. Analysis of KCl solutions for conductance measurements.

Sol'n No.	Mass of sample, g	meq X^- found	meq/g
9 a	12.10168	1.205019	0.0995745
9 b	10.08243	1.003805	.0995598
9 c	20.14008	2.005180	.0995617
		Average	0.0995654
10 a	10.56794	1.051805	0.0995279
10 b	8.71284	0.867100	.0995198
10 c	11.58117	1.152630	.0995260
		Average	0.0995246

The standard deviation of each mean (based on pooled standard deviation) is 0.0000038 meq/g (or 0.004 relative %).

Occasional analyses were performed on hydrogen-loaded ion exchange beads. The set of data cited below was taken in order to determine the effect of the duration of drying on the loading factor. Two of the samples were dried in a vacuum oven for 20 hrs at a temperature of 105 °C, and the other two were dried for 188 hrs under the same conditions. The samples were delivered into a coulometric cell with 1M KCl at pH = 7.00, and the liberated H^+ was reduced at a Pt cathode by passage of constant current to pH = 7.00. The results are given in Table 38.

Table 38. Analysis of H^+-loaded ion-exchange beads.

	Dried 20 hrs		
Sample No.	Weight	meq H^+ found	meq H^+/g of bead
15-1	0.2546 g	1.1938	4.689
15-2	.2633 g	1.2338	4.686
		Average	4.688
25-1	0.2663 g	1.2556	4.715
25-2	.1973 g	0.9295	4.711
		Average	4.713

Occasionally there is the opportunity to compare coulometric results with those of other laboratories. This was the case with a synthetic sea water, Standard Sea Water P50, issued by the I.A.P.O. Standard Sea Water Service, Charlottenlund Slot, Denmark. Our mercurimetric determinations of halides in this standard are summarized in Table 39. The ampoule value is based on conventional titrimetry. It is gratifying to see such excellent agreement between two independent measurements.

Table 39. Analysis of sea water standard P_{50}.

Aliquot No.	meq X^-/g sol'n (corrected to vacuum)
1	0.546474
2	.546569
3	.546520
	0.546521

Recalculated as "chlorinity", the results became 19.3757 °/oo as compared with 19.375 °/oo, the value appearing on the ampoule.

(G. Marinenko and C. E. Champion)

4. ELECTROANALYTICAL MEASUREMENTS

A. Introduction

The electroanalytical measurements program has become strongly oriented along the lines of ion-selective electrodes and their microanalytical applications. Although the major portion of this year's time has been used in organizing the Symposium on Ion-Selective Electrodes and in editing the proceedings of that meeting, some limited research and service analyses were undertaken and completed.

B. Symposium on Ion-Selective Electrodes

The Symposium on Ion-Selective Electrodes held at the National Bureau of Standards in Gaithersburg, Maryland, on January 30-31, 1969 was attended by approximately 450 physical and biomedical scientists. The widely divergent disciplines represented were matched by an equally broad spectrum of topics reviewing the state of the art of these electrochemical sensors.

Ten hour-long invited papers were presented by some of the foremost authorities on various aspects of this subject. In addition to the formal presentation of papers, several hours of discussion time were scheduled in order to provide a forum for the active exchange of information on novel applications, instrumentation, and experimental problems and techniques.

Lectures on the first day were concerned primarily with principles, characteristics, basic thermodynamic studies, and reference electrodes while the second day was devoted to interdisciplinary applications ranging from biomedical research and clinical applications to industrial analysis and control.

The first paper by George Eisenman (Univ. of Chicago) entitled "Theory of Membrane Electrode Potentials" dealt with an examination of the parameters determining the selectivity of solid and liquid ion exchangers and of neutral sequestering agents such as cyclic antibiotics and polyethers which offer

the possibility that the exquisite selectivities characteristic of living cells can be duplicated in an artificial electrode. The similarities and differences among the mechanisms of the three types of electrodes were discussed as well as their particular advantages and limitations.

The next paper by James W. Ross (Orion Research) summarized the work directed toward developing useful new ion-selective electrodes of the solid-state and liquid membrane types. In addition, he discussed the general characteristics of these electrodes and the future development of new electrodes of various types. This paper was followed by a similar presentation on heterogeneous membrane electrodes of the precipitate-impregnated type by Arthur K. Covington (Univ. of Newcastle upon Tyne, England). He also discussed the very important topic of reference electrodes. It was pointed out that, although interest is usually directed toward the indicator electrode, the function of the reference electrode should also be thoroughly understood. Liquid junction potentials and essential features, designs, and methods of utilization of reference electrodes were discussed.

James N. Butler (Tyco Laboratories) reviewed the use of solid-state and liquid ion exchange membrane electrodes in studies of the thermodynamics of solutions. Studies of this type range from the measurement of activity coefficients to studies of multiple equilibria in constant ionic media.

Roger G. Bates' (NBS) presentation on activity standards and standardization pointed out that problems arise because there is no unique way of defining the activity of a single ionic species but showed how the pH convention could be extended to yield standards for electrodes reversible to other cations and anions.

The paper by Edward W. Moore (Lemuel Shattuck Hospital) was concerned with studies in biological fluids using the calcium ion exchange electrode. Applications to biomedical

research and clinical medicine were presented in connection with studies of hyperparathyroidism, cirrhosis, and hypercalcemia of malignancy.

Raja N. Khuri (American Univ. of Beirut, Lebanon) reviewed the uses of both the glass and non-glass ion-selective electrodes in biomedical research. Problems associated with potentiometric measurements in biological systems both *in vitro* and *in vivo* were discussed.

A review of the uses of these sensors in physicochemical studies was given by Garry A. Rechnitz (State Univ. of New York at Buffalo). While devoted primarily to kinetics and complex ion studies, he also described some of the interesting problems raised regarding the method of operation of these sensors.

Truman S. Light (Foxboro Company) discussed industrial analysis and control using ion-selective electrodes in various modes of operation such as monitoring flowing streams by single or multiple electrodes, observation of a sample stream following reagent injection, and the use of ion-selective electrodes as end-point detectors in automatic process titrators.

Richard A. Durst (NBS) reviewed direct potentiometric techniques, potentiometric titrations, and the analytical applications of ion-selective electrodes to various problems including oceanographic, pollution, and agricultural studies.

The formal report of these proceedings will be published in book form. This, approximately 500-page volume, will include the complete texts of the invited lectures plus a transcription of selected segments of the recorded discussions. This NBS Special Publication [20] should be of considerable value in advancing the state of the art by providing a thorough evaluation of the subject and a comprehensive review.

C. Research Activities

1. Modification of a Silver Sulfide Ion-Selective Electrode for Microchemical Analysis

Previously, a fluoride electrode was modified for microchemical analysis by inverting the electrode, encircling the membrane with a sleeve, and placing the sample solution into this microcell [21,22]. In the case of the silver sulfide electrode, sample microcells may be formed by drilling depressions directly into the silver sulfide membrane. This soft, polycrystalline material is easily drilled with little tendency to fracture or cleave.

A cross-sectional view of the final electrode configuration is shown in Figure 10 with the drilled 5- and 10-µl depressions. A teflon cap is milled to fit snugly over the end of the electrode body and a 1 mm hole is drilled through this cap to accommodate the reference electrode probe. The purpose of the cap is to reduce evaporation of the small volumes of sample and to facilitate alignment of the reference probe and sample cell.

The 0.1N $AgNO_3$ internal reference solution of the silver sulfide electrode is not gelled with agar as used with the fluoride electrode [21], since the agar reacts with silver. Instead, the electrode is completely filled with the reference solution to eliminate problems from entrapped air bubbles. A silica gelled internal reference solution was also used with good results, but entails considerably more work to prepare.

Comparable results were obtained with both the 5- and 10-µl sample compartments. Figure 11 illustrates the response of the electrode (5-µl cell) to varying activities of silver in both buffered (with respect to silver) and unbuffered solutions. In the case of unbuffered silver nitrate solutions, the electrode response is Nernstian down to almost 10^{-7}M (point #6). However, for solutions buffered by the presence of various insoluble silver salts, the response is Nernstian (solid line)

down to the lowest level studied, approximately 10^{-25}M. Apparent deviations from Nernst response are more likely due to errors in calculating the silver activity than to non-Nernstian behavior of the electrode. These results suggest that the electrode must, at some point, begin to respond to some complex form of silver, since at the lowest silver activities, there are theoretically no free silver ions in the solution. In fact, at point #13 on the curve, the electrode is apparently responding to 1 millionth of an atom of silver (again assuming it is responding only to free, hydrated silver ions)! Certainly, further studies are needed to elucidate this rather anomalous electrode behavior.

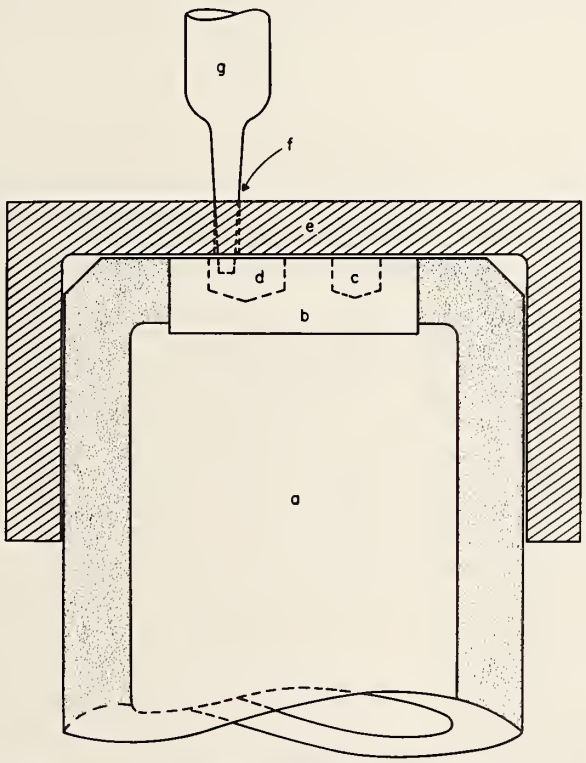

Figure 10. Inverted silver sulfide membrane electrode. (a) internal reference electrode compartment; (b) polycrystalline silver sulfide membrane; (c) and (d) sample solution cells: 5 and 10 µl, respectively; (e) teflon cap to prevent sample evaporation; (f) 1-mm diameter hole in cap for insertion of external reference electrode salt bridge; (g) reference electrode salt bridge containing 4% agar gel of saturated KNO_3.

