NBS TECHNICAL NOTE

425

Microchemical Analysis Section:

SUMMARY OF ACTIVITIES JULY 1966 TO JUNE 1967

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

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UNITED STATES DEPARTMENT OF COMMERCE
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NBS TECHNICAL NOTE 425

ISSUED OCTOBER 1967

Microchemical Analysis Section:

SUMMARY OF ACTIVITIES JULY 1966 TO JUNE 1967

Edited by John K. Taylor

Microchemical Analysis Section
Analytical Chemistry Division
Institute for Materials Research

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FOREWORD

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

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

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

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1967 we plan to issue these summaries for all of our sections. The following is the third annual report on progress of the 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; a.c. polarography; coulometry; electroanalytical measurements; microscopy; wet chemistry; conventional elemental microchemical analysis.

Activities during the reporting period are classified under research or analytical development. The classification is often arbitrary since nearly all of the analytical applications have required considerable efforts of both kinds. An attempt has been made to describe analytical methods briefly yet with sufficient detail to make them understandable to the experienced analyst. However, specific details will be made available to anyone interested in such matters.

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 1966 to JUNE 1967

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 1966 to June 1967. General activities are reported in the areas of gas analysis, polarography, potentiometry, coulometry, chemical microscopy, and classical microchemical analysis. Research accomplishments described in some detail include the following: high pressure mass spectrometry; high precision differential polarography; an improved coulometric technique for titration of halides; developments in micro null-point potentiometry; techniques for the accurate weighing of small liquid samples. A number of microchemical procedures which have been developed for the analysis of a variety of materials are also included.

1. MASS SPECTROMETRY AND GAS ANALYSIS

A. Research Activities

1. Introduction

The research activities of this laboratory during the past year were directed toward two principal goals. The first was the application of high pressure mass spectrometry to the development of a highly accurate method for the determination of low concentrations of carbon dioxide in nitrogen. The second objective was to explore methods of gas analysis with the eventual goal of developing highly accurate absolute methods suitable for the production of gaseous standard reference materials. The investigation of high pressure mass spectrometric techniques for the determination of carbon dioxide is substantially complete. Absolute methods of the requisite accuracy are generally lacking in the field of gas analysis and only a beginning has been made in this aspect of the problem.

2. High Pressure Mass Spectrometry

The preliminary results of the application of high pressure mass spectrometry to the accurate determination of low concentrations of carbon dioxide has been described in a previous report [1]. Complete details are contained in a manuscript now in preparation [2]. The principle effort since the previously described work has been concerned with the preparation of several additional mixtures which extend the range of concentration from 0.0187 to 0.0384 mole percent. The results obtained with these additional mixtures substantiate the previous results and showed that an accuracy of better than ± 1% of the amount of carbon dioxide can be achieved on analysis of a sample.

analysis. At no time was it possible to completely convert the oxygen to carbon dioxide. A wide range of temperatures and pressures were used but in all cases some of the oxygen either failed to react or reacted to form a mixture of carbon dioxide, carbon monoxide, and nitrogen oxides. The method shows promise, however, so that investigations to improve the cell are planned.

Further work on the determination of low concentrations of oxygen has been conducted as part of the Standard Reference Materials Program and will be discussed later in this report.

3. Hydrocarbons in Air and Water

Another application of high pressure mass spectrometry that shows signs of success is the determination of low concentrations of methane in nitrogen. The interest in this system lies in its eventual use as a step in the determination of trace hydrocarbons in water and in the possible preparation and distribution of a standard reference material consisting of low concentrations of hydrocarbons in air or in nitrogen.

The method involves the oxidation of the methane in nitrogen to carbon dioxide with subsequent accurate determination of the carbon dioxide by the previously described mass spectrometric technique. As a first step, a mixture of 1.34 mole percent hydrocarbon (as methane) in nitrogen was prepared. The mixture was allowed to flow at a rate of about 100 cc/minute through a 3/8" stainless steel tube packed with copper oxide heated in a tube furnace. Oxidation of the methane was neither complete nor reproducible. Even when no residual methane was present, as determined mass spectrometrically, it was not possible to produce the stoichiometric quantity of carbon dioxide. Analysis of the gases after passage revealed the presence of varying amounts of carbon monoxide.

Several applications of the method were investigated. The first of these was an attempt to determine low concentrations of oxygen in nitrogen by conversion of the oxygen to carbon dioxide with subsequent determination of the carbon dioxide by mass spectrometry. Several devices were constructed for this purpose, the most successful of which is shown in figure 1. The active element is a carbon filament produced by wrapping a graphite rod with cotton thread and carefully carbonizing it. The graphite is heated by passage of an electric current through the rod. The current is conducted into the cell through the platinum tubes attached to the copper rods which are soldered to the glass-to-metal seals. Standard taper joints allow easy access to the cell.

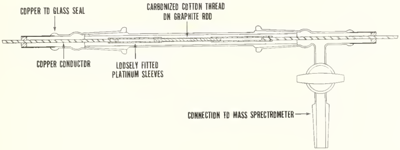

Figure 1. Device for conversion of oxygen to carbon dioxide.

A study of the efficiency of the device was made using known mixtures of low oxygen concentration. The mixtures were admitted to the cell which was connected to the inlet system of the mass spectrometer and the carbon was heated. After the reaction had gone to completion (about 1 min.), a portion of the gas in the cell was withdrawn for mass spectrometric

A carefully measured quantity of oxygen, more than sufficient for the combustion of methane, was added to the above mixture changing the calculated hydrocarbon content from 1.34 to 1.29 mole percent. It was now found that complete oxidation did occur. A mass spectrometric analysis of the dried gas after oxidation yielded the following results:

	1.33 mole percent
	1.34 " "
	1.33 " "
Average	1.33 mole percent

For the present and until further results are obtained by gravimetric determination of the carbon dioxide, the concentration of hydrocarbon is considered to be the average of the mass spectrometric results and the measured pressure of the individual components.

This mixture was then used to produce, by dilution, a second mixture whose calculated hydrocarbon content was 0.0207 mole percent. This sample was oxidized by passage over copper oxide and a portion was collected for mass spectrometric analysis. Results obtained for the analysis of five separate portions obtained on the same day gave the following results:

	0.0204 mole percent
	0.0206
	0.0206
	0.0208
	0.0207
Average	0.0206 mole percent CO_2

Results obtained after this were considerably higher and it was found that the oxidized sample contained oxygen far in excess of the amount added to the original mixture. Oxygen readily reacts in the ionization region of the spectrometer with tungsten carbide and, when rhenium filaments are used, with residual hydrocarbon to produce carbon dioxide and carbon monoxide. Furnace temperatures ranged from about 700 to about 1100° Celsius. At 1000° Celsius the dissociation pressure of oxygen over copper oxide is about 100 mm [3] which represents a significant amount. While some of the oxygen reacts with the materials of the tube and probably with reduced copper in cooler portions of the tube, enough gets through to seriously interfere with the analysis. The residual methane at lower temperatures indicates that the reaction is not complete even at flow rates as low as 50 ml/minute.

Before further dilution of the 0.0207 mole percent hydrocarbon mixture is made, some further investigation and redesign of the apparatus will be necessary.

4. Variations in Atmospheric Composition

The purpose of the development of a highly accurate mass spectrometric method for the determination of carbon dioxide was to provide standard reference materials by which the atmospheric carbon dioxide could be monitored for expected long-term increases. A similar interest has arisen concerning possible long-term variation in the oxygen content of the atmosphere. A preliminary program to study analytical methods for oxygen determinations was begun in cooperation with the Environmental Science Services Administration.

The program is divided into two parts. The first is the evaluation of commercially available instruments for the precise (± 0.01 mole percent oxygen in air) determination of oxygen while the second is the development of an absolute laboratory method for the determination of oxygen with an accuracy of better than ± 0.01 mole percent.

About the only rapid and precise instrumental methods available are based on measurement of the paramagnetic properties of oxygen [4]. An instrument utilizing the "Pauling" principle was obtained. The manufacturer did not claim the requisite precision but a technique was developed which provides highly satisfactory measurements. Two samples of air with lowered oxygen content were prepared by dilution with nitrogen from a third sample having an assumed oxygen content of 20.99 mole percent. The analytical results are shown below. The values are those measured against the assumed 20.99% mixture.

Determination	Mixture #2	Mixture #3
1	20.90	20.85
2	20.91	20.86
3	20.91	20.87
4	20.91	
	20.91 mole percent	20.86 mole percent

The calculated concentration of mixture #2 is 20.91 while that of mixture #3 is 20.84%. The error involved in the calculated concentration is about ± 0.02 mole percent.

The results for determination #3 were obtained by a person completely unfamiliar with the instrument and principle of operation and who had been given only brief instructions concerning the technique. The results indicate that the instrument can do what is needed - that is, produce results of the required precision in situations outside the laboratory.

Methods for the absolute determination of oxygen at atmospheric concentrations are few and not very satisfactory. Flowing gas volume measurements are difficult to make with an accuracy better than 1%. Accordingly, methods which would depend on adsorption from a flowing stream inherently lack accuracy. The measurement of oxygen by adsorption from static volumes has been the classical technique for accurate oxygen analysis and an excellent example of a monumental determination of this type appeared in 1912 [5]. However, the great care necessary for the construction of the equipment and the degree of experience required of the operator make this technique infeasible.

In 1841 Dumas and Boussingault [6] determined oxygen by weighing both the oxygen and the nitrogen. The oxygen was removed with hot copper. Large glass vessels were used and their results indicate a moderate degree of accuracy. Phosphorus has also been used to remove oxygen from air but not in a totally gravimetric method. This suggested the use of phosphorus and a gravimetric procedure as a possible relatively simple method for the absolute determination of oxygen.

The method is based on the use of the weighing flask shown in figure 2. The flask contains a few grams of phosphorus which are introduced through the base of the stop-cock into an inert atmosphere. The stopcock plug is inserted and the flask is evacuated. The phosphorus is carefully melted while pumping on the flask. It is agitated, cooled, and then remelted. This treatment eliminates any water carried over with the phosphorus or occluded in it. The tightly packed glass wool in the stopcock plug serves to filter out any particulate oxides of phosphorus in the subsequent evacuation.

The difficulties associated with the precise weighing of large volumes and the unavailability of a high capacity analytical balance limited the size of the bulbs to 200 ml. The weight of air contained in a bulb of this size is about 0.25 gram at 700 mm. A balance was available with sufficient capacity and capable of a sensitivity of 0.01 milligram. If the procedure was successful it should have been theoretically possible to determine atmospheric oxygen concentration to ± .005 mole percent.

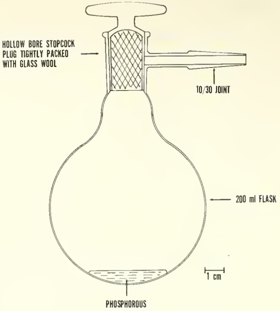

Figure 2. Flask for oxygen determination.

The procedure is as follows: air from a single cylinder of compressed air is dried over magnesium perchlorate and admitted to the carefully weighed bulb to a pressure of about 700 mm. The bulb is hung from the arm of a balance from whose other arm hangs a tare bulb of almost identical mass and volume. After a constant weight is obtained, the bulb is connected to a vacuum system, cooled with liquid nitrogen and evacuated. This is necessary since the vapor pressure of phosphorus is sufficiently high at room temperature to introduce a serious error in weighing. Other coolants were tried but only ice, which did not cool sufficiently, and liquid nitrogen appeared to leave no residue on the surface of the bulb. After pumping, the bulb is detached and all traces of grease are removed from the ground joint with carefully applied methylene chloride or other highly volatile solvent. The portion of the bulb that had been immersed in liquid nitrogen is then carefully washed with distilled water and dried prior to reweighing. The procedure yields the weight percent of carbon dioxide and oxygen. It is necessary to determine independently both the carbon dioxide and argon, but with less accuracy than that required for oxygen.

Results were disappointing and the reason is probably concerned with the cooling, evacuating and washing operations. The result obtained for sixteen determinations was 23.16 ± 0.06 weight percent of oxygen.

The rather high value of the average deviation eliminates this method from further consideration. However, by simply replacing phosphorus with a 1:1 sodium-potassium alloy a second method is available. The cooling prior to evacuation is no longer necessary and also the glass wool plug can be eliminated.

This method is in a preliminary stage of investigation but five good initial results have been obtained. The value for the weight percent of oxygen (the carbon dioxide is removed from the sample in this procedure) is 23.144 ± .008. The average deviation is now within the required limits and it is believed that it can be reduced with subsequent and more refined techniques.

B. Standard Reference Materials

1. Introduction

At present three types of gaseous mixtures are under investigation as possible standard reference materials. They are carbon dioxide in nitrogen, air of accurately known oxygen content, and inert gases containing traces of oxygen. The preparation of a standard air of known oxygen content was originally begun for the Environmental Science Services Administration and the entire work is described in the previous section. The analytical methods involved in the production of the carbon dioxide standard have already been described [1,2]. Further work on the preparation of the samples for distribution is outlined below. The experimental work on trace oxygen is included in this section because the work has been entirely supported by the Office of Standard Reference Materials.

