NBS TECHNICAL NOTE

455

# Microchemical Analysis Section:

## Summary of Activities July 1967 to June 1968

**U.S. DEPARTMENT OF COMMERCE**
**National Bureau of Standards**

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[2] Located at Boulder, Colorado 80302.

[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

UNITED STATES DEPARTMENT OF COMMERCE
C. R. Smith, Secretary
NATIONAL BUREAU OF STANDARDS • A. V. Astin, Director

# NBS TECHNICAL NOTE 455

ISSUED OCTOBER 1968

# Microchemical Analysis Section:

## Summary of Activities
## July 1967 to June 1968

Edited by John K. Taylor

Microchemical Analysis Section
Analytical Chemistry Division
Institute for Materials Research

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

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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 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 abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1968 we plan to issue these summaries for all of our sections. The following is the fourth annual report on progress of the Microchemical Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

# PREFACE

This report summarizes the current program and activities of the Microchemical Analysis Section of the Analytical Chemistry Division. The Microchemical Analysis Section has the primary mission to make contributions to the science and technology of analysis of small samples. Its program includes fundamental studies to improve the precision, accuracy and sensitivity of analytical methods as well as the development of new and improved methods of chemical analysis applicable to wide areas of materials research. As a closely related activity, the section provides analytical measurements of high reliability to the various research programs of the Bureau and to the Standard Reference Materials programs.

Research projects are active in the following analytical competence areas: gas analysis by mass spectrometry and other techniques; polarography; coulometry; electroanalytical measurements; microscopy; wet chemistry; conventional elemental microchemical analysis.

Activities during the reporting period are classified either as research or analytical development. The classification is often arbitrary since nearly all of the analytical applications have required considerable efforts of both kinds. During the year, a number of analytical methods have been developed or studied in sufficient detail to verify their applicability to the demanding requirements of standard reference material certification. An attempt has been made to describe a number of these, briefly, yet with sufficient detail to make them understandable to an experienced analyst. However, specific details will be made available to anyone interested in such matters.

Much of the work during the year has been concerned with the analysis of standard reference materials. In addition, these materials have been used frequently to verify the accuracy of analytical procedures. They are referred to by an identification such as SRM #1604, 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 specify adequately the 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 1967 to JUNE 1968

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 1967 to June 1968. 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: determination of trace amounts of oxygen in gases, development of a coulometric method for precise analysis of boric acid, improvements in microdetermination of silver and fluorine by null-point potentiometry, the electrochemical generation of fluoride ion, preparation of resin-bead particle standards, and determination of trace elements by the nuclear track technique. A number of microchemical procedures which have been developed for the analysis of a variety of materials are also included.

Key Words: Coulometric analysis, Gas analysis, Methods of chemical analysis, Microchemical analysis, Microscopic analysis, Polarographic analysis, Specific ion electrodes.

# 1. GAS ANALYSIS

## A. Introduction

The functions of the Gas Chemistry Laboratory are threefold; research into gas analytical methods, the analysis and production of gaseous standard reference materials, and service analysis of research materials and other materials. These functions are not independent of each other but rather are interrelated. For instance, much of the research is directed toward the analysis of standard reference materials and some of the service work requires prior development of analytical methods. For this reason there will be some overlapping of the three sections of this portion of the report.

## B. Research Activities

### 1. Determination of Atmospheric Oxygen

In a previous report [1], initial research on a method for the determination of atmospheric oxygen was described. This work has since been completed and published [2]. The method involves reaction of the oxygen with either phosphorous or a sodium-potassium alloy. When corrected for the difference in carbon dioxide, which is removed when using the sodium-potassium alloy, the results are identical. It was found that the cylinder of air examined had an oxygen content of 23.157 weight percent with a 95% confidence limit of 0.017% based on 36 determinations. This value is equivalent to 20.959 mole percent. The currently accepted value for the concentration of oxygen in the atmosphere is 20.945 ± 0.002 mole percent [3]. The contents of the cylinder from which the 36 samples were obtained was analyzed for its carbon dioxide content. This was found to be quite low and when the correction for the reduced carbon dioxide content was applied to the original value, the corrected value became 20.953 mole percent. In order to resolve the still remaining discrepancy of 0.008 mole percent, a sample of pure dry atmospheric air was obtained. It was compared with the cylinder sample and a difference of 0.008 mole percent was observed. Thus, the discrepancy was resolved and the validity of the gravimetric method was proved. These results are also in substantial agreement with the results obtained by Benedict in 1912 [4].

### 2. Trace Oxygen Analysis

Considerable effort has been devoted to the development of absolute methods for the determination of oxygen in gases. Such methods are needed to accurately analyze a series of standard reference materials consisting of nitrogen containing oxygen at levels ranging from a few parts per million up to a thousand parts per million or more.

An attempt was made to determine low concentrations of oxygen in inert gases by expanding the sample into a closed Hersch-type cell [5] and integrating the current produced by the oxygen. A knowledge of the coulombs produced, in addition to the cell volume and sample pressure, should allow calculation of the oxygen concentration. After considerable experimentation, this method was abandoned, since results were generally non-reproducible. The major problem was obtaining a reproducible value for the cell volume; this seemed to fluctuate due to varying rates of loss of water vapor.

An attempt was made to determine the oxygen content of some of the intermediate mixtures by gravimetric methods. Two reagents were tried; manganous oxide (MnO), and phosphorous coated on silica gel. The MnO appeared to be quite ineffective in removing all the oxygen and the results were very low. The phosphorous reagent was prepared by dissolving phosphorous in carbon disulfide and then soaking silica gel in this solution. The solution was then evaporated and the reagent was packed into absorption tubes. Again the results were disappointingly low. Therefore, gravimetry as a method for the determination of oxygen at low concentrations was abandoned.

A successful method for the analysis of trace concentrations of oxygen in inert gases was developed utilizing a modification of the Hersch cell [5]. The cell design used for analyses, which are described later, is shown in figure 1. The cell consists of a cathode made from ribbons of silver foil one mil in thickness and an anode consisting of a small sheet of lead, separated from the silver by a Teflon sheet. The electrolyte was a two-molar solution of sodium hydroxide.

Four cells are connected in series to assure complete electrochemical reduction of the oxygen. The current output in terms of the voltage drop across appropriate resistors is measured at two different flow rates. The difference in voltage is a direct measure of the difference in the rate of consumption of oxygen and hence allows a calculation of the absolute oxygen content. The apparatus with its attendant valving, volume measuring device and saturator to allow correct calculation of the volume is shown schematically in figure 2.

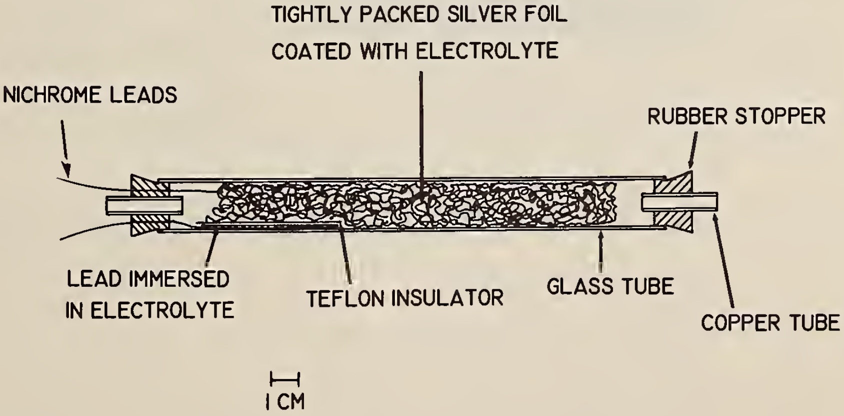

Figure 1. Modified Hersch cell for determination of oxygen concentrations above 1 ppm.

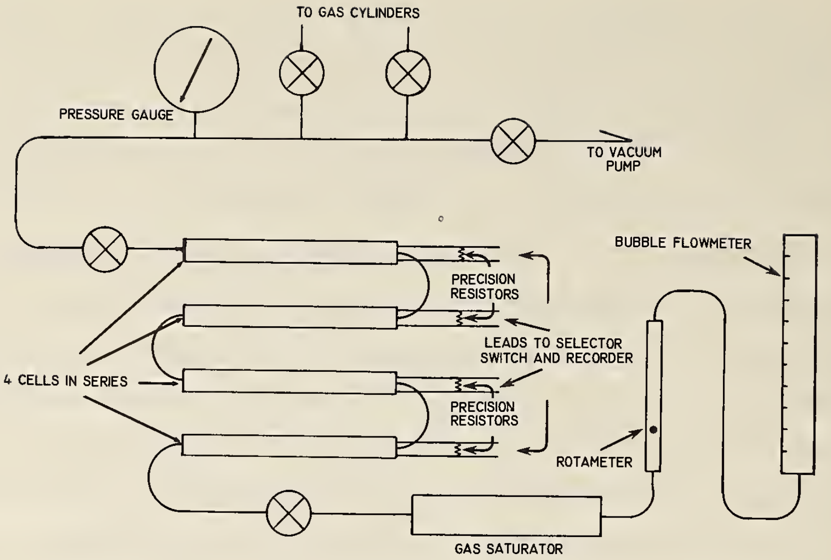

Figure 2. Apparatus for determining concentrations of oxygen in inert gases at concentrations above 1 ppm.

This method is described in a publication [6] which should be consulted for experimental details. The results of an experiment are calculated from the equation

$$M_{O_2} \times 10^6 \text{(ppm)} = 0.2127 \frac{(E_f - E_i)T}{(f_f - f_i)p'r}$$

where

$M_{O_2} \times 10^6$ = oxygen concentration in parts per million by volume (ppm)

$E_i$ = the sum of all cell outputs at the initial flow rate (mV)

$E_f$ = the sum of all cell outputs at the final flow rate (mV)

$f_i$ = initial flow rate ($cm^3/s$)

$f_f$ = final flow rate ($cm^3/s$)

T = temperature in degrees Kelvin

r = load resistance of cell (ohms)

p' = atmospheric pressure corrected to dry air at room temperature (atmospheres).

Using this new technique, oxygen concentrations as low as one ppm may be determined. Below one ppm, residual currents, produced by leakage or diffusion of atmospheric oxygen into the system, tend to obscure the small currents produced by the oxygen in the gas being analyzed.

An improved apparatus designed for concentrations of oxygen below the ppm level has been designed. This cell design is shown in figure 3 and the complete apparatus is shown photographically in figure 4. In use, all joints are lubricated with a small amount of high vacuum grease and tightly clamped.

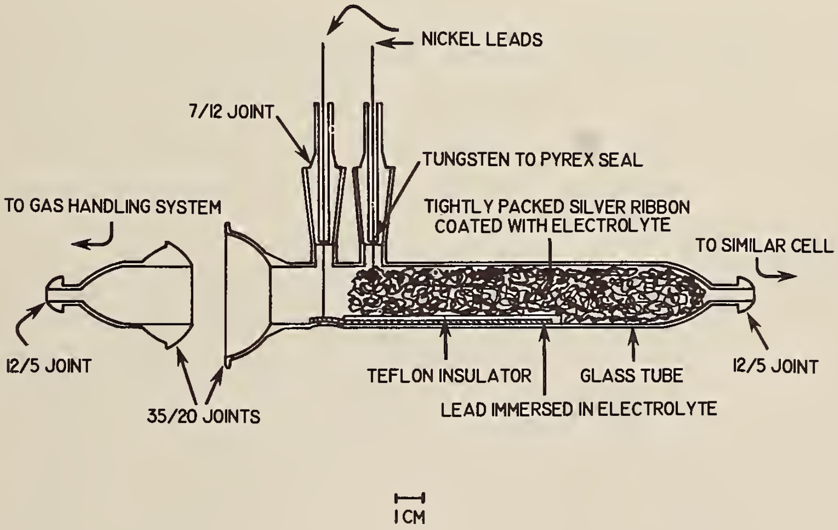

Figure 3. Galvanic cell designed for the detection of oxygen at concentration levels below 1 ppm.

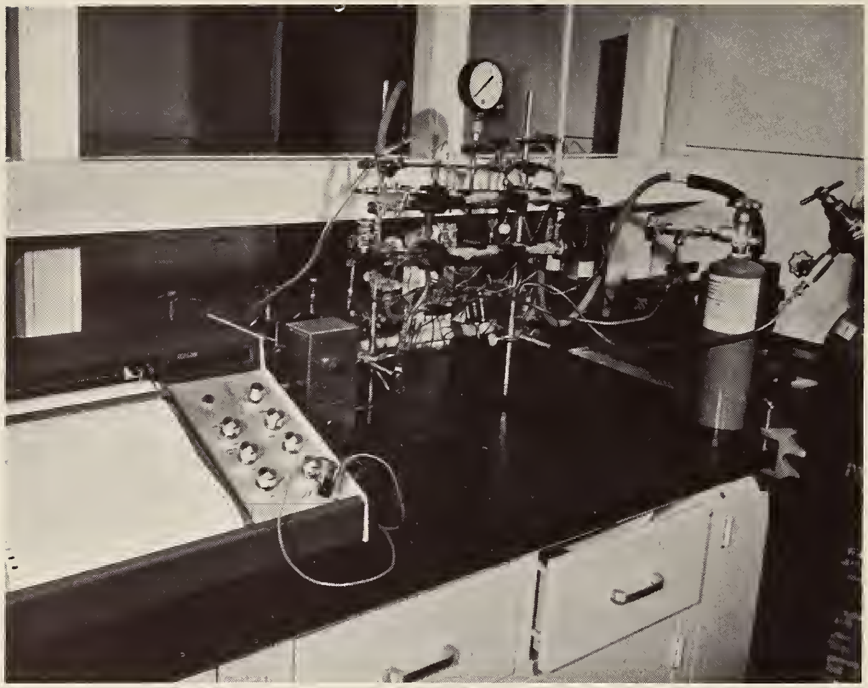

Figure 4. Photograph showing arrangement of cells in series.

### 3. Determination of Carbon Dioxide

A previous publication from this laboratory described a method for the accurate determination of low concentrations of carbon dioxide in nitrogen [7]. A method has now been developed for the accurate and direct mass spectrometric analysis of carbon dioxide in air. In essence, it consists of removal of the oxygen with phosphorous with subsequent mass spectrometric analysis with an accuracy of better than 1%. Samples are collected in bulbs containing phosphorous which are immediately analyzed by comparison with one of the NBS standard reference materials consisting of carbon dioxide in nitrogen (SRM's 1601, 1602 and 1603).

Using this method, a large number of samples were collected in a rural area near the National Bureau of Standards site at Gaithersburg, Maryland. The results are of great interest because they indicate rapid fluctuations in the carbon dioxide content of the atmosphere. This is in agreement with observations made by Dr. C. D. Keeling of the Scripps Oceanographic Institute [8].

The National Bureau of Standards method for determination of atmospheric carbon dioxide has also been described in a publication [9].

### 4. Determination of Argon

Moissan, in 1903, made a world-wide survey of the argon content of the atmosphere [10]. His value of 0.934 mole percent has recently been challenged by Sinya Oana, whose value is 0.917 mole percent [11]. Both of these investigations utilized the same method, that is removal of all the reactive constituents of the air with calcium with subsequent measurement of the residual pressure presumed to be argon.

We have attempted to determine the argon by an independent method based on high pressure mass spectrometry, in which a comparison is made between a carefully prepared standard and a sample of clean dry atmospheric air. This procedure consists of carefully weighing a quantity of nitrogen in a bulb after which slightly more than one percent of argon is added and the bulb reweighed. This is used to calibrate the mass spectrometer by measuring the mass (40) to (28) ratio. A sample of ordinary air is then measured in the same manner. Preliminary results indicate that the true value for the concentration of atmospheric argon may be lower than that reported by either of the previous investigators. Their high results may be due to the equilibrium pressure of nitrogen over calcium nitride. Much further work will be necessary before a definitive value can be given.

## C. Standard Reference Materials

### 1. Oxygen in Nitrogen

Certified gas standards consisting of oxygen in nitrogen have been prepared, analyzed, and are now being distributed by the Office of Standard Reference Materials. These are summarized in table 1.

Table 1. Standard reference materials certified for oxygen content.

| SRM No. | Oxygen Concentration |
|---|---|
| 1604 | 0.000303 ± 0.000004 mole percent |
| 1605 | .00103 ± .00001 mole percent |
| 1606 | .0112 ± .0001 mole percent |
| 1607 | .0212 ± .0002 mole percent |
| 1608 | .0978 ± .0007 mole percent |
| 1609 | 20.95 ± .02 mole percent |

The methods of analysis have been described earlier in this report.

Work is currently in progress on three new gaseous standards. These are sulfur dioxide in air, carbon monoxide in air, and a hydrocarbon in air.

### 2. Sulfur Dioxide in Air

The major problem with sulfur dioxide is its reactivity. Consequently, the first phase of this program was concerned with selection of a suitable container. Initially, three duplicate mixtures were prepared in stainless steel cylinders. Of each duplicate pair, one was equipped with a brass valve and one with a stainless steel valve. The nominal concentrations of sulfur dioxide in nitrogen were 6, 115, and 2350 ppm by volume, respectively. The mixtures were periodically analyzed over a period of one month by the peroxide method [12] and it was observed that the 6 ppm mixture continually decreased while the values for the higher concentration remained constant within the limitation of the experimental error.

Subsequently, two more mixtures were prepared in larger stainless steel cylinders. The concentrations were 15 and 300 ppm. Periodic analysis of these samples produced results with a spread of less than ± 1% from the mean.

Portions of the 15-ppm mixture were transferred to two mild steel cylinders. The concentration of sulfur dioxide immediately dropped to 8 ppm in one cylinder and to 4 ppm in the other. These concentrations continued to decrease significantly over a period of two weeks.

Because of the observed behavior, effort will be devoted at present to certification of standards containing relatively high concentrations of sulfur dioxide. These standards will be useful for source control rather than atmospheric analysis. Concurrently, further investigation will be continued to determine a suitable container for the lower concentrations.

### 3. Hydrocarbon in Air

A proposal to produce a series of hydrocarbon-in-air standards was accepted and work has begun on their preparation and analysis. Mixtures will be made using methane as the hydrocarbon component and the concentrations will be approximately 100, 10, and 1 ppm.

Hydrocarbon analyses are to be performed using an instrument utilizing flame ionization. In order to use this instrument, calibration standards are necessary. The relationship between hydrocarbon concentration and instrument response should be linear. Hence, a standard of relatively high concentration (200-300 ppm) and one of zero concentration could be used to calibrate the instrument for subsequent analysis of mixtures of hydrocarbon in air.

A standard containing 207 ppm methane in nitrogen was available; this concentration was determined by converting the methane to carbon dioxide and determining the carbon dioxide mass spectrometrically as well as from the measured pressure involved in compounding the mixture.

Using the flame-ionization technique, with the above calibrant, the hydrocarbon content of several cylinders of compressed air was found to be in the 3-ppm range. To provide air of zero hydrocarbon concentration, removal of the hydrocarbon contained in the compressed air was necessary. Neither a column of molecular sieves nor a column of cooled, activated charcoal inserted in the air line, were effective in completely removing the hydrocarbon in the compressed air. However, it appears that a Vycor tube filled with cupric oxide and heated to about 1050°C will remove all hydrocarbon in air passed through it. Using this technique, the same instrument response is obtained when air containing about 4.5 ppm hydrocarbon, air containing about 2 ppm hydrocarbon, and nitrogen containing about 0.2 ppm hydrocarbon are passed through the hot cupric oxide into the instrument. Preliminary results using the 207-ppm mixture and compressed air passed over hot copper oxide (after which the air is presumed to be hydrocarbon free) as calibrants, indicate that results from the hydrocarbon analyzer are reproducible. For example, an air sample, analyzed on three different days, gave results of 2.98, 2.91 and 2.92 ppm hydrocarbon.

After several mixtures are analyzed to verify the linearity of response and also to provide calibration standards at the lower levels, work will proceed on the preparation of the standard reference materials.

## D. Research Materials Service Analysis

### 1. General

The analysis of research materials is a significant part of the activities of this laboratory. The nature of samples range from relatively pure materials to very complex mixtures. Typically, there are complicating factors that preclude a routine determination. Frequently, method development or modification is involved.

Analyses performed during the past year are summarized in table 2. Several of the more interesting determinations are outlined below.

Table 2. Summary of gas analytical services.

A. Mass Spectrometric Analysis

| Material | Number of Samples | Sample Size | Determined |
|---|---|---|---|
| | | Organic Substances | |
| Reaction product | 1 | 2 ml STP | Molecular weight |
| Ethane | 1 | 10 ml STP | $H_2$, $CH_4$, $CO_2$, butane |
| Gases evolved from plastics | 1 | $10^{-6}$ moles | p-xylene, p-tolualdehyde |
| | | Inorganic Substances | |
| Air | 2 | Cylinder | $CO_2$ |
| Condensates from reaction | 1 | 10 ml STP | $CO_2$, HCl, $H_2S$ |
| $N_2O$ | 1 | Cylinder | $H_2$, $O_2$, Ar |
| Air | 1 | Cylinder | $H_2$ |
| He | 1 | 50 ml STP | $H_2$ |
| $N_2$ | 1 | Cylinder | He |
| $SF_5Cl$ | 2 | Cylinder | $SOF_2$, $SO_2$, $SO_2F_2$, $SiF_4$ |

Table 2. (Continued)

| Material | Number of Samples | Sample Size | Determined |
|---|---|---|---|
| | | Inorganic-Organic Mixtures | |
| Atmospheres within sealed tape recorders | 2 | 500 ml STP | Organic vapor contamination of the $N_2$ atmosphere |
| Product of reaction | 2 | 0.1 ml STP | $H_2$, $CH_4$ |
| Reaction atmosphere | 2 | 2 ml STP | $H_2$, $CH_4$, $N_2$, $O_2$, Ar |
| $H_2$ | 1 | 10 ml STP | $CH_4$, $H_2O$, Air |
| Air | 1 | Cylinder | $CH_4$ |
| Air | 1 | Cylinder | Pentane |
| | | Isotopically Altered Compounds | |
| Helium-3 | 3 | 30 ml STP | He-4, $H_2$, $H_2O$, $N_2$, $O_2$ |
| Helium-3 | 19 | 30 ml STP | He-4 |
| Nitrogen-15 | 1 | 100 ml STP | Nitrogen-14 |
| Carbon-13 enriched ethyl acetate | 2 | 0.07 ml | Carbon-12 ethyl acetate |
| Helium-3 | 1 | Cylinder | Helium-4, $H_2O$, $N_2$, $O_2$, Ar, $CO_2$ |
| $D_2$ | 2 | 1 ml STP | HD, $H_2$ |
| $D_2$ | 3 | Cylinder | $H_2$, HD |

Table 2. (Continued)

| | | | |
|---|---|---|---|
| | | Pure Chemicals | |
| He | 1 | 500 ml STP | $N_2$, $O_2$, Ne, Ar |
| He | 1 | Cylinder | $CH_4$, $C_2H_6$, $O_2$ |
| $NO_2$ | 1 | Cylinder | Impurities |

## B. Nuclear Magnetic Resonance Analysis

| Material | Number of Samples | Sample Size | Determined |
|---|---|---|---|
| Reaction products | 5 | 5 ml of a 10% solution | Structure |
| Unsaturated hydrocarbon plus reactant | 2 | 5 ml of a 10% solution | Change in the ratio of saturated to unsaturated material over a period of time |

## C. Gas Chromatographic Analysis

| Material | Number of Samples | Sample Size | Determined |
|---|---|---|---|
| Preservative solutions | 3 | 10 ml | Methanol, ethanol, water, formaldehyde |
| Bromo organic compounds | 2 | 10 ml | Purity |

## D. Preparation of Gas Mixtures

Compounded one mixture of 14 ppm carbon monoxide in nitrogen.

Compounded for methane in air mixtures

(a) 2.02 ppm

(b) 2.02 ppm

(c) 8.09 ppm

(d) 8.09 ppm.

## 2. Analysis of Heavy Water

A method was developed and is now being used to monitor the deuterium oxide content of heavy water contained in the NBS nuclear reactor. The preliminary work has been described in the report of last year [1]. The method consists of comparing the absorption of a sample of deuterium oxide to that of a standard at 2.95 μ using an infrared spectrometer. The standards are prepared from a sample of deuterium oxide of known concentration. A series is prepared by the careful addition of weighed quantities of water to weighed quantities of deuterium oxide.

The heavy water for installation in the NBS reactor consisted of 75 drums, each containing 55 gallons of deuterium oxide. The values obtained on analysis of these drums ranged from 99.73 to 99.80 mole percent deuterium oxide. These values could be determined to ± 0.005 mole percent.

Periodic analyses of the deuterium oxide in the reactor have shown little additional contamination by light water.

## 3. Reaction Product Analysis

Another analysis involved an experiment in kinetics which was solved using a nuclear magnetic resonance spectrometer (NMR). The problem was to determine the rate at which various reactants would add across the double bond of an unsaturated organic molecule. The reactant and unsaturated molecule were added to an NMR tube at a very low temperature. The tube was sealed and stored at low temperature until analyzed, at which time it was quickly warmed to the temperature of the NMR probe and a spectrum of the significant peaks was obtained. These peaks, occurring in regions corresponding to saturated and unsaturated bonds, were periodically measured and their areas determined. From these data it was possible to determine the rate constant for the reaction.

### 4. Gas Contaminant Identification

A third problem was concerned with the premature failure of sealed tape recorders carried in space satellites. The project in which these recorders were used was sponsored jointly by the National Aeronautics and Space Administration and the European Space Research Organization. Their suspicion was that possible volatile organic substances might be contaminating the supposedly inert atmosphere within the recorders causing failure of the tape or the coating on the tape.