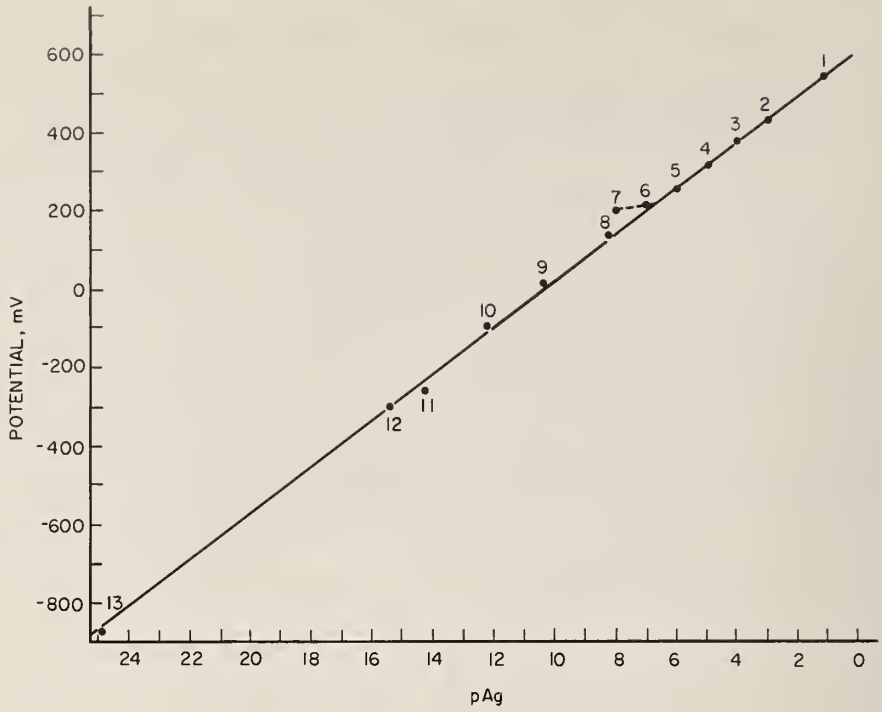

Figure 11. Silver sulfide electrode response to silver activity (test solution vol. = 5 µl).

(Solid line: 59.2 mV/pAg)

Point	Solution Composition	∿ pAg (calc)	E(mV)
1.	10^{-1}M $AgNO_3$	1.1	+ 550
2.	10^{-3}M "	3	+ 438
3.	10^{-4}M "	4	+ 385
4.	10^{-5}M "	5	+ 323
5.	10^{-6}M "	6	+ 260
6.	10^{-7}M "	7	+ 225
7.	10^{-8}M "	8	+ 213
8.	Sat'd AgI	8.2	+ 150
9.	Sat'd AgI + 10^{-6}M KI	10.3	+ 21
10.	Sat'd AgI + 10^{-4}M KI	12.3	- 91
11.	Sat'd AgCl + 1M $Na_2S_2O_3$	14.2	- 256
12.	Sat'd AgCl + 0.1M KI	15.5	- 298
13.	0.1M Na_2S + 1M NaOH	24.9	- 872

2. Construction and Characteristics of a Fluoride Ion-Selective Microelectrode

The feasibility of constructing a fluoride microelectrode suitable for studies in microliter volumes of sample solutions has been demonstrated. This basically simple and straightforward technique illustrates the potentiality of such ion-selective electrodes in studies similar to those in which glass microelectrodes are currently used. Although still about two orders of magnitude larger than the smallest glass microelectrode [23], the characteristics of this first fluoride microelectrode are encouraging enough to prompt further work in the miniaturizing of this and other ion-selective electrodes.

Previously, small volumes (5 to 50 µl) could be studied with the conventional ion-selective electrodes using the inverted electrode technique, such as was demonstrated with the fluoride electrode [21,22], or the drilled-well electrode, as described above for the silver sulfide electrode. Although these systems allow measurements on small volumes of solution, these electrodes cannot be used for measurements *in situ* but, rather, the sample has to be placed in the microelectrode cell. In contrast, while this fluoride microelectrode is still too large for most *in vivo* measurements, it would be applicable to certain *in situ* studies where the solution volume is a limitation or in conjunction with other microelectrodes, where simultaneous measurements must be made on a limited volume of sample or on a continuous basis. In such cases, the inverted microelectrodes would not suffice.

The microelectrode (Figure 12) is constructed from a section of polyethylene tubing drawn out to a 2-mm (o.d.) neck at the lower end. A small, cone-shaped piece of lanthanum fluoride is inserted into this narrow end of the tube and heat sealed into place. In the first design, the microelectrode was used in this form, but was later refined as shown in the enlargement of the tip (Figure 13). In this latter design, the tip was painted with polystyrene coil dope which, after drying,

was scraped away to expose a small, well-defined area of the crystal tip.

In addition, the first form of the electrode employed a mercury contact to the inner surface of the lanthanum fluoride membrane. This type of contact proved unsuccessful, and the internal reference electrode system was used. This consisted of an internal 0.1M NaF-0.1M KCl solution into which dipped the silver-silver chloride reference electrode. The electrode was connected to the meter by shielded cable.

The final form of the microelectrode tip (Figure 13) was an exposed conical portion of the LaF_3 crystal of approximately 1.5 µl volume. This small area electrode had a relatively low resistance of 900 KΩ.

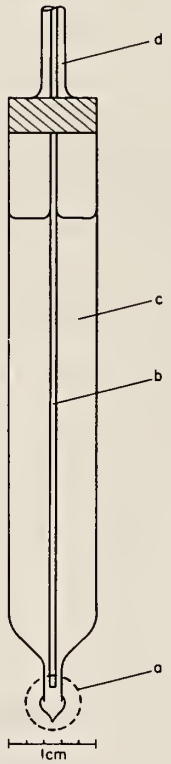

Figure 12. Fluoride microelectrode.

(a) Microelectrode tip (see enlargement - Figure 13).
(b) Silver-silver chloride internal reference electrode.
(c) 0.1M NaF-0.1M KCl solution.
(d) Shielded lead to pH-millivolt meter.

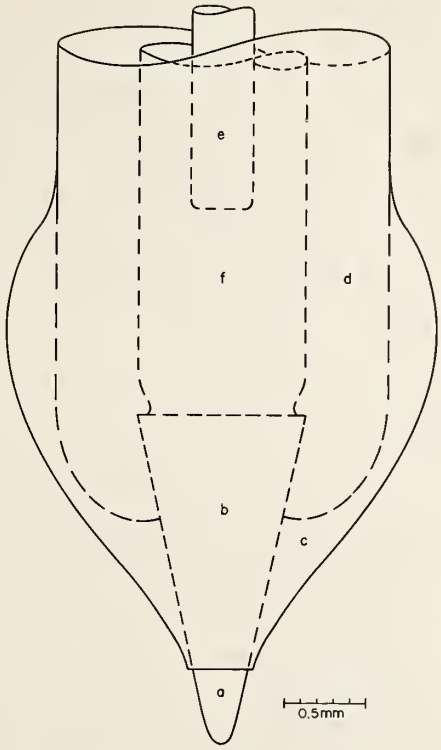

Figure 13. Detail of fluoride microelectrode tip. (a) lanthanum fluoride tip (uncoated), volume ∿ 1.5 µl; (b) LaF_3 crystal body [insulated with (c) polystyrene coil dope]; (d) polyethylene tube (electrode body); (e) silver-silver chloride internal reference electrode; (f) NaF-KCl (each 0.1M) reference solution.

With respect to the original form of the microelectrode, i.e., mercury internal contact and uncoated (fully exposed) membrane tip, the principal problem was poor long-term stability. Although the slopes of individual calibration curves, run within one hour's time, were approximately Nernstian (average slope: 57.7 mV/pF), the variation in the E° of this electrode was on the order of ± 20 mV from day to day.

The depth of immersion of this uncoated electrode tip had little effect on the potential. The emf shifted about 2 mV negative over the 1-mm length of the exposed crystal. This is not too surprising, however, since even when just a small portion of the tip enters the solution, it is very likely that a film of the solution coats the entire crystal. The small variations in emf that do occur are probably due to fluoride activity variations within the thin solution film.

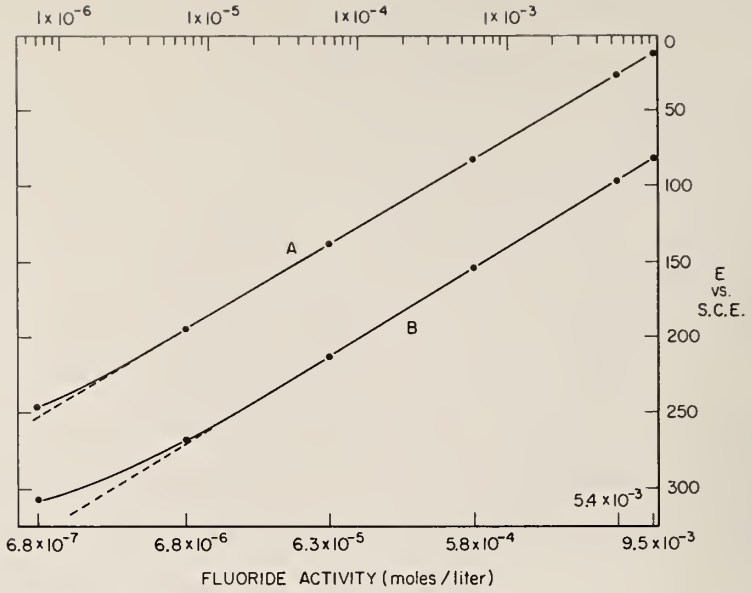

Figure 14. Microelectrode response to fluoride activity.
Curve A - Original design electrode (mercury internal contact and uncoated membrane tip).
Curve B - Improved electrode design (Ag-AgCl internal reference and partially coated tip).

Using the "improved" version of this electrode, i.e., Ag-AgCl internal reference and coated tip, the response to fluoride activity shown in Figure 14 was obtained. Although deviating noticeably from Nernstian response in the micromolar range, the slope in the more concentrated solutions is improved (59.5 mV/pF). The coated electrode showed no depth of immersion effect, and the long-term E° variations were improved by a factor of ten to ± 2 mV (possibly due to room temperature variations; measurement cell not thermostated).

All of the measurements were made on macro volumes of stirred solutions (approx. 25 ml) against a normal-size saturated calomel electrode. Using a micro capillary reference electrode in conjunction with this micro fluoride electrode, measurements could be made on 2-µl sample volumes. Further miniaturization is possible along similar construction lines which could lead to intracellular fluoride determinations.

D. Analysis of SRM Gold-Silver Metal Microprobe Wires

The composition of four Au-Ag alloys (20 mil wire form), intended for use as electron microprobe standard reference

materials, was determined by a gravimetric procedure in which preferential dissolution of one of the constituents was affected prior to analysis. Due to the uncertainties in the previously reported values [1], redeterminations of the gold content of the alloys were performed using a slightly modified procedure. The low silver alloys were again inquartated with enough high-purity silver to increase the silver content to between 70 and 80%. At this level, all of the alloys can be easily dissolved in 1:1 nitric acid. The gold residue is filtered and ignited. Instead of weighing at this point as before, the gold is dissolved in aqua regia, and a small quantity of residual material (presumably AgCl from undissolved silver occluded by the gold and silicate material from the inquartation crucible) is removed by filtration. The gold is then reprecipitated with sulfurous acid, filtered, ignited, and weighed.

The results are given in Table 40 and supercede all previously reported data. There appears to be no difference, within the precision of the results, between the composition of the lead and trail ends of the alloys.

Table 40. Values for gold.