2. Carbon Dioxide in Nitrogen

Six carefully analyzed master cylinders of carbon dioxide in nitrogen have been prepared. Three of these, representing concentrations between 310 and 380 parts per million have been transferred to 2-liter cylinders at a final pressure of about 500 psi (figure 3). The manifold for filling 20 cylinders at a time is shown in figure 4. The remainder of the mixtures will be retained as reference materials for the analysis of future mixtures.

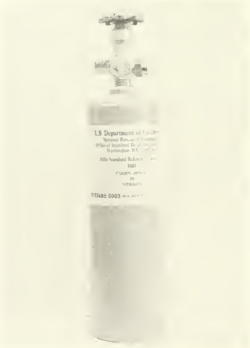

Figure 3. NBS Standard Reference Material number 1601.

Figure 4. Filling twenty small cylinders from master mixture.

The carbon dioxide-nitrogen system is relatively inert and little or no alteration of the composition should occur in storage. However, at least one sample from each batch will be retained for periodic comparison with known standards. Determinations were made to confirm that no change occurs during transfer from the large cylinder to the small ones. Also, it has been verified that no change occurs during room temperature storage in a 2-liter cylinder for sixty days, nor was any change observed during a period of 45 days in a cylinder kept at a temperature of 60° C. No change in composition was observed for either cylinder during stepwise reduction of its pressure from 500 psi to atmospheric pressure. However, on standing at atmospheric pressure at a temperature of 60°C for five days, the residual gas showed an increase of about 1 relative percent in its carbon dioxide content attributed to desorbtion from the cylinder walls. This behavior should have no significant detrimental effect on the usefulness of this reference material.

3. Trace Oxygen in Inert Gases

In 1960 Hersch [7] described a galvanic cell for the determination of oxygen. It consists of a silver-gauge cathode and a lead-foil anode separated by a film of potassium hydroxide absorbed in a sheet of porous plastic. The galvanic current is proportional to the oxygen content of the gas which is reduced at the cathode. The original cell design described by Hersch was modified to provide more efficient contact between the flowing gas and the electrode. The cell is shown in figure 5. It is incorporated into the gas manifold shown in figure 6 and schematically in figure 7. The gas washing bottle serves two purposes. It was found that cells exposed to dry gas at flow rates of about 100 ml/minute rapidly lose sensitivity and fail to respond after about 3 days' use. This probably occurs because of dehydration of the electrolyte. It was found that if the gas is saturated with water vapor the sensitivity remains essentially constant for a period of weeks. Accordingly, the gas washing bottle is filled with an ammoniacal cuprous chloride solution and copper turnings. Thus gas passing through it is not only saturated with water vapor but is also reduced in oxygen content and can serve as a "zero" oxygen reference gas.

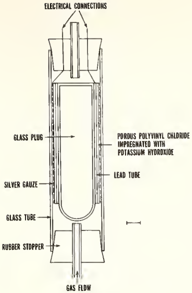

Figure 5. Experimental cell for determination of low concentrations of oxygen.

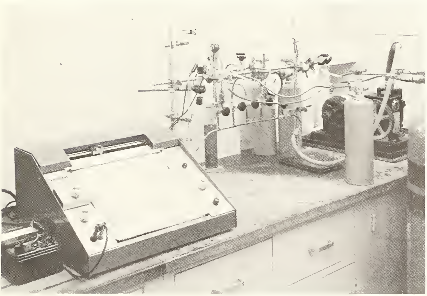

Figure 6. Apparatus for determination of trace quantities of oxygen.

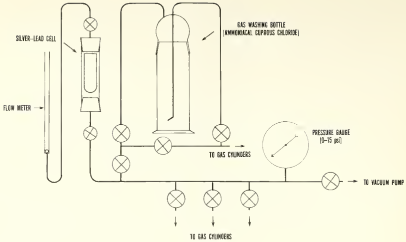

Figure 7. Manifold arrangement of apparatus for determination of trace quantities of oxygen.

A tube which can be substituted for the gas washing bottle is filled with manganous oxide and is also used to remove oxygen from the gases. The efficiency of the ammoniacal cuprous chloride and the manganous oxide has not yet been determined.

The remainder of the manifold is designed to allow easy switching between mixtures of varying oxygen content. It is constructed of copper tubing wherever possible because even short lengths of plastic or rubber tubing make it impossible to measure low concentrations of oxygen.

The current output of the cell was determined by measuring the voltage drop across a 250 Ω resistance with a recorder. It was found that at a flow rate of 100 ml/minute the cell response was about 0.3 mV/ppm (1.2 μA/ppm) in the concentration region below 100 ppm. Above 100 ppm the response decreases somewhat. The response below 100 ppm is essentially linear while above 100 ppm it becomes non-linear. Reproducibility of the curve from day to day is excellent while the output for a fixed concentration may vary somewhat.

From this preliminary work it appears that the method will be capable of an accuracy of about ± 2% over a concentration range from 100 ppb to 1000 ppm of oxygen in a gas.

A new cell is being designed and mixtures of accurately known oxygen content are being prepared. When these are completed, the accuracy and the lowest detectable limits of the method will be fully evaluated. In addition, a study will be made of the stability of composition of mixtures of oxygen in inert gases as related to the type of container and storage conditions.

C. Analytical Services

1. Introduction

The analytical services of this laboratory have been widely varied both as to type of sample and analytical technique. Described below are two analyses presented as examples of the types of problems which are submitted. The first is typical of many urgent requests for analytical services presented by other government agencies. The second is an example of cooperation within the National Bureau of Standards on a problem of mutual interest.

2. Identification of Combustion Products

The first problem was to aid in the investigation of a fatal blaze by the isolation and identification of volatile combustion products retained in the lung tissue of the victim. A portion of the lung tissue of the victim was removed during autopsy and immediately frozen. A portion of this sample was placed in a container, as shown in figure 8, and while the tissue was still frozen, the container was evacuated. The tissue was then allowed to thaw slowly and periodically samples of evolved gases were analyzed mass spectrometrically. It was necessary to concentrate the gases and also to remove residual air as well as the large quantities of water vapor evolved during the process. The volatile components were first collected at liquid nitrogen temperature in a trap which was then evacuated and warmed prior to the analysis of its contents. Water vapor was removed in an adsorption tube packed with magnesium perchlorate.

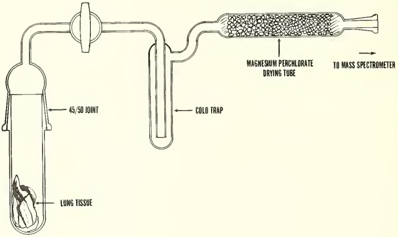

Figure 8. Apparatus for evaluation and collection of gases evolved from lung tissue.

This procedure enabled the isolation and identification of at least ten foreign substances suspected of being products of combustion of the fatal fire.

A portion of lung tissue from a victim of an accident not involving a fire was analyzed in a similar manner as a control. None of the compounds found in the first lung tissue were present in the second.

3. Determination of Light Water in Deuterium Oxide

The second analytical problem of special interest involves the periodic analysis of numerous samples of deuterium oxide for the light water content. The heavy water is to be used as the moderator in the National Bureau of Standards reactor. The analyses are to include initial analyses of heavy water as received from the supplier and periodic analysis of the heavy water in the reactor to detect any contamination with light water through the heat exchanger.

The requirements of the analysis necessitate a glove box whose atmosphere can be saturated with heavy water. This is shown in figure 9. The gas washing bottle seen at the rear of the box is filled with 99+% heavy water. The drying tower removes light water from a stream of air which is then saturated with heavy water and admitted to the glove box. The box is constantly flushed with this stream of saturated air.

The method of analysis is an infrared technique which requires carefully prepared standard mixtures. These standards are prepared from accurately weighed quantities of light and heavy water. All transfers of samples and standards to the infrared cells are performed in the glove box. The band at 2.95 μ due to DOH is measured using an infrared spectrometer. Preliminary results indicate that the method is capable of detecting differences in concentration of light water of about 0.02 mole percent in the range from 99.0 to 99.8 mole percent heavy water.

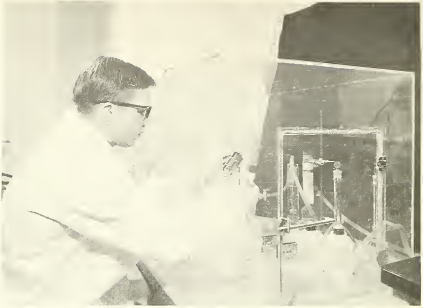

Figure 9. Glove box for transferal of heavy water samples to infrared cells.

4. Summary of Analytical Services

The following table gives a summary of the types of analyses performed during the past year and the number in each category.

Table 1. Summary of gas analysis services.

Material	Number of Samples	Sample Size	Determined
		Pure Chemicals	
N_2	1	Cylinder	Purity
Ar	1	Cylinder	Purity
NH_3	1	Cylinder	Monomethylamine, dimethylamine, trimethylamine

Table 1. (Continued)

Material	Number of Samples	Sample Size	Determined
Pure Chemicals (Continued)			
Monomethylamine	1	Cylinder	NH_3, dimethylamine, trimethylamine
Dimethylamine	1	Cylinder	NH_3, monomethylamine, trimethylamine
Trimethylamine	1	Cylinder	NH_3, monomethylamine, dimethylamine
Vinyl fluoride	1	5 ml STP	Purity
1,1-Difluoroethylene	1	5 ml STP	Purity
1,1,2-Trifluoroethylene	1	1 ml STP	Purity
Helium-3	3	30 ml STP	Helium-4, H_2, N_2, O_2, H_2O
Helium-3	20	30 ml STP	Helium-4
Nitromethane	2	10 ml	Nitroethane, nitropropane
Hydrogen	1	Cylinder	H_2O, N_2
Argon	2	Cylinder	N_2, O_2
Argon	2	Cylinder	H_2O, N_2, O_2, CO_2, and "other contaminants"
Organic Substances			
Gases evolved from lung tissue	5	5 ml STP	CH_4, HCN, C_2H_2, fluoromethanes, fluoroethanes, benzene, toluene, hydrocarbons, oxygenated hydrocarbons

Table 1. (Continued)

Material	Number of Samples	Sample Size	Determined
		Inorganic Substances	
Gaseous products of powder combustion	2	60 ml STP	H_2, H_2O, N_2, CO, CO_2, Ar
Gaseous products of polimerization of compounds of C-F and Si-F	1	10 ml STP	Molecular weights and composition of fragments
Si_2F_6	1	10 ml STP	Purity and cracking pattern
BF_3, B_2F_4, $C_2H_3BF_2$	4	1 ml STP	Atom percent B^{10} in each sample
Air	1	Cylinder	Impurities - none
Impurities in commercial fluorine	4	2 ml STP	N_2, O_2, Ar, CO_2, CF_4, SO_2F_2, SiF_4, C_2F_6, SF_6, C_3F_8, C_4F_8
Xenon	2	30 ml STP	Isotopic distribution
Atmosphere from a dry box	2	25 ml STP	H_2, N_2, O_2, Ar, CO_2
N_2-O_2 mixture	1	Cylinder	N_2 and O_2
NH_3BH_3	1	1×10^{-4} g	Cracking pattern and impurities
NH_3BH_3	1	1×10^{-3} ml STP	Cracking pattern and impurities
Argon	2	250 ml STP	Air
N_2, O_2, and CO_2 mixtures	4	Cylinder	N_2, O_2, and CO_2

Table 1. (Continued)

Material	Number of Samples	Sample Size	Determined
		Inorganic Substances (Continued)	
Air and CO_2 mixtures	4	Cylinder	Air and CO_2
Unknown gases	2	30 ml STP	Air, H_2
Unknown gases	6	10 ml STP	N_2, O_2, $C_2CL_3F_3$
		Inorganic-Organic Mixtures	
Gaseous products of reaction	1	0.1 ml STP	H_2, CH_4, H_2O, N_2, O_2
Gaseous products of reaction	1	0.1 ml STP	H_2, CH_4, H_2O, air, chloroform
Vinyl fluoride-difluoroethylene	1	1.0 ml STP	$C_2H_2F_2$, C_2H_3F, perfluorinated hydrocarbons
Products of fractionation	2	1 ml STP	cis-1,2-difluoroethylene, trifluoroethylene, chloroform, perfluorocarbons
Products of reaction	1	2 ml STP	Air, C_2H_2, PH_3, CO_2, high molecular weight hydrocarbon
Atmospheres within sealed recorders	11	500 ml STP	Organic vapor contamination of the N_2, He atmosphere

Table 1. (Continued)

Material	Number of Samples	Sample Size	Determined
		Deuterated Compounds	
Mixtures of C_2H_4, C_2H_3D, $C_2H_2D_2$, C_2HD_3, CD_4 as products of reaction	4	1×10^{-6} mole	Relative amounts of each in the mixtures
Mixtures of deutero methanes	4	5 ml STP	CH_4, CH_3D, CH_2D_2, CHD_3, CD_4, N_2, O_2
Deuterium	2	Cylinder	H/H&D ratio

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

2. POLAROGRAPHIC ANALYSIS

A. Introduction

The polarographic program during the past year has continued its emphasis on development of methods of improved precision, accuracy, sensitivity, and efficiency. These methods have been applied to a wide variety of samples encountered in the standard reference materials and service programs.