Recorders prepared by both groups were obtained. They were placed in an oven under conditions similar to what they would experience in actual usage. Samples of the atmospheres within the recorders were then removed through a small valve inserted into the recorders. The samples were then examined mass spectrometrically. Some samples were introduced directly while others were passed through a cold trap. In the case of these, the volatiles were pumped away with subsequent warming and those substances not volatile at the low temperature were determined.

Varying amounts of organic materials were found in each recorder. This data will be used by the concerned agencies together with their knowledge of the components in the recorders in order to remedy the problem.

### 5. Atmospheric Oxygen Survey

An example of a combined service and development project is a cooperative effort between the Environmental Science Services Administration and the National Bureau of Standards for the investigation of a method for the determination of atmospheric oxygen in samples of air collected on a world-wide cruise of the research ship Oceanographer. It was necessary for the Bureau to develop a technique which would allow analysis of small samples at atmospheric pressure with an accuracy of 0.01 mole percent or better. The apparatus is shown schematically in figure 5 and photographically in figure 6.

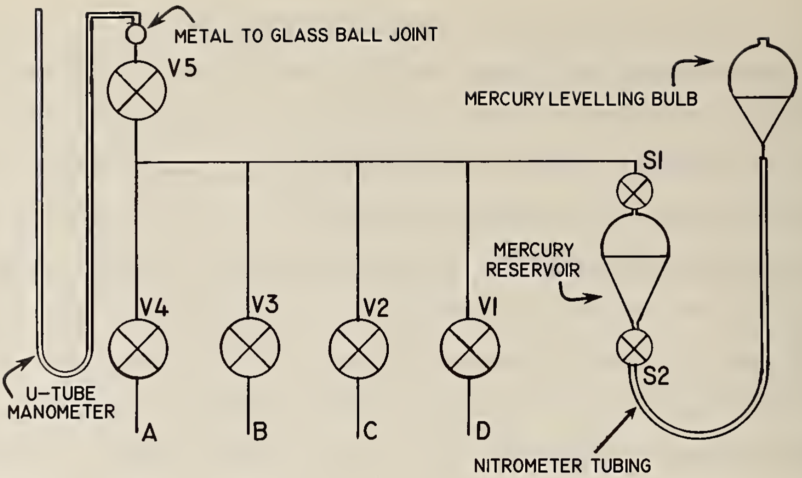

Figure 5. Schematic of gas handling system for admitting gases to oxygen analyzer at one atmosphere from a container at lower pressure.

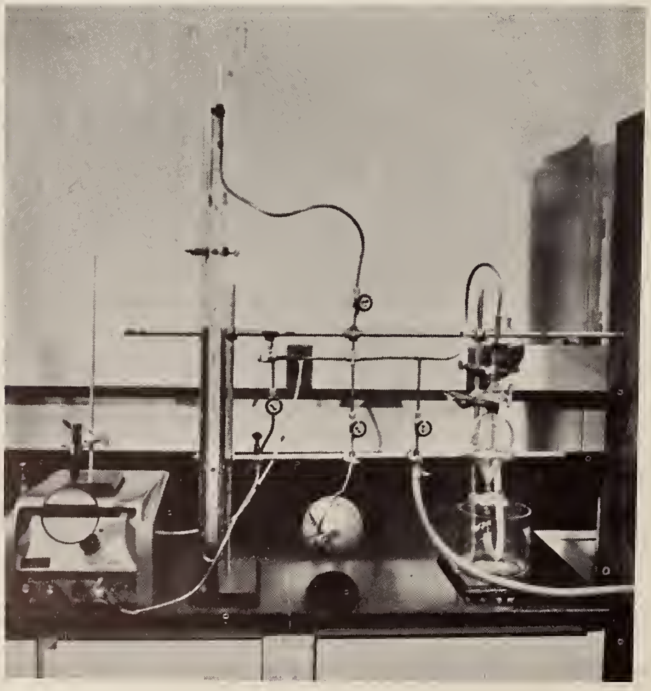

Figure 6. Photograph of apparatus shown in figure 5.

In use, the sampler is connected at B, the mercury is transferred to the levelling bulb and stopcock 2 is closed. The whole system is evacuated through valve 2 at line C with only valve 4 closed. Valve 2 is then closed and the cylinder valve is opened allowing the sample to fill the system. Valve 3 is then closed and stopcock 2 is opened slowly until enough mercury has entered the reservoir tó bring the pressure to about a torr above atmospheric. Stopcock 2 is then closed, valve 4 is opened momentarily to equalize the pressure with the atmosphere. Valve 4 is then closed and measurements of the oxygen content are made using an instrument utilizing the paramagnetic properties of oxygen. Next, the system enclosed by valves 2, 3, 4, 5, and stopcock 1 is evacuated. Valve 2 is then opened and a new sample is allowed to flow into the restricted portion of the system. Mercury is again allowed to flow into the reservoir after opening stopcocks 1 and 2. Valve 5 is opened and the pressure is raised again to slightly over one atmosphere.

The same procedure is followed in introducing more samples from the same flask. The procedure can be continued as long as there is sufficient mercury in the reservoir to allow compression of the sample to one atmosphere. The tubing is 1/4-in. soft copper and the operation is so rapid and the cell volume is so small that no contamination from previous samples from the same container trapped in the reservoir or manometer is likely to occur.

Because the measurements are made at atmospheric pressure, a barometer capable of estimation of the atmospheric pressure with a repeatability of ± 0.03 mm is necessary to correct all calculations to the same pressure.

Personnel aboard the Oceanographer will sample air at selected locations by filling one-liter stainless steel flasks which will be evacuated immediately before sampling. The sample will be drawn through a probe sufficiently long to obtain an uncontaminated sample of air. The air is dried by means of a drier filled with magnesium perchlorate attached to the probe. It is anticipated that at least 50 samples will be collected from this cruise. Subsequently, a second research ship, the Eltanin, will obtain a similar number of samples which will also be analyzed in the same manner.

The apparatus will allow about five samples per container to be analyzed.

(E. E. Hughes, W. D. Dorko, and J. M. Ives)

# 2. POLAROGRAPHIC ANALYSIS

## A. Introduction

The polarographic program during the past year has been largely devoted to the analysis and development of methods of analysis of standard reference and other research materials. Since a scarcity of reliable methods exists in many areas of microchemical, trace, and high precision analysis, considerable effort has been exerted in these directions in this laboratory. The resultant polarographic methods were demonstrated to be advantageous in most cases in sensitivity, accuracy, and time required for analysis. Some of the procedures will be given in the following report as well as some collaborative data obtained by other analytical techniques for the same materials.

## B. High Precision Polarographic Analysis

### 1. Analysis of Lead and Zinc Cyclohexanebutyrates

Procedures utilizing the improved comparative polarographic method developed here [13] have been applied to several organic standard reference materials. Not only were the methods used for the certification analysis, but also provided quick and accurate information on sample homogeneity.

The procedure for the determination of zinc in zinc cyclohexanebutyrate, SRM 1073b, was as follows: After drying over phosphorous pentoxide for about 48 hours, samples weighing approximately 0.6 g were slowly ashed to about 700 °C. The residues were then wet ashed with nitric acid and hydrochloric acid, evaporated to dryness, dissolved in 10 ml of concentrated hydrochloric acid and water and diluted to one liter. Zinc was then measured comparatively at about - 1.0 V vs. a mercury pool anode using reference solutions prepared in the same manner from melting point zinc, SRM 43e.

Preliminary analyses of nine separate lots of the sample showed no significant differences. The lots were then combined by rotating and tumbling in a large jar. Four samples were taken from the blended material, identified as follows: top, 1/3 down, 2/3 down, bottom. Quadruplicate determinations were made on each sample except the one taken 2/3 down which was analyzed in triplicate. The results are shown in table 3.

Table 3. Zinc in zinc cyclohexanebutyrate.

| Sample designation | Zinc, percent | Standard deviation, s |
|---|---|---|
| Top | 16.68 | 0.06 |
| 1/3 down | 16.60 | .14 |
| 2/3 down | 16.67 | .06 |
| Bottom | 16.67 | .09 |
| General average | 16.66 | |

The method for the determination of lead in lead cyclohexanebutyrate, SRM 1059b, was as follows: After storing in a desiccator over phosphorous pentoxide for about 24 hours, samples weighing about 0.27 g were ashed slowly to 500 °C. The residues were dissolved in 10 ml of hydrochloric acid and diluted to one liter. Lead was then measured comparatively at about - 0.5 V vs. a mercury pool anode using solutions prepared from melting point lead, SRM 49d, as reference standards.

The material was received in 12 bottles, each containing about 150 g of the compound. Six bottles were selected at random and four were analyzed in duplicate and two in triplicate. The results are shown in table 4. It is seen that the average deviations between different bottles were somewhat greater than those between replicates on a single bottle, suggesting that the differences found between bottles were real.

Table 4. Homogeneity check of six different bottles of lead cyclohexanebutyrate.

| Sample designation | Pb, % | Avg. dev. per determination | Average Pb, % | Deviation from general average |
|---|---|---|---|---|
| 0-4 | 36.55<br>36.26 | 0.14 | 36.41 | 0.35 |
| 0-10 | 36.59<br>36.70 | .06 | 36.64 | .12 |
| 0-11 | 37.38<br>37.29<br>37.43 | .05 | 37.37 | .61 |
| 0-12 | 36.62<br>36.76 | .07 | 36.69 | .07 |
| 0-20 | 36.31<br>36.55<br>36.48 | .09 | 36.45 | .31 |
| S-29 | 36.66<br>37.12 | .23 | 36.89 | .13 |
| General average | 36.76 | .11 | | .26 |

The several lots were then combined and blended by rotating and tumbling in a large jar. Four samples were taken from the blended material and identified as follows: top, 1/3 down, 2/3 down, bottom. Duplicate determinations were made on each sample by the method already described. The results are shown in table 5.

A high degree of agreement is shown between duplicates, with an average deviation of about 0.02% absolute or 0.05% relative. There is still an apparent small discrepancy between the values found for the four samples, but it is within the tolerances for homogeneity required for this standard.

Table 5. Determination of lead in various portions of blended lead cyclohexanebutyrate.

| Sample designation | Pb, % | Avg. dev. per determination | Average Pb, % | Deviation from general average |
|---|---|---|---|---|
| Top | 36.715<br>36.668 | 0.023 | 36.692 | 0.038 |
| 1/3 down | 36.760<br>36.690 | .035 | 36.725 | .071 |
| 2/3 down | 36.560<br>36.570 | .005 | 36.565 | .089 |
| Bottom | 36.650<br>36.620 | .015 | 36.635 | .019 |
| General average | 36.654 | .020 | | .054 |

### 2. Analysis of Copper-Zinc Alloys

Polarography is a superior technique for precise analysis of copper base alloys as illustrated for the following sample. A binary copper-zinc alloy which came to our laboratory through the service analysis program was found by electron microprobe analysis to be especially micro-homogeneous. Since their criteria for homogeneity are considerably more rigorous than for many other techniques, it seemed desirable to have an accurate analysis on this particular sample in order that it could be used as a microprobe standard. Since the microprobe measurements are precise to within about 0.5% or better, an accuracy greater than this was desired for the copper-zinc analysis.

The procedure used was as follows: Approximately 0.2-g samples of metal drillings were dissolved in dilute nitric acid, and evaporated to dryness. The residues were dissolved in hydrochloric acid and diluted to one liter with pyridine and water so that the final concentration was approximately 0.5 M in both pyridine and pyridinium chloride. The solutions were measured by comparative polarography, using reference solutions prepared from melting point copper, SRM 45d, and melting point zinc, SRM 43e. The results showed a composition of 76.75% copper and 23.21% zinc with average deviations in both cases of less than 0.1%.

## C. Major Constituent Analysis

### 1. Analysis of Metal-Organic Complexes

Single cell cathode ray polarography is particularly suitable for the rapid determination of many metal constituents in organic or biological matrices.

For some studies made in the Polymers Division by Dr. E. Horowitz and Miss M. Solarczyk on the behavior of certain transition metal-polymer systems, the exact composition of some copper, nickel, zinc, manganese, or iron-8-hydroxyquinolates prepared by them was needed. The methods used were as follows: Fifty mg of the copper quinolate was treated with 0.5 ml of sulfuric acid and several additions of nitric acid to destroy organic material. The samples were then fumed to dryness and the residues were dissolved in 4 ml of hydrochloric acid and water. Eight ml of pyridine was added, the samples were diluted to 100 ml, and copper measured at about - 0.4 V vs. the mercury pool anode. Nickel was determined in a similar manner except the peak was measured at about - 0.8 V vs. a mercury pool anode.

Zinc was determined in the same supporting electrolyte as copper and nickel after slow ignition of 50-mg samples. Zinc was then measured at about - 1.1 V vs. the mercury pool anode.

Manganese was determined using 50-mg samples after slow ignition. The residue was dissolved in a few drops of hydrochloric acid, evaporated to dryness and diluted to 100 ml with 0.1 M potassium chloride. Manganese was then measured at about - 1.6 V vs. a mercury pool anode.

The organic material was destroyed in 25-mg samples of two different iron quinolate samples by fuming with perchloric acid and nitric acid. The residues were dissolved in 2.5 ml of 1+1 perchloric acid, 12.5 ml of 2 M sodium acetate, 2.5 ml of 0.1 M EDTA, and diluted to 25 ml. Iron was then measured at about - 0.3 V vs. the mercury pool anode. The results on the quinolates are shown in table 6.

Table 6. Analysis of metal-quinolates.

| | Cu, % | Ni, % | Zn, % | Mn, % | Fe, % | |
|---|---|---|---|---|---|---|
| Found | 16.11 | 11.55 | 16.55 | 14.66 | 13.57 | 13.54 |
| | | 11.69 | 16.26 | 14.52 | 13.51 | 13.65 |
| Reported | 16.1 | 11.6 | 16.4 | 14.6 | 13.5 | 13.6 |

Small crystals containing major-constituent amounts of copper and minor-constituent amounts of either cadmium or lead were analyzed for both metals concurrently in the same solution by cathode ray polarography. The samples which were copper pyridine N-oxides doped with small amounts of either cadmium or lead, were of interest in some electron-spin resonance studies made in the Inorganic Materials Division.

Organic material was destroyed in a 25-mg sample of the copper-cadmium compound by fuming with nitric acid and perchloric acid. The residue was dissolved in 0.5 ml of 1+1 hydrochloric acid, diluted to 50 ml, and copper was measured at about - 0.25 V and cadmium at about - 0.7 V vs. a mercury pool anode. The results showed 19.4% copper and 0.36% cadmium.

The copper-lead sample was analyzed in a similar manner using approximately 30-mg samples except that it was necessary to utilize the subtractive mode of operation of the cathode ray polarograph for the determination of the lead. The peak resulting from the reduction of the small amount of lead, following the very large copper peak, is not well enough defined for quantitative measurement. By using a solution in the second cell containing an amount of copper similar to that of the sample and no lead, the large copper peak is electrically subtracted and a well-defined lead peak results. Copper was measured in the single cell at about - 0.25 V vs. a mercury pool anode and lead, by the dual-cell mode of operation at about - 0.5 V vs. a mercury pool anode. Results are shown in table 7.

Table 7. Copper and lead in metal-organic complex.

| | Copper, percent | Lead, percent |
|---|---|---|
| Sample no. 1 | 19.81 | 0.17 |
| Sample no. 2 | 19.95 | .19 |
| Reported | 19.9 | .18 |

### 2. Determination of Zinc in Corrosion Products

A small amount of corrosion product resulting from the contact of a mixed hydrazine rocket fuel with the zinc coating of a rocket fuel container was submitted for determination of zinc. Knowledge of the zinc content would then give an indication of the amount of corrosion which had occurred. A 3-mg sample was dissolved and evaporated to dryness with nitric acid and perchloric acid followed by dissolution in a pyridine-pyridinium chloride supporting electrolyte. Zinc was then measured at about - 1.1 V vs. a mercury pool anode and found to be 30.4%.

## D. Minor Constituent Analysis

Cathode ray polarography has been very useful for the determination of a number of elements in solders and steel. The methods developed could be used directly without time-consuming separations.

### 1. Determination of Lead in Leaded Steel

A method described last year [1] for SRM 130a has been utilized for analysis of a leaded steel needed to verify conformance with the lead specification. A 400-mg sample was dissolved in 10 ml of 1+1 hydrochloric acid and saturated potassium chlorate solution was added to oxidize carbides and the solutions evaporated to about 6 ml. The iron was then reduced by gentle heating with hydrazine hydrochloride and 5 ml of saturated sodium formate and 2 ml 0.5% starch solution. After dilution to 25 ml, lead was measured at about - 0.5 V vs. a mercury pool anode.

### 2. Determination of Copper, Bismuth, and Nickel in Solders

Methods were developed for the determination of bismuth, copper and nickel in lead-tin solders, SRM 127b and 1131. Bismuth and copper or nickel and copper could be determined concurrently in the same supporting electrolyte; however, for the certification analyses, they were each measured in a separate supporting electrolyte. The methods are as follows: For the determination of copper and, under some conditions, bismuth, 1-g samples were dissolved in a 4+1 mixture of hydrobromic acid and bromine, 10 ml of perchloric acid was then added and the solutions evaporated to perchloric acid fumes several times to remove tin. SRM 127a was also taken through the procedure as a control. The solutions were then boiled vigorously to convert the lead bromide to perchlorate and diluted to 25 ml. Ten-ml aliquots were evaporated to dryness twice with nitric acid and the residues dissolved in 1 ml of 5% nitric acid and 4 ml of a 20% sodium tartrate solution. Copper was then measured at about - 0.3 V vs. a mercury pool anode. Bismuth could also be measured at about - 0.5 V; however, in view of the relatively small volume and high concentration of lead tartrate, it was thought that some co-precipitation of bismuth might occur with the lead tartrate and that the amounts of bismuth present in the sample might be better determined at higher dilutions. The results are shown in table 8 as well as those later obtained by other techniques. The polarographic values represent individual samples while those by other techniques are averages as reported by the analysts.

Table 8. Copper in SRM's 127a, 127b, and 1131.

| Sample | Copper, percent<br>Polarographic | Spectrographic | Neutron activation | Average |
|---|---|---|---|---|
| 127a (cert. 0.004) | 0.0037 | | | |
| | .0038 | | | |
| | .0040 | | | |
| 127b | .011 | 0.011[a] | 0.010[b] | 0.011 |
| | .011 | | | |
| | .011 | | | |
| | .010 | | | |
| 1131 | .010 | .010[a] | | .011 |
| | .009 | | | |
| | .011 | | | |
| | .012 | | | |

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[a] M. M. Darr, Spectrochemical Analysis Section.

[b] P. D. LaFleur, Activation Analysis Section.

For the determination of nickel in the solders, 2-g samples were dissolved and tin was removed in a manner similar to that described above for the determination of copper. The samples were diluted to 100 ml and 1 g of sodium sulfate was added to precipitate lead. The solutions were mixed well, lead sulfate was allowed to settle, and a 25-ml aliquot was taken from the clear supernatant liquid. The aliquot was evaporated to dryness, the residue dissolved in 3 ml 1+6 hydrochloric acid and 2 ml of pyridine and nickel measured at about - 0.85 V vs. a mercury pool anode. Copper could also have been measured in the same solution at about - 0.4 V. The results are shown in table 9.

Table 9. Nickel in SRM's 127a, 127b, and 1131.

| Sample | Nickel, percent<br>Polarographic | Spectrographic | Spectrophotometric |
|---|---|---|---|
| 127a (cert. 0.002) | 0.0025<br>.0021 | | |
| 127b | .011<br>.012 | 0.015[a] | 0.011[b] |
| 1131 | .011 | .014[a] | .009[b] |

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[a] M. M. Darr, Spectrochemical Analysis Section.
[b] E. R. Deardorff, Analytical Coordination Chemistry Section.

Bismuth was determined using 2-ml aliquots of the solution from which the aliquots for copper were taken. The aliquots were evaporated to dryness with hydrochloric acid and dissolved in 5 ml of 5% hydrochloric acid. Bismuth was then measured at about - 0.2 V vs. a mercury pool anode. The results are shown in table 10.

Table 10. Bismuth in SRM's 127a, 127b, and 1131.

| Sample | Bismuth, percent<br>Polarographic | Spectrographic |
|---|---|---|
| 127a (cert. 0.036) | 0.038<br>.038 | |
| 127b | .065<br>.065 | 0.062[a] |
| 1131 | .066<br>.068 | .064[a] |

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[a] M. M. Darr, Spectrochemical Analysis Section.

### 3. Determination of Copper and Zinc in Aluminum Alloys

Copper and zinc may be very conveniently determined polarographically in aluminum alloys. Preliminary attempts to use a pyridine-pyridinium chloride supporting electrolyte did not give very precise results, probably owing to some occlusion of copper by the gelatinous aluminum hydroxide precipitate. A copper-zinc-aluminum alloy received was analyzed by dissolving 50-mg samples in dilute hydrochloric acid, diluting to 25 ml with 0.1 N hydrochloric acid and measuring copper at about - 0.2 V and zinc at about - 1.0 V vs. a mercury pool anode. An aluminum-copper alloy was analyzed in a similar manner. The results are shown in table 11 and represent the average of four determinations.

Table 11. Determination of copper and zinc in aluminum alloys.

| Sample | Zinc, percent | Copper, percent |
|---|---|---|
| Cu-Zn-Al | 1.89 ± 0.03 | 5.63 ± 0.04 |
| Cu-Al | | 3.83 ± .04 |

## E. Small Sample Analysis

The work on samples weighing as little as several hundred μg has continued. Methods developed in this laboratory have played a vital role in determination of the composition of thin metallic films being developed for electronic circuitry by Harry Diamond Laboratories and also of thin films developed in research programs at the Naval Ordnance Laboratory. The methods have been extended to include the analysis of the source material remaining on a tungsten filament after vacuum deposition of the film onto a glass slide.

### 1. Analysis of Antimony-Bismuth Films

The method developed for the determination of both bismuth and antimony in thin films is described in ref. [1]. The samples analyzed during the past year have ranged from about 70 to 97% bismuth and the total sample weight has been as little as 184 µg. Ordinarily, samples are too small to weigh so that composition is calculated from the analytical measurements, assuming no differential losses during analysis. One sample of the binary source alloy was submitted for analysis in sufficient quantity that preliminary weights could be taken, hence an additional check on the accuracy of the method was provided. The results for this alloy are shown in table 12.

Table 12. Determination of bismuth and antimony in thin film deposition source material.

| | Wt found, mg | | |
|---|---|---|---|
| Wt taken, mg | Bismuth | Antimony | Total |
| 332.7 | 238.1 | 91.0 | 329.1 |

The apparent error of - 1% is well within the limit of single cell polarographic measurements. Greater accuracy could of course be provided if needed by use of the comparative mode of operation of the cathode ray polarograph.

### 2. Analysis of Copper-Nickel-Chromium-Aluminum Films

A number of thin films have been analyzed for copper, nickel, chromium, and aluminum largely by the methods described in ref. [14]. The amounts ranged from 2 to 100 µg of copper and aluminum, 43 to 3600 µg of nickel, and 35 to 900 µg of chromium. A number of filaments used for vaporizing the source material were also submitted for analysis in order to determine the amount of unvaporized material remaining. The source material was removed by prolonged digestion in quartz with nitric acid, then with nitric acid and hydrochloric acid. Some tungsten was also dissolved and precipitated as tungstic oxide. The resulting solutions were diluted to 25 ml and 10-ml aliquots were taken for the concurrent determination of copper and nickel in a pyridine-pyridinium sulfate supporting electrolyte and 5-ml aliquots for the determination of chromium in 1 M sodium hydroxide as already described in ref. [14].

For the determination of aluminum, 5-ml aliquots were evaporated to dryness with 5 drops of hydrochloric acid, the residue dissolved in 2 drops of 50% hydrochloric acid, transferred to a separatory funnel and diluted to 10 ml with $H_2O$. Two ml of acetic acid and 10 ml of 2 M sodium acetate were added to give a pH of about 4.5. Ten ml of a saturated sodium diethyldithiocarbamate solution was added and copper and nickel extracted with 15, 10, 10, and 5-ml portions of chloroform. One ml of 6% cupferron was added, the solution allowed to sit for 2 minutes and aluminum was extracted with 15, 10, 5, and 5-ml portions of chloroform. The extracts were evaporated to dryness in quartz. One ml of perchloric acid and 2 ml of nitric acid were added and the solutions were boiled and evaporated to dryness to destroy organic material. The residues were treated with 10 drops of 50% hydrochloric acid, evaporated to dryness on low heat, and dissolved in 0.5 ml of 6 M perchloric acid. Five ml of 2 M sodium acetate and 2 ml of Superchrome Garnet Y were added, the solutions diluted to 50 ml and transferred to polyethylene bottles. After heating in a water bath for 10 minutes and cooling, aluminum was measured on the cathode ray polarograph at about - 0.7 V vs. a mercury pool anode. The aluminum found ranged from 14 to 25 µg with a blank of 1.7 µg.

### 3. Analysis for Lead in Lead-Tin-Telluride

Several lead-tin-telluride film source materials were submitted for the determination of lead with a desired error of less than 1%. In the previous thin film samples, both lead and tin determinations were needed necessitating separations as described in ref. [1]. However, lead alone may be determined in 1 M sodium hydroxide with no interference from tin. The material was dissolved in nitric acid and perchloric acid, evaporated to dryness, the residue dissolved in hydrochloric acid and made 1 M in sodium hydroxide. Lead was then measured on the cathode ray polarograph. The results illustrating the precision achieved are shown in table 13.