Nominal: Au, %	Ag, %	Found: Au, %
20	80	22.46
40	60	40.06
60	40	60.04
80	20	80.13

E. Analysis of Miscellaneous Materials

1. Determination of Fluoride in Dust Samples

The versatility of the fluoride ion-selective electrode to unusual analytical problems is illustrated by its application to the determination of fluoride in a sample of dust. The analysis of fluoride in this sample was performed using combustion in an oxygen flask and determination with the fluoride ion-selective electrode. Three determinations were made using 0.2-0.3g samples. The results were

63 ppm
122 ppm
78 ppm
Mean 88 ppm.

Washed laboratory sand and dust from the NBS grounds were also analyzed. No fluoride was detected within the sensitivity of the method which is approximately 2 ppm with this size sample. The variation in the results of the sample could be caused by inhomogeneity of the sample or incomplete combustion of the fluorine compounds in the sample.

The oxygen flask method was used (by R. A. Paulson) for the combustion using a polycarbonate flask. Fifty µl of diethylene glycol was added to the sample as a combustion aid. Ten ml of 0.1M potassium nitrate solution was used as the absorbant. The same solution was used to wash out the flask and the final volume was 25 ml. A fluoride ion-selective electrode and a plastic silver-silver chloride reference electrode in an all plastic system were used for the direct potentiometric determination of the fluoride. The electrode system was calibrated with standard fluoride solutions in the range from 10^{-3}M to 10^{-5}M.

2. Determination of Fluoride in Acid Mixtures

In support of NBS calorimetry research, analyses were performed on aqueous mixtures of hydrofluoric acid and (a) HCl and (b) HNO_3.

In the first case, the fluoride determinations in the HF-HCl mixtures were performed by the potentiometric titration with a standard $LaCl_3$ titrant using a fluoride ion-selective indicator electrode. The analyses were carried out on 0.5-0.9g aliquots of the four fluoride sample solutions resulting from the reaction of ClF_5 and NF_3O with mixtures of H_2 and O_2. Results ranged from 0.5 to 0.8 meq F^-/g soln.

Fluoride was determined by direct potentiometry in HF-HNO_3 mixtures produced by the thermal decomposition of fluorinated, substituted triazines. Approximately 2-ml samples of the mixtures were weighed, neutralized, and diluted to 25 ml prior to direct potentiometric measurement with a fluoride electrode. The analysis results ranged from 2.4 to 7.7 x 10^{-2} mmole F^-/g solution for 12 separate samples, and agreed well with the theoretically calculated fluoride contents.

(R. A. Durst)

5. COMPLEX EQUILIBRIA STUDIES

A. Introduction

Frequently analytical procedures involve complex equilibria which are not well understood. Knowledge of the chemistry involved in such systems is of interest from a purely theoretical standpoint, in that the methods do not have to be accepted empirically, and from a practical standpoint, in that improved methods are possible only when existing methods are understood. During the past year the boric acid-borate-mannitol system [24] and several lanthanide-nitrate systems have been investigated.

B. Research Activities

1. Aqueous Boric Acid-Borate-Mannitol Equilibria

The stoichiometry and equilibria of the boric acid-borate-mannitol system have been the subjects of extensive studies. It is generally thought that mannitol reacts with borate to yield complexes of the borospiran structure with mannitol-to-boron ratios of 1:1 and 2:1. While Tung and Chang [25], Boeseken and Vermaas [26,27], Deutsch and Osoling [28], Ross and Catotti [29], and Torssell [30] agree that both 1:1 and 2:1 complexes are formed, they report widely divergent formation constants. Antikainen [31] reports that, over the range of mannitol solubility, the 2:1 complex is incompletely formed and the ratio of complexed mannitol to complexed boron does not exceed 1.8. Very recently Nickerson [32] has reported that only a 1:1 species is formed and proposes the previous workers have been in error since they presupposed a 2:1 complex and interpreted the data to fit that model. While results from this laboratory do not support the conclusions of Nickerson, his criticism does, at least in some cases, have merit.

The boric acid-borate-mannitol system has therefore been reinvestigated to establish unequivocally the stoichiometry of the system and tc obtain reliable values for the equilibrium

constants involved. In those cases where the experimental data seemed reliable, the data of previous workers were re-evaluated according to the stoichiometry found in this work. Reassessment of these data has revealed a number of misinterpretations which, once resolved, yield consistent results. Several instances of such data reassessment are discussed below.

a. Experimental. Commercially available boric acid, sodium metaborate, sodium tetraborate (borax), mannitol, and deuterated solvents were used.

A 60 MHz nuclear magnetic resonance spectrometer was used to obtain the proton magnetic resonance spectra of a 0.5M mannitol solution and 0.5M mannitol solutions containing excess borate and boric acid. The spectrum of an additional mannitol-boric acid sample containing DCl to repress the ionization of boric acid was obtained. All spectra (Figure 15) were obtained in D_2O and the chemical shifts measured relative to acetone internal standard.

All pH measurements were obtained using an expanded scale pH meter and a glass-reference combination electrode. The pH meter was calibrated using pH 4, 7, and 10 buffers. All measurements were at 25.0 ± 0.5°.

For experiments with large amounts of mannitol present, a boric acid or borax solution of twice the desired concentration was prepared and 50-ml aliquots were delivered to 100-ml volumetric flasks. The desired amount of mannitol was weighed, dissolved in the minimum amount of distilled water and transferred quantitatively to the volumetric flask. The solution was diluted to volume, mixed thoroughly, and the pH of the resulting solution was measured. Plots of pH vs. log mannitol concentration were obtained in this manner for borax concentrations of 1.000×10^{-3}M to 5.000×10^{-2}M. Typical examples of these plots are shown in Figure 16. A similar plot for a 0.200M boric acid solution is shown in Figure 17.

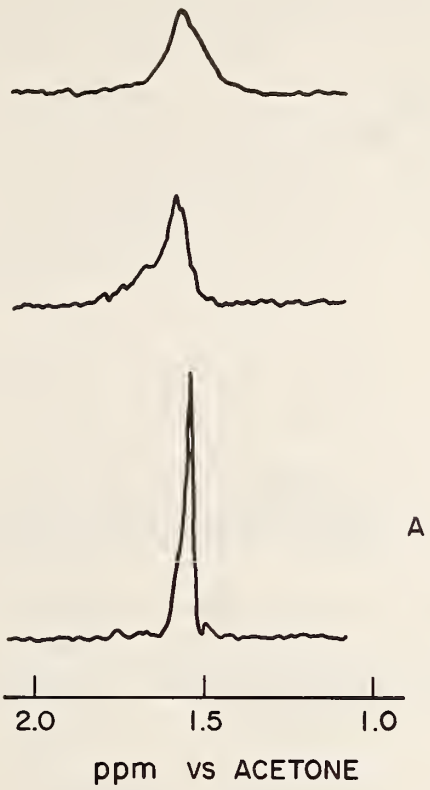

Figure 15. Proton magnetic resonance spectra in D_2O of: A) 0.5M mannitol; B) 0.5M mannitol, 1.0M boric acid; C) 0.5M mannitol, 1.0M sodium metaborate. Addition of DCl to B returned spectrum to A.

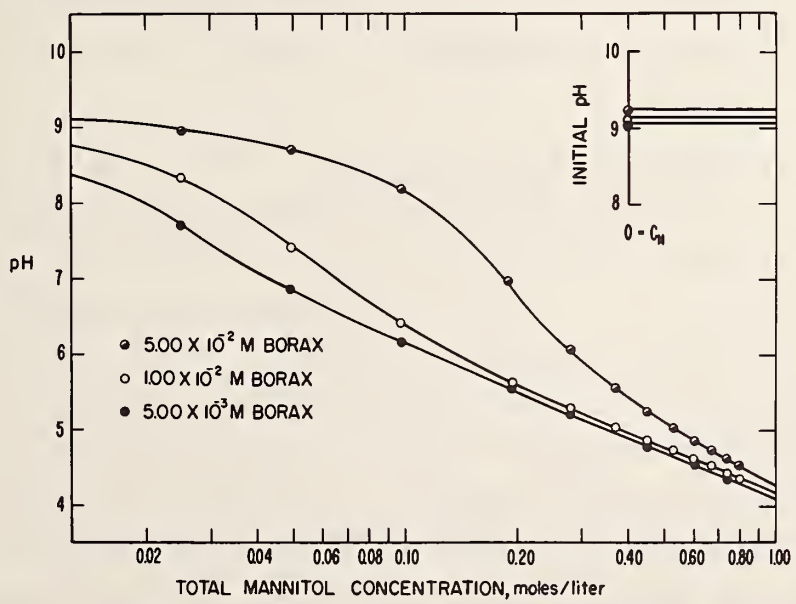

Figure 16. pH of mannitol-borax solutions in which mannitol concentration was varied, borax concentration was held constant.

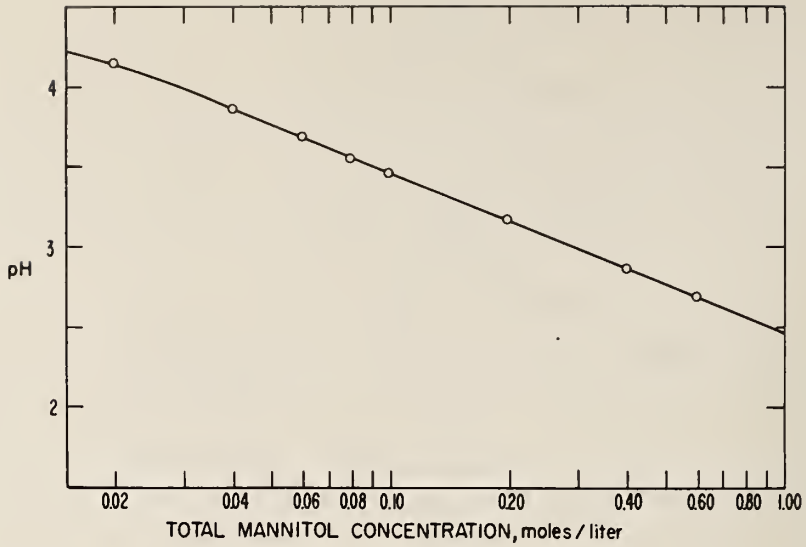

Figure 17. Formation constants for BM^- calculated from changes in pH of a 10^{-2}M borax solution to which small amounts of mannitol were added. See Table 41.

For experiments with small amounts of mannitol present, a 1.000 x 10^{-2}M mannitol solution was delivered in small increments to 100.00 ml of the appropriate boric acid-borate solution from a 5-ml buret. Measurements of pH were taken to the nearest 0.001 pH unit after each addition of mannitol. Data from a typical titration of this kind are shown in Table 41.

b. Results and discussion. The proton magnetic resonance spectrum of 0.5M mannitol in D_2O is shown in Figure 15, curve A. The eight non-alcoholic protons of mannitol are so similar that only a single resonance appeared in the spectrum at about 1.5 ppm vs. acetone. In the presence of 1.0M borate, curve C, the singlet was considerably broadened. If mannitol forms a borate complex, this broadening would be expected due to a small change in the chemical shift of protons on the carbons carrying boron bonded oxygen as well as coupling of these protons to boron. In the presence of 1.0M boric acid, curve B, the mannitol singlet was only slightly

broadened, presumably due to complexation of the small equilibrium concentration of borate. In the presence of boric acid and enough DCl to repress its ionization, the spectrum was the same as that of mannitol alone, indicating no complex formation. Mannitol was therefore considered to react only with the borate anion and not with boric acid.