B. High Precision Polarographic Analysis

The double differential technique developed in this laboratory [8] has been applied to the analysis of a number of different materials where a precision better than that obtained with ordinary polarography was required. Procedures have been developed for the determination of cadmium in binary precious metal alloys and in double salts of the element. Methods for the determination of lead and zinc in metal organics have been studied and further work has been done on the determination of iodide in solutions. Several of these procedures will be outlined in the following sections.

1. Analysis of Cadmium-Silver Alloys

Sufficient alloy is weighed and the volume is selected to produce a final solution that contains about 50-100 ppm of cadmium. The alloy is dissolved in nitric acid and the silver is precipitated as the chloride. After filtration, the filtrate is evaporated to remove excess acid. The residual cadmium salt is dissolved in the supporting electrolyte of 1 N hydrochloric acid and transferred to a volumetric flask. The solution is measured polarographically by the comparative technique using standards preferably within 5 percent of the concentration of the analytical solution.

For illustration, an alloy containing 17.88 percent cadmium was analyzed using a 0.25 g sample and a final volume of 500 ml. Duplicate determinations agreed within 0.04 percent. The silver content could be determined gravimetrically by weighing the precipitated silver chloride.

2. Analysis of Cadmium-Gold Alloys

Binary alloys containing 0.5 to 7 percent cadmium have been analyzed using the following procedure. Sufficient alloy is weighed to produce a solution containing 50-100 ppm of cadmium in the dilution chosen; however, higher or lower concentrations may also be accurately measured. The metal is dissolved in aqua regia and gold is separated by precipitation with sulfur dioxide. The filtrate is evaporated to remove excess acid and finally the residue is dissolved in the supporting electrolyte of 1 N hydrochloric acid and adjusted to volume in a volumetric flask. Cadmium standards are prepared as already mentioned.

In order to check for possible cadmium occlusion, the gold precipitates were dissolved in aqua regia and reprecipitated. No cadmium was found in the filtrate so that this step is not necessary.

3. Determination of Cadmium in Salts

The cadmium content of salts, particularly the double salts of cadmium, and sodium sulfate may be conveniently analyzed by the comparative polarographic technique. In this case, the sample is merely dissolved in the supporting electrolyte, 0.1 N hydrochloric acid, and made up to volume to contain about 100 ppm of cadmium. Several salts containing 33 to 46 percent of cadmium have been analyzed in this manner.

4. Determination of Iodide in Ammonium Iodide Solutions

The comparative technique can also be used for the determination of iodide in solutions such as ammonium iodide. The iodide must be oxidized to iodate by heating gently with bromine water. Sodium carbonate and potassium chloride are then added to give solutions approximately 0.1 M in each prior to polarographic measurement. The comparative method has the advantage that accurate results may be obtained on small samples. One sample submitted consisted of one ml of ammonium iodide solution containing approximately 0.17 mg of ammonium iodide. This sample was diluted to 50 ml so that duplicate 20 ml-aliquots could be taken and treated as described above. Results on the duplicates showed an average deviation equivalent to 0.0003 mg/ml with respect to the original sample.

C. Major Constituent Analysis

Polarographic methods have proved to be extremely useful for rapid analyses where the precision attainable by conventional techniques is sufficient. Often several elements may be determined concurrently in the same solution using a minimum of sample. Some examples selected from recent experience are outlined in the following sections.

1. Determination of Zinc and Nickel in Nickel-Doped $ZnSiF_6 \cdot 6H_2O$

Polarography as a microchemical technique is quite advantageous when several determinations are needed on a limited supply of sample. In one instance a sample of $ZnSiF_6$ which had been doped with nickel for some EPR studies was submitted for determination of both zinc and nickel. Duplicate 5 mg samples were used, and silicon and fluorine were removed by addition of 6 drops of concentrated perchloric acid followed by fuming to dryness. The residues were dissolved in 0.2 ml of 50% perchloric acid, water, and 0.2 ml of pyridine and diluted to 10 ml. Nickel and zinc were then measured polarographically at about -1.0 and -1.3 V, respectively, vs. a mercury pool anode.

The excellent agreement which can be obtained is shown in table 2.

Table 2. Determination of nickel and zinc in nickel-doped $ZnSiF_6$.

	Found in sample, %	Calibration factors, μg/div. x 10^5
Ni	6.9, 6.7	0.414, .417
Zn	13.8, 13.9	.541, .537

2. Determination of Copper and Nickel in Alloys

Several samples of copper and nickel foil in which the copper-to-nickel ratio ranged from 50-50 to 80-20 were analyzed in order to both determine the composition and to check for possible inhomogeneity among samples of a given lot. In this particular case, the samples weighed from 50 to 100 mg each. The metals were dissolved in dilute nitric acid, evaporated to dryness, and the residues dissolved in 20 or 40 ml of hydrochloric acid and water. Twenty or 40 ml of pyridine was added and the samples were diluted to 500 or 1000 ml, depending on the copper and nickel concentration. Copper was measured at about -0.4 V and nickel at -0.9 V. The results showed an average deviation between duplicates of 0.07% for copper and 0.3% for nickel.

A silver alloy containing approximately 25% nickel was also checked polarographically for specification conformance.

Two hundred-mg samples were dissolved in dilute nitric acid and diluted to 45 ml with water. After heating to boiling, 3% hydrochloric acid was added dropwise to precipitate the silver. The solutions were allowed to set until cold, then were filtered, and the precipitate was washed with 0.5% nitric acid and finally with water. The silver could then be determined gravimetrically if desired. The filtrates containing the copper and the nickel were evaporated to dryness, the residues were dissolved in 20 ml of hydrochloric acid, 100 ml of water, and 40 ml of pyridine, and diluted to 500 ml. Copper and nickel were then measured respectively at about -0.5 and -1.0 V vs. a mercury pool anode. The results are shown in table 3.

Table 3. Determination of copper and nickel in silver alloy.

	Found in sample, %	Calibration factors, μg/div. x 10^3
Copper	24.47, 24.84	0.848, .844
Nickel	0.499, .494	.480, .444

D. Trace and Minor Constituent Analysis

Recent work on a variety of metals and alloys, particularly standard reference materials, has proved the advantages of polarographic methods. Generally, the polarographic determinations could be made directly with no prior separations on rather complicated matrices yielding results of comparable or improved accuracy over more time-consuming conventional wet methods.

1. Determination of Lead in Leaded Steels

The determination of lead in many matrices has been particularly successful by polarography. Often it can be determined directly with no separation. The formate-buffer method [9] for lead can be applied to its direct determination in steels where 0.05% or greater is present. Copper in amounts above 0.005% can also be determined in the same solution. This method was applied to a leaded steel, SRM 130a. The sample was also checked by this analyst by two gravimetric techniques, lead molybdate and electrodeposition of lead, used by other analysts.

For the polarographic determination, 1-g samples were dissolved in 10 ml of 50% hydrochloric acid and a small amount of potassium chlorate solution was added as an oxidizing agent. The solutions were evaporated to about one-half the original volume after which were added 5 ml of 20% hydrazine hydrochloride, 5 ml of saturated sodium formate solution, and 2 ml of 0.5% starch solution. The solutions were heated just below the boiling temperature to reduce the iron. In some cases, additional hydrazine hydrochloride was necessary for complete reduction. The solutions were then cooled and diluted to 25 ml and lead was measured at about -0.5 V vs. a mercury pool anode. Copper could also be measured at about -0.25 V. Large amounts of tin, arsenic, titanium, or molybdenum may interfere with the lead determination and excesses of antimony and molybdenum may interfere with the copper determination.

In the lead molybdate procedure, 5-g samples were dissolved in 17.5 ml of concentrated hydrochloric acid and 100 ml of water and diluted to 250 ml with hot water. The solutions were gassed with hydrogen sulfide, then filtered and the precipitate washed with 1% hydrochloric acid. The precipitates and paper were then treated with 5 ml of perchloric acid and repeated additions of nitric acid to destroy organic material. The resulting solutions were diluted to 50 ml and free sulfur was filtered off. After evaporation to reduce the volume of the solutions some silica appeared, making necessary an additional filtration for its removal. The volume of the filtrates was then adjusted to 75 ml, and 2 g of tartaric acid was added, and the solutions were boiled until the lead molybdate coagulated. The lead molybdate was then filtered, ignited at 600°C and weighed.

For the electrolytic determination of lead as PbO_2, 5-g samples were dissolved and lead separated with hydrogen sulfide as described above. Lead was then plated onto a platinum anode at 0.2 amps and weighed as PbO_2.

The results, as well as those obtained by other analysts, and the certified value are shown in table 4.

Table 4. Comparisons of methods for lead in leaded steel, SRM #130a.

% Lead			
Polarographic	Gravimetric	Other analysts	Certified value
0.228	0.229^a $.227^b$	0.229^a, 0.228^a $.223^a$, $.225^a$ $.231^a$, $.229^b$ $.227^a$	0.228

^{a}PbS-$PbMoO_4$

^{b}PbS-PbO_2

The polarographic values are in excellent agreement with those obtained by the gravimetric techniques. The polarographic procedure required less than an hour, compared with several days for either of the other two procedures. The polarographic method also has the additional advantage of requiring a smaller amount of sample.

2. Determination of Lead in Nickel Oxide

Trace amounts of lead may be determined in nickel oxide also without separations. The method is rapid and simple and gives results which are in good agreement with those obtained by other procedures. One-gram samples were dissolved in dilute nitric acid, five ml of perchloric acid was added, and the samples fumed almost to the appearance of salts. Water and hydroxylamine hydrochloride were added and the solutions were diluted to 25 ml. Lead was measured at about -0.45 V using the method of standard additions. The results are shown in table 5.

Table 5. Determination of lead in nickel oxide.

SRM	Pb, %	Determinations	Standard deviation
671	0.0014	3	0.0003
672	.004	2	.0003
673	.0004	6	.00004

The peaks were not well-defined for the lowest range. For concentrations smaller than those measured, better results would be obtained by an initial separation of the lead by some means such as solvent extraction.

3. Determination of Copper, Lead and Cadmium in Intermediate Purity Zinc

Polarography is one of the few techniques whereby several elements may be determined concurrently in the same solution. This has been illustrated to great advantage in some recent homogeneity checks and determinations in intermediate purity zinc, SRM #683. Not only was it possible to determine copper, lead, and cadmium at the same time, but the average deviation in the ppm range was generally better than the 2 to 5 parts in 100 normally obtained by the single cell direct mode of operation and was considerably better than the precision usually obtained in the trace ranges by many other methods.

During this investigation, it was noted that an extreme dependence existed between the amount of zinc present and the concentration of copper, cadmium, and lead found. In fact the concentration found varied almost inversely with sample size. This was attributed to the sizeable decrease in diffusion coefficients of copper, cadmium, and lead which occurred in the rather concentrated solution of zinc chloride (see also ref. [10]).

The variation in the calibration factors for copper and lead with the amount of zinc present is shown in table 6.

Table 6. Effect of zinc concentration on peak currents of copper and lead.

	Sensitivity ppm/μA	
Zinc, g/ml	Cu	Pb
0.00	1.2	1.3
.30	1.9	2.3
.48	2.9	4.3
.50	3.2	4.5

In preparing the calibration curves, it was therefore necessary that the same amount of zinc be present in the standard solutions as was in the sample to be analyzed. Duplicate samples weighing 3 to 5 grams of each lot of the intermediate purity zinc were dissolved in 15 ml of concentrated hydrochloric acid after the samples had first been etched with dilute nitric acid, rinsed, and dried to remove surface impurities. The solutions were evaporated to dryness below 100°C, dissolved in 2 drops of hydrochloric acid and water, and diluted to 10 ml. Copper, lead, and cadmium were then measured subtractively against a blank at about -0.2, -0.5, and -0.7 V vs. a mercury pool anode, respectively.

The results on SRM #728 are shown in table 7.

Table 7. Determination of copper, lead, and cadmium in three lots of intermediate purity zinc, SRM #728.

	Amount, ppm		
Sample designation	Cu	Pb	Cd
Lot 1	5.76	10.81	1.12
Lot 2	5.82	10.84	1.17
Lot 3	5.89	10.92	1.10
General average	5.825	10.857	1.13
Pooled average deviation of duplicates	± .08	± .003	± .02
Pooled average deviation of any lot from the general average	± .04	± .04	± .03

Except for lead, the average deviations of duplicates within any lot is essentially the same as the average deviation of any one lot from the total average, thus indicating that, within the limit of the measurement error, there is no difference in the copper, lead, or cadmium content in these three lots. The increased precision for lead is probably owing to the extremely well-defined lead peak obtained in these solutions.