Table 13. Lead in lead-tin-telluride.

| Sample | Lead, percent | Average deviation, percent |
|---|---|---|
| R-28 | 31.256<br>31.440 | 0.092 |
| 2236-34 | 31.641<br>31.774 | .067 |

## F. Trace Analysis

The bulk of the work in trace analysis in this laboratory during the past year has been devoted to the analysis of and development of methods of analysis for ppm and ppb-level constituents of several high purity metal standard reference materials. The polarographic methods developed are very sensitive and selective and give results in excellent agreement with those obtained by other techniques.

### 1. Determination of Trace Constituents in Zinc

The methods developed for the concurrent determination of copper, cadmium and lead in zinc and results on some of the samples have already been described in ref. [1]. The methods proved extremely useful for both homogeneity testing and certification analysis of both standards. Lots 1, 2, and 3 of zinc, SRM 728, were shown to be homogeneous with respect to these elements, however, inhomogeneities were suspected in lots 2 and 3 of zinc, SRM 683. Additional samples of lots 2 and 3 were, therefore, submitted for analysis. Samples from each lot, weighing 10.5 to 10.9 grams, were dissolved in 30 ml of concentrated hydrochloric acid and diluted to 50.0 ml with water. Duplicate 20-ml aliquots of each solution were evaporated to dryness and the salts dissolved and diluted to 10.0 ml with 0.1 N hydrochloric acid.

Table 14 lists the results of the individual determinations and the average value for each sample, as well as the general average value for each element. The agreement between duplicate determinations is considerably better than between samples, particularly for lead, thus indicating some inhomogeneity of the material.

Table 14. Copper, lead, and cadmium in pure zinc composition standard, SRM 683.

| Sample designation | Copper, ppm | Lead, ppm | Cadmium, ppm |
|---|---|---|---|
| 2B36-1 | 6.13 | 9.60 | 0.93 |
| | 6.36 | 9.60 | .91 |
| | 6.25 | 9.60 | .92 |
| 2-A36-1 | 6.17 | 11.58 | 1.06 |
| | 6.25 | 11.47 | 1.06 |
| | 6.21 | 11.53 | 1.06 |
| 2-B15-1 | 6.32 | 10.28 | 1.19 |
| | 6.32 | 10.28 | 1.17 |
| | 6.32 | 10.28 | 1.18 |
| 2-A15-3 | 6.65 | 11.58 | 1.21 |
| | 6.65 | 11.58 | 1.21 |
| | 6.65 | 11.58 | 1.21 |
| 3-A15-1 | 6.49 | 11.29 | 1.16 |
| | 6.71 | 11.62 | 1.18 |
| | 6.60 | 11.46 | 1.17 |
| 3-B15-1 | 6.47 | 11.53 | 1.12 |
| | 6.65 | 11.87 | 1.19 |
| | 6.56 | 11.70 | 1.16 |
| 3-A26-1 | 6.43 | 9.63 | 1.11 |
| | 6.61 | 9.63 | 1.14 |
| | 6.52 | 9.63 | 1.12 |
| General average | 6.44 | 10.83 | 1.12 |
| Pooled average deviation per determination | 0.06 | 0.06 | 0.01 |
| Average deviation of samples from general average | .14 | .85 | .07 |

As a result of these measurements and also of residual resisitivity ratios obtained at the NBS laboratory in Boulder, lots 2 and 3 were not used and only lot 1 was considered to have sufficient homogeneity for certification.

Determinations of iron and aluminum were also needed for both zinc standards. Limited time was available for these determinations; hence it seemed desirable to develop a direct method requiring no separations. The use of the Solochrome Violet RS or Superchrome Garnet Y complexes of iron and aluminum as discussed earlier in ref. [1] was first considered because of the extreme sensitivity of the method. It was found, however, that the presence of zinc caused a depression of the normal aluminum and iron-dye complex peak heights. This difficulty was circumvented by preparation of the standard curve with addition of increasing amounts of iron and aluminum to the zinc sample to be analyzed. Although iron and aluminum could be determined concurrently in the same solutions with Solochrome Violet RS, it was found that better results for aluminum could be obtained with Superchrome Garnet Y. Equivalent amounts of lead, which is a possible interference in the method, were also added to the calibration standards. The results are shown in table 15.

Table 15. Determination of iron and aluminum in zinc SRM 683 and 728.

| SRM | Element | Found, ppm | s | n | $\frac{ts}{\sqrt{n}}$ | Certified value |
|---|---|---|---|---|---|---|
| 683 | Al | 2.8 | 0.7 | 6 | 0.7 | |
| 683 | Fe | 2.3 | .6 | 6 | .6 | 2.2 |
| 728 | Al | 2.8 | .8 | 9 | .6 | |
| 728 | Fe | 2.5 | .4 | 6 | .4 | 2.7 |

Additional verification of this work is planned involving separation of the iron and aluminum. However, the blank resulting from the additional operations and reagents required may cause difficulties.

## 2. Determination of Trace Constituents in High Purity Zinc

A small amount of exploratory work has been done on the determination of copper, cadmium and lead in the high purity zinc, SRM # 682, by anodic stripping. The instrumental sensitivity was more than adequate for the determinations at this level, however, the blank value, particularly for copper and lead, limits the amount which can be determined. All the containers used were subjected to repeated cleaning with hot concentrated hydrochloric acid until an actual analysis of 0.1 N hydrochloric acid solution which had been heated in the container showed no higher contamination than that of 0.1 N hydrochloric acid alone. A blank was also measured after each sample to verify lack of contamination of the electrolysis vessel. The method used was as follows: Approximately 1-g samples were dissolved in 7 ml of hydrochloric acid and evaporated to dryness. The residue was dissolved in 5 ml of 0.1 N hydrochloric acid and the anodic dissolution peaks were measured after pre-electrolysis into a mercury drop extruded from a micrometer syringe. The results are shown in table 16. It should be noted that one erratic polarographic result for lead of 0.2 ppm was obtained. It is not known if this is the result of chance contamination or of actual sample inhomogeneity.

Table 16. Copper, cadmium, and lead in high purity zinc.

| | ppm | | | |
|---|---|---|---|---|
| Element | Polarographic | Atomic absorption | Spectrophotometric | Spark source mass spectrometry |
| Cu | 0.03 | 0.044[a] | 0.040[b] | |
| Cd | .05 | | | 0.1[c] |
| Pb | .03 | | | |

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

[b] R. W. Burke, Analytical Coordination Chemistry Section.

[c] R. Alvarez and P. Paulsen, Spectrochemical Analysis Section.

### 3. Determination of Copper, Lead, and Iron in High-Purity Platinum

For the polarographic determination of traces of iron in SRM 680 and iron, copper, and lead in SRM 681, complete separation of platinum should be achieved. Several methods were considered such as dithizone extraction (copper and lead), cupferron extraction (iron), and ion-exchange (copper, lead, and iron). A cupferron extraction procedure was first tried with both samples and complete iron recovery with standard solutions was achieved. The procedure was somewhat inconvenient to use, however, owing to the precipitation of ammonium chloroplatinate resulting from the cupferron hydrolysis during the extraction. However, the organic layer could be passed through a filter paper plug, eliminating any precipitate in the extract.

The procedure was as follows: One-gram samples of SRM 681 or 0.5-gram samples of SRM 680 were dissolved in aqua regia and evaporated to incipient dryness three times with hydrochloric acid. The residues were dissolved in 1 ml of hydrochloric acid and water and diluted to 10 ml in a separatory funnel. One ml of 6% cupferron was added and the iron cupferrate extracted with four 5-ml portions of chloroform. The organic layer was evaporated to dryness and fumed with nitric and perchloric acids to destroy organic matter. The residues were dissolved in 0.5 ml of 6 M perchloric acid, 2.5 ml 2 M sodium acetate and 1 ml of 0.05% Solochrome Violet RS, and diluted to 25 ml. The solutions were allowed to stand 15 min, then iron was measured on the cathode ray polarograph at about - 0.8 V vs. a mercury pool anode. An alternate ion exchange separation procedure was also tried with SRM 681 in which iron, copper, and lead were eluted with 0.1 M and 8 M hydrochloric acid and all three determined concurrently in an oxalic acid, ammonium hydroxide, ammonium chloride supporting electrolyte. Iron was measured at about - 0.1 V, copper,

- 0.2 V, and lead, - 0.6 V vs. a mercury pool anode. The results are shown in table 17.

Table 17. Iron, copper and lead in high purity and doped platinum.

| Sample | Element | Found, ppm | s | n | $\frac{ts}{\sqrt{n}}$ |
|---|---|---|---|---|---|
| 680 | Fe | 0.75 | 0.2 | 2 | 1.8 |
| 681 | Fe | 5.0 | 1.0 | 6 | 1.0 |
|  | Cu | 5.2 | 2.0 | 5 | 2.5 |
|  | Pb | 10.3 | 0.7 | 5 | 0.9 |

These elements were also determined by a number of other techniques and a summary of all the results obtained is shown in table 18.

Table 18. Comparison of iron, copper, and lead determinations in platinum, SRM 680 and SRM 681.

ppm found

|  |  | NBS |  |  | Other analysts |  |  |  |
|---|---|---|---|---|---|---|---|---|
| Sample | Element | Polarographic | Isotope[a] dilution mass spectrometry | Activation analysis[b] | A[c] | B[c] | C[c] | Cert. value |
| 680 | Fe | 0.75 |  |  | 1.4 | 2.6 | 0.6 | 0.7 |
| 681 | Fe | 5.0 |  |  | 3.5 | 6.2 | 5.6 | 5.0 |
|  | Cu | 5.2 | 6.0 | 5.0 | 6.3 | 3.0 | 5.6 | 5.1 |
|  | Pb | 10.3 | 14 |  | 8.5 | 15.0 | 9.1 | 12.0 |

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[a] R. A. Alvarez and P. Paulsen, Spectrochemical Analysis Section.

[b] G. W. Smith, Activation Analysis Section.

[c] Emission Spectrographic Analysis.

By comparison of these results, it is seen that the polarographic methods give very reliable results in such high purity metal analysis.

## 4. Determination of Copper and Iron in High Purity Gold

For the determination of iron in samples of high purity gold rod and wire, extraction of iron was not considered since gold is also extracted with most solvents. However, the ion-exchange separation which removed platinum so effectively also proved to be suitable for gold removal. Preliminary investigation of a method of analysis was made using the samples of the gold rod. Considerable difficulties were experienced because of the high iron blank coming probably from reagents and the atmosphere. Two-gram samples were used and an iron blank corresponding to about 2 ppm was obtained. This resulted in iron values for the rod ranging from 0.2 to 0.5 ppm giving an average value of 0.33 ppm and a standard deviation of 0.14 ppm. The experimental conditions were then altered to use smaller amounts of reagents and also to utilize containers that would more effectively exclude atmospheric contamination. This resulted in a lowering of the blank to a value corresponding to about 0.5 ppm of iron. The values obtained for the wire as well as those obtained by spectrophotometry are shown in table 19.

Table 19. Iron in high-purity gold wire.

| | Iron found, ppm | | |
|---|---|---|---|
| | Polarography | Spectrophotometry | |
| | | A[a] | B[b] |
| | 0.42 | 0.45 | 0.36 |
| | .45 | .47 | .44 |
| | .35 | .46 | |
| | .41 | | |
| Avg | 0.41 | 0.46 | 0.40 |

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[a] D. H. Christopher, Analytical Coordination Chemistry Section.

[b] R. W. Burke, Analytical Coordination Chemistry Section.

Copper was later determined in the gold, polarographically, using a similar ion-exchange separation procedure. Blanks still remained somewhat of a problem, being of the order of 0.1 - 0.2 ppm. On three aliquots of the rod, values ranging from 0.1 to 0.2 ppm were obtained resulting in an average value of 0.18 ppm. Results on the wire are shown in table 20.

Table 20. Copper in high purity gold wire.

| | Copper found, ppm | | |
|---|---|---|---|
| | Polarography | Spectrophotometry[a] | Activation Analysis[b] |
| | 0.24 | 0.13 | 0.12 |
| | .23 | .12 | .11 |
| | .26 | .14 | .21 |
| | | .12 | .16 |
| | | | .18 |
| | | | .15 |
| Avg | 0.24 | 0.13 | 0.16 |

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[a] R. W. Burke, Analytical Coordination Chemistry Section.

[b] W. D. Kinard, P. D. LaFleur, and D. A. Becker, Activation Analysis Section.

### 5. Analysis for Pollutants

One of the great potential areas of contribution for the polarographic techniques and experience acquired here would seem to be in the field of water and air pollution. As a result of some talks and publications describing polarographic work done here, interest has been generated as to the possible polarographic contribution to analysis of a number of trace metals in materials such as atmospheric fallout, water, milk, urine, and blood. At present, lack of agreement between different analysts and different techniques such as spectrophotometry, atomic absorption, and spectroscopy, leaves doubt as to the true values in several important problems. The application of polarography in these analyses would certainly result in improved methods in some cases. A preliminary analysis has been made in this laboratory of a dust fallout sample supplied by another laboratory. It was possible to determine lead, cadmium, and zinc concurrently in the same supporting electrolyte. The values obtained were consistent with those expected for a sample of this type. A number of other elements could have been determined at the same time had they been of interest in this particular problem.

(E. J. Maienthal)

# 3. COULOMETRIC ANALYSIS

## A. Introduction

The coulometric analysis program is concerned with the development of analytical methods of highest reliability and their utilization in the analysis of standard reference materials as well as materials of importance to various research programs of the National Bureau of Standards. During the past year, considerable effort has been devoted to the development of a method for assay of boric acid and to numerous determinations of boric acid for several purposes. Fundamental studies have resulted in the establishment of accurate values for the electrochemical equivalents of two materials, leading to a redetermination of the faraday. Methods already developed have been employed in the determination of chromium in several materials. These developments will be described in the following sections.

## B. Research Activities

### 1. Development of a Method for Precise Analysis of Boric Acid

The expanding use of boron and its compounds in nuclear reactor technology and the NBS program concerned with the issuance of the standard reference material for neutron flux monitoring necessitated the development of methods for precise and accurate determination of this element. The most widely used method for the determination of milligram amounts of boron is titration of boric acid, complexed with some polyol such as mannitol. These methods, however, are somewhat empirical in nature, particularly with respect to the amount of polyol required for titration, and generally precise to only a few parts per thousand. Le Duigou and Lauer recently reported a method for precise coulometric determination of boron [15]. Their precision for 150-mg samples of boric acid was of the order of 0.02%. However, they found a disagreement between the coulometric value and the value obtained by conventional acidimetric titration. This discrepancy was of the order of 0.1%. This fact alone was sufficient to intrigue our interest in the coulometric behavior of this system.

In aqueous solutions, boric acid is a very weak acid (pK - 9.2). Accordingly, titrations of boric acid must be conducted in some complexing medium which increases its dissociation constant. Mannitol has been most widely used and appeared to be most promising. The first two questions to answer were: What concentration of mannitol is necessary and sufficient to permit precise and accurate analysis of boric acid, and does the concentration of mannitol have an effect on the coulometric assay of boric acid? A number of samples of boric acid were analyzed in the following electrolytes: 1M KCl-0.25M mannitol; 1M KCl-0.75M mannitol; 1M KCl-1.5M mannitol (sat'd). The analyses showed no significant difference (within 0.005%) between the results in the three media for sample sizes of boric acid ranging from 1 to 6 meq. Beyond 6 meq, the latter two electrolytes gave identical results but in 0.25M mannitol, the slope of the potentiometric curve near the equivalence point was too small to permit accurate evaluation of the end point (i.e., the amount of mannitol is insufficient to complex all of the boric acid).

From the standpoint of the magnitude of inflection, an electrolyte containing 1.5M mannitol is superior, however, its viscosity is rather high which presents some inconvenience in forcing this solution through the fritted glass disks of the coulometric cell as well as homogenization of the solution during the course of analysis. Hence, as a matter of convenience, a concentration of 0.75M mannitol was used throughout subsequent work. In addition, this duplicates the medium used by Le Duigou and Lauer, thus its use permits investigation of the possible systematic sources of error noted by these authors.

The accuracy of coulometric acidimetry conducted in 1M KCl solution has been verified previously; however, in these boric acid analyses the supporting electrolyte is not just 1M KCl but it is also 0.75M with respect to mannitol. To investigate possible bias, HCl solutions, single crystal oxalic acid dihydrate, and acid potassium phthalate, respectively, were analyzed coulometrically in 1M KCl both with and without mannitol. This choice of acids was made to cover a large range of $pK_a$ values which would include the $pK_a$ of mannitoboric acid (in 0.75M mannitol, the apparent $K_a$ of boric acid is $4.17 \times 10^{-5}$). The results of analyses of these acids in mannitol medium were identical (within 0.003%) with the results obtained in the absence of mannitol. Accordingly, the accuracy of coulometric acidimetry is unaffected by the addition of mannitol to 1M KCl. It was also noted that the pH of the inflection points on the potentiometric titration curves, obtained with the use of the glass-saturated calomel electrode system, is virtually unaffected by the presence of mannitol.

In further studies of bias, the boric acid sample size was varied from 20 mg to 1.0 g. The assay values found were identical. Thus, for sample sizes ranging over 1.5 orders of magnitude, there is no apparent bias in the analytical method.

Boric acid of known purity is not available for evaluating the accuracy of the method. However, the absence of analytical bias due to composition of electrolyte and to sample size support the conclusion that the method is highly accurate.

The precision of analysis of boric acid is illustrated in figure 7 which represents the data for homogeneity studies on boric acid Lot No. 92511. Open circles represent determinations with 600-mg samples, and dark circles - those with 200-mg samples. The numbers adjacent to the points represent the sequence for each replicate analysis. Excluding sample

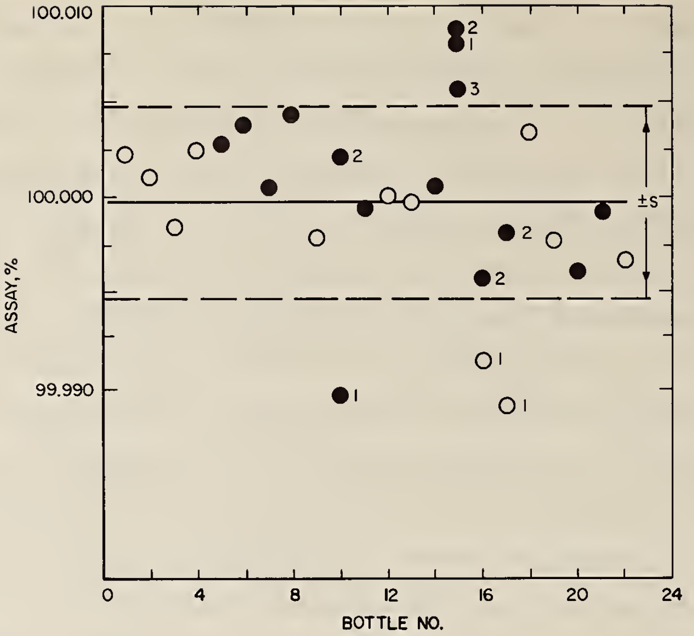

Figure 7. Homogeneity studies of boric acid.

No. 15 (which appears to be a material of somewhat different composition), the standard deviation of a single determination is 0.0049%, which also includes any inhomogeneity of the material.

### 2. Determination of Strong Acid in Crystalline Boric Acid

In analyzing boric acid solutions, such as solutions of separated boron isotopes for use in the calibration of a mass spectrometer, it is necessary to show that the titrated hydrogen ion is contributed totally by boric acid. In other words, it is necessary to prove that there is no other acid in this boric acid. Direct titration of strong acid, in the presence of boric acid in 1M KCl solution, was not found to be sufficiently sensitive due to buffering effect of boric acid. Thus, it was impossible to resolve less than a few hundredths of a percent of strong acid in the boric acid. Another method needed to be developed and the obvious path was to resort to preconcentration of strong acid. Removal of boric acid by extraction into an organic layer, consisting of 5% solution of 2-ethyl-1,3-hexanediol in chloroform was attempted and found unsatisfactory because a large amount of HCl was lost in the process.

The procedure finally developed for this purpose is based on the 20-fold decrease of solubility of boric acid in water between 100 and 0°C. A special sealed tube procedure was devised to recrystalize the boric acid from which the supernatant liquid could be removed for determination of its strong acid content. The results of analysis of SRM Boric Acid, Lot No. 92511 show that it contains 5.5 ppm of strong acid. Thus, after applying the correction for the strong acid, the $B/H^+$ ratio in this material corresponds to $0.999991 \pm 0.000013$ on the molar basis. The uncertainty of this ratio represents the 95% confidence interval of the mean, based on 17 degrees of freedom. This method requires large amounts of material (1 to 2 g), and thus is infeasible for the evaluation of the stoichiometry of $H_3{}^{10}BO_3$ and $H_3{}^{11}BO_3$ isotopically "pure" samples due to considerations of cost and availability of material. Consequently, a micro method had to be developed for the determination of strong acids in boric acid solution. The key to this problem was to establish the amount of strong acid in the SRM Boric Acid Lot 92511. This was done as described above. Subsequently, solutions containing known, widely varying concentrations of boric acid were prepared and their pH was measured. A three-dimensional calibration graph was constructed relating the following three parameters: pH, concentration of boric acid, and the concentration of strong acid (HCl). Thus, knowing accurately the total acid concentration from coulometric analysis and the pH of the boric acid solution, one can calculate the concentration of strong acid by the method of successive approximations. The accuracy of such determination is limited by the number of reiterations that one wishes to make. The sensitivity of the three-dimensional calibration graph is such that 0.002% of strong acid in the original samples of boric acid can be easily determined with an accuracy of a few relative percent.

### 3. Electrochemical Equivalents of Benzoic and Oxalic Acids

In the course of coulometric studies during the past several years, a number of highly accurate assays have been made of two materials, namely benzoic acid and oxalic acid dihydrate. Since the purity of these materials has been evaluated by independent methods, the coulometric assays may be calculated to yield values for the electrochemical equivalents of these acids. These constants are not only interesting in their own right but they permit a redetermination of the faraday by a method not heretofore used, namely acidimetric coulometry. The details of this work are discussed in a recent publication [16] and are summarized in the following. The acid was analyzed spectrochemically to determine the concentration levels of electrochemically active elements. Trace levels of Cu were detected but the amount does not affect the electrochemical equivalent of the acid by more than a few parts in $10^7$. This, of course, is insignificant in comparison with the other uncertainties of this determination.

From thermometric measurements, the purity of this acid was estimated to be 99.997 mole percent, while calorimetric evaluation indicated it to be 99.999 mole percent. Acidimetric intercomparison of acids through sodium carbonate as a transfer material gave an assay of 99.9955 ± 0.0014%, where the uncertainty represents the 95% confidence interval for the mean based on 7 degrees of freedom plus an allowance of 0.0008% for the uncertainty in the purity of $Na_2CO_3$ [17].

The oxalic acid dihydrate was single-crystal material grown by J. L. Torgesen and J. Strassburger of the NBS

Crystal Chemistry Section from acetone-water mixtures by the temperature dropping technique [18]. Optically clear fragments of single crystals were selected for titration. Analysis of this material revealed the impurities shown in table 21.

Table 21. Impurities found in oxalic acid dihydrate.

| Element | ppm by Weight | Method of Analysis | Possible Form |
|---|---|---|---|
| Li | < 1 | flame photometer | $LiHC_2O_4 \cdot H_2O$ |
| Na | 39 | " " | $NaHC_2O_4 \cdot H_2O$ |
| K | < 1 | emission spectrometry | $KHC_2O_4 \cdot H_2O$ |
| Rb | < 1 | " " | $RbHC_2O_4 \cdot H_2O$ |
| Mg | < 1 | " " | $MgC_2O_4 \cdot 2H_2O$ |
| Fe | < 1 | " " | $Fe_2(C_2O_4)_3 \cdot 5H_2O$ |
| Si | < 1 | " " | $SiO_2$ |

On the basis of the above analyses, taking sodium as 39 ppm and all other elements as 0.5 ppm and assuming that these impurities exist in this material in some form equivalent to the molecular compositions shown in column 4 of table 21, its purity would be estimated as 99.9871%.

It is rather difficult to assign limits of uncertainty to the assay of this material, but an attempt is made to place reasonable bounds on the errors which might be involved. The error due to an uncertainty in the sodium content of 2 ppm would result in a correction uncertainty of 0.0006%. Taking the middle of the range for the content of the rest of the elements seems to be a reasonable approximation. This would contribute a correction of 22 ± 9 ppm to the assay of the material, where the uncertainty represents the 95% confidence limit to the error in the correction, using Eisenhart's procedure [19] of assuming a binomial distribution for the actual impurities. Thus, if the assumptions of the effective form of the impurity are correct, the purity of this material is uncertain by 0.0015%.

The coulometric method used is basically the same as described in ref. [20]. It consists of the reduction of hydrogen ions derived from the weighed acid at the platinum cathode according to the reaction

$$H^+ + e^- \rightarrow 1/2\ H_2.$$

The titration is carried out in 1M KCl solution. A glass electrode-saturated calomel electrode system is used for measuring the change of hydrogen-ion concentration as a function of the passed charge to identify a differential potentiometric inflection point. The supporting electrolyte (1M KCl) is initially acidified to facilitate the removal of $CO_2$, swept with scrubbed nitrogen and then pretitrated to a pH of 7.00 by passing small increments of charge. The charge consumed in going from the end point of pretitration to the differential pH inflection is taken as equivalent to the amount of hydrogen ion which was introduced with the weighed acid.