Table 41. Titration of 100 ml 9.389 x 10^{-3}M borax with 1.000 x 10^{-2}M mannitol.

ml. Titrant	pH	(B^-) x10^3 mol/l	(BM^-) x10^4 mol/l	(M) x10^5 mol/l	log K_1
0	9.110	9.389	-	-	-
0.50	9.108	9.299	0.43_0	0.68	2.83
1.00	9.106	9.210	0.85_5	1.35	2.84
1.50	9.104	9.123	1.27	2.11	2.82
2.00	9.102	9.036	1.69	2.71	2.84
2.50	9.100	8.951	2.09	3.49	2.83
3.00	9.098	8.867	2.49	4.23	2.81
4.00	9.094	8.700	3.28	5.66	2.82
5.00	9.090	8.540	4.02	7.60	2.79
6.00	9.087	8.400	4.58	10.80	2.70
7.00	9.084	8.265	5.10	14.42	2.63

$$(HB) \cong (HB)_{initial} = (Borax) = (B^-)_{initial}$$

$$(B^-) = \frac{(HB)K_a}{(H^+)}$$

$$(BM^-) = (B^-)_{initial} - (B^-)$$

$$(M) = (M)_{total} - (BM^-)$$

$$K_1 = \frac{(BM^-)}{(B^-)\,(M)}$$

(1) Determination of the maximum mannitol to boron ratio and the formation constant of the highest complex. Having established that mannitol (M) reacts only with borate (B^-) the increase in acidity of a boric acid (HB) solution upon adding mannitol was considered to occur in two steps. The dissociation (hydrolysis) of boric acid,

$$B(OH)_3 + H_2O = B(OH)_4^- + H^+$$

which may be written more conveniently as

$$HB = B^- + H^+ \qquad K_a$$

followed, upon the addition of mannitol, by formation of some complex(es),

$$B^- + nM = BM_n^- \qquad K_n$$

The overall reaction which was followed by monitoring pH was therefore

$$HB + nM = BM_n^- + H^+ \qquad K_o = K_a K_n$$

Previous investigators have studied this reaction by monitoring the pH of a boric acid solution upon addition of mannitol in increments. As will be seen, this has led to a variety of interpretations and erroneous conclusions due largely to the fact that extremely small initial borate concentrations are present. In this work, borax was used instead of boric acid, hence (HB) = (B^-) initially. The pH of solutions of constant borax concentrations was measured after adding various amounts of mannitol. Typical plots of pH vs. log total mannitol concentration are shown in Figure 16.

For the overall reaction above,

$$K_o = \frac{(BM_n^-)\ (H^+)}{(HB)\ (M)^n}$$

solving for pH,

$$pH = - n \log (M) - \log K_o - \log \frac{(HB)}{(BM_n^-)}$$

At high mannitol concentrations, (M) was approximately equal to the total mannitol concentration, C_m. It can be seen from Figure 16 that the minimum pH's obtained experimentally were on the order of 5. The source of hydrogen ion must have been the dissociation of boric acid and, since hydrogen ion concentrations of 10^{-5}M were negligible to within a percent or better compared to the initial concentration of boric acid, (HB) was considered to be the initial boric acid concentration and borate from the dissociation of boric acid was considered to to be negligible. Finally, if the formation constant of the complex was large, all of the borate could be considered to be in the form BM_n^- at high mannitol concentrations.

When these three approximations are valid, the previous equation simplifies to

$$pH = - n \log C_m - \log K_o$$

and the plot of pH vs. log C_m has slope - n and intercept - log K_o. In Figure 16 it can be seen that the approximations hold for 0.005M and 0.01M borax. The linear portions with a slope of -2 indicate a 2:1 mannitol-to-boron ratio for the complex. (The maximum C_m's are approaching the solubility limit of mannitol so that 2:1 represents the complex of maximum ratio). At high borax concentration, 0.05M, the curve approached but did not quite reach a linear portion of slope -2. Presumably, the assumption that all borate was present as BM_2^- did not hold.

The intercept of the 0.01M and 0.005M borax curves with the pH axis at log C_m = 0, were found to be 4.16 and 4.08, respectively. The pH values at C_m = 0 showed a slight change in the initial pH of boric acid with concentration. Measurements of pH of borax solutions at C_m = 0 were, in fact, measurements of pK_a. The small changes in pK_a with borax con-

centrations were expected and were found to be in good agreement with those predicted from theory [33]. Therefore, K_o, being a product of K_n (in this case K_2) and K_a, should also have varied slightly with borax concentration.

From the values of pK_o and pK_a, taken from Figure 16, log K_2 was calculated. From four determinations of log K_2 with borax concentrations between 0.001 and 0.01M, values of 4.96, 4.98, 4.99, and 4.99 were found (average = 4.98).

(2) Determination of the formation constant of the 1:1 complex. Formation constants for the 1:1 mannitol-borate complex were determined by adding small amounts of mannitol solution from a buret to 100 ml of a boric acid-sodium borate solution. Table 41 shows part of the data for a typical titration of this kind. The initial concentrations of mannitol, boric acid, and borate were corrected for dilution and the pH measured after the addition of each increment of mannitol solution. Since changes in hydrogen ion concentration were of the order of 10^{-12}M when mannitol was added and since the source of hydrogen ion was boric acid, the concentration changes of the latter were of the order of 10^{-12}M or negligible compared to the total boric acid concentration. Therefore, (HB) was taken as equal to the initial borax concentration. Using K_a (from initial pH) and the measured pH, the concentration of free borate (B^-) was calculated. Negligible amounts of borate were formed from boric acid and the original borate concentration equaled the sum of free borate plus complexed borate. Thus the concentration of complex (BM^-) was obtained by subtracting (B^-) from the initial borate concentration. Finally, the concentration of free mannitol was obtained by subtracting the concentration of complex from the initial mannitol concentration and values for K_1 were calculated.

Values for K_1 are given in the last column of Table 41. They are essentially constant at low mannitol concentrations and begin to decrease as mannitol concentrations increase.

This relationship is seen graphically in Figure 18 and is just the effect that would be predicted if the formation of a higher complex becomes important at appreciable mannitol concentrations. The agreement of calculated K_1 values at low mannitol concentration can be interpreted as proof of the existence of the 1:1 complex. The value of the formation constant of the 1:1 mannitol-borate complex was taken to be the limit as mannitol approaches zero. In Figure 18 this value corresponds to a log K_1 of 2.83. For other boric acid-borate concentrations and ratios, values of 2.70, 2.75, and 2.89 were obtained, the average being 2.79.

Since K_2 is the product of the first and second successive formation constants, β_1 and β_2, of the mannitol-borate complex and K_1 is β_1, the successive constants were calculated.

$$B^- + M = BM^-M \quad ; \quad \beta_1 = K_1$$

$$BM^- + M = BM_2^- \quad ; \quad \beta_2 = \frac{K_2}{\beta_1}$$

$$\log \beta_1 = 2.79; \quad \log \beta_2 = 2.19$$

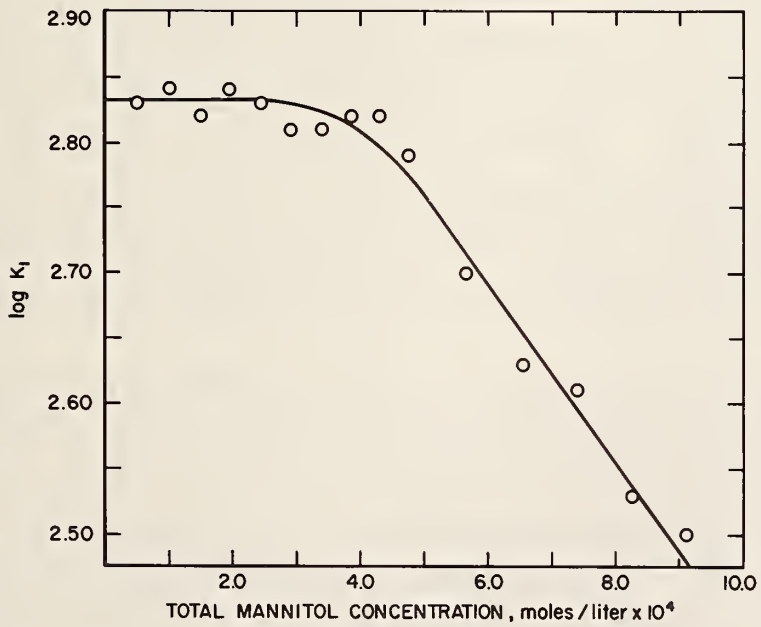

Figure 18. pH of mannitol-boric acid solution in which mannitol concentration was varied, boric acid concentration was held constant.

Since the second successive formation constant is very nearly as large as the first, the formation of the second complex becomes important as soon as an appreciable amount of the first complex is formed. It is evident, therefore, that values of K_1 must be obtained in the limit of zero mannitol concentration especially when boric acid, and hence a very low borate concentration, is used initially. Failure to recognize the possibility of very similar successive constants has led previous investigators to erroneous conclusions.

Deutsch and Osoling [28] reported values of 2.5 and 4.7 for log K_1 and log K_2, respectively. However, their calculation of these constants was based on the assumption that at (HB)>>(M) only a 1:1 complex is formed. The formation constants were calculated by these authors using a rather complex algebraic relationship in which K_1 was calculated from pH measurements of a boric acid solution to which small amounts of mannitol were added. The calculation of K_2 required prior knowledge of K_1. The values of K_1 and K_2 reported by Deutsch and Osoling have been questioned by later workers [29,32]. It appears that the reported value of K_1 is in error since, under the experimental conditions used, the mannitol concentration was significantly greater than the borate concentration and the 2:1 complex was formed. Data in the Deutsch and Osoling work are further confused by the fact that the initial boric acid solution contained a small amount of some alkaline impurity and the pH of the initial solution was higher than predicted from K_a.

The value of K_1 obtained by Deutsch and Osoling is therefore in error (but fortuitously close to the correct value). By assuming only a 2:1 complex, a value of $K_2 = 10^{4.6}$ can be calculated from the data used by these authors for calculating K_1. Applying an approximate correction for the alkali error, calculated from K_a and the initial pH, brought the K_2 value to $10^{5.0}$ in excellent agreement with the value obtained in this laboratory.

Values of K_2 reported by Deutsch and Osoling show considerable scatter (mean deviation, 39%), the scatter being introduced by an incorrect value of K_1. Recalculation of K_2 using the original data, a correct value for K_1, and an approximate correction for the alkali error gives K_2 very close to $10^{5.0}$

Similarly, values of K_2 in excellent agreement with those obtained in this laboratory can be calculated from the data of Boeseken and Vermaas [27] and Ross and Catotti [29]. These workers reported K_o ($K_o = K_2 K_a$) to be $10^{-4.2}$ and $10^{-4.0}$, respectively. Using appropriate values of K_a, K_2 was calculated and log K_2 values of 5.0 and 5.2 were obtained. No measurements of K_1 were obtained by these authors.