Copper, cadmium, and lead were also determined by the same technique on various portions of the bars of different lots of intermediate purity zinc, SRM #683, and the results are shown in table 8.

Table 8. Determination of copper, lead, and cadmium in bars of intermediate purity zinc, SRM #683.

Sample designation	Amount, ppm Cu	Pb	Cd
1-36A-4	6.10	10.83	1.07
2-37B-3	5.85	10.34	1.01
3-27A-3	5.88	9.60	1.09
3-27A-7	6.01	10.45	1.01
3-27B-3	5.91	10.40	1.04
	5.95 ± .08	10.32 ± .30	1.04 ± .03

Duplicate samples were not taken; however, it is seen that in this case the average deviation of the results for lead is greatly outside the measurement error shown by the determinations on SRM #728. Additional work on this sample is planned in which duplicates of individual samples will be used.

4. Determination of Cadmium in Cadmium^{109} Solution

Two ml of a solution 0.1 N in hydrochloric acid containing cadmium^{109} which had been used in some radioactive tracer work was measured directly at about -0.7 V without dilution, using the solution as its own supporting electrolyte. The cadmium concentration was found to be 0.61 ppm. The presence of a small amount of lead, estimated to be about 0.2 ppm, was also detected. This was an unsuspected impurity in this material.

E. Small Sample Analysis

The work started earlier on small sample analysis has been continued on additional nickel-chromium-copper-aluminum and antimony-bismuth thin films and has also been extended to include thin films of lead selenide and lead-tin-telluride.

1. Analysis of Antimony-Bismuth Thin Films

Because of the errors which would be involved in weighing the very small amount of film, about 90 to 200 micrograms, deposited on a glass plate weighing approximately 5 to 10 grams, it was necessary to determine both antimony and bismuth to obtain the relative amounts of each. On the basis of calibration curves, the results obtained by single-cell operation were thought to have an error no greater than 2 to 5%. It was possible in one case to check the magnitude of this error, using a larger amount of sample. The source material, consisting of a binary mixture of pure antimony and bismuth, was dissolved in hydrochloric acid together with a few ml of 30% hydrogen peroxide and diluted to 250 ml. Ten ml of 50% sulfuric acid was then added to a 5-ml aliquot of the solution and the solution evaporated to fumes at low heat. The solutions were diluted with 10 ml of water, heated to boiling, and 5 ml of water saturated with sulfur dioxide was added. The solution was then boiled until all sulfur dioxide was expelled. Five ml of 50% hydrochloric acid was added, the solution was diluted to 250 ml, and bismuth and antimony were measured at -0.1 and -0.2 V, respectively. The results are shown in table 9.

Table 9. Determination of bismuth and antimony in film deposition source material.

	Found		
Sample taken, mg	Bi, mg	Sb, mg	Total sample, mg
7.121	5.417	1.690	7.107

For the analysis of the thin films, all volumes were cut 5 or 10 fold.

2. Analysis of Lead Selenide Thin Films

The lead selenide films, which were prepared by Gerald Hoff, Naval Ordnance Laboratory, could be analyzed using a variety of supporting electrolytes. Lead may be measured in a 1 M sodium hydroxide supporting electrolyte with no interference from selenium. Since it was desired in this case to know the lead composition with an error no greater than 1%, it was necessary to measure by the comparative mode of operation. The films, which were deposited on a crystal of sodium chloride, were stripped with hydrochloric and nitric acid, evaporated to dryness, and dissolved and diluted to sufficient volume with 1 M sodium hydroxide to give a concentration of approximately 50 ppm. Lead was then measured comparatively against standards in the same manner and the results are shown in table 10.

Table 10. Determination of lead in lead-selenide thin films.

Sample designation	Pb found, mg
#1	1.634 ± .005
#3	3.989 ± .039

3. Analysis of Lead-Tin-Telluride Thin Films

The lead-tin-telluride films were prepared in connection with some lattice parameter studies by R. F. Bis, Naval Ordnance Laboratory [11]. For these films of varying ratios, both the lead and tin content were needed with an error of less than 2%. The method of determining the total amount of lead and tin, which are reduced at the same potentials, in a hydrochloric acid supporting electrolyte and then determining lead alone by making the solution 1 M in sodium hydroxide to obtain tin by difference, does not yield sufficiently accurate results.

However, with twin cells it seemed possible that the lead peak could be subtracted electronically from the lead and tin peak thus giving more accurate results. Investigation of this approach was made with several standard solutions ranging in final concentration from 20 to 60 ppm of lead and 10 to 30 ppm of tin. Duplicate aliquots were taken; one was treated with hydrobromic acid and bromine mixture to remove all tin. Both aliquots were then made up to volume in 6 M hydrochloric acid. The solution containing lead alone was placed in one cell and that containing lead and tin in the second cell. Measurement was then made with cell one alone, which gave the peak height of lead, then cell two was measured against cell one to obtain the peak height for tin. Although this simple procedure would be adequate for many purposes, average deviations of 3% were obtained which were too large for the samples under study. Investigation of a complexing media with sufficient resolution to allow simultaneous determination of lead and tin showed similar errors. It appeared then that the most accurate results would be obtained by separating lead and tin and using the twin cell mode of operation. It was subsequently shown that complete recovery of both lead and tin in the amounts to be found in these samples could be achieved by a cupferron extraction of the tin.

The procedure adopted was as follows: The solutions were diluted to 30 ml in about 6% hydrochloric acid, cupferron was added, and the tin cupferrate extracted with 5-ml portions of chloroform. The organic material was destroyed in the tin extract by fuming with nitric and sulfuric acids and in the aqueous portion containing lead and tellurium by fuming with nitric acid and perchloric acid after removal of hydrochloric acid on a steam bath. The tin residues were dissolved in 25 ml of hydrochloric acid and diluted to 50 ml, and the lead-tellurium residues were dissolved in 5 ml of hydrochloric acid and diluted to 50 ml.

The recovery of both lead and tin was complete and the standard curve in the expected region of the samples was linear. The results shown in table 11 for the analysis of typical thin films illustrate the utility of the method.

Table 11. Determination of lead and tin in lead-tin-telluride thin films.

	Found, mg	
Sample designation	Lead	Tin
46	0.309	0.253
47	.216	.457
48	.427	.343
49	.177	.099
50	.284	.103
51	1.05	.050

F. Ultra Trace Analysis

Anodic stripping techniques are generally most advantageous for concentrations of the order of 10^{-7} or 10^{-8} M. In this laboratory a Sargent* fast-scan polarograph in conjunction with a Kemula-type electrode, as shown in figure 10, has been used for a variety of determinations in water and high purity reagents. Cathode ray polarography has also been used in cases where sufficient sample is available for concentration of the ions in question to the $10^{-7}\underline{M}$ level. Anodic stripping was used for the determination of copper, cadmium, and lead in the continuing analysis of a number of reagents prepared in other laboratories. Some typical results are shown in table 12.

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*See last paragraph of preface.

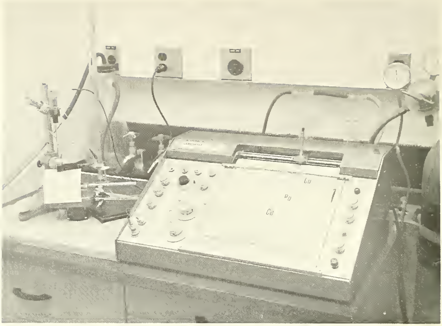

Figure 10. Apparatus for anodic stripping polarography.

Table 12. Determination of copper, cadmium, and lead in reagents.

	Found, ppb						
	Commercial	Commercially purified			Laboratory purified[a]		
	HCl	HNO_3	HCl	HF	HNO_3[a]	HCl[a]	HF[a]
Cu	23	b	19	b	b	b	b
Cd	< 1	b	3	b	b	b	b
Pb	4	2	4	29	1	0.6	0.5

[a] Prepared by Marcia Newell of the U. S. Geological Survey.

[b] Not examined for Cd and Cu.

For these determinations 10- or 20-ml samples were evaporated to dryness with the addition of a few drops of nitric or perchloric acid and the residues dissolved in 5.0 ml of 0.1 N hydrochloric acid. The anodic dissolution peaks were then measured after a 5-min pre-electrolysis into the mercury drop.

The distilled water in the new facilities at Gaithersburg has been analyzed over a period of time to determine its suitability for use in various other determinations being performed. When the system was first installed, approximately 150 ppb of copper, 13 ppb of lead, and 20 ppb of zinc were found. However, repeated flushings of the pipes and tanks with distilled water resulted in considerable improvement. The results over a 6-month period are shown in table 13.

Table 13. Analysis of distilled water.

	Found, ppb			
Date sampled	Cu	Pb	Zn	Cd
5-9-66	4	8	5	-
5-10-66	3	-	5	-
6-7-66	-	0.6	-	-
7-14-66	-	1	-	-
12-19-66	0.5	.6	-	< .02

The distilled water of another government laboratory was also checked for lead in order to detect possible contamination arising in several steps of a process for the production of a fish protein concentrate. For this analysis, a 20-fold concentration by evaporation was made and the solution measured in 1 N hydrochloric acid. Their original distilled water was found to contain about 10 ppb of lead while rinsings from a blender used in a procedure to monitor the process contained about 20 ppb. Ash samples of the fish concentrate were also checked for lead. Samples which had been ashed by the Bureau of Commercial Fisheries were treated with 1 ml of nitric acid, 2 ml of hydrobromic acid-bromine mixture, to remove any tin present, followed by addition of 2 ml of 50% perchloric acid and evaporation to dryness. The residue was treated with 2 ml of 50% hydrochloric acid, evaporated to dryness, and dissolved by heating with 5 ml of 50% hydrochloric acid and about 10 ml of water. The solution was then diluted to 25 ml and lead was measured subtractively at about -0.5 V vs. a mercury pool anode. This method offers considerable improvement in sensitivity and time required for analysis over the AOAC spectrophotometric method which is subject to many separations and/or interferences.

Table 14. Analysis of reactor water.

	ppm				
Sample	Al	Fe	Cu	Cd	Pb
A	0.02	< 0.1	-	-	-
B	.17	< .1	-	-	-
C	.15	< .1	-	-	-
D	-	-	0.22	-	-
E	-	-	.03	-	-
F	-	-	.18	-	-
G	-	-	.02	-	-
H	-	-	.16	-	-
I	-	-	.004	0.0009	0.0006

A number of samples of reactor water have also been checked for several elements including copper, cadmium, lead, iron, and aluminum. Copper, cadmium, and lead were done by methods similar to those just described. Iron and aluminum were measured concurrently after formation of a complex with Solochrome Violet RS by a method similar to that described previously for aluminum [12]. Iron is reduced at about - 0.7 V and aluminum at about - 0.8 V vs. a mercury pool anode. Typical results on various samples are shown in table 14.

(E. J. Maienthal and S. F. Cooper)

3. COULOMETRIC ANALYSIS

A. Introduction

The coulometry program has several objectives: the development of new, and the improvement of existing, methods of highly precise and accurate analysis; absolute determinations of stoichiometry of standard reference and research materials; performance of high precision custom analyses in support of other research programs and needs of the National Bureau of Standards; and development of precise methods of microchemical analysis. Significant progress has been achieved in all of these areas. In this report a brief description is given of some of the highlights of the work.

Facilities and coulometric equipment used in this laboratory have been described previously [1,12], and are the same with one exception. An ultramicro balance has been acquired, the performance of which will be described briefly.

B. Analysis of THAM

THAM (2-amino-2-hydroxymethyl-1,3-propanediol), a compound which is widely used as physiologically active material, has been issued by NBS as a calorimetric standard. In the course of selection of material to be issued, five different lots of THAM were submitted for coulometric determination of purity on the basis of acidimetric titrations.

Attempts to titrate THAM coulometrically by a direct procedure, as was done previously [13] with sodium carbonate according to the reaction $2H_2O \rightarrow 4H^+ + 4e + O_2$, failed. The coulometric titer for THAM fell several percent below 100%. Systematic surveys of the literature from 1947 to 1966 revealed no attempts to titrate THAM coulometrically. In general, its electrochemical oxidation has not been previously studied.

However, there are several articles on attempts to coulometrically carry out acidimetric titration of aromatic amines, which were unsuccessful due to oxidation of amines themselves. The electrochemical oxidation of the aromatic amines has been attributed to oxygen, liberated at the anode. The electrochemical oxidation mechanism of THAM is at present under investigation in collaboration with Alexander Fatiadi of the Organic Chemistry Section.

An indirect coulometric procedure developed in this laboratory for the alkalimetric titration of THAM circumvents the difficulties associated with its electrochemical oxidation. This method consists of the coulometric back titration of excess hydrochloric acid which is added by weight to THAM samples. A differential potentiometric inflection point of ΔpH/C as a function of charge is taken as the titration end point. The hydrochloric acid is of azeotropic composition and its actual hydrogen ion concentration is determined coulometrically. Table 15 summarizes the alkalimetric assay of five lots of THAM with corresponding standard deviations of the means for each set.

Table 15. Acidimetric assay of five different lots of THAM.