The assembled coulometric cell is shown in figure 8. The anode and the cathode compartments are 180-ml electrolytic beakers connected horizontally by a 25-mm o.d. tube, approximately 6 cm in length, in which three sintered glass disks of coarse, medium, and fine porosity, respectively, are sealed. Each of the two intermediate compartments thus formed has a tube with a stopcock to enable filling and emptying by applying vacuum or nitrogen pressure. The volume of the compartment between the coarse and the medium frit is about 10 ml and between the medium and the fine frit, about 20 ml.

The advantage of using a cell of relatively small volume is two-fold. The sensitivity of the end-point detector system is increased and impurities in the supporting electrolyte, although remaining at the same concentration, are reduced with respect to the total amount present by the inverse of the ratio of volumes.

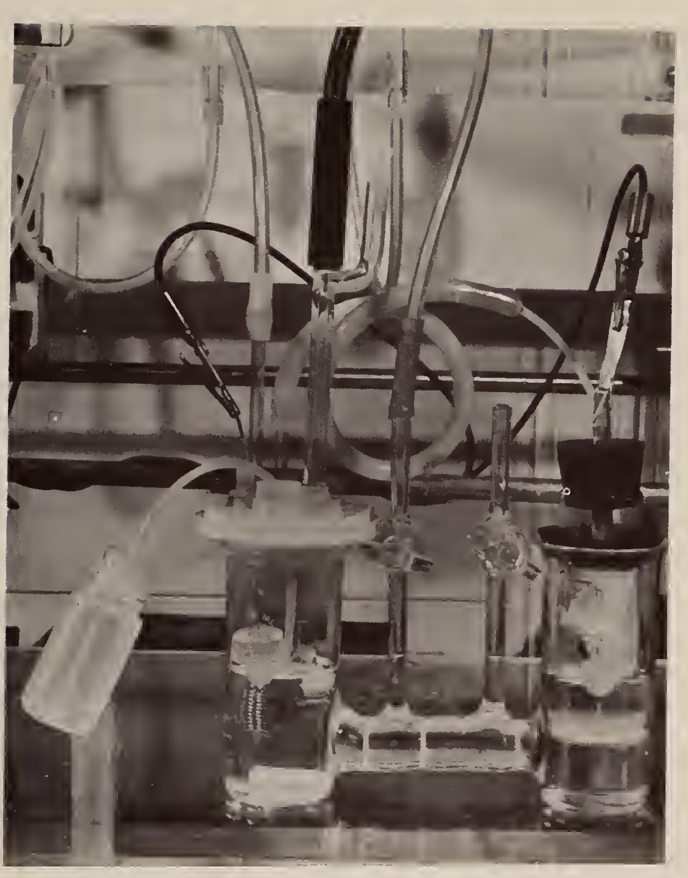

Figure 8. Coulometric titration cell for precise acidimetry.

The molded polyethylene cathode compartment cover is held in place by a polyethylene lock ring. In it are mounted: a combination glass-calomel electrode, an inlet for nitrogen to be passed over the solution, a nitrogen outlet tube connected to a trap, a platinum cathode, and a 15 cm long x 3 mm o.d. polyethylene tube bent upward at the end (forming approximately a 30° angle with the main stem of the tube) and connected on the outside to a polyethylene bottle. This polyethylene system can be used for delivery of liquid samples and for withdrawing some of the solution from the cell and ejecting it at the walls and the top of the cell, thereby rinsing any material which might have been deposited on the top or the sides of the cell as a result of gas liberation during the course of electrolysis.

The nitrogen outlet tube is made from a cut-down 10-ml pipet. Prior to titration, a drop of distilled water is introduced into the bulb of this pipet. After completion of the titration, this drop is delivered into the cell. Thus, any spray which might have been expelled into the tube is returned to the cell.

A polyethylene cap is mounted about 1 cm above the top edge of the cathode. The purpose of this cap is to catch most of the spray from the cathode resulting from the liberation of gaseous hydrogen.

An agar gel plug (3 g of agar per 100 ml of 0.1N KCl) is cast into the bottom of the anode compartment to prevent liquid from entering or leaving this compartment. A corrugated silver sheet serves as the anode.

The whole cell assembly is mounted on a stage with a magnetic stirrer under the cathode compartment. A 3/4-in Teflon encapsulated stirring magnet is used in the cell for agitation of the solution.

The high precision electrical and timing circuits, enabling measurements of charge passed through the cell to within ± 0.0001% have been described previously [20,21].

Samples of both benzoic and oxalic acid were weighed by substitution on a 20-g capacity microbalance. The standard deviation of the weighing process was 0.003 mg. The weighings were free of systematic errors except for the uncertainties in the standard weights, which were less than 0.003 mg. The weight of each sample was corrected for air buoyancy, based on the density of the air which prevailed at the time of weighing.

In general, the same titration procedure was followed as described in ref. [20] except that the stirrer was operated only during dissolution of the samples. The reason for turning off the stirrer during the titration is three-fold: (1) to eliminate swirling of gas bubbles liberated at the cathode into the bulk of the solution, thereby minimizing spray loss of the analyzed material, (2) to minimize transfer of impurities in the supporting electrolyte to the electrode surface, and (3) to minimize transfer of the investigated acid into the intermediate compartments.

After electrolysis at about 101.78 mA for a period of time sufficient to react with about 99.95% of the sample, the current was interrupted. The intermediate compartments were flushed by applying nitrogen pressure or vacuum as needed and the stirrer was turned on. The 6.43 mA current was then passed incrementwise, where each increment corresponded to about 0.02 C. The intermediate compartments were flushed after passage of each increment of charge. The cell wall and cell cover were rinsed by withdrawing and expelling catholyte from the cell by means of the polyethylene rinse system, as described earlier. Following the rinse, the pH of the solution was measured to the nearest 0.001 pH unit and recorded. At the end of the titration a differential plot of $\Delta pH/\Delta C$ was constructed to locate the inflection point.

Nineteen titrations of benzoic acid were carried out. The data are summarized in table 22. Column 2 gives the weight of benzoic acid corrected to the weight in a vacuum and for an assay of 99.9955% based on the data of Bates and Wichers [17]. Column 3 shows the number of coulombs which were required to bring the pH of the solution to the inflection point, determined graphically. Column 4 shows the value of the electrochemical equivalent of benzoic acid, calculated on the basis of columns 2 and 3. The mean value of the electrochemical equivalent of benzoic acid is 1.265715 ± 0.000036 mg/C, where the uncertainty includes 0.000014 mg/C as the limits for a 95% confidence interval for the mean, based on 18 degrees of freedom and 0.000022 mg/C for effects of known sources of possible systematic error.

Table 22. Electrochemical equivalent of benzoic acid.

| Run No. | Wt of benzoic acid, g[a] | Coulombs required to titrate | Electrochemical equivalent mg/C |
|---|---|---|---|
| 1 | 1.000521 | 790.4920 | 1.265694 |
| 2 | 1.001966 | 791.6338 | 1.265693 |
| 3 | 1.001297 | 791.0651 | 1.265758 |
| 4 | 1.001155 | 790.9952 | 1.265690 |
| 5 | 1.002562 | 792.0710 | 1.265747 |
| 6 | 1.001457 | 791.2400 | 1.265680 |
| 7 | 1.000902 | 790.7553 | 1.265754 |
| 8 | 1.000968 | 790.8079 | 1.265753 |
| 9 | 0.999579 | 789.7362 | 1.265712 |
| 10 | 1.000006 | 790.0681 | 1.265721 |
| 11 | 1.000286 | 790.3129 | 1.265683 |
| 12 | 1.000543 | 790.5234 | 1.265671 |
| 13 | 0.999576 | 789.7482 | 1.265689 |
| 14 | 0.999337 | 789.5385 | 1.265723 |
| 15 | 0.999645 | 789.7800 | 1.265726 |
| 16 | 1.001315 | 791.1064 | 1.265714 |
| 17 | 0.999768 | 789.8663 | 1.265743 |
| 18 | 1.000402 | 790.3957 | 1.265697 |
| 19 | 1.001581 | 791.2968 | 1.265746 |
|  |  | Mean | 1.265715 |

Uncertainty (95% confidence limit for the mean) = 0.000014 mg/C.

[a] The weight given in this column is corrected for the buoyancy of the air and for purity of 99.9955%.

The results of coulometric titrations of 12 samples of oxalic acid dihydrate are summarized in table 23. Column 2 gives the weight of oxalic acid, corrected to the weight in a vacuum and corrected for impurities (see section on materials). Column 3 shows the charge which was passed in bringing the weighed amount of material in solution to the inflection point of the pH titration curve. Column 4 is the value of the electrochemical equivalent of oxalic acid dihydrate calculated on the basis of columns 3 and 4. The mean value of the electrochemical equivalent of oxalic acid dihydrate was found to be 0.653293 ± 0.000023 mg/C. The uncertainty figure includes 0.000009 mg/C as the limit for a 95% confidence interval for the mean based on 10 degrees of freedom and 0.000014 mg/C for effects of known sources of possible systematic error.

Table 23. Electrochemical equivalent of oxalic acid dihydrate.

| Run No. | Wt of oxalic acid dihydrate, g[a] | Coulombs required to titrate | Electrochemical equivalent mg/C | Deviation from mean $\Delta \times 10^5$ |
|---|---|---|---|---|
| 1 | 0.395404 | 605.2321 | 0.653310 | 1.7 |
| 2 | 0.396684 | 607.2161 | 0.653283 | 1.0 |
| 3 | 0.502996 | 769.9497 | 0.653284 | 0.9 |
| 4 | 0.381987 | 584.7072 | 0.653296 | 0.3 |
| 5 | 0.617067 | 944.5720 | 0.653277 | 1.6 |
| 6 | 0.484968 | 742.3577 | 0.653281 | 1.2 |
| 7 | 0.570579 | 873.4824 | 0.653223 | 7.0 |
| 8 | 0.490940 | 751.4959 | 0.653284 | 0.9 |
| 9 | 0.441219 | 675.3761 | 0.653294 | 0.1 |
| 10 | 0.626781 | 959.3928 | 0.653310 | 1.7 |
| 11 | 0.538062 | 823.6150 | 0.653293 | 0.0 |
| 12 | 0.509745 | 780.2558 | 0.653305 | 1.2 |
| | | Mean | 0.653293 | |

Uncertainty (95% confidence limit for the mean) = 0.000009 mg/C.

---

[a] The weight given in this column is corrected for the buoyancy of the air and for purity of 99.9871%.

Note: The value obtained in Run No. 7 was excluded from the calculations since it differs from the mean by more than 3 times the standard deviation.

## 4. Redetermination of the Faraday

Values for the faraday have been calculated from the electrochemical equivalents of benzoic acid and oxalic acid dihydrate, described in section B.3., together with the accurately known equivalent weights of these materials. These values are interesting because they were obtained by a method not heretofore used for such a purpose, hence they contribute an independent confirmation of the reliability of this constant.

Taking the equivalent weight of benzoic acid as 122.12467 and its electrochemical equivalent, determined in this investigation as $1.265715 \times 10^{-3}$ g/C, the faraday becomes 96,486.7 ± 2.5 C/g-equiv, and using 63.03326 as the equivalent weight of oxalic acid dihydrate and $0.653292 \times 10^{-3}$ g/C as its electrochemical equivalent, the faraday value is found to be 96,485.4 ± 3.4 C/g-equiv.

Recently, Hamer [22] recalculated some of the faraday values reported by earlier investigators. To focus attention on the results obtained in this laboratory, Hamer's table is included here for comparison. The first eight entries of table 24 are from Hamer's table. The ninth entry is based on work conducted in this laboratory and published earlier this year [21]. Entries ten and eleven are based on the electrochemical equivalents of benzoic and oxalic acid.

A practical problem concerned with units should be pointed out. Although the National Academy of Sciences-National Research Council recommends 96487.0 ± 1.6 C/g-equiv as the value of the faraday, this value is not consistent with the electrical units as presently maintained by NBS and thus throughout the USA [23]. The above faraday (96487.0 C/g equiv) is expressed in terms of the absolute coulomb. Since coulometry is an "absolute" method of analysis, one must use a value for the faraday consistent with his electrical measurements. Electrical instruments and components in the USA are calibrated in terms of the NBS volt, ohm and ampere.

Table 24. Summary of values for the faraday.

| | Values | | |
|---|---|---|---|
| Method | NBS (legal) basis | Absolute basis 1[a] | Absolute basis 2[b] |
| Silver deposition | 96476.9 ± 2.3 | 96478.1 ± 2.3 | 96478.0 ± 2.3 |
| Iodide oxidation[c] | 96487.7 ± 2.0 | 96488.9 ± 2.0 | 96488.8 ± 2.0 |
| Iodide oxidation[d] | 96488.7 ± 2.0 | 96488.9 ± 2.0 | 96488.8 ± 2.0 |
| Oxalate oxidation [26] | 96481.6 ± 3.0 | 96482.8 ± 3.0 | 96482.7 ± 3.0 |
| Omegatron [27] | 96487.3 ± 0.9 | 96486.1 ± 0.9 | 96486.2 ± 0.9 |
| Silver dissolution [28] | 96485.4 ± 2.4 | 96486.6 ± 2.4 | 96486.5 ± 2.4 |
| Silver dissolution[e] | 96485.4 ± 1.6 | 96486.6 ± 1.6 | 96486.5 ± 1.6 |
| Silver dissolution[e,f] | 96485.8 ± 1.6 | 96487.0 ± 1.6[g] | 96486.9 ± 1.6 |
| Iodide oxidation[h] | 96485.5 ± 3.2 | 96486.7 ± 3.2 | 96486.6 ± 3.2 |
| Benzoic acid reduction[i] | 96486.7 ± 2.5 | 96487.9 ± 2.5 | 96487.8 ± 2.5 |
| Oxalic acid reduction[i] | 96485.4 ± 3.4 | 96486.6 ± 3.4 | 96486.5 ± 3.4 |

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[a] based on the relation 1 NBS ampere = 1.000012 absolute ampere

[b] based on the relation 1 NBS ampere = 1.000011 absolute ampere

[c] based on the silver/iodide weight ratio [24,25]

[d] based on coulombs used to liberate iodine [24,25]

[e] based only on the vacuum values of Craig, Hoffman, Law, and Hamer [28]

[f] using 107.8685 for the atomic weight of silver

[g] value recommended by the National Academy of Sciences-National Research Council [23]

[h] calculated on the basis of the coulometric titration of $As_2O_3$ with electrogenerated iodine reported in [21]

[i] values obtained in this work.

Accordingly, one must use the faraday on the "NBS" (legal) basis (96485.8 NBS C/g-equiv). Alternately, the use of the "absolute" faraday must entail the introduction of corrections to the NBS coulomb in order to convert it to the absolute basis. The magnitude of this correction is still a subject of some debate, nontheless it is between 11 and 12 ppm.

Returning to the faraday calculated in this work, it is apparent that the overall agreement of faraday values obtained in this laboratory with the accepted value is remarkably good. This fact contributes to the confidence in the value of the faraday, since the reduction of hydrogen ion has not been thus far utilized for the determination of the faraday, and this reaction offers another independent method for the evaluation of this important physical constant.

Some corollaries may be drawn from this work. The data obtained indicate that acidimetric coulometers can be made to operate at a high level of precision. If the original acid content is known accurately, they can also be made to provide accurate measurement of the charge which passes through them. Thus, to have an accurate coulometer for the purpose of coulometric analysis or any other current-time integrating purpose, where current is neither constant nor a linear function of time but varies in some complex manner, a sample of acid of known purity or concentration can be conveniently utilized. Even in the case of the unavailability of accurately assayed acid, constant-current coulometric analysis of the available material can provide the necessary assay. One of the practical advantages of such coulometers over the silver coulometer is their simplicity and convenience of handling.

The results of this work, supported by other evidence on the accuracy and precision of coulometric analysis [20,21,29, 30,31,32] pave the way for a change of philosophy in the field of primary chemical standardization. The concept of absolute purity, as defined by a perfect single crystal of a given material, should be considered as criterion for the preparation of high purity materials but not for the chemical analytical determination of purity. In analytical chemistry, a much more universal and unified concept correlating a common property of a broad spectrum of materials through the use of electrochemical equivalents is preferable. The conformance of a given material to its theoretical electrochemical equivalent should define the absolute purity. The faraday, then, would in fact be the primary chemical standard.

Although s similar proposal was made in 1958 by P. S. Tutundzic [33]; objections were raised and the proposal was not widely accepted. Perhaps the proposal was premature since the state of the art of coulometry was far below that of conventional chemical analysis at that time. The efforts of those in the field of precise coulometric analysis since that time have advanced the technique to the point that most of these previous objections are no longer valid. It is, therefore, the belief of the authors that for the unification of primary chemical standardization, the approach of a material to its theoretical electrochemical equivalent offers the most rational criterion for purity wherever applicable. Having the faraday as the standard, future efforts, not only of chemists but also of physicists, would contribute to accurate definition of this standard. Even now, however, the uncertainty of the faraday is about one order of magnitude smaller than that of chemical standards commonly used.

### 5. Effect of Photodecomposition of AgCl on Coulometric Determination of Chloride

The photochemical reduction of silver chloride has long been considered as a source of error in halide determinations. Because of the high precision of coulometric analysis, this complication assumes added significance.

The photochemical reaction of interest may be represented by the equations

$$2\ AgCl + 2\ h\nu \rightarrow 2\ Ag + Cl_2$$

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HClO$$

$$HClO \rightarrow H^+ + Cl^- + [O].$$

In coulometric chloridimitry, the indicator electrode system (Ag-glass electrode) is reversible to silver ions and chloride ions. It therefore offers a direct means for monitoring the photo-reduction product ($Cl^-$) and hence the rate of the photodecomposition, itself.

Experiments were conducted in which KCl samples varying in size from 20 to 130 mg were titrated with silver ion electrogenerated in the dark. Following the completion of titration, the fluorescent lights of the laboratory were turned on and the emf of the indicator electrode was measured as a function of time. On the basis of a previously constructed calibration curve, an equation was fitted to the data, representing the rate of decomposition of AgCl (more accurately, the rate of production of $Cl^-$). The equation is of the form

$$R = at + bt^2 + ct^3$$

where R is the amount of $Cl^-$ produced in μ equiv., t is time in hours and a, b, and c are experimentally determined constants. For the conditions in this laboratory, the equation was found to be

$$R = 0.490t - 0.090t^2 + 0.010t^3$$

When the elapsed time required for a titration is substituted in this equation, the amount of photodecomposition should be calculable and applicable as a correction for over-titration of a given sample.

To verify the accuracy of the equation, 3 samples of KCl were analyzed in the dark and 3 in the light. The results of analysis are summarized in table 25. It can be seen that the accuracy of the results is improved by almost an order of magnitude when the correction is applied. Thus a difference of 0.0160% between samples analyzed in the dark and in the light, is reduced to only 0.0002% by use of the correction. The standard deviation of a single determination is changed only slightly from 0.0038 to 0.0035%.

Table 25. Effect of light on argentimetric titration of KCl.

| Number | In dark | In light | In light (corrected) |
|---|---|---|---|
| 1 | 99.9619 | - | - |
| 2 | - | 99.9831 (1 hr) | 99.9653 |
| 3 | 99.9640 | - | - |
| 4 | - | 99.9766 (0.5 hr) | 99.4646 |
| 5 | 99.9623 | - | - |
| 6 | - | 99.9764 (1 hr) | 99.9589 |
| Average | 99.9627 | 99.9787 | 99.9629 |
|  | s = 0.0012 | s = 0.0038 | s = 0.0035 |

## C. Analysis of Standard Reference Materials

### 1. Homogeneity Studies of Boric Acid

The boric acid to be issued as a standard reference material was received in a shipment consisting of 22 containers. To determine the homogeneity of the material, samples were taken from all bottles and analyzed by the previously developed coulometric titration of mannitoboric acid, as described in section B.1. The samples were weighed by substitution and the true mass was computed by applying corrections for the buoyancy of the air. The results of analysis are summarized in table 26. With the exception of sample no. 15, all assay values fall within ± 0.005% of the mean. Taking all values, the average assay is 99.9997% and the standard deviation of a single determination is 0.0049%.

Table 26. Boric acid homogeneity studies.

| Date of analysis | Sample no. | Assay |
|---|---|---|
| 10-31-67 | 17 | 99.9889 |
| 11-2-67 | 12 | 99.9999 |
| 11-3-67 | 1 | 100.0022 |
| | 4 | 100.0024 |
| | 9 | 99.9978 |
| 11-6-67 | 13 | 99.9997 |
| | 2 | 100.0010 |
| 11-7-67 | 3 | 99.9983 |
| 11-8-67 | 22 | 99.9964 |
| | 18 | 100.0032 |
| 11-9-67 | 16 | 99.9910 |
| | 19 | 99.9975 |
| 11-13-67 | 7 | 100.0004 |
| | 10 | 99.9896 |
| 11-14-67 | 20 | 99.9960 |
| | 11 | 99.9993 |
| 11-15-67 | 21 | 99.9990 |
| | 5 | 100.0028 |
| | 15 | 100.0078 |
| | 14 | 100.0005 |
| 11-16-67 | 8 | 100.0042 |
| | 6 | 100.0037 |
| 11-20-67 | 10[a] | 100.0020 |
| | 15[a] | 100.0089 |
| | 16[a] | 99.9955 |
| 11-21-67 | 17[a] | 99.9975 |
| | 15[a] | 100.0055 |
| | Average | 99.9997 |

---

[a] Repeat runs

From examination of the data it appears that errors are random with respect to the sequence of analysis (neglecting the three systematically high values for sample no. 15). Since there is only a slight chance that the three samples for the bottle number 15 would be high by more than one standard deviation, we conclude that the results of analysis of this bottle are high not due to random scatter, but more likely because the material in it is significantly different from the rest of the bottles. Excluding sample 15, the assay of the remaining apparently homogeneous material is 99.9987 ± 0.0018, where the uncertainty figure represents the 95% confidence interval for the mean, based on 23 degrees of freedom.

In the final evaluation of the stoichiometry of the SRM boric acid, the 22 original samples were combined into four composites. Composites containing equal amounts of samples were made as follows: Composite I- 6, 8, 15, 18 and 5; Composite II - 10, 16, 17, 20 and 22; Composite III - 3, 9, 19, 21, 11 and 13; Composite IV - 2, 7, 12, 14, 1 and 4. These materials were used in subsequent studies.

The final evaluation of the assay of all four composites is shown in figure 9. In the figure each circle represents an individual titration plotted in the sequence in which it was carried out. Shading of circles represents individual composites: blend of all; Composite I; Composite II; Composite III; Composite IV. It can be seen that there is no systematic difference in the assay as a function of titration sequence. There is also no apparent difference between the four composites (within the precision of the method).

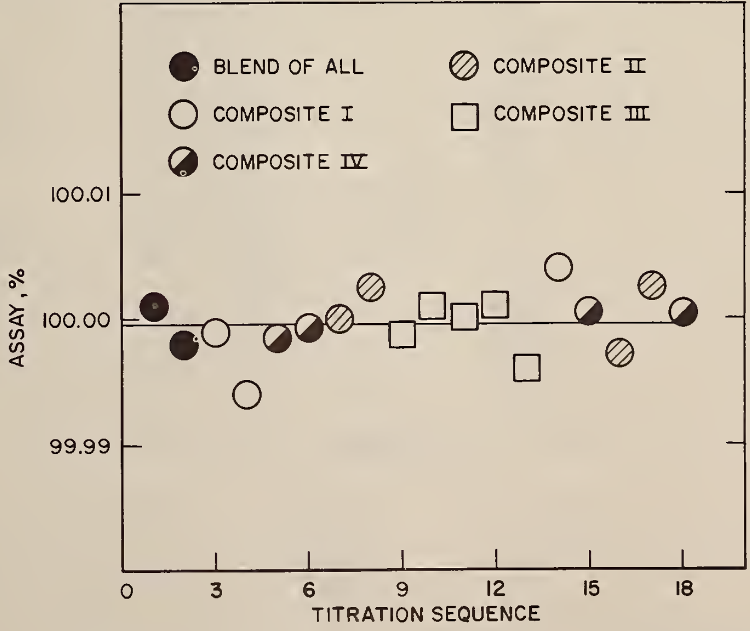

Figure 9. Effect of titration sequence and composite number on the assay of boric acid.

Table 27 summarizes this data for numerical evaluation of the results. On the basis of this data, it can be concluded that the acidimetric assay of boric acid Lot No. 92511 is 99.9997 percent. This value is not corrected for the strong acid in the boric acid, since from the standpoint of an acidimetric standard the assay must reflect the total available hydrogen ion. On the other hand, correction must be applied when one is concerned with $B/H^+$ ratio. After applying the correction for the strong acid, the $B/H^+$ ratio in this material corresponds to 0.999991 ± 0.000013 on the molar basis where the uncertainty represents a 95% confidence interval of the mean, based on 17 degrees of freedom.

Table 27. Assay of boric acid, Lot No. 92511. (Equilibrated at 34% relative humidity for at least 30 min.)

| Sample No. | Composite No. | Assay, % | Δ, ppm |
|---|---|---|---|
| 1 | Blend of all | 100.0008 | 12 |
| 2 | " | 99.9978 | 19 |
| 3 | I | 99.9990 | 7 |
| 4 | I | 99.9941 | 56 |
| 5 | II | 99.9983 | 14 |
| 6 | II | 99.9992 | 5 |
| 7 | III | 99.9998 | 1 |
| 8 | III | 100.024 | 27 |
| 9 | IV | 99.9987 | 10 |
| 10 | IV | 100.0009 | 12 |
| 11 | IV | 100.0002 | 5 |
| 12 | IV | 100.0012 | 15 |
| 13 | IV | 99.9961 | 36 |
| 14 | I | 100.0042 | 55 |
| 15 | II | 100.0007 | 10 |
| 16 | III | 99.9973 | 24 |
| 17 | III | 100.0025 | 28 |
| 18 | II | 100.0006 | 9 |
|  | Average | 99.9997 |  |

$s = 0.0025$

$\frac{ts}{\sqrt{n}} = 0.0013$

### 2. Effect of Relative Humidity on the Stoichiometry of Boric Acid, Lot No. 92511

The study of the behavior of this lot of boric acid indicates that this material is somewhat deficient in water, i.e., apparently it was prepared under conditions which resulted in the formation of small amounts of $B_2O_3$. This conclusion is supported by the following evidence. Samples weighed directly from the original boric acid containers and permitted to sit in the room at 28 percent relative humidity for 30 minutes gained weight, as illustrated in table 28.