Torssell [30] reported values of log K_1 = 2.75 and log K_2 = 5.06 for the formation of mannitol-borate complexes in excellent agreement with the 2.79 and 4.98 obtained in this laboratory. Torssell's method, also using additions of mannitol to boric acid and measurement of pH, involved extrapolating to zero mannitol to obtain K_1 and thus precluded the assumption that only a 1:1 complex is formed at any given concentrations.

Nickerson [32] has recently reported a number of arguments to support the conclusion that mannitol reacts with boric acid in a one-to-one ratio only. This conclusion, based on the argument that only one mole of product, HBM, was formed per mole of B reacting rather than two moles of product, H^+ and BM^- (or BM_2^-), is weakened by the fact that it was later assumed that HBM is a strong acid and dissociates to give in fact two moles of product. Furthermore, treating the data as though only one mole of product were formed resulted in the questionable conclusion that the boric acid in solution must exist as a dimer. While boric acid polymerization is known, it is well established that at concentrations of boric acid $\geq$0.025M, only monomer and borate ion are present while at higher concentrations the predominant polymeric species is a

cyclic trimer composed of two boric acids and one borate [34-36].

A number of plots of pH vs. log mannitol concentration for various amounts of mannitol added to boric acid, the concentration of the latter being held constant, were reported by Nickerson [32]. Experiments of this type have been repeated in this laboratory. A typical example is shown in Figure 17. The results of these experiments are in excellent agreement with those of Nickerson. The pH vs. log mannitol concentration plots obtained in this manner have a slope of -1. However, the conclusion of the previous author, that the slope of -1 implies a 1:1 complex, is incorrect.

Since the starting material in these experiments was boric acid, the borate concentration was always very low and, at high mannitol concentrations, the formation of the highest complex (of 2:1 mannitol to boron ratio) was expected. The observed changes in pH were the result of dissociation of boric acid and the formation of an equivalent amount of mannitol-borate complex. Although an objection to equating the concentration of liberated hydrogen ion with the concentration of complex has been raised [32], the large concentration of mannitol relative to borate allowed this assumption. (It has been previously shown that the assumption that hydrogen ion concentration and complex concentration are equal was not required when the starting material was borax.)

The overall reaction following the addition of mannitol to boric acid was as before:

$$HB + nM = BM_n^- + H^+ \quad ; \quad K_o = K_a K_n$$

and

$$K_o = \frac{(BM_n^-)\ (H^+)}{(HB)\ (M)^n}$$

Solving for pH

$$pH = - \log K_o - \log (HB) - n \log (M) + \log (BM_n^-)$$

Since

$$(BM_n^-) = (H^+)$$

$$pH = - \frac{(\log K_o + \log [HB])}{2} - \frac{n}{2} \log C_m$$

when the total mannitol concentration, C_m is large compared to the concentration of complex.

Plots of pH vs. log total mannitol concentration at constant boric acid concentration have a limiting slope -1. As can be seen from the previous equation, this slope is consistent with a 2:1 mannitol-to-borate complex. Furtheremore, extrapolation of the curves reported by Nickerson and those obtained in this laboratory (Figure 17) to log mannitol equal 0 followed by multiplication of the intercept by -2, and subtraction of log (HB) and log K_a gave values for log K_2, the formation constant for (BM_2^-). The average value 5.00 is in agreement with the 4.98 calculated from data obtained in this laboratory and previously discussed.

By a similar treatment, the additional equilibrium data of Nickerson can be shown to agree with those obtained in the present work. Thermochemical data reported by Nickerson [32] to indicate only a 1:1 combining ratio are inconclusive as these were obtained at concentrations were one would not expect complete formation of a 2:1 complex.

Table 42 summarizes values of formation constants reported by various authors and recalculated values obtained from their data. The apparent anomalous behavior of the boric acid-borate-mannitol system can be seen to result from misinterpretation of the experimental data rather than the nature of system.

Table 42. Formation constants of borate-mannitol complexes.

	Previously Reported $\log K_1$, $\log K_2$	Recalculated $\log K_1$, $\log K_2$
This work		2.79, 4.98
Deutsch and Osoling [28]	2.5 , 4.7	...[a], 5.0
Torssell [30]	2.75, 5.06	...[b], ...[b]
Nickerson [32]	$\log K_c = -1.92$[c]	...[a], 5.00
Ross and Catotti [29]	$\log K_o = -4.0$[d]	...[a], 5.2
Boeseken and Vermaas [27]	$\log K_o = -4.2$[d]	...[a], 5.0

[a]Values of K_1 are unobtainable from data in this work.

[b]Reported values are in agreement with those obtained in this laboratory and therefore not recalculated.

[c]K_c is equilibrium constant for the reaction $1/2\ H_2B_2 + M = HBM$.

[d]$K_o = K_a K_2$.

2. Lanthanide Metal-Nitrate Equilibria

Ion exchange, solvent extraction, and conductivity data obtained for aqueous lanthanide nitrate solutions have frequently been interpreted in terms of a metal-nitrate interaction. Although nitrate salts are usually classified as strong electrolytes, such interactions are not unreasonable for highly charged metal ions such as the lanthanides. Infrared spectroscopic and ion-selective electrode data obtained for a number of lanthanide nitrate systems [notably La(III) and Ce(IV)] suggest complexation rather than ion pair formation. These results, which are of a preliminary nature, are discussed below. The systems are currently being studied in detail with the goal of explaining 1) lanthanide "catalyzed" nitrate reduction at the DME [37], 2) the behavior of the Ce(IV)-Ce(III) electrochemical couple in nitrate solution, and 3) the mechanism of Ce(IV) oxidations of organic compounds (electron transfer via bridging nitrates).

When nitrate is bound to a metal ion, the symmetry of the nitrate is lowered from D_{3h} to C_{2v} and a corresponding increase in the number of infrared active vibrations should occur. Figure 19 illustrates the infrared spectra of solids containing free nitrate and complexed nitrate. The existence of the hexanitratocerate(IV) anion has been demonstrated by x-ray crystallography [38]. In addition the loss of degeneracy (i.e., frequency separation) of the assymetric stretching frequencies of bound nitrate are a measure of the dissimilarity of the nitrate oxygens and, therefore, a crude measure of metal-oxygen covalency. In lanthanum nitrate solutions, for example, the frequency separation is much larger than in calcium nitrate solutions where ion pairing is believed to occur [39,40]. The lanthanum nitrate bond therefore contains some covalent character - hence complex formation rather than ion pairing.

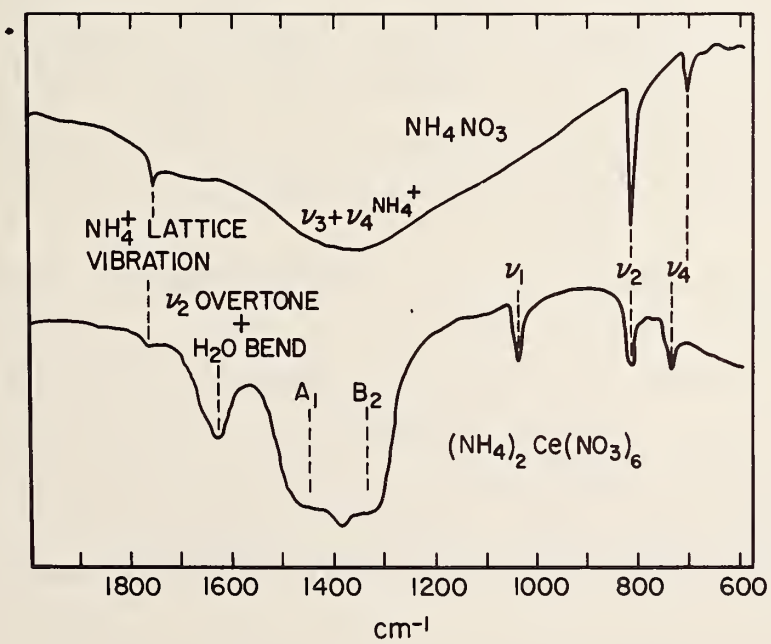

Figure 19. Infrared spectra of solids containing free and complexed nitrate.

Nitrate ion selective electrode measurements are consistent with 1:1 and higher lanthanide-nitrate complexes. The equilibria involved in the formation of these complexes is currently under study.

(J. W. Knoeck)

6. MICROSCOPIC AND CLASSICAL MICROCHEMICAL ANALYSIS

A. Introduction

The demands of modern science and technology have outmoded many of the established microchemical techniques. As a consequence, new procedures, possibly definable as ultramicrotechniques, have arisen to make possible the analysis of smaller and smaller samples. The program here has been mainly concerned with the detection and identification of micro amounts of materials and the development and preparation of ultramicrochemical standards. Of interest also is the determination of trace elements in various materials and the microchemical analysis of organic and inorganic materials.

B. Ultramicrochemical Standards

During the past two years we have cooperated with the Separation and Purification Section in the development of microstandard ion-exchange beads. These standards are metal ion-loaded ion-exchange beads from 5μ to 25μ in diameter. In this size range the weight of metal ion present will vary from a few pg to a few ng. Merely having a concentrated source of material in this range can be useful for a number of tests, such as limit of detection, but with proper characterization the amount of material present can be stated within 10% or better.

Microbead standards differ from the usual standards in several ways:

1) The weight of metal ion present in an individual bead is found from an optical measurement of its size.

2) These beads do not have the inherent stability usually associated with standards. They are especially sensitive to the water vapor present in air and in absorbing water they increase in size.

3) It is very difficult to make standardization analyses on individual beads.

However, if the metal ion content, water content and density of a fairly large batch of beads is known the relationship of the metal ion content to the bead diameter can be stated with a certainty of a few percent. This laboratory helped in this characterization in several ways which will be described in the following sections.

1. Water Content Measurements

Drying loaded ion exchange beads of this size (5-25μ) at 120 °C under vacuum for 16 hours will remove practically all the water from them. However, larger sized beads (∿ 100μ) may require several days to come to constant weight. Dry ion-exchange beads absorb water rather rapidly so that it is much simpler to handle individual beads in a controlled atmosphere in the 20-40% relative humidity range. Studies have been made of the rate of absorption of water by loaded beads exposed to 30% relative humidity. One-gram samples of beads, dried 16 hours at 120 ° under vacuum were placed in a humidity chamber containing a saturated solution of calcium chloride at 23 °C. Weight measurements were made at intervals. Results are given in Tables 43 and 44. All had reached constant weight after nine days.

Table 43. Percent gain in weight from the dry state at 30% RH.

	Time			
Cation on beads	5.5 hours	24 hours	3 days	9 days
Sodium	3.2	10.4	14.9	15.9
Calcium/sodium	3.4	11.8	16.8	17.7
Copper/sodium	3.4	13.1	22.0	23.3
Lead/sodium	3.2	9.1	10.9	11.3
Calcium	3.2	10.8	14.8	15.3
Copper	3.3	11.9	17.6	18.3
Lithium	3.5	12.2	17.5	18.2

Table 44. Percent gain in weight from the dry state at varying relative humidities.