Lot	Assay, %	$s/\sqrt{n}$ %*
A	99.959	0.001
B	99.936	.003
C	99.905	.002
D	99.875	.003
Single crystal	99.952	.014

*$s/\sqrt{n}$ represents the standard deviation of the mean.

A few exploratory experiments were conducted to determine the cause for the low assay of THAM. Preliminary experiments were run to determine the effect on its assay of drying of THAM at 110° C. This was previously investigated by Riddick and co-workers [14,15]. Riddick's data indicate that a 10-hour drying period at 110° C causes decomposition of THAM, a lower assay, and a change in its appearance. A 38-hour drying of three different lots of THAM at 110° C produced no change in the appearance of lot B or of single crystals but produced a significant change in the appearance of lot D.

Following the 38-hour drying at 110° C, the assay value of lot B increased to 99.964 but the assay of lot D decreased to 99.785. The behavior of the unrecrystallized lot D, then, is qualitatively in agreement with the data of Riddick, but the behavior of recrystallized THAM is different. The assay of the recrystallized THAM increased upon drying at 110° C, indicating volatilization of an impurity (such as mother liquor).

Study of weight loss as a function of time also indicates the possible existence of some readily volatile impurity in the material. It is also apparent that THAM itself is quite volatile at 110° C. This is indicated by a plot of the rate of weight loss for lot B, shown in figure 11. The integration of the shaded area would represent the weight loss of material above that which is lost by the volatilization of THAM itself. This latter rate of about 0.0195% per hour appears in the region beyond the 17-hour exposure time at 110° C. The evaluation of the integral shows that the volatile material weight loss is about 0.04%, which is in a reasonable agreement with the increase in the assay of THAM B after the 38-hour drying period, as determined by titration.

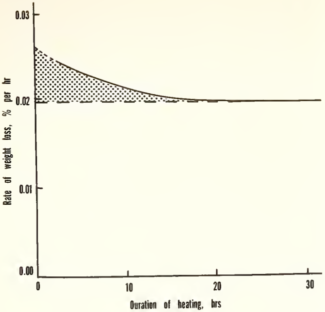

Figure 11. Stability of THAM during heating at 110° C.

Additional work with THAM is planned as follows: elucidation of the mechanism of the electrochemical oxidation of THAM; establishment of conditions necessary to obtain stoichiometry approaching 100.000%; study of reasons for deviation of the available lots of THAM from 100% stoichiometry; investigation of the possible absorption of CO_2, and measurement of the concentration of CO_2 in these solids.

C. Improved Coulometric Titration of Halides

During a period of several years, this laboratory has acquired considerable experience with the coulometric titration of halides using electrogenerated silver ions. In the past, an acetic acid-sodium nitrate supporting electrolyte has been used together with a biamperometric indicator system. Recently, effort has been devoted to the improvement and possible simplification of this system, making it more versatile to enable analysis of samples containing from a few hundred milligrams to samples containing microgram amounts of halides. Thus all aspects of the titrations were reconsidered. As a result of this critical reconsideration, a modified potentiometric end-point system was developed which enables titration of halides to be accomplished with even higher precision than that previously reported.

Biamperometric end-point detection was used in the previous work. The principle objection to this detector is irreproducibility of indicator current due to changes in stirring rate, positioning of electrodes and obstruction of electrodes by the precipitate. Thus for each titration a complete titration curve has to be plotted to enable extrapolation to the residual current.

The electrode system now chosen is an old one but it is used in a somewhat nonconventional manner. A glass electrode is used as a reference electrode while a silver-silver chloride electrode serves as the indicator. On the basis of the research of Craig and coworkers [16] on the stability of silver in perchloric acid medium and on the current efficiency of generation of silver ion in this electrolyte, a supporting electrolyte consisting of 1 $\underline{M}$ $HClO_4$ - 1 $\underline{M}$ $NaClO_4$ was chosen.

The system can be represented as follows:

$$Ag/AgCl(s),\ HCl|glass|HClO_4(1\underline{M}),\ NaClO_4(1\underline{M}), Cl(x), AgCl/Ag.$$

The advantages of the new indicator system are the following:

1. Elimination of losses of unknown by diffusion into the liquid junction.
2. Minimization of polarization of the indicator

electrode by use of a high resistance indicator circuit.

3. Stability of the end-point voltage.
4. Feasibility of titration to a preselected end-point voltage with significant reduction of the time of analysis.
5. Feasibility of titration using a microcell.

The e.m.f. of the above cell at the equivalence point is independent of the amount of chloride in the sample and is determined strictly by the solubility product of AgCl and hydrogen ion concentration (which do not change). Thus one can simply titrate to the preselected e.m.f. in the vicinity of the equivalence point.

A typical set of analytical results is shown in table 16 together with the standard deviation of a single determination.

Table 16. Determination of macro amounts of chloride.

mg Cl^- added		mg Cl^- found	
99.44		99.4418	
99.44		99.4473	
99.44		99.4416	
99.44		99.4425	
	Average	99.4433	s = 0.0028 mg

This system has been used for the analysis of single crystal KCl, SRM rubidium chloride, and synthetic sea water samples, for example.

A cell of this type was designed and constructed which enables titration of halides in only 1 ml of electrolyte. The cell is shown in figure 12. A sealing tube with a fine-porosity fritted glass disk is the titration compartment. A coil of high purity silver wire is both the generator anode and the indicator electrode. The glass reference electrode is placed in the perchloric acid medium outside the titration compartment thus reducing the number of probes to be inserted into the small titration volume. A drawn-out polyethylene tube is used to deliver nitrogen into the titration compartment. The nitrogen stream is used to stir and mix the solution. In this cell, amounts of chlorides as small as 200 ng have been titrated with a standard deviation of 12 percent.

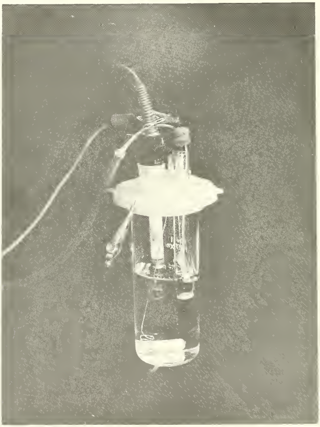

Figure 12. Coulometric cell for microtitrations of halides.

D. Coulometric Determination of Silver in Alloys

Determination of silver by conventional gravimetric or volumetric procedures in Ag-Cu-Ni alloys would normally present no difficulty if an accuracy of a few tenths of one percent suffices. On the other hand if an accuracy better than 0.1 percent is necessary, conventional methods would involve relatively cumbersome and tedious procedures.

A simple coulometric method was developed which produces results accurate to at least 0.05%. The method involves dissolution of silver with 1:1 nitric acid in 150 ml Erlenmeyer flasks, removal of the excess nitric acid by evaporation with sulfuric acid, addition of a known but excess amount of potassium chloride, previously analyzed by the above-described method, and finally the coulometric back titration of the excess chloride. A set of typical results of analysis of 100 mg samples of alloy is given in table 17.

Table 17. Coulometric analysis of silver alloy.

Sample No.	Ag, %	
1	74.94	
2	74.81	
3	74.89	
Average	74.88	s = 0.04%

This procedure, however, points out the need for SRM alkali metal halide standards which could be conveniently used without the requirement of preliminary assaying.

E. Mass Measurement Problems in Coulometry

This section describes three aspects of mass measurement confronting those working in the field of coulometry which, however, are not necessarily unique to coulometry:

(1) accurate mass measurement; (2) mass measurement of micro and ultramicro samples; (3) weighing of liquid samples.

For relatively large masses (1 g, for example) conventional microbalances are sufficiently sensitive to enable determination of weight precise to a few parts in 10^6. Since coulometry is an absolute method of analysis, absolute mass measurements are a prerequisite for accurate analysis. The most reliable method for such mass measurements is substitution weighing, where the mass of the specimen is replaced by an appropriate compliment of accurately calibrated weights and the remaining inequality of the two masses is obtained from the calibrated visual scale of the microbalance. To insure the accuracy of such mass comparisons and to eliminate the determination of the rest point of the empty balance, the above intercomparison may be carried out as a series.

Subsequent to such intercomparison, one must conduct tedious, time-consuming, multistage calculations which introduce the possibility of arithmetical errors. For this reason, a computer program "MASS" was written which reduces the chances of error to a minimum. The data necessary for accurate calculation of mass by means of this computer program are as follows: sample number; the weights used, each identified by its number; the residuals read from the optical scale of the balance; temperature in the balance case; pressure; relative humidity; density of sample; equivalent weight of unknown.

On the basis of the above data, the computer furnishes the following information: corrected sum of weights; volume of weights; average of residuals; sensitivity of the balance; weight of sample in air; air density; true mass; calculated number of meq; estimate of the number of coulombs required to titrate the sample. The computation time for one sample through the use of this program is about 2 seconds.

One of the significant features of this program is that the corrected mass values and volumes of individual weights of the set of weights, used in this laboratory, have been committed to the memory of the computer as a matrix, thus one only needs to specify the weight designations to obtain accurate mass values.

To enable accurate mass measurements of smaller samples (ca. 100 mg or less) a quartz-fiber torsion balance has been obtained. It is a two pan balance capable of weighing safely samples up to 250 mg in mass. To test the performance of such a balance under laboratory conditions, a comparison of two 100-mg weights was made over a period of several days. The results of this comparison are shown in figure 13. The data are plotted as a correction to one of the weights, taking the mass of another weight as standard, as a function of time. Such mass measurements can be done with at least 0.5 μg precision even when such systematic trends as occurred on 3-15-67 are present, corresponding to a precision of 5 parts in 10^6.

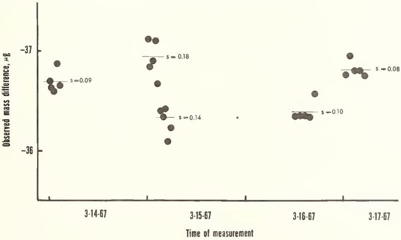

Figure 13. Intercomparison of two 100-mg tantalum weights over a period of time.

Since the two tantalum 100-mg weights were compared in these experiments by the substitution method, it is difficult to attribute such phenomena as the drift on 3-15-67 to balance performance. One must therefore conclude that the mass of one of the weights or of both weights was changing during that day. This may, at first, sound ridiculous yet on the other hand the surface finishes of the two weights were not identical even to the naked eye and a greater adsorption of moisture on the surface of the "rougher" weight could explain this occurrence. Even a monolayer of water 1 cm^2 in area would weigh approximately 0.03 μg. This experience points out the care which must be exercised in measurements of small mass or small mass-difference. Factors which might play a significant role are adsorption on the surface of specimens and accumulation of dust on the weights, specimens, and balance pans.

The third aspect of mass measurement, that of solutions and liquid samples, is another area of interest. Generally the equipment available for such purposes (weight burets in particular) is bulky and massive, and often exceed the capacity of modern microbalances (e.g. in excess of 20 g). Evaporation from the tips of syringes presents another problem. In this laboratory, a method was developed for weighing liquid samples in a 1-ml disposable syringe. Figure 14 shows such a syringe intact (A) and disassembled (B). The parts are: (1) silicone rubber piston with polyethylene handle; (2) glass body of syringe; (3) platinum needle with Lucite hub; (4) silicone rubber disk such as a septum used in gas chromatography. The function of all parts with the exception of (4) is self-explanatory. This rubber disk is used to prevent evaporation from the tip. Such a system filled with water (1 ml) weighs about 7 g and can be conveniently handled on practically any microbalance, enabling mass measurements to a few micrograms.

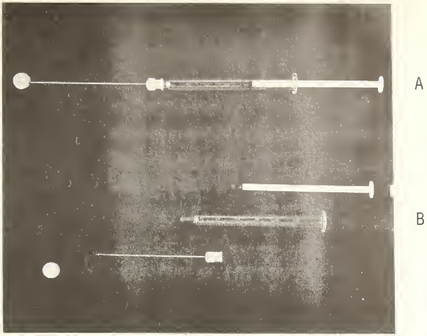

Figure 14. Use of a 1-ml syringe as a micro weight buret.

The loss of water from such a closed system was checked over a period of several days. The rate of weight loss is linear and corresponds to 100 µg/hr. Even if as much time as an hour intervenes between weighing the full syringe and reweighing it after delivery of a 100-µl sample, an accuracy of at least 0.1% can be obtained.

(G. Marinenko and C. E. Champion)

4. ELECTROANALYTICAL MEASUREMENTS

A. Introduction

A research program primarily concerned with the development and evaluation of novel techniques and instrumentation to improve the sensitivity, accuracy, and precision of trace and microchemical electroanalysis was initiated in August 1966. Two studies have been successfully completed to date: (1) the development of the technique of modified linear null-point potentiometry; (2) the evaluation of a modified fluoride activity electrode for use in microanalysis. In addition, a brief study was made on the response characteristics of an iodide-selective rubber membrane electrode.

Preliminary work has been started combining the modified fluoride electrode with the technique of linear null-point potentiometry to achieve a relatively simple microanalytical method of high sensitivity and precision for the determination of fluoride.