The data in figure 10 show that at 28% RH, the time which is required to weigh out a sample (approx. 15 min.) is insufficient for this material to absorb sufficient water to attain stoichiometry. At 34% RH, analyses of samples weighed in the same period of time show that the stoichiometry of this material corresponds exactly to $H_3BO_3$. Once the stoichiometric amount of water has been absorbed, the exposure of the material, even to a very dry atmosphere, does not result in the loss of water, and the composition of material corresponds to stoichiometric $H_3BO_3$.

Table 28. Absorption of water by boric acid.

| Sample Number | Initial wt of $H_3BO_3$ | Wt. of $H_3BO_3$ after 30-min exposure to 28% RH | $2x10^{-6}$g | Change in weight, percent |
|---|---|---|---|---|
| 1 | 1.351348g | 1.351484g | + 136 | + 0.010 |
| 2 | 1.340345 | 1.340394 | + 49 | + .004 |
| 3 | 0.934555 | 0.934655 | + 100 | + .011 |
| 4 | 1.685807 | 1.685968 | + 161 | + .010 |
| 5 | 2.249267 | 2.249379 | + 112 | + .005 |
| 6 | 1.343683 | 1.343823 | + 140 | + .010 |
| | | | Average | + 0.008% |

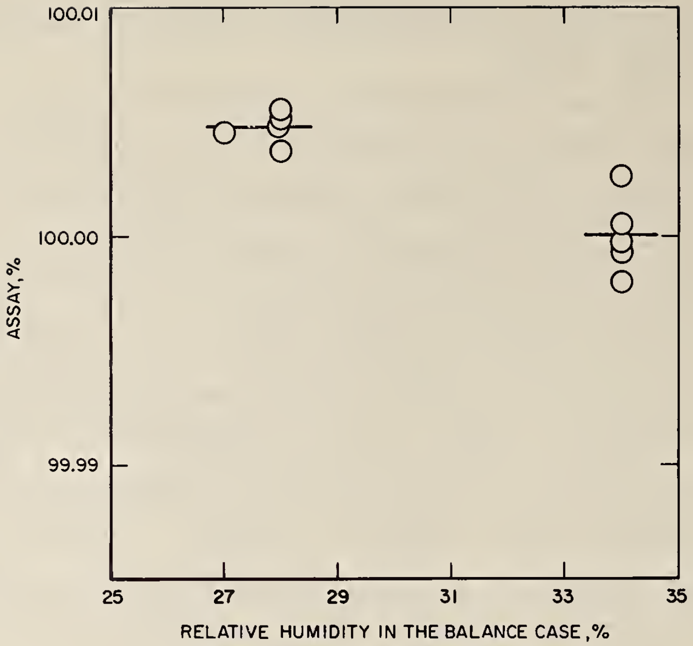

Figure 10. Effect of relative humidity in the balance case on the approach of boric acid to $H_3BO_3$ stoichiometry (15 min. exposure time).

Additional information on the effect of the relative humidity of the environment on the stoichiometry of $B_2O_3$-$H_2O$ system at 25°C was obtained in controlled humidity experiments. Boric acid was initially exposed to room atmosphere (approx. 34% RH) for several hours, in the course of which the material absorbed water and achieved stoichiometric composition (as illustrated in figure 7). Subsequently, boric acid was placed into controlled humidity environments. After at least a four-day exposure to a controlled atmosphere with an occasional mixing of the crystals, samples were weighed out for analysis. The results of these analyses are shown in figure 11. It can be seen that in the 0-52% relative humidity range, the assay of boric acid remains constant and close to stoichiometric $H_3BO_3$. Beyond 52% relative humidity, additional water is sorbed by boric acid, reaching 0.02% (referred to the weight of stoichiometric boric acid) at 95% relative humidity.

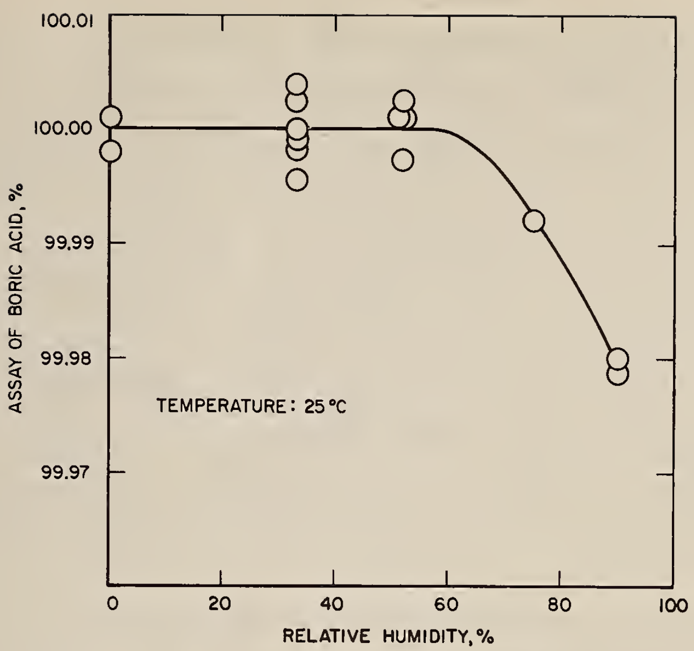

Figure 11. Effect of the humidity of the environment on the assay of boric acid.

It is concluded that initial exposure of this lot of boric acid to humid atmosphere is beneficial as it provides moisture necessary to achieve stoichiometric $H_3BO_3$. Subsequently the material is stable and can be stored at any humidity below ∿ 60%. Considering even drastic environmental conditions, such as variation of humidity between 0 and 90%, the material changes its stoichiometry by only 0.020%. This probably occurs due to adsorption of water on the surface of polycrystalline boric acid.

### 3. Development of a Procedure for Precise and Accurate Preparation and Aliquoting of Separated Boron-Isotope Boric Acid Solutions

The following problems were investigated to develop techniques for the preparation of solution for calibration of a mass spectrometer: Evaluation of precision of aliquoting relatively small amounts of boric acid solutions, to establish the suitability for accurate mixing of desired ratios of separated boron isotope solutions ($^{10}B$ and $^{11}B$); establishment of suitable conditions for accurate preparation and storage of boric acid solutions without significant changes in the composition of the latter (storage for about 1 week); development of a reliable procedure for delivery of boric acid solution aliquots into the coulometric titration cell; evaluation of any possible bias which might be associated with the size of boric acid solution aliquots; development of a method for the determination of small amounts of strong acids which might be present in the separated isotope solutions, without consuming large amounts of the costly solutions for this purpose.

Most of the solutions needed were prepared, stored and aliquoted by Keith Sappenfield, 310.06. The material used for the preparation of solutions was Composite II of the SRM Boric Acid Lot No. 92511.

The procedure developed for the aliquoting of solutions was similar to that described in ref. [1] with one exception: instead of 1 ml syringes, 10 ml polyethylene syringes were used as the weight burets. The solutions were prepared of such concentrations that samples as large as 10 ml and as small as 1 ml would bracket the sample sizes of separated isotope solutions which would be required for accurate mixing of known boron isotope ratios (about 0.3 meq/g of solution).

From such a syringe, solutions were weighed by difference into 4 oz polyethylene flasks. A closed syphon arrangement (similar to the one described in ref. [34] was constructed which fitted tightly over the 4 oz polyethylene flasks and led into the coulometric titration cell. Using this arrangement, solution samples could be quantitatively transferred into the titration cell without disassembling the coulometric cell. Such an arrangement is highly desirable since in this closed system nitrogen, flowing over the electrolyte in the cell, keeps the atmospheric carbon dioxide out of the cell.

Two sets of experiments were initially conducted to establish the precision of aliquoting, transfer and titration. Equal size samples of boric acid solutions were aliquoted on the same day and titrated soon thereafter (1 to 2 days after aliquoting). The results of these analyses are summarized in table 29. It appears from these initial experiments that the standard deviation of a single measurement (of the adopted procedure for weighing, transfer, and coulometric process) is about 0.00005 meq/g (on the percentile basis, the standard deviation of a single determination is about 0.017%).

Subsequently the procedure was refined and investigation was made of the effect of the sample size (aliquot size) on the analytical determination of boric acid. The samples were weighed out on the same day. The data obtained in these experiments are shown in table 30. It can be seen from these data that there is no systematic difference between analytical results for the larger and the smaller aliquots (within 0.01%).

Table 29. Precision of aliquoting and analysis of boric acid solutions.

| Solution | Aliquot No. | Wt of aliquot, g | meq found | meq/g |
|---|---|---|---|---|
| I | 1 | 10.95358 | 2.988735 | 0.272855 |
| Prepared & aliquoted by K. Sappenfield | 2 | 10.05553 | 2.742278 | .272713 |
| | 3 | 10.45754 | 2.852758 | .272794 |
| | 4 | 10.27975 | 2.804252 | .272794 |
| | | | Average | 0.272789 |
| II | 1 | 19.63511 | 2.964446 | 0.276145 |
| Prepared & aliquoted by K. Sappenfield | 2 | 10.59936 | 2.926541 | .276105 |
| | | | Average | 0.276125 |

Estimated precision: s = 0.000047 meq/g

Table 30. Effect of the size of boric acid solution aliquot on the coulometric determination of boric acid concentration.

| Solution | Aliquot No. | Wt of aliquot, g | meq found | meq/g | $\Delta x10^6$ |
|---|---|---|---|---|---|
| b | 3 | 10.20413 | 2.834423 | 0.277772 | 6 |
| Prepared & aliquoted by K. Sappenfield | 4 | 2.02505 | 0.562549 | .277795 | - 17 |
| | 5 | 2.20348 | .612081 | .277779 | - 1 |
| | 6[a] | 1.14274[a] | .324266[a] | .283762[a] | |
| | 7 | 1.17222 | .325603 | .277766 | + 12 |
| | | | | 0.277778 | |
| I | 1 | 6.828209 | 1.193722 | 0.174822 | + 24 |
| Prepared & aliquoted by G. Marinenko & C. Champion | 2 | 8.370246 | 1.463594 | .174857 | - 11 |
| | 3 | 8.755848 | 1.531033 | .174858 | - 12 |
| | | | | 0.174846 | |
| II | 1 | 8.493900 | 1.281755 | 0.150903 | + 1 |
| Prepared & aliquoted by G. Marinenko & C. Champion | 2 | 8.303518 | 1.253004 | .150900 | + 4 |
| | 3 | 21.30825 | 3.215547 | .150906 | - 2 |
| | 4 | 9.040497 | 1.364261 | .150906 | - 2 |
| | | | | 0.150904 | |

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[a] This sample is excluded from the consideration. A gross error (2%) was apparently involved in handling it.

A very significant point needed clarification. What are the most suitable conditions and containers for storing boric acid solutions without any significant changes in concentration? Polyethylene bottles stoppered with rubber septa and stored in room atmosphere were investigated first but found to be unsuitable. This conclusion is supported by the evidence shown in table 31. Solution "b" was prepared and aliquoted on Dec. 7, 1967, then aliquoted again on Dec. 12 and finally on Dec. 15. The data of table 31 show the averag concentration of solution on the various days of aliquoting. It can be seen that the increase in concentration of solution due to evaporation is non-linear. This is understandable since even a constant rate of evaporation of water would produce greater effect toward the end, since samples are being taken out for analysis from the bottle leaving a smaller and smaller amount of residual solution. Therefore, a loss of a given amount of water would produce a greater concentration change in the smaller residual volume. Thus, concentration changes with time become more significant as more and more samples are taken out from the storage bottle.

Table 31. Concentration changes of solution (b) stored in polyethylene bottle in room atmosphere.

| Date of aliquoting | Concentration, meq/g |
|---|---|
| Dec. 7 | 0.277666 |
| Dec. 12 | .277778 |
| Dec. 15 | .279337 |

Storage of solutions in glass at 90% and at 100% relative humidity produces no noticeable concentration change over significant periods of time. This is illustrated by the data in table 32. It can be seen that solution "1", for example, changed only 0.002% over a period of 20 days. This apparent difference must be contributed by the random error component, since the apparent concentration is decreasing and not increasing, while the concentration change of solution 2 (table 32) is in the opposite direction and of the order of 0.002% in four days.

Referring to table 32, the last column shows percent recovery. These values are based on the ratio of meq $H_3BO_3$/g of solution calculated from the weight of boric acid originally used in preparation of the solution, to the meq $H_3BO_3$/g of solution found by coulometric analysis. The average of this column is 100.0025 with 0.0021% as the 95% confidence interval for the mean, based on 7 degrees of freedom, while the assay of the solid boric acid is 99.9997 with 0.0013% as the 95% confidence interval for the mean, based on 17 degrees of freedom. It can be seen that the two means are within 0.0028% of each other and their 95% confidence intervals overlap.

Table 32. Stability of $H_3BO_3$ solution stored in glass bottles in 90-100% RH atmosphere.

| Date of Aliquoting | Sol'n no. | meq/g calc. | meq/g found | Recovery, % |
|---|---|---|---|---|
| 1-3-68 | 1 | 0.277604 | 0.277609 | 100.0018 |
| " | " | " | .277622 | 100.0067 |
| 1-23-68 | " | " | .277617 | 100.0047 |
| " | " | " | .277603 | 99.9996 |
| 1-4-68 | 2 | 0.150901 | 0.150903 | 100.0013 |
| 1-5-68 | " | " | .150900 | 99.9996 |
| " | " | " | .150906 | 100.0034 |
| 1-8-68 | " | " | .150906 | 100.0029 |
| | | | Average | 100.0025 |

$$\frac{ts}{\sqrt{n}} = 0.0021\%$$

### 4. Determination of Chromium in Ferrous Alloys

The high precision coulometric method for titration of hexavalent chromium developed in this laboratory consists of the reduction of dichromate ion in sulfuric acid-ferric ammonium sulfate solution with electrogenerated ferrous ion. The precision and accuracy of the method was verified and found equal to a few parts in $10^5$ [30].

The method is exceptionally well suited for the determination of chromium in ferrous alloys, if the latter are treated in an appropriate manner to convert all chromium to the hexavalent state. Of necessity, the other major constituent, iron, would then be in the ferric state and would not interfere with the analysis.

Two methods of dissolution and oxidation of chromium have been used in conjunction with the above coulometric titration procedure: (1) perchloric acid dissolution and oxidation and (2) sulfuric acid dissolution and ammonium persulfate oxidation of chromium.

Ferrochromium, SRM 196, and cast irons, SRM 66 and SRM 51, were dissolved and oxidized by the first method. These two materials illustrate the wide range of applicability of the method since the chromium content in them ranges from 79% in ferrochromium to 1/10 of a percent in cast iron 51.

The use of perchloric acid dissolution in the analysis of ferrochromium is very convenient as it eliminates the need for a sodium peroxide fusion. One of the difficulties with perchloric acid oxidation, however, is the formation of chromyl chloride which may be lost by volatilization. This difficulty, however, may be overcome by the use of a glass refluxing apparatus with condenser, which permits recovery of $CrO_2Cl_2$ in the condensate (amounting to about 0.2% of the total chromium). The accuracy of the recovery of chromium was verified by analyzing a known $K_2Cr_2O_7$ sample, prereduced with hydrogen peroxide and subjected to the same oxidation procedure as the alloys. The recovery for 100 mg to 1 g samples of dichromate was 99.991%.

The results of analysis of 0.6 to 1.1 g-samples of ferrochromium SRM 191 are summarized in table 33.

A similar material was used in the analysis of SRM cast irons. The results of analysis are shown in table 34.

Since the dissolution of stainless steel is not a difficult problem, a different method of dissolution and oxidation was used in the analysis of SRM stainless steels 101f and 101g.

Table 33. Determination of chromium in ferrochromium, SRM 196.

| Titration no. | Chromium assay, percent |
|---|---|
| 1 | 70.853 |
| 2 | 70.857 |
| 3 | 70.864 |
| 4 | 70.864 |
| 5 | 70.845 |
| 6 | 70.854 |
| 7 | 70.908 |
| 8 | 70.858 |
| 9 | 70.879 |
| 10 | 70.904 |
| 11 | 70.899 |
| 12 | 70.856 |
| 13 | 70.860 |
| 14 | 70.913 |
| 15 | 70.913 |
| Average | 70.875 |

Average 70.875 $s/\sqrt{n} = 0.007\%$

Table 34. Results of analysis of three randomly selected bottles for each of the two SRM cast irons.

Chromium, wt. percent

| 6g (6) | 6g (15) | 6g (23) |
|---|---|---|
| 0.3547 | 0.3630 | 0.3625 |
| 0.3560 | 0.3592 | 0.3573 |
| 0.3656 | 0.3597 | 0.3554 |
|  |  | 0.3653 |
| 0.3588 | 0.3606 | 0.3601 |

6g overall average 0.3599% Cr, $s = 0.0038$

$$\frac{ts}{\sqrt{n}} = 0.0029$$

| 5ℓ (1) | 5ℓ (9) | 5ℓ (15) |
|---|---|---|
| 0.1458 | 0.1419 | 0.1463 |
| 0.1422 | 0.1465 | 0.1502 |
| 0.1464 | 0.1502 | 0.1504 |
| 0.1448 | 0.1462 | 0.1490 |

5ℓ overall average 0.1467% Cr, $s = 0.0027$

$$\frac{ts}{\sqrt{n}} = 0.0021$$

The samples were dissolved in sulfuric acid, oxidized with ammonium persulfate using silver nitrate as catalyst and potassium permanganate as the indicator of the completeness of oxidation, and removal of the latter with HCl. The resulting solution was diluted and aliquoted by weight for analysis.

In order to establish the analytical precision in handling the solution, aliquoting and titration of small samples, duplicate aliquots were analyzed for some of the solutions. The differences of duplicate aliquots from their means (new mean for each individual solution) were used to evaluate the solution handling and titration uncertainty. The standard deviation of a single determination was found to be 0.0022 absolute percent (0.012 relative percent).

The results of analysis of the two stainless steel samples (101f and 101g) are summarized in table 35. The first column of the table shows the solution preparation number. The second column indicates the bottle designation from which the sample was weighed. The third column shows the size of the solid sample taken for the preparation of that particular solution. The fourth column shows the results of analysis for the given solution or aliquot. The fifth column shows the average of the results of two aliquots or the result of a single titration for the given solution.

On the basis of these determinations, it can be concluded that the two lots of stainless steel samples (101f and 101g) are homogeneous within the experimental uncertainty for sample sizes ranging from 130 mg to 2.3 g. Taking the vanadium values as 0.029 and 0.32 wt. percent for 101g and 101f, respectively, their corrected chromium content is: 101g - 18.435% and 101f - 18.474%.

Table 35. Analysis of SRM stainless steel for chromium.

101g

| Sol'n No. | Bottle No. | Wt. of sample, g | Wt. % Cr[a] | Ave wt. % Cr[a] |
|---|---|---|---|---|
| 1 | 7 | 0.17 | 18.44 | |
| " | " | " | 18.440 | 18.442 |
| 2 | 7 | 0.15 | 18.463 | |
| " | " | " | 18.456 | 18.460 |
| 3 | 1 | 0.13 | 18.451 | 18.451 |
| 4 | 3 | 0.19 | 18.443 | 18.443 |
| 5 | 7 | 0.24 | 18.439 | |
| " | " | " | 18.440 | 18.440 |
| 6 | 3 | 2.29 | 18.446 | 18.446 |
| | | | Average | 18.447 |
| | | | $\frac{ts}{\sqrt{n}}$ = | 0.008% |

101f

| Sol'n No. | Bottle No. | Wt. of sample, g | Wt. % Cr[a] | Ave wt. % Cr[a] |
|---|---|---|---|---|
| 1 | 3 | 2.29 | 18.486 | |
| " | " | " | 18.484 | 18.485 |
| 2 | 5 | 0.15 | 18.486 | 18.486 |
| 3 | 3 | 0.23 | 18.486 | 18.486 |
| 4 | 5 | 0.25 | 18.482 | |
| " | " | " | 18.488 | 18.485 |
| 5 | 3 | 2.26 | 18.484 | |
| " | " | " | 18.481 | 18.483 |
| | | | Average | 18.485 |
| | | | $\frac{ts}{\sqrt{n}}$ = | 0.002% |

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[a] uncorrected for vanadium

### 5. Assay of EDTA by Acidimetric Coulometry

Acidimetric titration offers a simple and convenient method for the coulometric assay of EDTA and related complexons. In principle, weighed samples of the complexon are added to a supporting electrolyte of 1M $CaCl_2$ which has been previously neutralized. This results in the liberation of hydrochloric acid (4 equiv. per mole in the case of EDTA and 2 equiv. per mole in the case of $Na_2$ EDTA). The acid so produced is titrated coulometrically as already described.

The performance of the method is illustrated by the assay of a lot of reagent grade disodium salt of EDTA, shown in table 36.

Table 36. Assay of $Na_2$ EDTA.

| Sample No. | Weight of salt, g | Assay, % |
|---|---|---|
| 1 | 0.987682 | 99.998 |
| 2 | 1.305296 | 99.998 |
| 3 | 0.746620 | 100.005 |
| Average | | 100.000, s = 0.004% |

### 6. Analysis of Ion Exchange Beads

In connection with work conducted on ion exchange bead microstandards (D. H. Freeman, 310.09), it was necessary to develop a method for precise determination of the ion exchange capacity of a cation exchange resin in the $H^+$ form and an anion exchange resin in the $Cl^-$ form.

In the case of the RH resins, the supporting electrolyte in the cell was 1M NaCl. Thus, when the ion exchange beads were delivered into the cell, the following reaction took place:

$$RH + NaCl \rightarrow RNa + HCl.$$

The liberated hydrochloric acid was determined by coulometric acidimetric titration. The results of analysis obtained for RH ion exchange beads are shown in table 37.

In the case of the RCl resin, the supporting electrolyte in the cell was 1M $HClO_4$-1M $NaClO_4$. The exchange reaction was

$$RCl + ClO_4^- \rightarrow RClO_4 + Cl^-.$$

The chloride ion produced by this exchange reaction was determined by argentimetric coulometric titration. The results obtained for RCl ion exchange beads are given in table 38.

Table 37. Analysis of RH ion exchange beads.

| Sample No. | Approx. bead diameter, µ | Wt of resin, mg | meq found | meq/g of resin |
|---|---|---|---|---|
| Ionac C-240 | 250 | 270.44 | 1.30127 | 4.8117 |
| | | 400.61 | 1.92763 | 4.8117 |
| | | | Average | 4.8117 |
| Ionac RH (10-30µ) | 20 | 81.31 | 0.40210 | 4.945 |
| | | 125.85 | 0.62315 | 4.952 |
| | | | Average | 4.948 |
| Chromo RH (10µ+) | 15 | 278.23 | 1.39271 | 5.006 |
| | | 116.38 | 0.58003 | 4.984 |
| | | | Average | 4.995 |
| Chromo RH (10µ-) | 5 | 249.49 | 1.25760 | 5.041 |
| | | 117.76 | 0.59190 | 5.027 |
| | | | Average | 5.034 |

Table 38. Analysis of RCl ion exchange beads.

| Sample No. | Wt of resin, mg | meq found | meq/g of resin |
|---|---|---|---|
| Ionac RCl | 100.65 | 0.37083 | 3.445 |
| | 37.36 | 0.12863 | 3.443 |
| | | Average | 3.444 |
| Ionac A-540 | 101.276 | 0.364806 | 3.6021 |
| | 160.139 | 0.576735 | 3.6015 |
| | 190.767 | 0.687236 | 3.6025 |
| | | Average | 3.6020 |

In the case of RH resin, beads of several diameters were submitted for analysis. For ease of plotting, capacity was plotted with respect to the logarithm of diameter of the beads (see figure 12). The results of analysis indicate that the $H^+$ capacity (meq $H^+$/g) depended upon the diameter of the beads. It appears that, at some diameter of the exchange bead, the $H^+$ capacity reaches a limiting value, determined only by the molecular configuration of the polymer. At this limiting diameter of beads and below it, all of the side chains which are involved in the ion exchange process are exposed to the solution and can participate in the ion exchange process. Above this limiting diameter, some of the active groups may be isolated within the bulk of the beads and are thus effectively shielded from the reactants.