Cation on beads	Relative humidity 30 %	50 %	70 %
Sodium	15.9	18.3	28.7
Calcium/sodium	17.7	19.8	29.0
Copper/sodium	23.3	26.1	37.4
Lead/sodium	11.3	12.4	17.8
Calcium	15.3	16.8	25.3
Copper	18.3	20.5	30.4
Lithium	18.2	21.1	34.7

2. Density Measurements

The density of dry beads has been determined using the pycnometer method for solids. In order to have the beads as dry as possible, approximately 1 gram was dried and weighed in the bulb of a 10-ml pycnometer. Dry cyclohexane was used as the liquid to keep the beads as dry as possible. The densities of four metal-ion loaded ion exchange beads which are possible standard reference materials were determined by this method and found to be as follows:

Calcium	1.500
Sodium	1.504
Copper	1.633
Lead	2.097

The range of densities present in a sample of loaded ion exchange beads is of special interest because it is an indication of the uniformity of loading the beads. The density gradient column is very convenient for determining the density of small objects. The beads here are too small to be seen individually but 25 mg will form a cloud where the density of each bead matches that of the liquid. The columns were prepared using the method of Oster and Yamamoto [41]. The liquids used were mixtures of methylene chloride, chloroform, carbon

tetrachloride, and methylene iodide. They were so chosen that the liquids in the top and bottom bulbs of the gradient tube differed by approximately 0.1 density units. The tube was allowed to stand at least 24 hours before the beads were added. The dried beads were mixed with a small amount of the upper liquid before adding to the column. After equilibrium had been reached the height of the band of beads was measured. Samples of the liquid were taken 2 cm above and 2 cm below the band and the density determined with a small pycnometer. By assuming a linear gradient between the two points it is possible to calculate the density of the top and bottom of the bead band and also the average density of the beads. Floats of known density will be used in future experiments to prove that there is a linear gradient present. In the case of the calcium loaded beads (SRM #1800) the density range was found to be 0.005 density units.

Other tests have been made to aid in characterizing the microbead standards. Two of these are the capacity determination and the sulfur determination.

3. Capacity of the Hydrogen Form

The capacity of the hydrogen form of the ion exchange beads is determined by titration with 0.05N sodium hydroxide solution after the addition of sodium chloride. An excess of the base is added until the pH is about 11. When equilibrium has been reached as shown by a constant pH, the excess sodium hydroxide is titrated slowly with 0.05N hydrochloric acid to a pH of 7. From these titrations the number of equivalents of exchangable hydrogen ions can be calculated. The beads are then filtered on a porcelain filter, dried and weighed. The capacity is reported as milliequivalents per gram of dry sodium resin. This latter step is necessitated because the hydrogen form is very difficult to dry.

4. Sulfur Determination

The percentage of sulfur in the beads when compared to

the percentage of metal is an indication of the efficiency of loading. There should be an equivalent of metal for each equivalent of sulfur in fully loaded beads. It has been found that the Carius combustion with fuming nitric acid at 250 °C will destroy the beads completely. Sulfur is then precipitated and weighed as barium sulfate using the conventional micro-gravimetric method.

5. Handling Techniques

The metal-loaded ion exchange beads are cast on a clean microscope slide for ease in handling and shipping. The beads initially are dispersed in dry cyclohexane in a concentration of 1 mg/ml. Twenty-five microliters of this slurry, spread on a microscope slide, will usually give a well dispersed sample of about 500 beads.

In use, the slide is examined under a microscope and isolated beads of the desired size are selected and measured using a filar micrometer. A bead so selected can be transferred by hand (40x magnification) using a needle with a very fine point. Needles are usually made of tungsten wire or glass. As Walter C. McCrone has many times pointed out, such transfers are more easily made if the operator practices clean living and makes use of all possible supports.

C. Clean Room

The horizontal laminar flow Class 100 clean room which has been in the planning and construction stages for some time has now been completed. A general description was given in a previous report [1]. The layout is repeated in Figure 20.

This clean room is divided into two sections by a perforated aluminum wall. The HEPA filter bank is on the left and the air flow is from left to right. The microscope tables are located in the cleanest part of the Class 100 room. The Class 1000 room is so marked to indicate that it is for work which does not require as high a level of cleanliness. However most of the time, and especially if the Class 100 area is not occupied, this area will meet Class 100 standards.

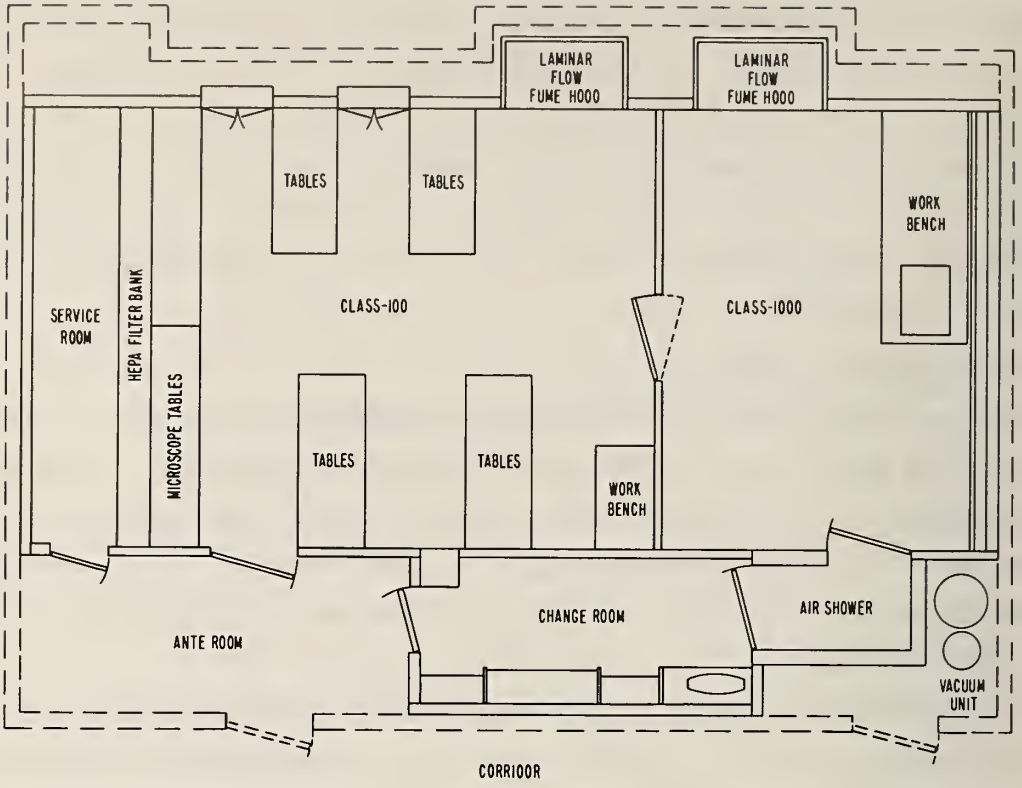

Figure 20. Plan of the clean room facility.

A forward light-scattering airborne particle counter is used to monitor the clean room. It is located in the anteroom with the sensor in the clean room.

Each section of the room has a vertical laminar flow fume hood. The air for the hood enters through HEPA filters in the top. A portion of the air exits through a slot in the forward part of the hood floor forming an air curtain. Only a small amount of air enters the hood from the clean room. These hoods are intended for handling volatile solvents, for light chemical procedures and for handling samples which could contaminate the clean room. The hoods were not planned for chemical work requiring large amounts of acids.

Views of the clean room complex are given in Figures 21, 22, 23, 24, and 25.

Figure 21 shows the anteroom in the foreground, the change room and the air shower. The change room contains the wash

basin and hand drier. The pass-through is also in the change room.

Figure 22 shows the entrance from the air shower into the Class 1000 area. A high speed centrifuge is on the right.

Figure 23 shows the fume hood in the Class 100 area. The baffle wall separating the two areas of the room is on the right.

Figure 24 shows a portion of the microscopy table in the cleanest portion of the room.

Figure 25 shows another part of the microscope table. It also shows the emergency exit to the anteroom and the pass-through to the change room.

Figure 21. Anteroom, change room, and air shower. The change room is equipped with wash basin and hand drier. The pass-through is also located in the change room.

Figure 22. Entrance from the air shower into the class 1000 area.

Figure 23. Verticle laminar flow fume hood in Class 100 area. The baffle wall separating the two areas is on the right.

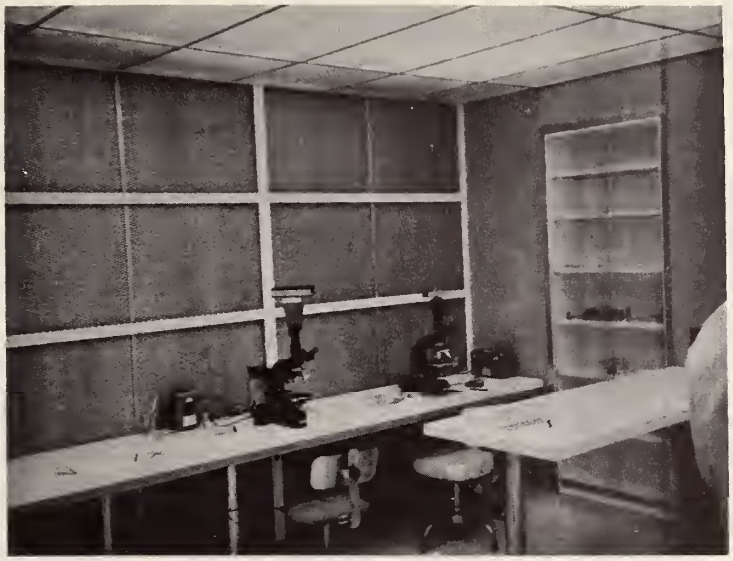

Figure 24. Microscopy table in cleanest portion of the room.

Figure 25. Pass through, emergency exit and portion of microscopy table.

D. Applications of the Nuclear Track Technique to Trace Analysis

The successful application of the nuclear track technique [42-45] to the determination of traces of uranium in biological material [1] has prompted an investigation of its extension to the determination of other trace-level elements. A search is in progress to identify candidate elements capable of producing tracks either by emitting a charged particle or a fission fragment after a nuclear reaction. In addition, studies are being made of detectors and detection conditions in order to increase selectivity.

Elements being considered at this time produce tracks in plastic through two types of nuclear reactions. The first of these is the (n, α) reaction which produces shallow alpha tracks in cellulose acetate (CA) or cellulose butyrate (CAB) as a result of bombardment of the target element with thermal neutrons. Lighter elements such as lithium and boron undergo this reaction. The other reaction type (γ, f) produces fission tracks in Lexan (a polycarbonate) when the target elements are bombarded with a high energy bremsstrahlung beam. In this case the target nuclei are heavier elements such as thallium, lead, bismuth, thorium, and uranium.

1. Determining Elements by the (n, α) Reaction

In order to determine elements by tracks produced from (n, α) reactions, the track-registration characteristics must be known for the materials being considered as detectors. Fleischer and co-workers found that the requirement for a charged particle to produce a track in a material was based on the mass of the charged particle entering the detector. Their work further showed CA and CAB to have the proper requirements for recording alpha tracks, but ruled out Lexan, mica, and Mylar as detecting materials [46-48].