B. Research Activities

1. Microchemical Determination of Silver by Modified Linear Null-Point Potentiometry

a. General Considerations. Precision null-point potentiometry [17] has been modified and applied with success to the microchemical determination of silver. The novel features of this technique, which result in significant improvement over the conventional method, include:

1) capability for analysis of solution volumes of 0.1 ml
2) coulometric generation of the reagent (Ag^+), in situ, for increased accuracy and prevention of dilution effects;

3) instrumentation utilizing operation amplifiers as voltage followers to prevent significant electrochemical reaction at the indicator electrodes;

4) semi-logarithmic plotting of the data (logarithm of the amount of reagent added vs. the concentration cell potential) whereby the equivalence point can be graphically evaluated by a linear extrapolation or interpolation to zero cell potential;

5) computer analysis of the data to obtain the equivalence point from the intercept of a least squares fit to a straight line.

b. Principle of the Method. In principle, null-point titrimetry is a very simple concentration cell technique based on the adjustment of the solution concentration in one of the electrochemical half-cells to the concentration of the analate half-cell as evidenced by zero cell potential at the equivalence point. This potential is measured between two identical indicator electrodes specific for the species being determined.

For the determination of silver, the concentration cell employed is

$$\mathrm{Ag}|\mathrm{Ag}^+(C_{NP}),\ \mathrm{H_2SO_4}(1\underline{N})\|\mathrm{H_2SO_4}(1\underline{N}),\ \mathrm{Ag}^+(C_{VS})|\mathrm{Ag}$$

where C_{NP} is the concentration of the null-point (analate) solution and C_{VS} is the variable (titrant) solution concentration. The e.m.f. of this cell is given by equation (1).

$$E = \frac{2.3RT}{F} \log \frac{(\mathrm{Ag}^+)_{NP}}{(\mathrm{Ag}^+)_{VS}} + E_j \qquad (1)$$

where $(Ag^+)_{VS}$ and $(Ag^+)_{NP}$ are the activities of silver in the variable and null-point solutions, respectively, and E_j is the liquid junction potential. If a large excess of an inert electrolyte, e.g., 1N H_2SO_4, is used in both half-cells, the liquid junction potential will be negligible since it depends on the difference in concentration between the solutions in the two half-cells. Also, the activity coefficients of silver in the null-point and titrant solutions will be practically equal due to the constant high ionic strength maintained in the two half-cells. Equation (1) thus simplifies to

$$E = \frac{2.3RT}{F} \log \frac{C_{NP}}{C_{VS}} \qquad (2)$$

where the cell e.m.f. is dependent only on the ratio of concentrations of silver in the null-point and variable solutions (C_{NP} and C_{VS}) when both half-cells are at the same temperature. By suitable cell design (described below), the half-cell temperatures are equal (approximately 25°C in these experiments), so that at the null-point, i.e., where the cell e.m.f. is equal to zero, $C_{NP} = C_{VS}$.

By plotting the logarithm of the amount of titrant added, either coulometrically or volumetrically, versus the cell e.m.f., a straight line having the theoretical Nerstian slope of 59.2/n mV per tenfold change in concentration should be obtained. Significant deviation from this value indicates improper cell behavior and consequently serves as a check on errors caused by drift of the cell potential during the titration.

c. Experimental Details. The concentration cells and associated instrumentation (figures 15 and 16) are of special interest, insofar as the solution volumes are concerned.

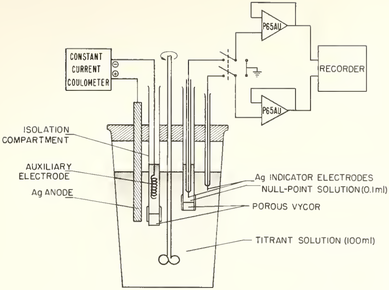

Figure 15. Concentration cell and schematic diagram of the experimental circuit.

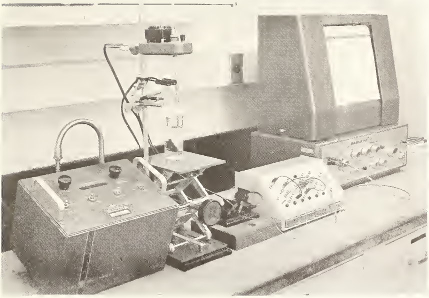

Figure 16. Null-point titration cell and associated instrumentation.

In this study, the 0.1 ml of solution being analyzed is contained in the null-point half-cell which is simply a plug of the porous Vycor rod connected to glass tubing by a sleeve of Tygon tubing [18]. This analate half-cell, which is immersed in the titrant solution, provides a low resistance contact between solutions yet prevents intermixing. The small sample solution volume of this immersion half-cell also permits rapid temperature equilibration between the solutions.

The variable-concentration solution, initially consisting of 100 ml of the inert electrolyte ($1\underline{N}$ H_2SO_4), is contained in a 180-ml tall-form beaker. In addition to the null-point half-cell with its silver indicator electrode, this titration half-cell accommodates a matching silver indicator electrode, the high-purity silver generator electrode, the auxiliary electrode isolation compartment, and a glass stirrer. Magnetic stirring was found to produce a.c. noise superimposed on the d.c. signal from the cell, hence it could not be used. The constant current source for the silver generation is calibrated to provide digital readout directly in microequivalents.

Inasmuch as the ratio of solution volumes in the titrant and null-point half-cells is 1000:1, the number of equivalents of silver generated in the titrant cell must be 10^3 times greater than the amount present in the null-point cell to achieve the same concentration. This "amplification" factor allows the determination of amounts of analate too small to be generated reliably by direct means. Furthermore, the volume ratio can be varied to achieve the optimum titrant generation rate for a given analysis.

The potentiometric circuit, shown schematically in figure 15, uses solid-state operation amplifiers as voltage followers between the silver indicator electrodes and the potential measuring device. A multirange potentiometric recorder is used for the latter purpose, rather than a more accurate potentiometer, to facilitate the direct and continuous observation of the cell potential equilibration and stability with time. The purpose of the voltage followers is to draw as little current as possible from the source while their extremely low impedance output follows the input exactly. The high input impedance prevents the occurrence of concentration changes in the null-point solution and disturbance of the equilibrium at the indicator electrodes (polarization) due to significant current flow during recorder off-balance.

The titration data are plotted on semi-logarithmic graph paper to obtain a linear plot of the logarithm of the amount of silver generated with respect to the cell potential. The equivalence point is then graphically evaluated by linear interpolation or extrapolation to zero potential. In this way, the null-point determination is based on a series of data points on both sides of the equivalence point, instead of only on a single measurement as in the conventional technique, thereby increasing the reliability of the null-point value.

Analysis of the data may be easily accomplished by computer techniques to obtain the equivalence point from the intercept of a least squares fit of the data to a straight line. The computer readout also provides the slope of the best straight line through the titration data points for comparison with the theoretical Nernstian slope.

d. Analytical Evaluation. Using these modifications of the null-point technique, standard 0.1-ml samples containing 0 to 13 µg of silver in 1N H_2SO_4 were analyzed. Table 18 shows the amount of silver present in the standard samples in micrograms and the amount of silver experimentally found for N determinations, expressed as an average of the graphical and computer analyses of the data. The errors reported define the range of applicability in terms of the accuracy of this method. It is obvious that below about 0.1 μg of silver (10 μM) there is a rapid decrease in accuracy. The slopes reported in the last column of the table indicate good Nerstian response in all concentration ranges within the precision of the measurements.

Table 18. Results of silver determinations.

μg of silver[a]				
Present	Found	N	Error (μg)	- Slope
12.94	12.89	7	- 0.05	59.1
1.29	1.32	8	.03	58.6
0.129	0.133	7	.004	58.7
.0129	.0223	6	.0094	58.8
.0065	.00187	7	.00122	58.3
.0	.00163	7	.00163	57.6

[a] sample volume = 0.1 ml

In figure 17, the equivalents of silver found are plotted vs. the equivalents taken. Ideally, this should be a straight line with a slope of 45°. Above 0.1 μg of silver, this relationship holds quite well, but below this value a positive deviation occurs. From this curve, it is calculated that 0.1 μg of silver can be determined with a positive error of only 5%, and at 0.065 μg the error is just under 10% (approximately 0.006 μg). Finally, for amounts below 0.01 μg of silver the error exceeds 100%, and the reproducibility of the method rapidly deteriorates. Qualitatively, the positive errors and the non-linearity in the titration curves at very low concentrations may be interpreted as a consequence of the spontaneous dissolution of the silver electrodes in the aerated sulfuric acid solutions.

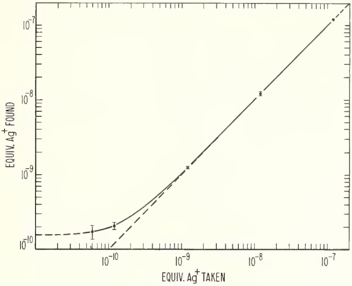

Figure 17. Accuracy of null-point potentiometry in the determination of silver.

Although interferences were not studied in detail, several selected cations were used which give some indication of the cationic tolerence levels in the silver determination. Instead of a purely chemical interference, such as anion complexation of precipitation of silver, the cationic interference may occur as a mixed potential of varying degrees of significance. Since the high-purity silver electrode is normally specific for silver ions, only those cationic species which can spontaneously reduce to the metallic state on the silver electrode (more noble than silver) or exist in two stable oxidation states in solution should produce an electrochemical interference. The cation interference study was performed by adding successively increasing amounts of the interfering ion to a constant concentration of silver and observing the effect on the cell potential. As evident from figure 18, Hg^{++} and Fe^{+3} interfere strongly while Ni^{++}, Cd^{++}, and Cu^{++} have very little effect on the potential. Cadmium shows the smallest influence on the concentration cell potential as would be expected for such an active metal. A deviation in potential is not observed until the concentration ratio of cadmium to silver is greater than 1000:1, i.e., >0.1 M Cd^{++}. Even at a ratio of 5000:1, the error in the silver determination amounts to less than 4%.

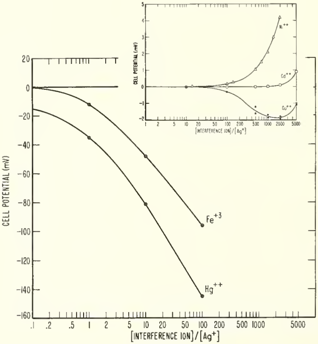

Figure 18. Cation interference curves at $[Ag^+] = 10^{-4}$ M.

Arbitrarily taking 10% (i.e., a potential shift of slightly over 2 mV) as the maximum tolerable error due to an interfering ion, it can be seen from figure 18 that the tolerance concentrations of the interfering ion when the silver concentration is 10^{-4}M are: $<10^{-5}$M Hg^{++}; 10^{-5}M Fe^{+3}; ~0.1M Ni^{++}; >0.5M Cu^{++}; and >0.5M Cd^{++}.

This technique offers several important advantages in addition to its intrinsic simplicity. By performing the titration in a cell other than the one containing the unknown, the sample solution is uncontaminated by the titrant solution and preserved for additional study, while the actual titration in the second cell is conveniently carried out in any desired volume of solution. This separation of titration and sample cells also permits the use of micro-volumes of the sample solution since the sample need only serve as a reference solution. As previously stated, the volume ratio between the sample and titration solutions acts as an "amplification" factor and permits the titration of amounts of material too small to be determined by an ordinary potentiometric titration. In addition, the use of the new highly-selective specific ion electrodes should permit the extension of this technique to many more elements with much higher interference tolerence levels. Work is presently in progress to use fluoride-specific electrodes in this way and to reduce the sample volume required to 0.01 ml.

2. Modified Fluoride Activity Electrode.

A fluoride activity electrode [19] has been modified for operation in the inverted position by conversion of the interior reference solution to a gel. Operation of the electrode in this position makes possible the use of the fluoride-sensitive membrane (a laser-type, rare earth fluoride single crystal) as the sample "container" and permits the determination of fluoride in sample volumes as small as 50 µl (figures 19 and 20) by direct e.m.f. measurement.

A calibration curve was obtained with this modified electrode for solutions containing $10^{-1}\underline{M}$ to $10^{-6}\underline{M}$ NaF in 0.1$\underline{M}$ KNO_3. The precision to which the fluoride concentration can be read from this calibration curve is calculated from the slope of the curve and the standard deviation of the e.m.f. measurements. In the concentration range from $10^{-1}\underline{M}$ to $10^{-3}\underline{M}$ NaF, the calculated standard deviation for a single determination is about 2%. Below $5 \times 10^{-6}\underline{M}$ NaF (i.e., less than 5 nanograms of fluoride), the determination of fluoride by this method is virtually useless due to the low calibration curve slope and is further impaired by the poor precision of the e.m.f. measurements. At the $10^{-5}\underline{M}$ NaF level, 10 nanograms of fluoride can be determined with an error of $\sim$ 0.7 nanogram.

In summary, the modified fluoride electrode exhibits a usable response over more than four decades of fluoride concentration ($10^{-1}\underline{M}$ to $5 \times 10^{-6}\underline{M}$) for sample volumes as small as 50 µl (table 19).