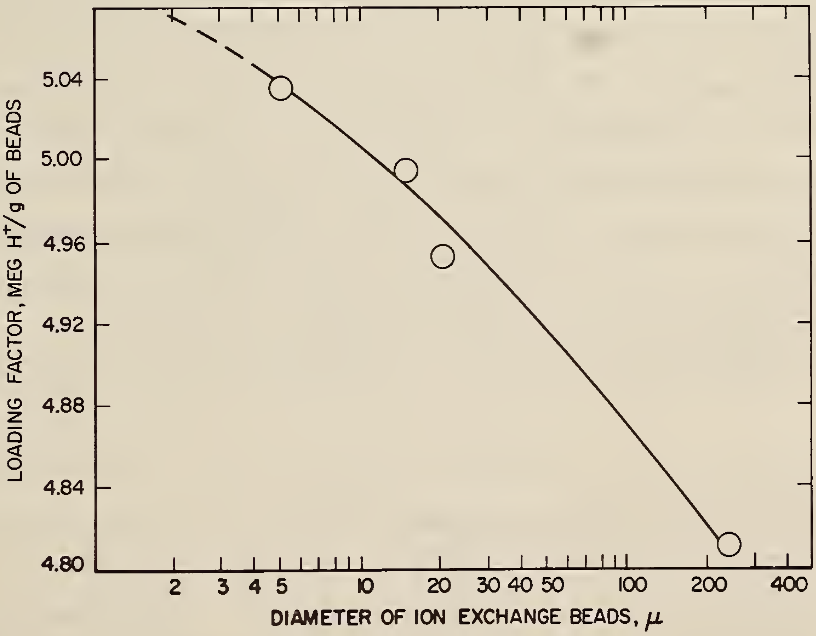

Figure 12. Loading factor of ion exchange beads as a function of bead diameter.

## D. Analysis of Research Materials

The precise coulometric technique and procedures developed in this laboratory are finding increasing applications to many NBS program areas. Most materials submitted to this division for analysis are now determined coulometrically when highly accurate assays are required. Analyses of standard reference materials were described in Section C. Several interesting applications for analysis of research materials are mentioned below.

Some calorimetric measurements made by the NBS Heat Division required the analysis of HCl solutions and HCl-HF solutions resulting from the combustion of halogenated hydrocarbons. Accurate analyses were required to decide whether simple acidimetric titrations, in the case of the former, and whether an acidimetric and argentimetric determination, in the case of the latter, would be definitive in determining the amount of calorimetric reaction.

The HCl solutions were analyzed coulometrically for both $H^+$ and $Cl^-$ with the results shown in table 39. Both kinds of determinations were made with an uncertainty of 0.0001 meq/g. The systematic difference between the $H^+$ and $Cl^-$ values indicated that the acid had reacted to a small extent with the metal of the calorimeter bomb. This unexpected conclusion was confirmed by a spectrographic examination of the acid which yielded impurities characteristic of the bomb. The calorimetric measurements could be corrected for this source of error.

In analyses of the HCl-HF solutions, all three elements were determined, with the fluoride analysis being accomplished by potentiometric titrimetry with a fluoride sensitive electrode (see Section 4.D.2. of this report). In these cases, a satisfactory ionic material balance was achieved when consideration was made for the acid reaction noted above.

Table 39. Analysis of calorimetric reaction products.

| | $H^+$, meq/g of sol'n | $Cl^-$, meq/g of sol'n | Ratio $\frac{H^+}{Cl^-}$ |
|---|---|---|---|
| | | Solution I | |
| | 0.7702 | 0.7704 | |
| | 0.7700 | 0.7700 | |
| Ave | 0.7701 | 0.7702 | 0.99987 |
| | | Solution II | |
| | 0.3628 | 0.3630 | |
| | 0.3628 | 0.3628 | |
| Ave | 0.3628 | 0.3629 | 0.99973 |
| | | Solution III | |
| | 0.3627 | 0.3629 | |
| | 0.3627 | 0.3629 | |
| Ave | 0.3627 | 0.3629 | 0.99945 |

Coulometric acidimetry and argentimetry have been used to establish the composition of a number of solutions used in electrolytic solution research, when an accuracy of parts in 10,000 or better was needed. Some of these have been hydrochloric acid in several non aqueous solvents such as N-methyl proprionamide (NMP), NMP-decalin, and NMP-cyclohexane for NBS Section 310.03. Also, sodium carbonate, sodium bicarbonate, and potassium dihydrogen tartrate were carefully assayed (to better than 1 part in 10,000) for use in establishment of the pD scale by Section 310.03.

(G. Marinenko and C. E. Champion)

# 4. ELECTROANALYTICAL MEASUREMENTS

## A. Introduction

Research in the electroanalytical measurements program has continued along lines initiated last year. Progress has been made on the development of linear null-point potentiometry and the use of ion-selective electrodes in microanalysis In addition, a number of SRM and service analyses were made, and several limited research projects were undertaken and completed.

## B. Research Activities

### 1. Improved Microdetermination of Silver by Linear Null-Point Potentiometry [35]

Significant improvements in the results obtained for the determination of submicrogram amounts of silver by linear null-point potentiometry (LNPP) [36] have been achieved by the use of several minor modifications of the technique. Except for external pregeneration of the standard silver solutions, the apparatus is identical to that previously described [36].

a. Experimental. Instead of coulometrically generating silver incrementally in the titration half cell, a series of standard silver solutions are coulometrically prepared in separate 100-ml volumes of the inert electrolyte, 1 N $H_2SO_4$. By the use of such pregenerated standard solutions the analysis time for a set of test solutions is reduced by a factor of about 4 or 5 to approximately 10 to 15 minutes per determination.

The standard solutions are prepared in accordance with the concentration of the unknown silver solution. The approximate concentration of the unknown is first determined by a direct emf measurement or by a preliminary null-point determination using standard solutions covering a wide concentration range. A test solution approximating the unknown concentration and a minimum of two solutions above and below this concentration are then coulometrically prepared. These five standard solutions permit the determination of the equilibrium null-point potential and provide two data points before and after the equivalence point for a reliable graphical or computer fit of the data to a straight line.

A 0.1-ml aliquot of the end point solution is taken from the standard solution (titrant) half cell (100 ml) and pipetted into the null-point (test solution) half cell. The porous Vycor null-point half cell is then immersed in the standard solution, and the matched indicator electrodes are inserted into each half cell. The cell potential is measured with a high impedance recording system as before [36]. There is an initial potential drift, caused by the dissolution of the silver electrodes, which is more pronounced in the more dilute silver solutions. After about five minutes, a limiting potential is reached which remains essentially constant for the remainder of the time required for a complete determination. This potential is used as the null point in subsequent determinations thereby compensating for the effect of silver dissolution. Once this null-point potential is established for the end point solution, the analyses of the unknown samples can be performed.

The 0.1-ml sample of the unknown is pipetted into the null-point cell, and the cell containing the standard silver solution of lowest concentration is used as the titrant half cell. After a stable emf is reached and recorded, the electrodes are rinsed, dried and the titrant half cell is replaced by the cell containing the next higher silver concentration. This substitution procedure is repeated until all of the standard solutions have been used and the data points recorded.

The data are evaluated as before, using both a graphical semilogarithmic plot and a linear least squares fit by computer. In the graphical analysis, the equivalence point is obtained by a linear interpolation to the equilibrium null-point potential. The equivalence point is obtained by computer techniques from the null-point intercept of a linear least squares fit of the data.

b. Results. Standard 0.1-ml samples containing 0.054 to 54 micrograms of silver in 1 N $H_2SO_4$ were analyzed. Several determinations were made at each concentration level and all showed good Nernstian behavior with the slopes of the titration curves approaching the theoretical slope of 59.2 mV/pAg unit. Also, the deviation from linearity previously observed at the lowest concentrations was not evident in this work, presumably due to the establishment of the dissolution equilibrium prior to the actual measurement of the cell emf.

A summary of results is given in table 40. An average five-fold decrease in the error over the previous study is observed between 0.05 and 2.7 µg of silver in a volume of 0.1 ml.

Table 40. Results of the LNPP determination of silver.

| $Ag^+$ taken µg/0.1 ml | $Ag^+$ found µg/0.1 ml | n | Error µg |
|---|---|---|---|
| $53.9_4$ | $54.0_7$ | 7 | $0.1_3$ |
| $5.39_4$ | $5.41_0$ | 9 | $.01_6$ |
| $0.539_4$ | $0.541_2$ | 9 | $.001_8$ |
| $.0539_4$ | $.0553_6$ | 7 | $.0014_2$ |

c. Discussion. The advantages of greater linearity of the titration curves, shorter analysis time, and improved accuracy, are achieved by pregeneration of the standard solutions and the establishment of an equilibrium null-point potential to reduce the error caused by dissolution of the indicator electrode in the null-point cell. In this study, 54 nanograms of silver were determined with an error of less than

2 ng, while at higher concentrations (above 10 μM) errors can be reduced to 1% or less using the improvements in the LNPP technique discussed.

### 2. Fluoride Microanalysis by Linear Null-Point Potentiometry [37]

The determination of fluoride at subnanogram levels in sample volumes of 10 μl has been achieved for the first time using the modified fluoride activity electrode [38] in combination with the concentration cell technique of linear null-point potentiometry (LNPP) [36]. The fluoride sample in the inverted fluoride electrode microcell is titrated by the addition of a standard fluoride solution to a second electrochemical half cell connected to the former by a salt bridge. The emf vs. titrant concentration data are plotted semilogarithmically and the equivalence point is obtained by a linear interpolation to the null-point potential.

The concentration cell employed is

$$\underset{10\ \mu l}{LaF_3|F^-(C_A),\ KNO_3(0.1M)}\|\underset{\text{salt bridge}}{KNO_3(0.1M)}\|\underset{100\ ml}{KNO_3(0.1M),\ F^-(C_T)|LaF_3}$$

where $LaF_3$ is the fluoride-specific membrane of the fluoride activity electrode, $C_A$ is the concentration of the fluoride solution being analyzed (i.e., analate solution), and $C_T$ is the concentration of fluoride in the titrant half cell. The emf of this cell is given by the Nernst equation for a concentration cell:

$$E = \Delta E - \frac{RT}{F} \ln \frac{(F^-)_A}{(F^-)_T} + E_j$$

where ΔE is a bias potential between the two fluoride activity electrodes due to differences in the inner reference solutions, $(F^-)_A$ and $(F^-)_T$ are the activities of fluoride in the analate and titrant half cells, respectively, and $E_j$ is the liquid junction potential. By the use of an excess of inert electrolyte (0.1 M $KNO_3$) throughout, the liquid junction potential between half cells becomes negligible, and the activity coefficients of fluoride will be practically equal due to the constant ionic strength maintained in the two half cells. Equation (1) thus simplifies to

$$E = \Delta E - \frac{RT \ln 10}{F} \log \frac{C_A}{C_T}$$

where the cell emf, corrected for the bias potential, is solely dependent on the ratio of fluoride concentrations in the analate and the titration half cells ($C_A$ and $C_T$) when both half cells are at the same temperature. Therefore at the null-point, where the cell emf is equal to zero, $C_A = C_T$.

The 10-µl sample microcell is illustrated in figure 13 to show details of the assembly. This microcell comprises the analate half cell. It consists of a fluoride activity electrode which has been modified [38] to operate in an inverted position by conversion of the inner reference solution (0.1 M NaF, 0.1 M KCl) to a gel (4% agar).

A 0.1 M $KNO_3$ salt bridge connects the analate and titration half cells. The salt-bridge junction to the microcell is made from a polyethylene tube drawn out to a fine capillary and filled with a 4% agar gel of 0.1 M $KNO_3$. The junction to the titration half cell is made through a porous Vycor plug [39].

The titration half cell consists of a 180-ml tall form beaker in which are inserted a second fluoride activity electrode (unmodified), a stirrer, and a polyethylene capillary tube from the microburet. The microburet, readable to 0.01 ml, contains the standard fluoride titrant solution. The titrant is prepared containing the 0.1 M $KNO_3$ inert electrolyte background to prevent ionic strength changes when it is added to the titration half cell.

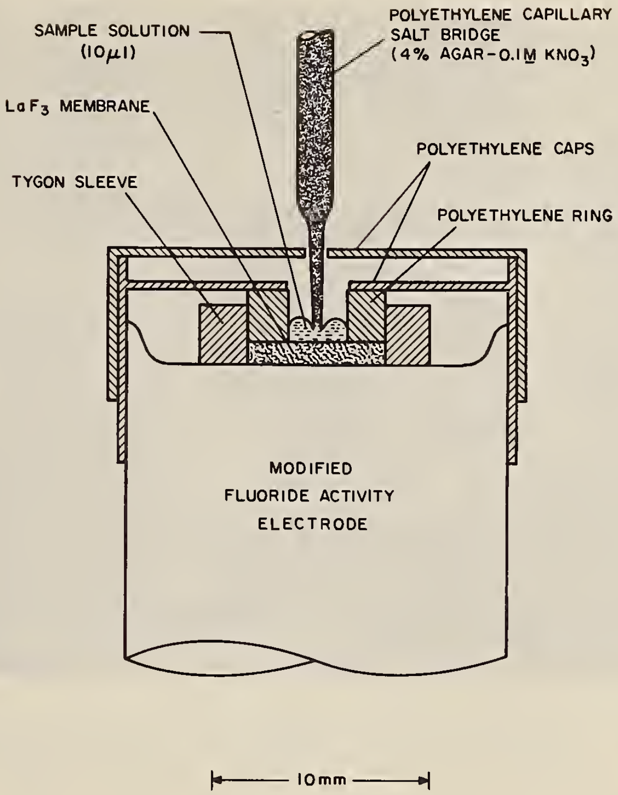

Figure 13. Fluoride electrode microcell.

The cell emf may be conveniently measured by connecting the electrode leads to an expanded scale pH meter (100 mV full scale) which serves as a voltage follower amplifier for a multirange potentiometric recorder. The cell emf can also be read directly from the pH meter with only slightly reduced precision, but the recorder facilitates continuous observation of the emf equilibration and stability. The microelectrode lead is connected to the glass electrode input jack of the pH meter while the second fluoride electrode connects to the unshielded reference electrode input. The pickup of electrical noise at this electrode does not constitute a serious problem in the emf measurement because of the relatively low resistance of the fluoride electrode (approximately 500k Ω). The emf is read from the recorder to the nearest 0.1 mV. The complete assembly is shown in figure 14.

Figure 14. Apparatus for fluoride determination by linear null-point potentiometry.

In addition to evaluating the equivalence point graphically, data analysis is easily accomplished by computer techniques whereby the equivalence point is obtained from the intercept of a linear least squares fit of the data. By this technique, the computer is programmed to take the logarithm of the X-value ($C_T$) before fitting the data and to print the antilogarithm of the X-intercept (equivalence point concentration, $C_T = C_A$) where the cell emf (or Y-value) is zero. The computer readout also provides the slope of the best straight line through the titration data points for comparison with the theoretical Nernstian slope. The results reported below are obtained in this way after an initial graphical inspection to determine any obvious anomalies in the titration data.

Standard 10 µl sample solutions containing 0.38 to 190 nanograms of fluoride in 0.1 M $KNO_3$ were analyzed. The results of these determinations are tabulated in table 41 for five measurements at each concentration level. At the lowest concentrations, the initial titration points exhibit a deviation from linearity caused by the slight dissolution of the lanthanum fluoride membrane not having reached equilibrium. This effect is predictable from the solubility product of $LaF_3$ and becomes a significant factor due to the extremely small volume of solution employed. However, this effect does not significantly affect the final results, as verified by the very small error observed, because the emf value used as the null point includes the same dissolution factor. That is, the null-point potential is obtained from measurements on identical half cell solutions over the entire concentration range studied. Since the measurements of these potentials are allowed to reach equilibrium, the concentration of fluoride in the microcell increases due to the dissolution of $LaF_3$ until the $K_{sp}$ is satisfied (this effect is negligible in the 100-ml titration half cell). The response of these two electrodes therefore only differs at very low concentrations.

Table 41. Results of fluoride determinations by LNPP.

| Fluoride taken | | Fluoride found | | | |
|---|---|---|---|---|---|
| | | | | Error | |
| Conc. (M) | ng | Conc. (M) | $\frac{s}{\sqrt{n}}$, % | % | ng |
| $1.00 \times 10^{-3}$ | 190 | $1.01_3 \times 10^{-3}$ | 0.3 | + 1.3 | 2.5 |
| $1.00 \times 10^{-4}$ | 19.0 | $1.01_0 \times 10^{-4}$ | .5 | + 1.0 | $0.1_9$ |
| $1.00 \times 10^{-5}$ | 1.90 | $1.01_4 \times 10^{-5}$ | .6 | + 1.4 | $.02_7$ |
| $5.0 \times 10^{-6}$ | 0.95 | $4.9_6 \times 10^{-6}$ | .6 | - 0.8 | $.00_8$ |
| $2.0 \times 10^{-6}$ | .38 | $2.0_1 \times 10^{-6}$ | 1.0 | + .5 | $.00_2$ |

The summary of results in table 41 gives the quantity of fluoride present in the standard test samples, both in terms of concentration and in nanograms per 10 µl sample, the concentration of fluoride found (average of 5 determinations) with the relative standard deviation of the mean, and the error expressed as a percentage and in nanograms. The error of the method is nearly constant at about 1% over the entire concentration range while the standard deviation of the mean as a percent of the mean increases with decreasing concentration from 0.3% to 1%. At the lowest fluoride concentration studied, 380 picograms of fluoride were determined with an error of only 2 picograms. This clearly ranks this technique as the most sensitive microanalytical method for the determination of fluoride.

### 3. <u>Electrochemical Generation of Fluoride Ion by Solid-State Transference</u> [40]

Fluoride ion has been electrochemically generated by means of the solid-state transport of fluoride ions through a permselective membrane of europium-doped lanthanum fluoride. The attainment of 100% current efficiency in such a system is based on the assumptions that, in a crystal of this type, the only mobile species is the fluoride ion (i.e., transference number of fluoride ion is unity), and no other sources of current inefficiency, e.g., leakage currents, exist. Consequently, when an electric current is passed through the crystal, the charge would be totally carried by the fluoride ion.

a. Apparatus. Using the very simple apparatus diagramed in figure 15 and shown in figure 16, a generation efficiency of 99.2 ± 0.5% (at the 95% confidence level) was achieved for nine generations of 1.00 mM fluoride. The apparatus consists of a fluoride generation compartment, the counter electrode compartment, a 90-volt d.c. source, two variable current-limiting resistors, a 100 Ω (0.01%) precision resistor and recorder for current monitoring, and the electrolysis cell into which the fluoride is generated. The generation compartment consists of a membrane of lanthanum fluoride sealed with epoxy cement into a polyethylene tube. The internal fluoride generation solution, 1 M NaF buffered at a

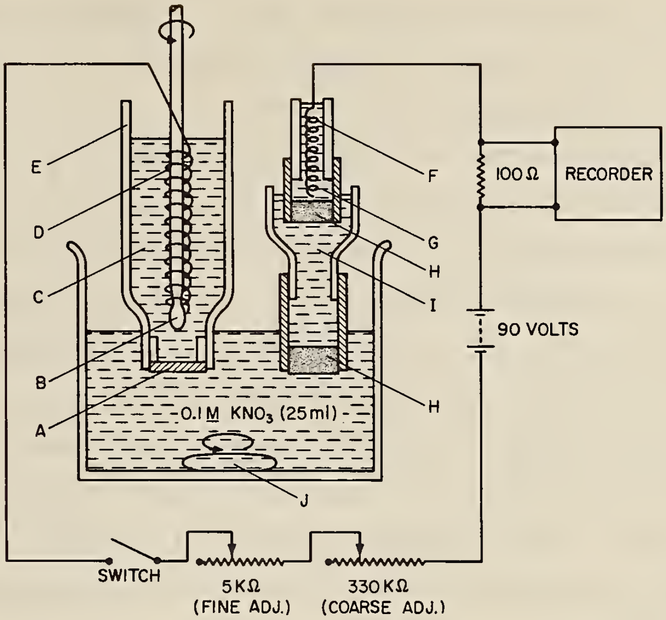

Figure 15. Electrochemical cell for fluoride generation.

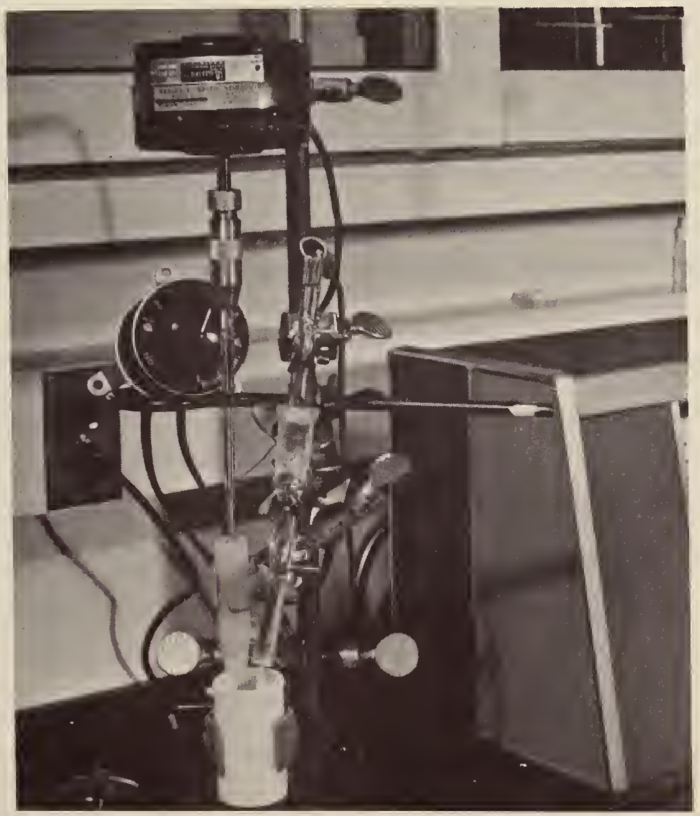

Figure 16. Fluoride generation cell.

pH of about 5.5 with HF, serves as the catholyte and supplies fluoride ion to the inner surface of the LaF crystal to prevent fluoride depletion in the membrane. The cathode is a spiral of platinum wire, and the catholyte is continuously stirred to prevent the formation of concentration gradients. The resistance of the $LaF_3$ membrane used (9 mm in diameter, 1.5 mm thick) is approximately 13k Ω. The double-junction counter electrode compartment contains a spiral platinum wire anode in a saturated $KNO_3$ solution at an initial pH of approximately 10 (with $NH_4OH$). Electrical contact to the intermediate salt bridge is made through a porous Vycor-$KNO_3$ liquid junction. The intermediate salt bridge contains saturated $KNO_3$, and contact with the electrolysis solution is made through a second porous Vycor-$KNO_3$ liquid junction.

b. Experimental. By applying a constant current of 0.670 mA (current density = 1.05 $mA/cm^2$) to the cell for a period of one hour, the passage of 2.412 coulombs of electricity should produce, at 100% current efficiency, $2.50 \times 10^{-5}$ equivalents of fluoride or a final concentration of 1.00 mM fluoride in the 25 ml of 0.1 M $KNO_3$ electrolyte. The current was manually controlled to better than ± 0.1% over the duration of the generation, and the time measurement was accurate to within ± 0.05%.

The efficiency of generation was calculated by analysis of the resulting electrolysis solution. The analysis was performed using the technique of "analate additions" potentiometry in which aliquots of the sample (analate) are delivered into a known volume of a standardized fluoride solution, and the analate concentration is calculated from the change in emf of a fluoride activity electrode. The precision of this technique at the millimolar level is 0.5% (expressed as the 95% confidence limits for the average of 20 determinations).

c. Results. The electrochemical generation of fluoride was performed nine times with an average efficiency of 99.2%. The 0.5% precision (95% confidence limits) corresponds to that for the measurement technique and therefore cannot be used as an estimate of the generation reproducibility.

The 0.8% inefficiency in the generation of fluoride by this method is assumed due to an inefficiency in the transport of fluoride ions across, and/or an undetected leakage around, the $LaF_3$ membrane. In this preliminary study with a relatively unsophisticated apparatus, the attainment of 99.2% current efficiency reproducible to within 0.5% indicates the potential use as a technique for the accurate generation of fluoride ion *in situ* for coulometric analysis in the laboratory or for automated fluoridation of water supplies. In a practical sense, since the generation efficiency can be established for a particular set of operating conditions, the current efficiency need not be 100% as long as it is reproducible.

### 4. Analate Additions Potentiometry

While the standard additions technique has been used extensively in various analytical methods, the inverse technique, herein called "analate additions", has apparently not received any attention. In this procedure, aliquots of the solution containing the species being determined (analate) are introduced into a known volume of a standard solution of that same species. The amount of analate is then calculated from some measureable change (depending on the method) produced by the analate. In the potentiometric determination of fluoride by this technique, the change in emf of a fluoride ion selective electrode is related to the analate concentration by the equation:

$$C_a = C_o\left[\left(\frac{V_o+V_a}{V_a}\right) 10^{\Delta E/S} - \left(\frac{V_o}{V_a}\right)\right]$$

where:

$C_a$ = concentration of analate

$C_o$ = concentration of standard solution

$V_o$ = volume of standard solution

$V_a$ = analate volume

$S$ = electrode response slope (mV/pF)

$\Delta E$ = emf (mV) change produced on addition of the analate

or, more simply, where:

$$N = \frac{V_O + V_a}{V_a}$$

$$C_a = C_o \left[ N \cdot 10^{\Delta E/S} - (N-1) \right]$$

The precision of this technique is dependent upon the precision in the measurement of ΔE. Under the present conditions, a standard deviation of about 0.2 mV is easily obtainable. The relative precision in measuring ΔE can be increased by taking larger aliquots, thereby increasing the emf change, but this introduces other complications such as changes in the ionic strength and liquid junction potential as well as the limitation set by the quantity of analate solution available.

The sensitivity of this technique is dependent only on the response slope, S, and is independent of the sample volume. Therefore, the aliquot added may be as small as necessary to give a useable response since the volume requirement for electrode immersion is already fulfilled by the standard solution. This technique is especially suited to small volumes of concentrated sample solutions where it is not desired to dilute as required for use in the standard additions method.

In this technique, the ionic strength will normally be established by the background electrolyte of the standard solution.