The etching conditions suggested by Fleischer and co-workers [46,48] and by Loveridge and McInnes [49] for CA and CAB have been studied but found to be unsuccessful. The conditions for CA, consisting of etching times of 3 hours at 25 °C produced slides which were very foggy. Additional experiments indicated that the etching temperature was the critical factor in obtaining properly etched slides. CAB required short

times of 8 minutes at 70 °C to obtain an optimum etched slide. But at these high temperatures the time appeared to be critical factor in obtaining slides and tracks that were not over etched. Further experiments with both materials proved that CAB was the more favorable plastic to be used as detecting material, if etched at 50 °C for 45 minutes in a 6.5N NaOH solution.

a. Detection of boron. The detection of boron by this technique is based primarily on the presence of boron-10 in the material. The alpha tracks are produced from the $^{10}B(n, \alpha)^{7}Li$ with a neutron cross section of 3840 barns.

(1) Experimental. Known amounts of the boron containing material were placed on the CAB slides in solution form, evaporated and covered with transparent tape. The slides (25 mm x 40 mm x 0.25 mm) were irradiated in the NBS reactor for 60 seconds at a neutron flux of $2.4 \times 10^{13} n \cdot cm^{-2} s^{-1}$. The slides are then etched in NaOH by the procedure described above and counted by using the Quantimet QTM [50], the procedure of which will be discussed in section C. The net number of tracks observed were compared with the net number of tracks obtained from simultaneously irradiated standards.

(2) Results. Irradiation of known quantities of boron shows that a linear relationship exists with the amount of boron present and the number of tracks formed. The detection limit for boron with a total integrated flux of $1.44 \times 10^{15} n \cdot cm^{-2}$ was found to be 4.3×10^{-12} grams per track.

b. Determination of lithium. The detection of lithium is also isotopic and is based primarily on alpha tracks produced from the $^{6}Li(n, \alpha)^{3}H$ reaction which has a thermal neutron cross section of 950 barns. The apriori assumption that the number of tracks formed is directly related to the total amount of the element present has to be made for lithium or any other element if quantitative results are desired.

(1) Experimental. The same experimental procedure outlined in the boron discussion is used for lithium detection.

(2) Results. Lithium also demonstrates a linear relationship between the amount present and the number

of tracks formed. The detection limits for lithium under the same conditions as cited for boron is 1.72×10^{-11} grams per track.

2. Determination of Elements by (γ, f) Reactions

The nuclear track technique has been limited previously to nuclear reactions induced by thermal neutron irradiations [45, 50-54]. These reactions have been of interest because of their large neutron cross sections which aid in their detection sensitivities. Currently, investigations are underway to study the radiation induced trails or tracks produced from the high energy bremsstrahlung beam of a linear accelerator (LINAC). The elements that produce fission tracks from the (γ, f) reactions have comparatively smaller cross sections and, consequently, their sensitivities will be smaller than the fission tracks produced from thermal neutrons.

Fission tracks have been produced in Lexan polycarbonate from thalium, lead, bismuth, thorium, and uranium by 35 MeV photon activation. However, a five-minute irradiation for a one-microgram sample indicated that only the latter three elements appear to be promising for quantitative measurements.

Since trace determination of bismuth by neutron activation analysis is limited, bismuth appeared to be especially interesting for focusing analytical attention. However, the sensitivity or detection limit for bismuth, 3.13×10^{-7} grams per track, was found to be less than those for thorium and uranium, 4.17×10^{-9} grams per track and 1.72×10^{-9} grams per track, respectively. Since the uranium and thorium sensitivities were greater than that of bismuth, a pre-irradiation separation had to be performed on the material to be analyzed.

a. Experimental procedure. The bismuth containing material was dissolved in dilute HNO_3. Then the solution was mixed with 10 ml of a complexing mixture, containing 50 grams of Na_2EDTA and 50 grams of NaCN dissolved in 1 liter of 1.5N NH_4OH. Next, 1 ml of a 2% solution of sodium diethyldithiocarbamate was added. The bismuth was then extracted with 10 ml of CCl_4 [55]. After addition of 1 ml of dilute HNO_3 to the CCl_4 layer, the mixture was heated until all of the CCl_4 was driven off. Droplets of 100 microliters of the resulting dilute HNO_3 solution were placed on Lexan slides that were

10 mm wide x 25 mm long x 0.25 mm thick in size. The slides were then evaporated, covered, and irradiated for a minimum of 5 minutes at a maximum bremsstrahlung energy of 35 MeV. After irradiation the slides were etched in 6.5N NaOH at 50 ± 2 °C for 45 minutes. The tracks were then counted and the values were compared with values obtained from standards irradiated simultaneously.

b. Conclusion. Analysis of both fractions of the solvent extraction layers showed by the nuclear track technique that all the uranium remained in the aqueous phase, while tracer experiments with ^{207}Bi and the nuclear track technique showed that 95% of the bismuth was extracted by the CCl_4. Therefore, the results demonstrate that trace quantities of bismuth and uranium can be analyzed in the same matrix.

E. The Quantimet-QTM

Nuclear tracks that have been produced in the plastic detectors have to be counted by some means. Normally this has been done by counting each track in a microscopic field of view by eye. This laboratory's procedure has been facilitated by utilizing the Quantimet QTM, an image analyzing computer microscope. The QTM consists of a microscope that is attached to a closed circuit television camera together with a small analog computer in line with a television monitor. The image being analyzed is displayed on the monitor and the measurements can be obtained from the monitor. Measurements that can be made by the QTM include area measurement, projection lengths, and image counting. In the case of track counting each track that is being counted in a field of view is marked by a flag or a line and the total number is given on the meter, as illustrated in Figure 26.

The use of the QTM as a tool for track counting is feasible provided the tracks are randomly orientated throughout the field of view. If the tracks are not randomly orientated but begin to overlap or form a cluster, the instrument will not be capable of detecting each track in the overlap or cluster. For instance, the QTM will give higher count values

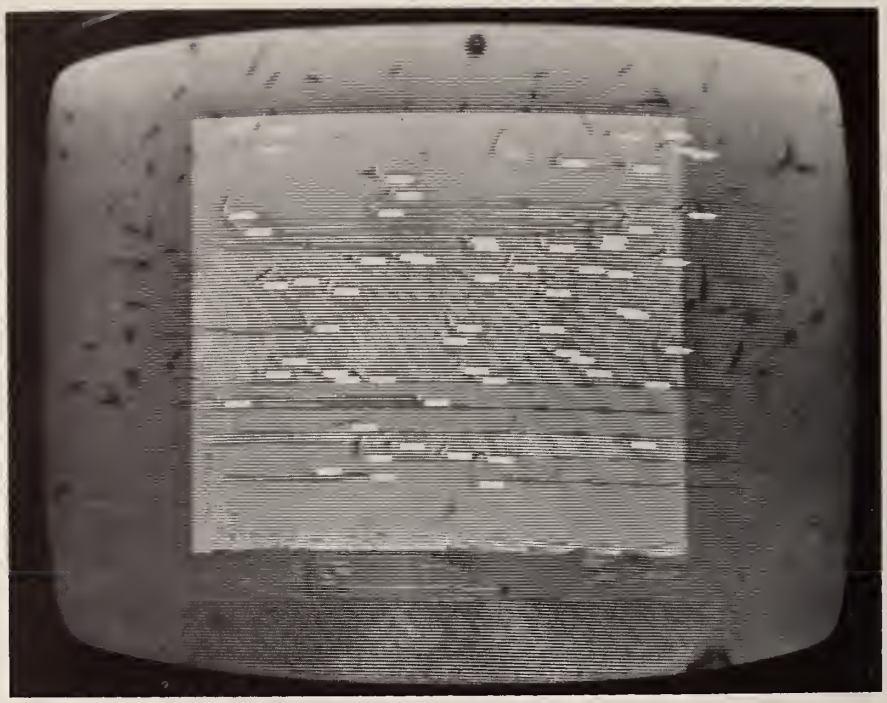

Figure 26. Bismuth fission-track counting by the QTM.

for a cluster of tracks than the actual number of tracks present. These higher values are obtained even though the acceptance angle is set at the minimum point at which two features lying in close proximity to one another can still be detected individually. Additional work will be needed to reduce the high track counting values of cluster but, even so, the QTM reduces both the time element and the eye fatigue involved in track counting.

(R. A. Paulson, B. S. Carpenter, and W. P. Schmidt)

7. INTERNATIONAL RESEARCH GRANTS PROGRAM

A. Introduction

The National Bureau of Standards awarded a grant to the Technion Research and Development Foundation on September 5, 1968, to apply anodic stripping voltammetry to trace analyses in Standard Reference Materials. The project is an extension of the work initiated in December 1965 and is under the supervision of Prof. Magda Ariel.

B. Mercury Coated Rotating Platinum Electrode (MCRPE)

Studies of the mercury coated rotating platinum electrode (MCRPE) have been continued and reported in a recent publication [56]. Various methods of coating the platinum with mercury have been studied. A method using a mercury drop of known weight was used whenever thick films (exceeding 15 μM) were desired, while the method recommended by Barendrecht [57] was used for thin films. When no cathodic potential is imposed on the electrode, the mercury film tends to coalesce into droplets with resulting electrode failure. Addition of surface active agents such as Triton X-100 has a retarding effect but often decreases sensitivity. Certain media (e.g., nitrates) seem to hasten electrode failure while others (acetate buffer, ammonia buffer, etc.) improve keeping qualities. Infrequently, electrodes may be regenerated by cathodisation, but for the stringent demands of trace analysis, complete dissolution of the film, cleaning of the platinum, and recoating are required.

Good results were obtained by electrodepositing a thin film of nickel on the RPE which was then coated by dipping in mercury. Excess mercury was removed by suction to leave a film 2-3 μM in thickness. Such electrodes had superior keeping qualities but should not be left exposed to the atmosphere.

The pre-electrolysis step for the MCRPE is similar to that for the hanging drop electrode. A slightly improved sensitivity

and resolution is found with stirred solutions down to 10^{-7}M. In the 10^{-7}M to 10^{-8}M range, quiescent solutions are advisable.

Due to its rigid construction, the MCRPE is very convenient to transfer from solution to solution which is another advantage of this electrode. Experimental studies have shown good reproducibility and linearity of response for lead and copper down to a concentration range of 10^{-8}M. These results are encouraging for further work to overcome problems of stability and reconditioning of electrodes.

C. Electrolysis Cell for Medium Exchange

A number of anodic stripping voltammetric (a.s.v.) determinations would be facilitated by carrying out the stripping process in a medium different from that in which the pre-electrolysis is performed. On the other hand, the transfer of the electrode from one medium to another offers the danger of loss of deposited metal by air oxidation or otherwise. Also there is the possibility of contamination by carry-over of the mother liquor to the stripping medium.

A system has been designed and constructed that facilitates the medium exchange process. It consists of the electrolysis cell proper and reservoirs to hold the sample solution and medium exchange solution, respectively. A pumpimg system is provided to interchange the solutions when desired. The system will be described in detail in a forthcoming publication.