Table 19. Response of the fluoride electrode and concentration error from the calibration curve.

Fluoride		Potential	Standard deviation of a single determination	
Conc.(M)	µg	mV vs. S.C.E.	%	µg
10^{-1}	95	25.8	2.1	2.0
10^{-2}	9.5	83.4	2.0	0.19
10^{-3}	0.95	142.7	1.9	.018
10^{-4}	.095	202.2	3.5	.033
10^{-5}	.0095	255.2	7.1	.00067
5×10^{-6}	.00475	268.3	17.2	.00082
10^{-6}	.00095	284.8	106	.00101

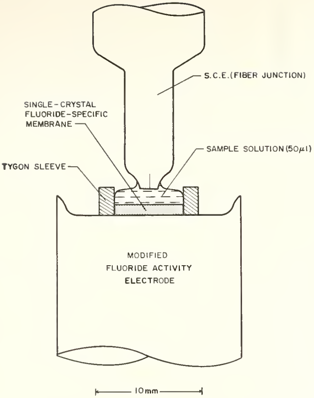

Figure 19. Fluoride electrode microcell and S.C.E.

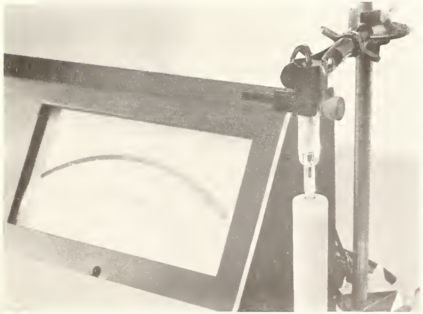

Figure 20. Fluoride electrode microcell assembly.

3. Response of the Iodide Selective Rubber Membrane Electrode.

A brief study was made of the response characteristics of an iodide selective membrane electrode [20]. This type of electrode consists of a polymerized silicone rubber membrane containing a relatively insoluble compound of the ion being measured, which in this case is silver iodide. The measured e.m.f. arises principally at the membrane-solution interface and is a phase boundary potential which responds to the anion activity in the solution.

Iodide solutions containing $10^{-1}\underline{M}$ to $10^{-5}\underline{M}$ KI were prepared, and the iodide electrode potential (vs. S.C.E.) was measured with an electrometer recorder. Equilibration of the iodide membrane in $10^{-1}\underline{M}$ and also in $10^{-4}\underline{M}$ iodide solutions gave comparable results in the measurement of solutions in the $10^{-1}\underline{M}$ to $10^{-3}\underline{M}$ range. However, equilibration in the $10^{-1}\underline{M}$ iodide solution could not be used if measurements below this concentration were to be made due to the apparent leaching of iodide from the membrane causing a continuous decrease in potential of about 1 to 2 mV/min. Using the $10^{-4}\underline{M}$ KI solution for equilibration, reproducible measurements could be made from $10^{-1}\underline{M}$ to $10^{-4}\underline{M}$ iodide. In all cases, the electrode was unusable at the $10^{-5}\underline{M}$ iodide level due to significant drifting and irreproducibility.

Although the electrode should exhibit a Nerstian response of 59 mV/pI, the calibration curve slope was actually almost double this value (approximately 115 mV/pI) in the range between $10^{-1}\underline{M}$ and $10^{-3}\underline{M}$ iodide and decreased to about 75 mV/pI between $10^{-3}\underline{M}$ and $10^{-4}\underline{M}$ KI.

From the foregoing observations, it is apparent that the particular electrode studied was not behaving normally. Instead, the electrode had a higher-than-normal response, and, in its useful range (10^{-1} M to 10^{-4} M KI), it was more sensitive to iodide activity than is theoretically possible. This type of abnormal behavior may be caused by solution leakage around or through the silicone rubber membrane. It was suggested [21] that this defect may have resulted during air shipment due to severe pressure changes on the electrode.

(R. A. Durst)

5. A.C. POLAROGRAPHY AND RELATED TECHNIQUES

A. Introduction

The increasing use of electroanalytical techniques for the detection and determination of trace constituents necessitates a corresponding consideration of the various factors which might affect the sensitivity of a given electroanalytical procedure. Adsorption at an electrode surface of either the constituent sought or an indifferent solution component can markedly change the electrode response by alterations in the double layer structure and the kinetics of an electron-transfer process. The primary objective of this program is to obtain a better understanding of the influence of adsorption processes on electrochemical measurements so that the knowledge gained can be used to increase the sensitivity of electroanalytical measurements in general, and to develop new procedures for the analysis of surface-active material in particular.

B. Instrumentation

In order to carry out the objectives of this program, a combination d.c. and phase-selective a.c. polarograph was constructed. The components of this instrument consist of an all solid-state d.c. and a.c. polarographic module which was designed and constructed here at the Bureau, a commercial solid-state power supply, and a high stability commercial oscillator, all mounted on a movable floor-model relay rack. In addition, there is an X-T recorder, also mounted on the relay rack, and a table model X-Y recorder. The arrangement of this apparatus is illustrated in figure 21.

The d.c. polarographic part of the module is based on a fairly conventional three-electrode, controlled potential, operational amplifier design. It contains an electronic scan unit which provides various d.c. scan rates in either an anodic or cathodic direction. A push button control activates the scan unit and a panel light indicates that the scan is operating. In addition, an automatic sweep limit control makes it possible to preset the desired final potential so that, once this potential is reached, the potential between the reference and indicator electrodes is automatically reset to the initial potential. By use of the manual scan unit, it is possible to apply a fixed potential accurate to within a few millivolts between the reference and indicator electrodes in order to calibrate the voltage axis of an X-Y recorder and/or supply an initial potential between ± 3 volts.

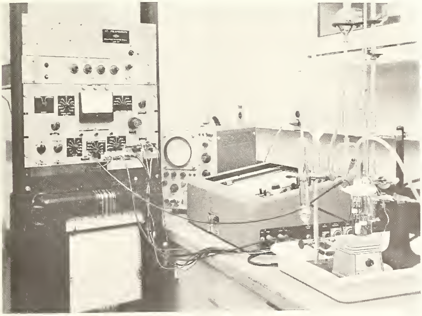

Figure 21. A.C.-D.C. polarograph, cell assembly, and related equipment.

The a.c. polarographic part of the module consists of a phase-sampling unit which analyzes the alternating current arising from the electrochemical cell when an alternating voltage is applied across it. This is accomplished by measuring that portion of the alternating current which is either in phase or 90° out of phase with respect to the applied alternating voltage peak maximum, or, alternately, measuring the difference of these two current components. In this manner, it is possible to measure the faradaic current arising from a charge-transfer process while eliminating the current contribution due to the double layer charging process (in-phase current measurements), the double layer capacity in the absence of a charge-transfer process (quadrature current measurements), or the double layer capacity during a reversible charge-transfer process (difference of the quadrature and in-phase current components). Details concerning the fundamental basis for these measurements can be found elsewhere [22].

With this instrument, alternating voltages with frequencies varying from 10 to 1000 Hz and amplitudes from 1 to 25 mV peak-to-peak can be applied to the electrochemical cell. The resulting alternating current is then amplified, sampled as discussed above, filtered, and again amplified before being fed to the current axis of the recorder. The time constant of the filter is variable, depending on the frequency employed.

By use of calibrated current outputs, the current axis of the recorder can be calibrated for both a.c. and d.c. measurements with current sensitivities ranging from 0.1 to 1000 μA full scale. Panel lights indicate when the potential control and current amplifiers are overloaded. In addition, many of the important points in the circuits are brought out to a test panel in the rear of the instrument in order to facilitate trouble-shooting and/or the rapid modification of the instrument, should the need ever arise. Individually shielded leads connect each electrode to the instrument.

Another feature of this instrument is a multi-functional test meter mounted on the front panel of the instrument. Depending on the settings of the instrument, it is used as a meter to adjust to zero any offset bias at the outputs of the operational amplifers, to align the in-phase and quadrature sampling circuits at each frequency, or to monitor the current or voltage while recording a.c. or d.c. polarograms.

In making these measurements, it is necessary to keep the solution resistance to a minimum. Therefore low resistance capillaries [23] were constructed and used in conjunction with a reference electrode which was positioned close to the DME via a Luggin-type capillary arrangement.

C. Research Activities

Currently, research is being directed towards correlating the adsorption of an electroactive species during the charge-transfer process, as determined by changes in the double layer capacity, with the appearence of d.c. polarographic maxima and the corresponding a.c. polarographic response. Initially, thallium adsorption on mercury is being studied as a function of the thallium ion concentration and the nature and concentration of the supporting electrolyte.

(T. F. Retajczyk, Jr.)

6. MICROSCOPIC AND CLASSICAL MICROCHEMICAL ANALYSIS

A. Introduction

During the past few years the aim of this laboratory has been to obtain more information from smaller samples. In line with this, the primary objective now is the handling and examination of particle samples, much of which must be done by observation with a microscope. To do this, a competence has been attained in the actual manipulation of particles so that they may be examined and transferred without loss and without contamination. The other objective is the elemental analysis of organic materials by microchemical means.

B. Facilities

A laboratory module has been equipped exclusively for ultramicrochemical work. A laminar flow clean bench, shown in figure 22, is used for operations which require the greatest freedom from contamination. This includes both the handling of particles and the microscopic examination of particles. A "white bench" is also used to prevent the contamination of samples. Associated equipment includes microscopes and accessories, a high speed centrifuge, an ultrasonic cleaning bath, an ultrasonic probe, micromanipulators, and membrane filter sampling and filtration apparatus. A low temperature asher (figure 23) [24,25] is used to remove organic material such as filtering media from particle samples without destroying their form and with minimum change of their chemical composition. A class-100 clean room is in the planning stage. It is discussed separately.

The microchemical facilities remain essentially as described in past reports [1,12].

Figure 22. Laminar flow clean bench.

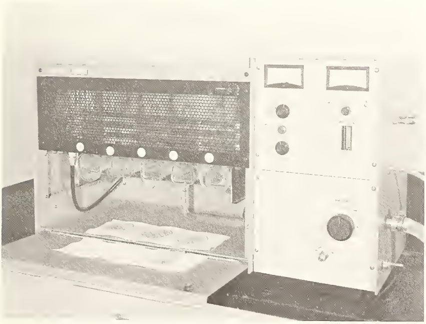

Figure 23. Low temperature ashing equipment.

C. Activities

1. Analysis of Particulates

As mentioned in the introduction, a principal objective is the handling, examination and identification of particulate matter in the size range of 1 to 10 µm. The handling and transferring of individual particles of this size require a high degree of manipulative skill. Considerable effort has been devoted to acquiring a competence in this line. In the analysis of particles, microscopy, ultramicrochemical tests, and nuclear track techniques are used. Particle samples are first collected by the usual methods used for atmospheric pollution sampling such as filters and tapes. In order to have sufficient knowledge of background conditions to be able to distinguish the unusual sample from the ordinary, a continuous surveillance of the NBS grounds and buildings is conducted. The samples so collected are examined microscopically and the particles of interest are transferred for analysis by the mass spectrograph, by the electron microprobe, or by ultramicrochemical tests. When uranium is of special interest, particles containing uranium are located by the fission track etching technique [26,27,28]. The sample, dispersed in collodion, is spread on a Lexan polycarbonate resin slide and irradiated with neutrons. Uranium-containing particles leave tracks formed by fission products in the plastic. After removal of the collodion film, the tracks are developed by etching the Lexan plate with sodium hydroxide solution, after which it is examined with a microscope. The particles associated with the tracks can be located by replacing the collodion layer in the same position on the Lexan slide. They can then be removed for subsequent tests.

2. Particulate Standards

A study of special interest is the preparation of particulate standards of uniform known size and known composition in which individual particles can be used as standards for the electron microprobe, the mass spectrograph, and for ultramicrochemical tests. Such particle standards have been made by dispersing NBS standards of known composition in liquids in which they are not soluble and collecting appropriate sizes by sedimentation techniques. While this provides a fraction containing particles in a narrow range of sizes, it is still necessary to pick and size the individual particles before use. A number of other methods for preparing particles will be investigated such as the spinning disk generator, the vibrating reed generator, and by the absorption of metal ions on ion exchange resins of uniform size. The latter technique is being developed by the Separation and Purification Section and will be discussed in the progress report of that Section [29]. The Microchemical Analysis Section is providing particle handling services for this investigation.

3. Microchemical Methodology

The microchemical activities of the laboratory are for the most part concerned, as in the past, with the elemental analysis of small samples. The equipment used was described in a previous report [1]. The carbon-hydrogen-nitrogen analyzer has been found to be very useful in the determination of water in inorganic materials, especially to determine the residual amounts of water present after drying in an oven or muffle furnace. In this method the sample is heated to 1050° C and any water driven off is separated by a gas chromatographic column and measured with a thermal conductivity detector.

No catalysts are used and organic materials must be absent. The apparatus is standardized with organic standards or with crystals of known water content.

Some of the results obtained by this method are given in table 20.