For the determination of fluoride by analate additions potentiometry, the following conditions were used: $V_o$ in all cases was 10 ml, $V_a$ was varied from 5 to 20 ml in 5 ml steps which resulted in $\Delta E$'s of 33 to 48 mV, and the response slope, S, of the electrode was evaluated as $56.3_5 \pm 0.2_0$ mV/pF. The analate solutions analyzed contained $1.00 \times 10^{-2}$M and $1.00 \times 10^{-3}$M NaF in 0.1 M $KNO_3$, and the respective concentration of the standard solutions was one order of magnitude less. For the two analate concentrations studied, a precision of 0.5% (95% confidence level for an average of 20 determinations) was obtained with this technique.

### 5. Determination of Dissolved Oxygen using an Amperometric Oxygen Sensor

A limited study of a commercial amperometric oxygen sensor was undertaken to evaluate its response over a wide range of dissolved oxygen with its eventual application to the determination of dissolved oxygen at trace levels. Briefly, the sensor consists of a gold cathode and silver anode, electrically connected by a thin layer of KCl gel. These sensor elements are separated from the sample solution by a gas-permeable membrane of Teflon. The sensor also contains a temperature-compensating thermistor. External electronics provide an 0.8V polarizing voltage, signal amplification and meter or recorder readout. In operation, oxygen gas diffuses through the membrane and is reduced, causing a flow of current proportional to the partial pressure of oxygen in the sample.

The apparatus developed and used in this study is shown in figure 17. The oxygen sensor is mounted in the base of a 2-cm o.d. glass tube with a rubber stopper and sealed into place with a coating of Glyptal. The bubbler is a medium porosity glass frit connected to the sensor tube by a ground

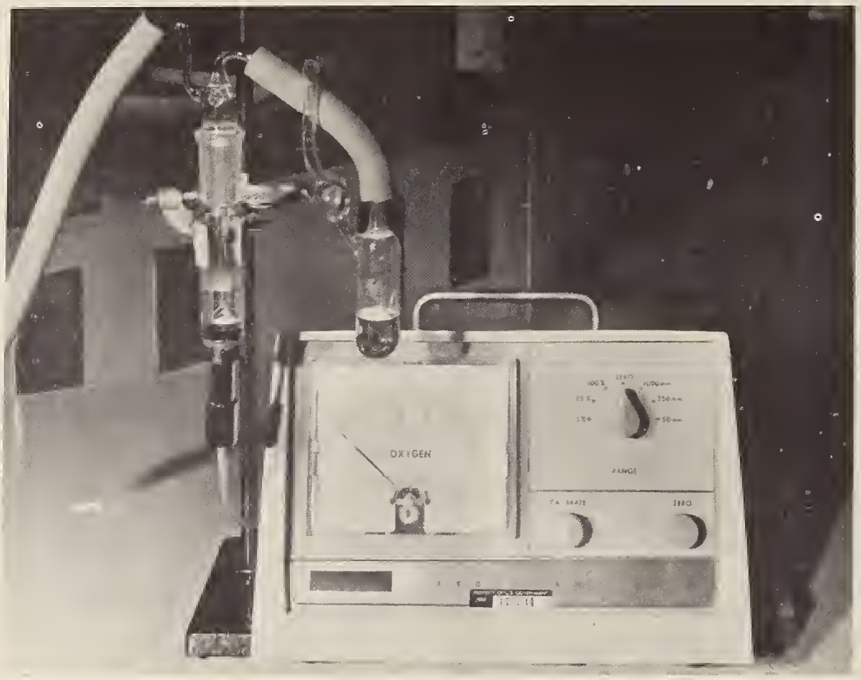

Figure 17. Oxygen cell and analyzer.

glass joint, and the exit tube is connected to a second bubbler to prevent the back-diffusion of atmospheric oxygen. The gas samples are equilibrated with 5 ml of distilled water contained in the tube above the oxygen sensor. Care was taken to prevent oxygen leaks by minimizing the number and length of rubber connections.

The analyses were performed by setting the readout meter to 8.3 ppm dissolved oxygen for an air-saturated solution of distilled water. The solution was then partially deaerated using nitrogen of known oxygen content from 70,660 ppm to 2 ppm. The gas-solution equilibration was monitored with a potentiometric recorder, and equilibrium was usually achieved in 10 to 30 minutes. The response was linear down to a meter reading of approximately 200 ppb dissolved oxygen (vs. the gas standards) and rapidly leveled off at about 50 ppb. Below 50 ppb, the uncertainty in the measurements was of the same order of magnitude (about 10 ppb) as the decrease to the lowest level of dissolved oxygen (∿ 30 ppb), and the readings were not a reliable estimate of the oxygen concentration. Table 42 gives the dissolved oxygen concentration corresponding to the gas-phase oxygen. The data are also plotted logarithmically in figure 18.

Table 42. Oxygen sensor response to dissolved oxygen.

| ppm $O_2$ (gas in $N_2$) | ppb $O_2$ (dissolved in $H_2O$) |
|---|---|
| 209,500 (air) | 8,300 (calibration point) |
| 70,660 | 2,800 |
| 2,638 | 150 |
| 112 | 35-50 |
| 2 | 25-40 |

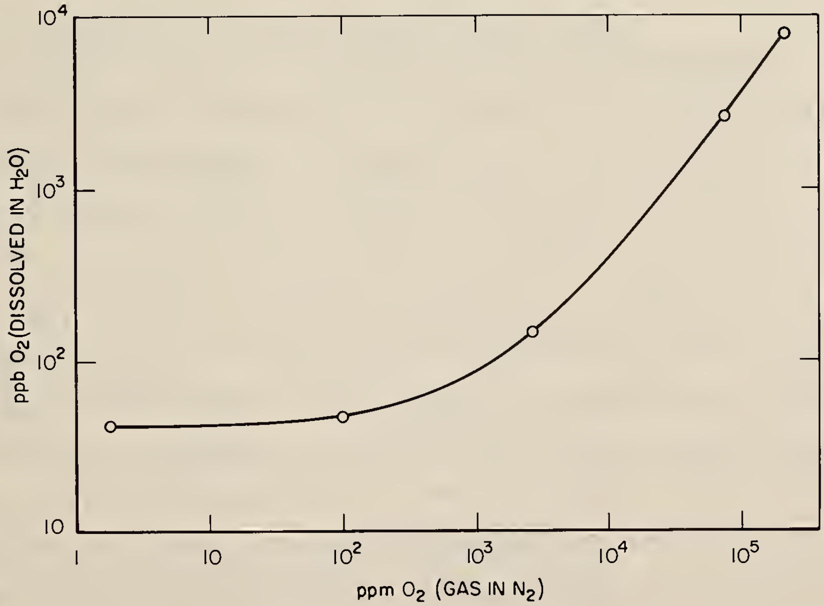

Figure 18. Oxygen sensor response to dissolved oxygen.

The lowest level to which a solution could be deoxygenated with the 2 ppm oxygen was 24.5 ppb oxygen. This lower limit may have been due to (1) the actual equilibrium oxygen concentration between the solution and gas phases, (2) equilibrium with oxygen leaks in the system, and (3) a residual current level in the sensing element itself.

The oxygen sensor provides a convenient and sensitive method for the determination of dissolved oxygen above 50-100 ppb in distilled water. Below this value, increased sensitivity and stability are needed for this method to be of analytical usefullness.

## C. Analysis of Standard Reference Materials

### 1. Analysis of Silver 2-Ethylhexanoate

Silver 2-ethylhexanoate is one of a series of stable, oil-soluble organic compounds of metals certified for use in the spectrographic analysis of trace elements in petroleum products. This compound is being issued by the National Bureau of Standards Office of Standard Reference Materials as SRM # 1077a.

Silver determinations were performed by both gravimetric and titrimetric methods on samples of the material taken from the top of stock bottles 1, 2, 3, and 4, and from the bottom of bottle 1. Samples consisting of 0.3 to 0.4 g of the material were ignited overnight in porcelain crucibles at 700°C. The residues were weighed assuming complete combustion of the organic material and conversion to metallic silver. The results are given in column 2 of table 43. The silver residues were then dissolved in 2+1 nitric acid, diluted to about 70 ml with distilled water, and titrated with standard NaCl. The end points were located potentiometrically, and the results are given in column 3. The results in columns 4 and 5 were obtained by a microgravimetric method (by R. A. Paulson) in which the silver was weighed as silver chloride after a sealed tube (Carius) oxidation with nitric acid. A sample weight of 10 mg was used.

The agreement of the analyses was excellent and indicates a silver content of 42.60 ± 0.05% (95% confidence level) for a stoichiometric purity of $99.0_0$%.

Table 43. Silver content of silver 2-ethylhexanoate.

| | Silver, percent | | | |
|---|---|---|---|---|
| Sample | Ignition Product | Titration | Carius | |
| T1 | 42.70 | 42.76 | - | 42.68 |
| T2 | 42.63 | 42.63 | 42.74 | 42.56 |
| T3 | 42.58 | 42.58 | 42.63 | - |
| T4 | 42.67 | 42.67 | 42.41 | 42.54 |
| B1 | 42.57 | 42.55 | - | 42.37 |
| Mean with 95% conf. limit | 42.63 ± 0.07 | 42.64 ± 0.10 | 42.56 ± 0.13 | |
| Pooled mean | 42.60 ± 0.05 | | | |

### 2. Analysis of *o*-Fluorobenzoic Acid

A sample of highly purified orthofluorobenzoic acid (*o*-FBA) intended for use as a microchemical standard reference material was carefully analyzed for evaluation of its purity and also to verify its fluorine content for certification purposes.

The determination of fluorine in *o*-FBA was carried out by decomposition of the organic material and the subsequent determination of fluoride by potentiometric titration with lanthanum (III) using a fluoride ion selective indicator electrode.

Several techniques were employed (by R. A. Paulson) to decompose the samples, with varying degrees of success. An apparent incomplete decomposition was observed with the sodium fusion (Ni-bomb), catalytic combustion (in quartz and platinum tubes), and Parr oxygen-bomb methods presumably due to the formation of carbon tetrafluoride. However, the low results observed could also be attributed to analytical error caused by iron or silicate interferences. The oxygen-flask method gave the most reliable and reproducible results. In this method, the sample, wrapped in moistened (with water or methanol) filter paper, is combusted in a Pyrex flask containing oxygen gas at approximately one atmosphere partial pressure and an absorbant (water or dilute NaOH).

In general, the La(III) titrations produced classical sigmoid-type titration curves in which the point of maximum slope (inflection point) was taken as the end point. The same point was taken in standardizing the lanthanum titrant solution against standard sodium fluoride solutions. In certain cases, the titration was abnormal in that a relatively small potential change was observed until 10 to 20% beyond the end point at which point a rapid emf change occurred which leveled off at potentials significantly past the end point potential. This effect is apparently due to either some type of adsorption phenomenon or a slow kinetic step in the nucleation of the insoluble lanthanum fluoride. Since this abnormal behavior was readily evident, the results of these titrations were discarded and not included in the data below.

For 14 determinations, an average fluorine content of 13.57% was found with a standard deviation of the mean of 0.07%. This value compares favorably with the theoretical value for o-FBA of 13.56% fluorine.

The material is being issued by the National Bureau of Standards Office of Standard Reference Materials as SRM 149, microchemical standard for fluorine determinations in organic materials.

### 3. Analysis of Au-Ag Metal Microprobe Standards

The composition of four Au-Ag alloys (20 mil wire form), intended for use as electron microprobe standard reference materials, was determined by a combination gravimetric/volumetric procedure in which preferential dissolution of one of the constituents ("parting") was affected prior to analysis.

In the case of the higher-content silver alloys (60 and 80% Ag), wire samples from the head, 1/4, 1/2, 3/4, and tail portions of the spool were combined and treated with 1+1 $HNO_3$ which preferentially dissolved the silver leaving a gold residue. The residue was filtered, ignited and weighed as metallic gold. The silver solution was potentiometrically titrated with a standard NaCl solution using a silver ion selective indicator electrode.

The higher-content gold alloys (60 and 80% Au; $HNO_3$ insoluble) were dissolved in aqua regia with considerable difficulty due to the formation of an impervious AgCl film on the alloy which passivated the surface and prevented further dissolution of the gold by aqua regia. To reduce this problem and facilitate dissolution, the 20, 40, and 60% Ag alloys were first rolled into approximately 3 mil ribbon. In addition, the 60% Au-40% Ag alloy required alternate treatments with $NH_4OH$ (to strip the AgCl from the ribbon surface) and aqua regia over a period of several days to completely dissolve the gold from a 1-gram sample. In this method, the gold is dissolved leaving the silver behind as the insoluble chloride. This residue is filtered, dried, and weighed as AgCl. The gold was precipitated as the metal by reduction with $SO_2$ followed by filtering, ignition, and weighing.

Due to the experimental difficulties encountered in the dissolution of the lower silver content alloys (less than 75% Ag), the alloys containing 20 to 60% silver were redetermined by an inquartation technique. In this technique, the alloys are fused with enough high-purity silver to increase the silver content of the alloys to between 75 and 80%. At this level, the alloys are easily dissolved in 1+1 nitric acid leaving a residue of metallic gold. The residue is filtered, ignited, and weighed. The silver content is obtained by difference.

The data listed in table 44 are the combined results from this technique and previous analyses with the reported values for silver obtained by difference.

Table 44. Au-Ag content of microprobe standards.

| Sample | Gold, percent | Silver, percent |
|---|---|---|
| 1 | 23.1 | 76.9 |
| 2 | 40.1 | 59.9 |
| 3 | 60.2 | 39.8 |
| 4 | 80.3 | 19.7 |

## D. Analysis of Research Materials

The development of a competence in the determination of fluoride has resulted in its application to analytical problems of interest to various research programs of the Bureau. Two such service analyses are described below in which are illustrated the wide variance in sample matrices encountered.

### 1. Determination of Fluoride in Sodium Carbonate Solutions

Sodium carbonate solutions containing fluoride from the fusion of $Na_2La_8Si_6O_{24}F_2$ with $Na_2CO_3$ were analyzed by a double standard additions technique using a fluoride ion specific electrode. After adjusting all sample aliquots to pH 6 and obtaining an electrode response curve by standard additions to the blank sodium carbonate solution (response 54.5 mV/pF), the fluoride concentration of the two sample solutions was calculated from the emf changes produced by the addition of two aliquots of a standard fluoride solution to each. The results are summarized in table 44.

Table 45. Fluoride in sodium carbonate.

| | Fluoride found[a] | | | Av dev |
|---|---|---|---|---|
| Sample | mg/ml | mg (total) | mM | mM |
| 1 | 0.040 | $6.3_2$ | 2.1 | 0.1 |
| 2 | .049 | $8.5_8$ | 2.6 | .3 |

---

[a] Average of two determinations.

## 2. Determination of Fluoride in HF-HCl Mixtures

Fluoride analyses were performed on two HF-HCl solutions resulting from the reaction of $ClF_3$ and $H_2$ in a platinum-lined Parr bomb. The determinations were carried out by the potentiometric titration of fluoride with 0.09578N $La(NO_3)_3$ using a fluoride ion selective indicator electrode. A single aliquot of each sample solution was titrated after adjustment to pH 6.5 ± 0.5. The results are given in table 46.

Table 46. Fluoride in HF-HCl mixtures.

| Sample | Aliquot wt | meq $F^-$/g sample |
|---|---|---|
| 1 | 0.62465 g | $0.660_9$ |
| 2 | .44537 g | $.681_1$ |

When combined with the coulometric results for hydrogen ion and chloride (by G. Marinenko), these data account for a material balance to an accuracy of about 2 parts in a thousand.

(R. A. Durst)

## 5. MICROSCOPIC AND CLASSICAL MICROCHEMICAL ANALYSIS

### A. Introduction

The activities of this laboratory include a number of programs which are related in that they are concerned with the analysis or characterization of very small amounts of matter. These programs include:

1. The detection and identification of micro amounts of materials;
2. The development and preparation of ultramicrochemical standards;
3. The determination of trace elements in various materials;
4. The microchemical analysis of organic and inorganic materials.

A parallel activity consists in developing and improving microscopic techniques and micromanipulative skills requisite for providing such services to other programs of the Division.

### B. The Detection and Identification of Microamounts of Materials

A principal objective of the program is the development of methodology and techniques for detection, handling, and identification of contaminants of the atmosphere. The collection of contaminants is done by the methods usually employed in atmospheric pollution studies such as by the use of impingers, filters, and tapes.

Frequently, only certain contaminants are of interest and these must be removed from the filter media and sometimes from a mass of other collected material. Ultrasonic vibration is used to dislodge contaminants from the filter or, if possible, the filter is dissolved in suitable solvents. Centrifugation is used to concentrate the contaminants before transferring them to slides for microscopic examination. The unique appearance and optical properties such as color, birefrengence, and index of refraction are used to help identify the actual crystal, compound, or object present. The excellent illustrations contained in McCrone's Particle Atlas [41] are often helpful in making identifications or in providing clues as to the nature of contaminants present. In some cases, ultramicrochemical tests can be applied but usually the particle is transferred so that an analysis may be made by various instrumental techniques. Because the amount of sample is ordinarily small, a high degree of manipulative skill is required for the handling and transferring of individual particles. It is also very necessary to have a clean environment. The work which is presently being done in a laminar flow clean bench will be moved soon to a laminar flow clean room now under construction.

## C. Ultramicrochemical Standards

Of special interest and importance is the preparation of ultramicrochemical standards. These standards should have a uniform known size and known composition so that measurement of the size under a microscope will permit the calculation of the amount of the element of interest present. Such standards are useful for determination of detection limits as well as for calibration of microchemical methods. They can also be used as standards for instrumental methods such as mass spectrometry and electron probe microanalysis which use very small amounts of material. While several other methods of preparation have been under consideration, the most promising is the addition of metal ions to ion exchange resins of uniform size. This technique was developed in cooperation with the Separation and Purification Section which provided batches of beads in the 1 to 10 μm size range.

There are several advantages to using ion exchange resins. The beads are essentially spherical so that the volume can be calculated from a measurement of the diameter. They are easily loaded to either full or partial capacity by treatment with a solution containing the desired ion. Since the loading characteristics of the resins are known or may be determined, the weight of the added ion can be calculated. The percentage of the ion can also be determined by chemical means using a sufficient amount of beads.

There are two problems which reduce the accuracy in determining the amount of ion present in the particle standard. One is the difficulty in accurately measuring the diameter of a bead, especially as it approaches 1 μm in size. Freeman [42] has given the conditions for the most accurate measurement of bead diameters. The other is that the size of a bead varies with its water content which is dependent on the humidity of the atmosphere to which it is exposed. By only working in an atmosphere of 30 to 40% R.H., this effect has been minimized.

The mass m* of a particular element within a single resin bead is given by [43]

$$m^* = \frac{\pi d^3 p e^*}{6 \Sigma e_i} (1-f)$$

where the bead volume is $\frac{\pi d^3}{6}$, p is the density, e* is the equivalent weight of the bound element of interest, and $\Sigma e_i$ is the equivalent weight of the resin including both the matrix and attached ions. The matrix in this case is a homogeneously sulphonated derivative of the copolymer of styrene and divinylbenzene with an equivalent weight of about 185. Some hydration is allowed for by taking the variable f as the fractional water content of the resin.

This laboratory has developed the technique for loading beads with various elements and placing individual beads on microscope slides for measurement of their diameters. Slide mounting also provides a convenient means to transport individual beads for later use in analytical calibrations.

## D. Determination of Trace Quantities of Uranium in Biological Materials

### 1. Background

A recently initiated program of the NBS Office of Standard Reference Materials to provide trace element standards in biological matrices has spurred an interest in development of sensitive analytical methods especially adaptable to biological analysis. Various materials such as dried blood, dried plasma, and botanical matter such as dried alfalfa, dried kale, and dried oak leaves have been proposed or are actually in preparation for this purpose. Accordingly, there is being pursued within the Division an extensive program to characterize these materials. During the past few years, a nuclear track technique has been developed for the detection of such fissile elements as plutonium, thorium, and uranium and even for a few nonfissile elements such as boron. The most extensive use of this new technique has been for the detection of uranium in inorganic materials for which purpose it has been found to be highly sensitive and very versatile. There is no reason to believe that it would not be useful for analysis of trace elements in organic materials, although no studies of this nature have been reported. Accordingly, it seems interesting to investigate the applicability of this technique to the analysis of biological materials, especially to the extent that it might be advantageous for standard reference material certification.

Fission occurs in natural uranium when it is exposed to radiation of the proper type [44,45]. In general, this radiation for uranium is thermal neutrons and photons. If an insulating material is placed in intimate contact with the uranium, the recoiling fission fragments which enter the absorber will leave along their paths atomically and electronically disturbed regions. This type of radiation damage occurs because the ionization density produced along the fission-fragment track is greater than the critical ionization density for the absorber. The fission tracks can be made optically visible by etching in a suitable solution. The tracking technique has been described in a series of papers by Fleischer, Price, Walker and other authors using several absorbing materials as detectors [46-50]. These authors have used the technique in a variety of studies for the purpose of dating of geological samples, and for detecting trace quantities of uranium in minerals, micas, and glass [51-53].

In the above-mentioned work, this technique was successfully employed in determining trace quantities of uranium in geological and metallurgical samples [54,55]. At NBS it was thought that the method could be applied to determine the uranium content of biological material. In the above-cited work, uranium was either determined or detected only on the surface of the materials without destroying the material. However, with biological materials, surface analysis is not feasible because of the porous nature of the organic matrix and the odd shape and size of the sample. Accordingly, biological materials must be prepared in solution form for analysis, thus providing a more uniform geometry for irradiation with the further advantage of reducing the bulk sample by several orders of magnitude.

Any optically clear insulating material could be used, in principle, to record fission fragment tracks, but because interferring nuclear reactions are possible, e.g., $^{10}B(n,\alpha)^{7}Li$, selectivity of the recording medium is essential. For this application, the material selected must be insensitive to alpha particles, high energy protons and recoil neutrons and record only fission fragment tracks. In a series of experiments, Fleischer, Price and Walker [51,52] found that Lexan (a polycarbonate, $C_{16}H_{18}O_3$) has the relatively high critical ionization density required to act selectively in the manner desired.

## 2. Experimental

The prototype standard materials selected for analysis, blood, plasma, and dried leaves were freeze-dried to remove most of the water, then ashed at a low temperature in an oxygen atmosphere using a low-temperature dry asher. Finally, the residue was digested in nitric acid, filtered, and diluted to a known volume. Carefully controlled drops of sample solution, delivered from a micropipette, were placed on Lexan slides, 20 mm wide x 40 mm long x 25 mm thick. The solutions were evaporated to dryness on a laminar flow clean bench. (An infrared heat lamp was used in early experiments to evaporate the solutions but this technique was abandoned because the heat lamp caused cracking of the Lexan.) Standard samples containing known amounts of uranium were mounted on Lexan detectors in an identical manner, in order to establish for specific irradiation conditions the relationship between the number of tracks observed and the weight of uranium present.

In order to prevent external contamination, the slides were packaged in polyethylene envelopes. After samples and standards were wrapped in plastic, they were exposed to a thermal neutron flux at the Naval Research Laboratory's swimming pool-type reactor for five minutes in an approximate flux of $3.5 \times 10^{11}$ $n \cdot cm^{-2} \cdot sec^{-1}$. After irradiation, the Lexan slides were etched in 6.5N NaOH at 50° ± 2 °C for 45 minutes [51]. Following the etching step, the fission tracks produced from the $^{235}U$ were counted with an optical microscope. The tracks observed in the case of the actual samples were compared with the number of tracks produced by the standards, irradiated under the same conditions, to determine the amount of uranium present.

NBS certified 950-A Uranium Oxide, $U_3O_8$, was used as a stock standard. The $U_3O_8$ was digested in nitric acid to convert the oxide to $UO_2(NO_3)_2$, then the solution was diluted to a specified volume with distilled water. Various known volumes of the prepared stock solution were spotted on Lexan slides in order to determine the relation of the number of tracks to the amount of uranium irradiated. The relation was found to be linear. Standards, samples and reagent blanks were irradiated simultaneously, then etched and counted. The purpose of the reagent blanks was to determine the contribution of uranium in the reagents which were used in the sample solutions. The preparation of these slides was identical to that of the standards and the samples. From the reagent blank it was possible to determine the contamination level that the reagents and Lexan slides contribute for each irradiation. The blank slides were found to contain an average of eight fission tracks, corresponding to $1.0 \times 10^{-11}$ grams of uranium.

Trace amounts of uranium also can be determined by counting the fission tracks induced by photons. In this case, the fission fragments are produced from the $^{238}U$ atoms. The samples and standards can be prepared in an analogous manner to that utilized for thermal neutron irradiation. In a preliminary study, standards were irradiated for five minutes in the National Bureau of Standards Linear Accelerator (LINAC). The photons used to induce fission were produced from an accelerated electron beam with a maximum energy of 35 MeV that bombarded a tungsten converter. The LINAC was operated at an integrated beam current of 20 μA. The fission tracks produced by the fragments from $^{238}U$ were developed and counted. The average weight of uranium per fission track was found to be $7.7 \times 10^{-11}$ grams.

## 3. Results

The technique described has been used for the determination of uranium in several samples of biological materials supplied by the Office of Standard Reference Materials, namely: dried mammalian blood, mammalian blood plasma, and dried leaves.

Six independent analyses of dried blood gave an average value of 0.55 ± 0.06 ppm for the uranium content. On the assumption that whole blood contains 15% "dried material" [56], the uranium content of whole blood is calculated to be 83 ppb.

Freeze-dried mammalian blood plasma was also analyzed. Five independent determinations gave an average value of 1.09 ± 0.25 ppm for its uranium content. On the assumption that plasma contains 6% "dried material" [56], the uranium content of plasma is calculated to be 66 ppb.