The usefulness of the apparatus has been demonstrated by application to the determination of trace metals (Zn, Cd, Pb, Cu) in iron base samples. While a.s.v. combined with conventional medium exchange could serve for the determination of copper in these samples [56], all four trace metals can now easily be determined, simultaneously, in a single sample aliquot.

(M. Ariel and co-workers)

8. PERSONNEL AND ACTIVITIES

A. Personnel Listing

John K. Taylor, Section Chief

Carolyn E. Smith, Secretary

Gas Analysis --

Ernest E. Hughes
Julian M. Ives

Polarography --

E. June Maienthal

Coulometry --

George Marinenko
Charles E. Champion

Electroanalytical Measurements --

Richard A. Durst
John W. Knoeck

Microscopy and Microchemistry --

Rolf A. Paulson
B. Stephen Carpenter
William P. Schmidt

B. Publications

1. R. A. Durst and J. W. Ross, "Electrochemical Generation of Fluoride Ion by Solid-State Transference", Anal. Chem. 40, 1343 (1968).

2. G. Marinenko and J. K. Taylor, "Electrochemical Equivalents of Benzoic and Oxalic Acid", Anal. Chem. 40, 1645 (1968).

3. E. E. Hughes, Book review: Gas Effluent Analysis, William Lodding, Ed., J. Am. Ceramic Soc. 5, 260 (1968).

4. J. M. Ives, E. E. Hughes, and J. K. Taylor, "Absolute Determination of Low Concentrations of Oxygen in Inert Gases by Means of Galvanic Cells", Anal. Chem. 40, 1853 (1968).

5. J. K. Taylor, "Modern Electrochemistry", Indus. Res. October 1968, p. 68.

6. J. K. Taylor, Editor, NBS Technical Note 455, "Microchemical Analysis Section: Summary of Activities, July 1967 to June 1968", U. S. Government Printing Office, October 1968.

7. R. A. Durst "Determination of Fluoride by Analate Additions Potentiometry", Mikrochem. Acta 3, 611 (1969).

8. C. E. Champion and G. Marinenko, "Errors in Coulometric Chloride Determinations Due to Photodecomposition of Silver Chloride", Anal. Chem. 41, 205 (1969).

C. Talks

1. R. A. Durst, "Specific-Ion Microanalysis by Linear Null-Point Potentiometry", Microchemical Workshop, American Microchemical Society, Pennsylvania State University, University Park, Pennsylvania, July 1968.

2. J. W. Knoeck and H. Diehl, "High Precision Constant Current Coulometric Assay of Primary Oxidizing Agents", 156th National Meeting, American Chemical Society, Atlantic City, New Jersey, September 1968.

3. C. E. Champion, G. Marinenko, and J. K. Taylor, "Coulometric Determination of Micrograms of Chromium", 156th National Meeting, American Chemical Society, Atlantic City, New Jersey, September 1968.

4. G. Marinenko and C. E. Champion, "High Precision Coulometric Analysis of Boric Acid", 156th National Meeting, American Chemical Society, Atlantic City, New Jersey, September 1968.

5. B. S. Carpenter, "Determination of Trace Quantities of Uranium in Biological Materials by the Nuclear Track Technique", 1968 International Conference on Modern Trends in Activation Analysis, National Bureau of Standards, October 1968.

6. J. W. Knoeck, "Nitrate Complexes of Cerium IV", Midwest Universities Analytical Chemistry Conference, Northern Illinois University, DeKalb, Illinois, November 1968.

7. J. K. Taylor, "What is Chemistry?", Col. E. Brook Lee Junior High School, Silver Spring, Maryland, November 1968.

8. J. K. Taylor, "Electrochemical Methods for Environmental Analysis", University of Michigan, Ann Arbor, Michigan, December 1968.

9. J. K. Taylor, "Electrochemical Methods in Trace Analysis", Seton Hall University, South Orange, New Jersey, December 1968.

10. R. A. Durst, "Careers in Chemistry", Earle B. Wood Junior High School, Rockville, Maryland, December 1968.

11. R. A. Durst, "Analytical Applications of Ion-Selective Electrodes", Symposium on Ion-Selective Electrodes, National Bureau of Standards, January 1969.

12. J. W. Knoeck and J. K. Taylor, "The Boric Acid-Borate-Mannitol System", 4th Middle Atlantic Regional Meeting, American Chemical Society, February 1969.

13. J. K. Taylor, "What is Chemistry?", Joyce Kilmer Junior High School, Vienna, Virginia, February 1969.

14. J. K. Taylor, "Relations of Electricity and Chemistry", Joyce Kilmer Junior High School, Vienna, Virginia, February 1969.

15. G. Marinenko and C. E. Champion, "Coulometric Titrations of EDTA", 4th Middle Atlantic Regional Meeting, American Chemical Society, Washington, D. C., February 1969.

16. E. J. Maienthal and J. R. Baldwin, "Analysis of Standard Reference Glasses by Cathode Ray Polarography", 4th Middle Atlantic Regional Meeting, American Chemical Society, Washington, D. C., February 1969.

17. B. S. Carpenter and C. Cheek, "Determination of Uranium in Biological Materials by Fission Track Counting", 4th Middle Atlantic Regional Meeting, American Chemical Society, Washington, D. C., February 1969.

18. E. E. Hughes, "A Mass Spectrometric Technique for the Accurate Determination of the Argon Content of the Atmosphere", 4th Middle Atlantic Regional Meeting, American Chemical Society, Washington, D. C., February 1969.

19. C. E. Champion, "Cyclic Voltammetric Study for the Exchange Rate of Cadmium with Calcium EDTA Complex", George Washington University, Washington, D. C., March 1969.

20. J. K. Taylor, "Careers in Chemistry", Good Counsel High School, Wheaton, Maryland, March 1969.

21. J. W. Knoeck, "Complex Formation and Ion Pairing in Metal Nitrate Solutions", University of Arizona, Tucson, Arizona, April 1969.

22. J. W. Knoeck and J. K. Taylor, "Nitrate Complexes of Lanthaanide and Actinide Metals - A Mechanism for Catalytic Nitrate Waves", 157th National Meeting, American Chemical Society, Minneapolis, Minnesota, April 1969.

23. J. W. Knoeck and J. K. Taylor, "Borate-Polyalcohol Complexes", 157th National Meeting, American Chemical Society, Minneapolis, Minnesota, April 1969.

24. E. J. Maienthal, R. A. Paulson, and J. K. Taylor, "Applications of Polarography to the Analysis of Air Pollutants", 157th National Meeting, American Chemical Society, Minneapolis, Minnesota, April 1969.

25. J. K. Taylor, "What is Chemistry?", St. Ann Junior High School, Arlington, Virginia, April 1969.

26. J. K. Taylor, "High Precision Electrochemical Analysis", University of Maryland, College Park, Maryland, May 1969.

27. J. W. Knoeck, "Complex Formation and Ion Pairing in Metal Nitrate Solutions", North Dakota State University, Fargo, North Dakota, May 1969.

28. J. K. Taylor, "Electrochemical Methods for Elemental Analysis", 10th Summer Symposium, ACS Division of Analytical Chemistry, University of Georgia, Athens, Georgia, June 1969.

D. Committee Activities

J. K. Taylor

Service Analysis Coordinator, Analytical Chemistry Division
Member, Review Board, Science Book List, American Association

for the Advancement of Science
Member, Board of Managers, Washington Academy of Sciences (WAS)
Elected member, Council of the American Chemical Society (ACS)
Member, Council Committee on Chemical Education, American Chemical Society
Member, Panel on Chemistry, Civil Service Board of Examiners
Member, Board of Managers, Chemical Society of Washington
Member of Council, The Polarographic Society of London
Member, Advisory Committee, Laboratory Guide, American Chemical Society
Chairman, Chemical Education Topical Group, Chemical Society of Washington
Member, ISO/TC 48 Laboratory Glassware and Related Apparatus
Chairman, Program Committee, Alpha Chi Sigma

R. A. Durst

Treasurer (to 9/68), The Capital Chemist, Chemical Society of Washington
Member, Member Services Committee, Chemical Society of Washington
Safety Representative, Microchemical Analysis Section
Chairman, Symposium on Ion-Selective Electrodes, National Bureau of Standards
Chairman, Symposium on Electroanalytical Measurements, 4th Middle Atlantic Regional Meeting, American Chemical Society
Elected member, Board of Managers, Chemical Society of Washington
Member, Education Committee, Chemical Society of Washington
Faculty member, Stonecrest Study Center
Member, Colloquium Committee, Analytical Chemistry Division, National Bureau of Standards

E. June Maienthal

NBS Reporter for Capital Chemist, Chemical Society of Washington

Editor, Analytical Chemistry Division Newsletter, NBS
Division Representative for NBS Standard

G. Marinenko

Member, Ad Hoc Committee on Electronic Data Systems, Division of Analytical Chemistry, NBS
Chairman, Refreshment Committee, Alpha Chi Sigma

R. A. Paulson

Member, Services Analysis Committee, Analytical Chemistry Division, NBS
Collaborator, Committee for Study of Microchemical Methods, Association of Official Agricultural Chemists

E. Standard Reference Materials Analyses

Material	Analyst	Determination	Technique
Stainless Steel 160b, 1155	GM & CEC	Cr	C
	EJM	Bi, Pb	P
	RAP	Mo, Ni	G
Ductile Iron 1140, 1140a, 1141, 1141a, 1142, 1142a	EJM	Bi, Pb	P
Special Steels 1261, 1265	EJM	Bi, Pb, Ti	P
Copper Organic 1080a	EJM	Cu	P
Calcium Carbonate	WPS	Acceptance Testing	G, M
	GM & CEC	Assay	C
Au-Ag Microprobe 481	RAD	Au, Ag	Pot
	GM	Ag	C, G
Plastic and Flint Clays 97a, 98a	RAP	C, H, Moisture	G, M
Boric Acid	GM & CEC	Assay	C
Potassium Dichromate	WPS	Acceptance Testing	G, M
	GM & CEC	Assay	C

E. (Continued)

Material	Analyst	Determination	Technique
Potassium Chloride	WPS	Acceptance Testing	G, M
	GM & CEC	Assay	C
Sodium Chloride	WPS	Acceptance Testing	G, M
	GM & CEC	Assay	C
KH_2 Citrate	GM & CEC	Assay	C
Sodium Oxalate	WPS	Acceptance Testing	G, M
Microstandard Particles 1800, 1801, 1802, 1803	WPS	Stability	G
	RAP & WPS	S, C, H, Density	G, M
	GM, RAP, WPS	Capacity	C, Pot
	EJM	Elemental Analysis	P
Standard Glasses for Trace Elements	EJM	Ni	P
Bilirubin	EJM	Mesobilirubin	P
Glucose	WPS	Ash, Moisture, Insolubles	G
Uric Acid	WPS	C, H, N, Ash, Insolubles	G, M
Creatinine	WPS	C, H, N, Ash, Insolubles	G, M

Key to Analyst

CEC - Charles E. Champion
RAD - Richard A. Durst
EJM - E. June Maienthal
GM - George Marinenko
RAP - Rolf A. Paulson
WPS - William P. Schmidt

Key to Technique

C - Coulometry
G - Gravimetry
M - Microchemical
P - Polarographic
Pot - Potentiometric

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