Table 20. Percent water determined with the carbon-hydrogen-nitrogen analyzer.

Sample	Weight	%H_2O
$KClO_3$-1	10 mg	0.22
		.17
-2		.08
-3		.14
-4		.09
		.11
-5		.56
Alumina-1	30 mg	.08
		.07
-2	40 mg	.05
		.04
Silica	25 mg	.09
		.12
U_3O_8	45 mg	.06
		.06
Be_3N_2	20 mg	1.16
		1.12
Beryllium aluminate	40 mg	0.15
		.16
		.23
		.16
$CaZnSi_2O_6$	4 mg	4.3
		4.3

A number of different types of material have been ashed in the low temperature asher (LTA) to test its operation. Filters were ashed in order to remove the organic material prior to the determination of the metals present in the residue by photometric, polarographic, or spectrochemical means. As many as six pieces (3 cm x 8 cm, each weighing approximately 0.5 gram) could be completely ashed overnight at 150 watts. With this material, as with a number of others, it was not always possible to obtain a quantitative measurement of the amount of ash present, since it is very light and fluffy and easily lost when the boat is removed from the combustion chamber. With some samples there is even evidence of partial loss of ash from the boat before the chamber is opened.

Filters are ideal in that they offer a large surface for oxidation. Compact materials oxidize much more slowly. For example, it was desired to determine spectrochemically the metallic elements present in polyethylene containers. A 3-gram polyethylene vial required 120 hours at 200 watts to ash completely because it melted down into a glob of material. Ion exchange resins are also slow to burn because of the relatively small surface exposed. A 2-gram piece of Teflon tubing lost 12% of its weight during 15 hours of ashing at 150 watts. The slow ashing in this case is due to the heat stability of this material.

Some of the materials ashed such as dried oak leaves and wool carpeting have a high amount of residue and therefore need frequent stirring to expose the unburned portion.

A number of small samples were ashed prior to examination of the inorganic structure with the electron microprobe. Preliminary work with blood, human skin and onion skin indicates that the LTA works well in ashing these materials.

D. Clean Room Facility

A laminar-flow clean room complex has been designed during the past year and construction is expected to begin during fiscal year 1968. This complex is to be used in conjunction with the work being done in microscopy, particle analysis, and air pollution as well as to provide essential clean room services for other divisional programs.

The general layout for the clean room facility is shown in figure 24. The facility occupies a total area of approximately 24 x 36 feet and consists of two clean rooms separated by a perforated wall partition together with rooms to prepare personnel for entry into the clean areas. Air flow is from left to right. A service room is provided for easy access to the filter bank. The design of this complex is such that all air-borne particles greater than 0.5 µm in size will be filtered out. To eliminate further environmental contamination the laminar air flow will be moving at an average velocity of 100 feet per minute down the room from the filter bank area and then recirculated.

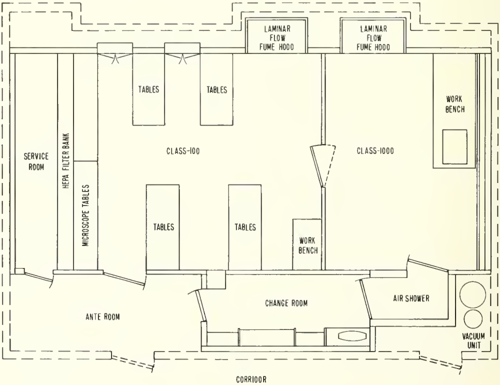

Figure 24. General layout for clean room facility.

All personnel using the clean room will be required to enter by way of the ante-room, then into the change room to vacuum their clothing and to put on special garments. After leaving the change room, the personnel will proceed to the air shower for a final cleaning before entry is made into the clean room. Upon entering the clean room, an individual will have the option of working in either the class 100 area, the highest level of cleanliness, or in the class 1000 area, a lower level of cleanliness, depending upon the nature of the work being done.

Microscopy work will be done in the cleanest part of the class 100 area which is directly in front of the HEPA filter bank wall. The chemical work will be conducted in the vertical laminar flow fume hoods. Finally, to minimize and eliminate dust collection and settling, all of the utilities will be recessed in the wall and a limited amount of storage space will be provided in the clean room.

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

7. INTERNATIONAL RESEARCH GRANTS PROGRAM

A. Introduction

The National Bureau of Standards awarded a grant to the Technion Research and Development Foundation, 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. Two contributions have resulted from this program during the past year and will be described briefly.

B. Trace Metal Determination in Silicates

An anodic stripping voltammetric method has been developed for the determination of zinc in silicates [30]. The method is sensitive and is not affected by interferences resulting from varying sample composition.

Samples of finely ground material (about 100 mg) are fused with boric acid-lithium fluoride in a platinum crucible. After removal of silica by heating with hydrofluoric acid and sulfuric acid, the cake is dissolved in hydrochloric acid to produce a clear solution which is made up to volume in a volumetric flask.

An appropriate aliquot of this solution, containing 0.1 to 5 μg of zinc, is passed through an anion-exchange column which has been preconditioned by the passage of 1 N hydrochloric acid through it. The zinc is eluted from the column, directly into the electrolysis cell, by passing 50-60 ml of water through it.

Samples decomposable by direct acid attack may be weighed into Teflon beakers, dissolved in acid, evaporated to dryness, after which the residue is dissolved in hydrochloric acid and transferred to the volumetric flask as before. Such samples which are also sufficiently low in iron content need not be passed through the column.

For voltammetric measurement, a hanging mercury drop electrode of the Kemula type is used. The solution, prepared as described, is adjusted to a pH of 4.5 by addition of acetate buffer and ammonia as required. After purging with nitrogen, it is pre-electrolyzed for 2-6 min at 1.2 V vs. SCE, while stirring the solution with a magnetic stirrer. On completion of pre-electrolysis, stirring is stopped, the solution is allowed to rest for 30 sec without breaking the circuit, and an anodic stripping voltagram is recorded at 800 mV/min from -1.2 to -0.8 V vs. SCE. Peak heights are measured and calibrated by the method of standard addition.

The method has been evaluated by the determination of zinc in NBS Standard Reference Material Opal Glass No. 91 and in 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 anion-exchange step effectively removes prevalent constituents of rock and silicate samples (e.g. manganese, vanadium, nickel, iron, etc.) that would be reducible in the voltage range employed. This step also removes platinum introduced in small amounts during sample solution. Platinum would otherwise interfere due to formation of zinc-platinum intermetallic compounds during the pre-electrolysis step or by the appearance of a hydrogen reduction wave, catalyzed by the platinum, at potentials in the vicinity of the zinc-oxidation peak. The possible use of the resulting zinc-peak deminishment for the determination of trace amounts of platinum is presently under investigation.

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

The combination of a.c. polarography with linear-scan anodic stripping voltammetry has been investigated using a phase-discriminating a.c. attachment [31]. The resolution and sensitivity was compared with those obtainable under the same conditions with conventional d.c. 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 a.c. anodic stripping combination shows that the latter shows 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 No. 91 (Opal Glass). The results obtained agreed with those found using conventional anodic stripping. The presence of platinum diminished the zinc peak height as observed in the previous work but no interference was observed when iron was present since the $Fe^{+3} \rightarrow Fe^{+2}$ reduction proceeds irreversibly and its sensitivity is accordingly very low. As a result, zinc can be determined in the presence of considerable amounts of iron.

If iron is not removed, the choice of pre-electrolysis potential is critical. At the potential chosen (-1.2 V vs. SCE) the reduction of ferrous iron to metal does not occur. At more negative potentials (up to -1.5 V) the height of the zinc peak decreased, probably due to the formation of compounds of the type Fe_XZn_Y [32].

(M. Ariel and coworkers)

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, EOD 4-24-67

Polarography --

E. June Maienthal
Sharon F. Cooper, EOD 2-20-67, part-time

Coulometry --

George Marinenko
Charles E. Champion, EOD 2-27-67

Electroanalytical Measurements --

Richard A. Durst, EOD 8-15-66
Erick L. May, Summer Employee - 1967

A.C. Polarography --

Theodore F. Retajczyk, Jr., EOD 10-13-66

Microscopy and Microchemistry --

Rolf A. Paulson
John R. Baldwin
B. Stephen Carpenter, EOD 4-24-67
William P. Schmidt

B. Publications

1. R. A. Durst, Porous Glass Salt Bridges, J. Chem. Ed. 43, 437-438 (1966).

2. E. J. Maienthal and J. K. Taylor, Application of Cathode Ray Polarography and Anodic Stripping Voltammetry to Trace and Micro Analysis, Paper No. 5, Book of Preprints - Symposium on Trace Characterization, NBS (1966).

3. R. A. Durst, Book Review: Chemical Principles in Calculations of Ionic Equilibria by Emil J. Margolis, Anal. Chem. 38, 74A-76A (1966).

4. R. A. Durst, Mechanism of the Glass Electrode Response, J. Chem. Ed. 44, 175-176 (1967).

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6. E. J. Maienthal and J. K. Taylor, Improvement of Polarographic Precision, Mikrochimica Acta (In Press).

7. E. J. Maienthal and J. K. Taylor, Polarographic Methods in Determination of Trace Inorganics in Water, accepted for publication as a chapter in Symposium on Trace Inorganics in Water, "Advances in Chemistry" series published by the American Chemical Society.

8. R. A. Durst, Photo-Polarographic Behavior of Irreversibly Reduced Inorganic Depolarizers, 11th Annual Report on Research, American Chemical Society-Petroleum Research Fund (1967).

C. Talks

1. J. K. Taylor, "The Science of Measurement", American University Summer Institute for Elementary School Teachers, Washington, D. C., July 1966.

2. E. J. Maienthal and J. K. Taylor, "Application of Cathode-Ray Polarography and Anodic-Stripping Voltammetry to Trace and Micro Analysis", Symposium on Trace Characterization, National Bureau of Standards, October 1966.

3. J. K. Taylor, "Relations of Electricity and Chemistry", St. Bartholomew's School, Bethesda, Md., October 1966.

4. J. K. Taylor, "Recruiting Ph.D's and Post-Doctoral Specialists", Executive Seminar in Recruitment, U. S. Civil Service Commission, Washington, D. C., October 1966.

5. J. K. Taylor, "Relations of Electricity and Chemistry", Parkland Jr. High School, Rockville, Md., December 1966.

6. J. K. Taylor, "Problem Areas in Professional Employment", Washington Academy of Sciences, Washington, D. C., February 1967.

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

8. E. J. Maienthal and J. K. Taylor, "Application of Linear Sweep Voltammetry to Analysis of Standard Reference Materials", Society for Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 1967.

9. E. J. Maienthal and J. K. Taylor, "Polarographic Methods in Determination of Trace Constituents in Water", American Chemical Society, Miami, Florida, April 1967.

10. R. A. Durst and J. K. Taylor, "Modified Null-Point Potentiometry", American Chemical Society, Miami, Florida, April 1967.

11. T. F. Retajczyk, "Alternation Current Polarography in Concentrated Salt Media", Catholic University, Washington, D. C., April 1967.

12. G. Marinenko, "Improved Technique for Coulometric Halide Titrations", American Chemical Society, Towson, Maryland, May 1967.

13. R. A. Durst, "Microchemical Determination of Silver by Linear Null-Point Potentiometry", American Chemical Society, Towson, Maryland, May 1967.

14. J. K. Taylor and G. Marinenko, "Coulometric Titrations", American Chemical Society, Claremont, California, June 1967.

15. R. A. Durst, "Null-Point Potentiometric Titrations", American Chemical Society, Claremont, California, June 1967.

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)
Chairman, ACS Division of Analytical Chemistry
Member, Panel on Chemistry, Civil Service Board of Examiners
Member, Board of Managers, Chemical Society of Washington
Member, Professional Relations Committee, Chemical Society of Washington
Safety Officer, Analytical Chemistry Division
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

Judge, Analytical and Inorganic Student Papers, ACS Meeting-in-Minature, Goucher College, Towson, Md.

Thesis Director in absentia, Boston College, Chestnut Hill, Massachusetts

E. June Maienthal

NBS Reporter for Capital Chemist, Chemical Society of Washington

Elected member, Board of Managers, Chemical Society of Washington

Editor, Analytical Chemistry Division News Letter

G. Marinenko

Member, Welcoming Committee, Chemical Society of Washington

R. A. Paulson

Member, Service Analysis Committee, Analytical Chemistry Division

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

E. Awards

J. R. Baldwin

Division of Analytical Chemistry Accomplishment of the Month, Honorable Mention, February 1967

R. A. Durst

Division of Analytical Chemistry Accomplishment of the Month,
First Place, January 1967
Honorable Mention, May 1967

E. E. Hughes and W. D. Dorko

Division of Analytical Chemistry Accomplishment of the Month, First Place, December 1966

E. June Maienthal

Division of Analytical Chemistry Accomplishment of the Month, First Place, November 1966.

R. A. Paulson

U. S. Department of Commerce Bronze Medal Award, February 1967

J. K. Taylor

U. S. Department of Commerce Gold Medal Award, February 1967

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