Determination of the uranium content of the dried leaves gave results which varied between 1.7 and 14.9 ppm. This variation is attributed to the inhomogeneity of the material.

## E. Analysis of Standard Reference Materials

### 1. Residual Fuel Oil

Of the many materials now classed as atmosphere pollutants, sulfur dioxide can be detected by human senses in lower concentrations than any other common pollutant. Consequently, it must be classed as one of the more objectionable pollutants, at least from the point of view of the man-in-the-street. At present, there are in force, or under consideration, regulations by various levels of government to control the amount of sulfur dioxide in smoke and stack gas by means of various scrubbing techniques, or of limiting the amount of sulfur in the fuel.

Of the sulfur dioxide emitted to the air over the United States in 1963 (greater than 23 million tons), about two-thirds stemmed from coal-burning powerplants and another 16 percent from residual fuel oil. The Petroleum Products Survey of the U. S. Bureau of Mines indicates that No. 6 fuel oil sold in the populous Northeastern area ranges from 0.52 percent to 2.9 percent in sulfur content. In the West, the maximum sulfur content exceeds 4 percent. In all probability, after much debate pro and con, there will be limits placed on the amount of sulfur in coal and fuel oil.

To provide a base for accurate analysis of fuel oil, the National Bureau of Standards has certified two new standard reference materials intended for use in the determination of sulfur in residual fuel oil. Designated NBS SRM 1621 and 1622, the new standards were prepared from commercial fuel oil supplied by the Esso Research and Engineering Co., Linden, New Jersey.

The sulfur content of the fuel oils was determined by combustion of one-gram samples in a Parr Oxygen Bomb, followed by gravimetric determination as barium sulfate. The method used differed from that designated as ASTM D129 in that any iron present was removed with ammonium hydroxide and filtered before the precipitation of the sulfate.

Two drums of oil were received containing oil with the nominal sulfur contents of 1 and 2 percent, respectively. Three samples were taken from each drum representing the top, middle, and bottom portions. Approximately ten determinations of sulfur were made from each portion of the 1 percent oil and six determinations of each portion of the 2 percent oil. Since there did not appear to be a significant difference between portions, the results for each oil were pooled.

To identify problems with respect to use or storage of the sample, tests were made to determine the loss of volatile constituents. Approximately six grams of oil were placed in 100-ml beakers and allowed to stand open at room temperature for a period of time. The results are shown in table 47.

Table 47. Loss of volatile constituents from fuel oils.

| | Percent loss | |
|---|---|---|
| Period of Exposure | 1% Oil | 2% Oil |
| 1 day | 0.39 | 0.40 |
| 2 days | .61 | .58 |
| 5 days | .94 | .91 |
| 7 days | 1.11 | 1.10 |

From this study it is concluded that no problem should arise during the routine weighing of analytical samples. Furthermore, no storage problem should develop, provided the sample container is closed when not in use.

In addition to the sulfur analysis, several routine determinations were made for descriptive characterization of the oil. Carbon and hydrogen were determined by the conventional micro-combustion method using 5-mg samples. Water was determined by the Dean-Stark distillation procedure (ASTM D-94). Sediment was determined by a method similar to ASTM D-475 using 20-g samples. Ash was determined by ASTM Method D-482 using 5-g samples.

The results of all analyses are summarized in table 48.

Table 48. Analyses of residual fuel oils.

| | |
|---|---|
| SRM 1621 | |
| Sulfur | 1.048%<br>s = 0.058<br>n = 30<br>95% Confidence Limit ± 0.021 |
| Carbon | 86.6% |
| Hydrogen | 12.1% |
| Water | Not detected (< 0.1%) |
| Sediment | 0.01% |
| Ash | 0.02% |
| SRM 1622 | |
| Sulfur | 2.138%<br>s = 0.029<br>n = 17<br>95% Confidence Limit ± 0.013 |
| Carbon | 85.3% |
| Hydrogen | 11.3% |
| Water | Not detected (< 0.1%) |
| Sediment | 0.01% |
| Ash | 0.05% |

### 2. Miscellaneous Analyses

The laboratory has provided a number of analytical services incidental to the preparation, purification, and certification of standard reference materials. Elemental analysis for carbon, hydrogen, nitrogen, sulfur, and halogen has been made on all of the organic materials now being prepared, purified and certified as standards. During the past year, three organo-metallic compounds, cholesterol, urea, creatinine, and uric acid, were extensively analyzed. Many analyses have been made of the ion exchange beads already mentioned, as well as intermediates prepared for the development of special exchange materials.

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

## 6. MISCELLANEOUS ANALYTICAL PROCEDURES

### A. Determination of Sulfur in Plastic Clay

The certification of two lots of plastic clay as standard reference materials (SRM 97a and 98a) required the determination of the sulfur content, estimated to be about 500 parts per million. Because the conventional methods for the determination of this element in minerals is cumbersome [57], a new technique was developed.

The method devised consisted in the combustion of a mixture of the clay with a high silicon steel (SRM 125), using conventional metallurgical analytical equipment. This latter material has a low sulfur content of 0.003 percent, and provides a fluid melt. Mixtures of clay with the steel in the ratios of 1:1, 1:2, and 1:3, respectively, were tried and the latter proved to be the most satisfactory.

Samples of clay of 0.5g were mixed with 1.5g of the steel, placed in combustion boats normally used for the determination of sulfur in metals, and burned in an ordinary resistance furnace at a temperature of at least 1440 °C. The resulting sulfur dioxide was absorbed in starch-iodide solution and titrated with potassium iodate according to the conventional procedure. The results of the analysis are given in table 49.

Table 49. Determination of $SO_3$ in clay.

| Sample | $SO_3$, percent |
|---|---|
| SRM 98 (control) | 0.077, .071 |
| Certificate value | 0.07 |
| SRM 98a | 0.315, .301, .320, .326 |
| Average | 0.315 |
| SRM 97a | 0.102, .104, .107, .104 |
| Average | 0.104 |

The sulfur content is calculated as $SO_3$. A sample of plastic clay SRM 98 was used as a control and the results found were in good agreement with the certified value.

The method appears to be quite satisfactory for the determination of sulfur in clay and should be applicable to other mineral products. It has the distinct advantage over the conventional method in being relatively rapid in that only about 8 minutes are required for each determination.

## B. Determination of Carbon and Sulfur in Copper Foil

Some investigations of the mechanical and physical properties of electrodeposited copper required determinations of small amounts (> 100 ppm) of carbon and sulfur in samples of foil, stripped from stainless steel electrodes. Modifications of conventional metallurgical analytical techniques proved to be satisfactory for this purpose, as outlined below.

The copper foil (thickness approximately 1 mil) was cut into 1/4-in. squares. For determination of carbon, samples of 1.5 g were placed in combustion boats, covered with 1.0 g of a low-carbon silicon steel (SRM 131) and ignited at 1300 °C in a stream of oxygen. The carbon dioxide was absorbed in ascarite-filled bulbs for gravimetric determination.

For determination of sulfur, direct combustion was satisfactory. Samples of the cut foil (1 to 2 g) were put in covered combustion boats and ignited at 1440 °C. The sulfur dioxide evolved was determined by starch-iodate titrimetry. The results of analysis are given in table 50 and table 51.

Table 50. Determination of sulfur in copper foil.

| Sample | S, % | Sample | S, % |
|---|---|---|---|
| 197-A | 0.0042 | 323-A | 0.0014 |
| 197-B | .0043 | 323-B | .0006 |
| 197-C | .0031 | 323-C | .0012 |
| Average | 0.0039 | Average | 0.0011 |

Table 51. Determination of carbon in copper foil.

| Sample | Carbon, percent |
|---|---|
| 10-A | 0.0054, .0072 |
| 10-B | .0054, .0036 |
| 10-C | .0036, .0072 |
| Average | 0.0054 |
| 193-A | 0.0036, .0072 |
| 193-B | .0054, .0054 |
| 193-C | .0036, .0054 |
| Average | 0.0051 |

## C. Analysis of Platinum-Chromium Alloys

The following procedure was devised and used for the analysis of some platinum-chromium alloys prepared for metallurgical studies of this system.

The samples contained 3 to 30 percent chromium and the remainder platinum. Approximately 160 mg of each alloy was available for analysis. Those containing less than 15 percent chromium could be dissolved completely in aqua regia. For higher chromium concentrations, acid dissolution resulted in residues which were fused with sodium pyrosulfate, followed by solution in water. The combined solutions were evaporated repeatedly with hydrochloric acid to remove the nitric acid. Finally, the residues were dissolved in dilute acid and diluted to 300 ml so that the final solution contained 5 percent hydrochloric acid.

The solution was heated to boiling and platinum was precipitated with hydrogen sulfide. The precipitate was filtered, ignited, leached, and reignited in a porcelain crucible and weighed as metallic platinum.

The filtrates from the above procedure were evaporated twice to fuming with sulfuric acid. The salts were dissolved in water and diluted to a volume of 300 ml. The chromium was oxidized with ammonium persulfate, using silver nitrate as catalyst, in the conventional manner, and titrated potentiometrically with ferrous ammonium sulfate.

The results of the analysis, reported in table 52, show the procedure to give reliable results as evidenced by the material balance achieved.

Table 52. Analysis of platinum-chromium alloys.

| Sample | Platinum, percent | Chromium, percent | Total |
|---|---|---|---|
| #1 (3% Cr) | 97.1 | 2.8 | 99.9 |
| #2 (6% Cr) | 93.8 | 6.2 | 100.0 |
| #3 (10% Cr) | 90.0 | 10.1 | 100.1 |
| #4 (15% Cr) | 85.1 | 14.8 | 99.9 |
| #5 (21% Cr) | 79.0 | 20.9 | 99.9 |
| #6 (29% Cr) | 71.8 | 28.1 | 99.9 |

(J. R. Baldwin)

# 7. INTERNATIONAL RESEARCH GRANTS PROGRAM

## A. Introduction

The National Bureau of Standards awarded a grant to the Technion Research and Development Foundation, Haifa, Israel, on December 1, 1965, to investigate "Trace Analysis by Anodic Stripping Voltammetry". Professor Magda Ariel, Chemistry Department, Technion, Israel Institute of Technology, is principal investigator. Dr. John K. Taylor, Chief, Microchemical Analysis Section, is the NBS project monitor. The project was completed in March 1968. The results are summarized in the following sections.

## B. Trace Metal Determinations in Silicates

An anodic stripping voltammetric (a.s.v.) method has been developed for the determination of zinc in silicates [58]. The method is sensitive and is not affected by interferences resulting from varying sample composition.

The method has been evaluated by the determination of zinc in NBS Standard Reference Material Opal Glass No. 91 and U. S. Geological Survey samples G-1 and W-1. This work shows the method highly reliable for determinations at the ppm level with standard deviations of 5 to 10 relative percent.

The determination of zinc in samples G-2, AQV-1, GSP-1, BCR-1, and PCC-1 was carried out by this method. Five of these standards have been analyzed by a neutron activation method by Brunfelt et al [59] and the present results show good agreement with those cited in Table II of their paper. A report showing standard deviations and details of the problems encountered in the determination of copper and lead is under preparation. The determination of copper by a.s.v. combined with medium exchange is best carried out at a mercury-film electrode (see section C below).

### C. Anodic Stripping Voltammetry with Superimposed A.C. Potential

The combination of ac polarography with linear-scan anodic stripping voltammetry has been investigated using a phase-discriminating ac attachment [60]. The resolution and sensitivity were compared with those obtainable under the same conditions with conventional dc stripping techniques.

Studies of resolution of neighboring peaks were conducted. For a species undergoing a two-electron reaction the error resulting from overlapping of two consecutive peaks of equal heights, differing in peak potential by 75 mV or more, does not exceed 1 percent.

For reversible reactants, a comparison of plain anodic stripping with the ac anodic stripping combination shows that the latter provides an increased sensitivity of about one order of magnitude. This increase is retained, though to a lesser degree, for slightly irreversible reactions.

The potentialities of the technique were demonstrated by the determination of zinc in NBS SRM 91 (Opal Glass). The results obtained agreed with those found using conventional anodic stripping.

### D. Studies of the Rotating-Film Electrode

This electrode, as described by de Vries [61], has been evaluated experimentally for a.s.v. The expected advantages were: improved sensitivity and resolution, adaptability to medium exchange and diminished susceptibility to changes in cell geometry. The main results showed:

1. The effective voltage range is narrower than that of the hanging mercury drop electrode and depends on the thickness of the mercury-film;
2. Sensitivity is 10 to 20 fold that of an HMDE;
3. The electrode behavior is greatly influenced by methods employed in coating, pretreatment and storage;

4. The theoretical assumption of an evenly spread film is not upheld by experiment; during electrolysis (rotation) a thicker mercury film forms round the electrode rim, while during stripping (electrode at rest) mercury tends to accumulate near the electrode center. Changes in electrode potential and/or the presence of surfactants also affect mercury distribution. These effects need to be controlled before good reproducibility is achieved;

5. For the determination of low copper concentrations in samples requiring medium exchange between the pre-electrolysis and the stripping steps, the mercury-film electrode gives good results.

### E. Water Purification

The extremely low concentrations of trace metals determined require the consistently reliable purity of the water employed. De-ionized water, while sufficiently free of ionic contaminants, often introduces nonionic contamination (from the ion exchange step); as a result, adsorption peaks may appear in the voltagrams and the shape of the stripping peaks of the metals (notably zinc) is affected.

Various purification methods were tried and the following has been finally adapted:

De-ionized water is filtered and then passed through a column filled with activated charcoal (which has been kept in an oven, at 950° in an inert atmosphere, for 2 hrs). The effluent is distilled in a Pyrex still and finally redistilled from a quartz still, by a non-boiling evaporation process.

The last stage is kept under constant recirculation so that freshly distilled water only is employed. Water treated by this method is practically free of interfering contaminants: after 30 min pre-electrolysis, hardly a trace of zinc stripping peak may be obtained; its zinc content has been shown to be less than 0.03 ppb.

## F. Theoretical Studies of Electrochemical Techniques

Theoretical Studies have been undertaken on several electrochemical techniques. A report dealing with potential-step electrolysis followed by linear potential-sweep voltammetry [62] was written, which was an extension of theory previously developed [63]. The results are of importance for an experimental technique for trace analysis described by Yarnitzky [64] and Ariel.

The problem of constant-current chronopotentiograms distorted by double-layer charging was attacked subsequently. This led to four reports [65-68]. These investigations were undertaken to clarify the usefulness of chronopotentiometry to a.s.v. methods.

(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
William D. Dorko
Julian M. Ives

Polarography --

E. June Maienthal

Coulometry --

George Marinenko
Charles E. Champion

Electroanalytical Measurements --

Richard A. Durst
Erick L. May (Summer Employee - 1967)

Microscopy and Microchemistry --

Rolf A. Paulson
John R. Baldwin
B. Stephen Carpenter
William P. Schmidt

## B. Publications

1. E. J. Maienthal and J. K. Taylor, "Improvement of Polarographic Precision by a Comparative Technique", Microchimica Acta (Wien) 1967, 939.

2. J. K. Taylor, "Measurement of Density and Specific Gravity", Treatise on Analytical Chemistry 7, part 1, 4561-4610 (1967).

3. R. A. Durst and J. K. Taylor, "Modified Linear Null-Point Potentiometry", Anal. Chem. 39, 1374-79 (1967).

4. R. A. Durst and J. K. Taylor, "Modification of the Fluoride Activity Electrode for Microchemical Analysis", Anal. Chem. 39, 1483-1485 (1967).

5. G. Marinenko and J. K. Taylor, "High-Precision Coulometric Iodimetry", Anal. Chem. 39, 1569 (1967).

6. J. K. Taylor, Editor, NBS Technical Note 425, "Microchemical Analysis Section: Summary of Activities, July 1966 to June 1967", U. S. Government Printing Office, October 1967.

7. R. A. Durst, Book review: *Glass Electrodes for Hydrogen and Other Cations*, George Eisenman, Ed., Record of Chem. Prog. **28**, 4 (1967).

8. J. K. Taylor, Book review: *Statistical Techniques for Collaborative Tests*, W. J. Youden, Capital Chemist **18**, 70 (1968).

9. R. A. Durst, "Fluoride Microanalysis by Linear Null-Point Potentiometry", Anal. Chem. **40**, 931 (1968).

10. R. A. Durst, E. L. May, and J. K. Taylor, "Improved Technique for the Microdetermination of Silver by Linear Null-Point Potentiometry", Anal. Chem. **40**, 977 (1968).

11. E. E. Hughes and W. D. Dorko, "Direct Mass Spectrometric Determination of Atmospheric Carbon Dioxide", Anal. Chem. **40**, 866 (1968).

12. E. J. Maienthal and J. K. Taylor, "Polarographic Methods in Determination of Trace Inorganics in Water", in *Trace Inorganics in Water*, Advances in Chemistry Series 73, R. F. Gould, Ed., American Chemical Society, 1968.

13. E. E. Hughes, "A Simple Technique for the Absolute Determination of Atmospheric Oxygen", Environ. Sci. Tech. **2**, 201 (1968).

14. E. E. Hughes and W. D. Dorko, "Accurate Mass Spectrometric Determination of Low Concentrations of Carbon Dioxide in Nitrogen", Anal. Chem. **40**, 750 (1968).

15. E. E. Hughes, Book review: *Gas Effluent Analysis*, W. Lodding, Ed., Marcel Dekker, Inc., New York, 1967, J. Am. Ceramic Soc. **5**, No. 8, Ceramic Abstracts, p. 260 (1968).

16. D. F. Freeman and R. A. Paulson, "Chemical Microstandards from Ion Exchange Resins", Nature **218**, 563 (1968).

C. Talks

1. J. K. Taylor, "Scientific Careers vs. Management Careers", U. S. Civil Service Commission, Washington, D. C., September 1967.

2. J. K. Taylor, "Electrochemical Methods of Trace Analysis", Wilmington Section, American Chemical Society, October 1967.

3. C. E. Champion and G. Marinenko, "Improved Methods for Coulometric Determination of Halides", Chicago Meeting, American Chemical Society, September 1967.

4. R. A. Durst and J. K. Taylor, "Modification of the Fluoride Activity Electrode for Microchemical Analysis", Chicago Meeting, American Chemical Society, September 1967.

5. E. J. Maienthal, S. F. Cooper, and J. K. Taylor, "Some Analytical Applications of Modern Polarographic Techniques", ORNL Gatlinburg Conference, October 1967.

6. G. Marinenko, C. E. Champion, and J. K. Taylor, "Coulometric High Precision Analysis", ORNL Gatlinburg Conference, October 1967.

7. J. K. Taylor, "Recent Advances in High Precision Chemical Analysis", University of Alberta, Edmonton, Alberta, Canada, October 1967.

8. J. K. Taylor, "What is Chemistry?", DeChantal School, Bethesda, Md., November 1967.

9. B. S. Carpenter, "Nuclear Track Technique for Determination of Trace Elements", Howard University, Washington, D. C., December 1967.

10. J. K. Taylor, "Electrochemical Separations: Principles and Practice", Analytical Chemistry Division Colloquium, December 1967.

11. J. M. Ives and E. E. Hughes, "Absolute Determination of Low Concentrations of Oxygen in Inert Gases Using Galvanic-Type Cells", Third Middle Atlantic Regional Meeting, American Chemical Society, Philadelphia, Pa., February 1968.

12. R. A. Durst, "Microanalysis of Fluoride at Subnanogram Levels by Linear Null-Point Potentiometry", Third Middle Atlantic Regional Meeting, American Chemical Society, Philadelphia, Pa., February 1968.

13. J. K. Taylor, "Electricity and Chemistry", T. C. Williams High School, Alexandria, Virginia, February 1968.

14. J. K. Taylor, "Electrochemical Methods", American Chemical Society, San Francisco, Calif., April 1968.

15. R. A. Durst, "Equilibria in Electrochemical Cells", National Institutes of Health, Bethesda, Md., February 1968.

16. R. A. Durst, "Fluoride Microanalysis by Linear Null-Point Potentiometry", American Chemical Society, San Francisco, Calif., April 1968.

17. R. A. Durst, "Electrochemical Generation of Fluoride Ion by Solid-State Transference", Chemical Society of Washington, May 1968.

18. J. K. Taylor and G. Marinenko, "Applications of Coulometry to High Precision Analysis", American Chemical Society, Akron, Ohio, May 1968.

19. B. S. Carpenter, "Applications of the Quantimet Analyzing Computer in Chemical Microscopy, Howard University, Washington, D. C., May 1968.

## 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.

R. A. Durst

Treasurer, The Capital Chemist, Chemical Society of Washington

Chairman, Auditing Committee, ACS Division of Analytical Chemistry

Member, Member Services Committee, Chemical Society of Washington

Chairman, Local Dinner Arrangements Committee (NBS meeting), Chemical Society of Washington

Safety Representative, Microchemical Analysis Section

E. J. Maienthal

NBS Reporter for Capital Chemist, Chemical Society of Washington

Elected member, Board of Managers, Chemical Society of Washington

Editor, Analytical Chemistry Division NewsLetter.

R. A. Paulson

Member, Services Analysis Committee, Analytical Chemistry Division

Collaborator, Committee for Study of Microchemical Methods, Association of Official Agricultural Chemists.

## E. Award

J. K. Taylor

American Institute of Chemists, Washington Section, Honor Scroll Award.

F. Standard Reference Material Analyses

| Material | Analyst | Determination | Technique |
|---|---|---|---|
| Cast Iron 6g | JRB | S,C (total),P,Si C (graphitic) | C,G,S |
| | EJM | Ti | P |
| | GM & CEC | Cr | F |
| Cast Iron 51 | JRB | S,C (total), C (graphitic), P, Si | C,S,G |
| | EJM | Ti | P |
| Cast Iron 51 | GM & CEC | Cr | F |
| Cast Iron 342a | JRB | C (total), C (graphitic), S, P, Si | C,G,S |
| | EJM | Ti | P |
| Steel 125b | JRB | S,C,P | C,S |
| Stainless Steel 101f | JRB | C,S,P,Si,Mn,V | C,S,Pot |
| | GM & CEC | Cr | F |
| Stainless Steel 101g | JRB | C,S,P,Si,Mn,V | C,S,Pot |
| | GM & CEC | Cr | F |
| Ductile Iron 1140, 1141, 1142, 1140a, 1141a, 1142a | JRB | C,S,P,Si,Mn | C,G,S |
| Cast Steel 1138, 1139 1138a, 1139a | JRB | C,S,P | C,S |
| Ferrosilicon 59a | JRB | Mn | S |
| Ferrochromium 196 | GM & CEC | Cr | F |
| | JRB | C,S,P | C,S |
| Solder 127b | EJM | Bi,Cu,Ni | P |
| Solder 1131 | EJM | Bi,Cu,Ni | P |
| Au-Ag Microprobe | RAD | Au,Ag | G,Pot |

| Material | Analyst | Determination | Technique |
|---|---|---|---|
| Au-Cu Microprobe | JRB | Au,Cu | G |
| Intermediate purity zinc 683 | EJM | Cu,Pb,Cd,Fe,Al | P |
| Intermediate purity zinc 728 | EJM | Cu,Pb,Cd,Fe,Al | P |
| High purity zinc 682 | EJM | Cu,Pb,Cd | P |
| H.P. platinum 680 | EJM | Fe | P |
| Doped platinum 681 | EJM | Fe,Cu,Pb | P |
| High purity gold 685 | EJM | Fe,Cu | P |
| Cobalt Glass | RAP | Water, $CO_2$, loss on ignition | G |
| Clay 97a, 98a | JRB | $SO_3$ | C |
| Boric Acid | GM & CEC | Assay for purity | F |
| $Na_2$ EDTA | GM | Assay for purity | F |
| Sucrose 17 | RAP | Moisture, ash | G |
|  | BSC | Reducing sugars | G |
| Dextrose 41 | RAP | Moisture, ash | G |
|  | BSC | Reducing sugars | G |
| Cholesterol 911 | RAP | C,H | M |
| Urea | BSC & WPS | Insol, ign. loss<br>C,H,N | G,M |
| Fluorine micro standard 149 | RAP & RAD | F | Pot |
| Lead organic 1059b | RAP | C,H | M |
|  | EJM | Pb | P |
| Zinc organic 1073b | RAP | C,H | M |
|  | EJM | Zn | P |

| Material | Analyst | Determination | Technique |
|---|---|---|---|
| Magnesium organic 1061b | JRB | Mg | G |
|  | WPS | C,H | M |
| Silver organic 1059b | RAP | C,H | M |
|  | RAD | Ag | Pot |
| Tin organic 1057b | JRB | Sn | G |
|  | WPS | C,H | M |
| Fuel oil 1621 | RAP,WPS,BSC | S,C,H | C,G,M |
| Fuel oil 1622 | RAP,WPS,BSC | S,C,H | C,G,M |
| $CO_2$ in nitrogen 1601, 1602, 1603 | EEH & WDD | $CO_2$ | Ms, G |
| $O_2$ in nitrogen 1604, 1605, 1606, 1607, 1608 | EEH & JMI | $O_2$ | Gal |

Key to Analyst

JRB - John R. Baldwin
BSC - B. Stephen Carpenter
CEC - Charles E. Champion
RAD - Richard A. Durst
WDD - William D. Dorko
EEH - Ernest E. Hughes
JMI - Julian M. Ives
EJM - E. June Maienthal
GM - George Marinenko
RAP - Rolf A. Paulson
WPS - William P. Schmidt

Key to Technique

C - Combustion
F - Coulometric
G - Gravimetric
Gal - Galvanic cell
M - Microchemical
Ms - Mass spectrometric
P - Polarographic
Pot - Potentiometric
S - Spectrophotometric

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