NBS TECHNICAL NOTE

403

Microchemical Analysis Section:

SUMMARY OF ACTIVITIES JULY 1965 TO JUNE 1966

Edited by John K. Taylor

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

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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 highly important. 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. At the National Bureau of Standards such publications fit logically into the category of a Technical Note. In 1966 we plan to issue these summaries for all of our sections. The following is the second annual report on progress of the Microchemical Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

This report summarizes the program and activities of the icrochemical Analysis Section of the Analytical Chemistry ivision. This section is new in name only, since the nalytical areas included in its program have been administraively linked for the past several years. Prior to April 1966, he section was known as the Analysis and Purification Section. t that time, the purification programs were transferred to he newly created Separations and Purification Section and the ame of the section was officially changed to its present one o more properly reflect its program emphasis.

The Microchemical Analysis Section has the primary mission o make contributions to the science and technology of analysis f small samples. Its program includes fundamental studies to mprove precision, accuracy and sensitivity of analytical ethods as well as the development of new and improved methods f chemical analysis applicable to wide areas of materials esearch. As a closely related activity, the section provides nalytical measurements of high reliability to the various esearch programs of the Bureau and to the Standard Reference aterials program.

Research projects are active in the following analytical ompetence areas: mass spectrometric gas analysis, polaroraphy, coulometry, stoichiometry, classical microchemistry. n addition, the section has considerable analytical experience nd investigates and develops methods incidental to specific nalytical problems in the following areas: gas chromatography, uclear magnetic resonance spectrometry, infra-red spectrometry. nvestigations in the area of microscopic analysis have just een activated and will include the development of ultra-micro echniques.

Activities during the reporting period are classified nder research or analytical development. The classification is often arbitrary since nearly all of the analytical applications have required more than incidental efforts of both kinds. Investigations which would appear to have considerable general applicability have been classified in the first group, while those more closely related to specific materials have been placed in the second category. In most cases, where analytical methods have been described, it has been attempted to describe the procedures used briefly, yet with sufficient detail to make them understandable to the experienced analyst. However, specific details could 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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JULY 1965 TO JUNE 1966

Edited by John K. Taylor

ABSTRACT

This report describes the scientific programs and research activities of the Microchemical Analysis Section of the Analytical Chemistry Division of the NBS Institute for Materials Research during the period July 1965 to June 1966. General activities are reported in the areas of gas analysis by mass spectrometry, polarography, coulometry, stoichiometry, and classical microchemical analysis. Research accomplishments described in some detail include: improvements in the sensitivity of gas analysis using high-pressure mass spectrometry; analysis of deuterated compounds by mass spectrometry; comparative polarographic analysis of high precision; polarographic methods for trace and ultra-trace determination of a number of elements; highly accurate coulometric iodimetric titration; a highly precise method for determination of magnesium based on its final weighing as magnesium sulfate; and a number of microchemical procedures for the analysis of a variety of materials.

1. MASS SPECTROMETRIC GAS ANALYSIS

A. Introduction

The primary gas analytical tool of this laboratory is a mass spectrometer. Many other techniques, however, are employed in instances where the mass spectrometer alone would not suffice for the analysis or where treatment of the sample is required before mass spectrometric analysis. The primary goal of the research effort has been to develop mass spectrometric techniques which minimize the necessity for the use of other techniques with the main purpose to increase the accuracy and sensitivity of the mass spectrometer, particularly in the field of trace analysis.

B. Facilities

The instrumentation available in this laboratory is essentially that described in last year's report [ref. 1, p. 6]. In addition, a Consolidated Electrodynamic model 21-620 mass spectrometer was available. This instrument lacks some of the features of the Consolidated 21-103C but was found to be quite useful for several phases of the research activity.

The mass spectrometer gas analysis laboratory was moved to the new Gaithersburg site in April 1966. A three module bay with darkroom facilities has been provided which houses the mass spectrometer, a nuclear magnetic resonance spectrometer and most other laboratory apparatus concerned with gas analysis and with the preparation of gas mixtures.

C. Research Activities

1. High Pressure Mass Spectrometry

a. General Considerations. Early attempts to detect low concentrations of helium 4 (1-300 ppm) in helium 3 by utilizing inlet pressures as high as 10 mm suggested the possibility of the application of high pressure mass spectrometry for the detection of trace constituents in other gas mixtures. It was early recognized that the number of gaseous systems which could be studied would be quite limited. The method would of necessity be more or less limited to inorganic systems or to systems in which the trace component was organic. A recent publication [2] shows that the method is quite applicable for the determination of trace constituents in helium. We have attempted to extend the method to other systems in which helium is not the major component.

The inlet system to the mass spectrometer was modified by the addition of a McLeod gage. The vacuum system exhausting the analyzer tube was modified to the extent that two pumping systems were provided to increase pumping speed. One system, an ion pump, was not suitable alone for high pressure operation particularly for the rare gases. A two stage mercury diffusion pump in parallel with the ion pump proved a satisfactory combination. This system has been further modified in hopes of further increasing the pumping speed but no results have as yet been obtained.

Several preliminary experiments indicated that a maximum inlet pressure exists for a given gas above which the total ion yield decreases rapidly. This pressure, with the pumping system used, was around 5 mm for such gases as nitrogen, carbon dioxide and argon. The effect seems to depend somewhat on the rate at which the gas can be pumped away. The reason for the maximum is no doubt the increase in ion-molecule collisions in the ionizing region and in the analyzer tube which would directly reduce the number of ions reaching the collector.

b. Spectra of Carbon Dioxide at Various Pressures. An extensive study was made of the effect of pressure on the mass spectral pattern of carbon dioxide. The results, shown in table 1, indicate no large variation in pattern over a pressure range from 0.5 to approximately 10 mm but some slight changes do occur.

Table 1. Variation with pressure of ion yield[a] for carbon dioxide.

ressure in millimeters of Mercury	Ions				
	C^+(12)	O^+(16)	CO_2^{++}(22)	CO^+(28)	CO_2^+(44)
9.6	16.3	13.7	1.63	12.2	100
8.5	13.6	12.6	1.65	11.3	100
7.7	13.0	12.2	1.65	11.2	100
4.4	10.6	11.3	1.79	10.8	100
2.5	9.8	10.9	1.79	10.7	100
2.2	9.8	11.0	1.81	10.7	100
2.0	9.7	11.0	1.82	10.9	100
1.2	9.2	10.6	1.89	10.5	100
0.6	9.2	10.8	1.85	10.9	100
0.5	9.2	10.8	1.86	10.8	100

Ion yields are expressed as the percentage of ion current relative to that at (44).

The pattern is expressed as the percentage of ion current at the lower masses relative to that at the parent ion mass (44)*. The decrease in the relative amounts of the fragment ions with decreasing pressure really represents an increase in the amount of the parent ion with decreasing pressure. This immediately suggests the possibility of increased thermal effects in the ionizing region resulting from the greater density of the gas at higher pressure. It is interesting to note that the only ion which does not decrease with decreasing pressure is the (22) which is the doubly charged parent ion. This further suggests that the added thermal energy at higher pressures affects the production of the doubly charged parent ion to an even greater extent than the parent ion itself.

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[*] Mass numbers are expressed as the singly charged ion at the mass number indicated, e.g. (X). If and when a doubly charged ion is discussed, it will be so stated.

The next step was an attempt to determine approximately the minimum detectable quantity of a substance that could be directly determined using high inlet pressures. Mixtures were prepared by successive dilution of concentrated mixtures prepared in small (1 liter) stainless steel pressure vessels. Some problems due to adsorption were encountered and to minimize these effects, dilutions were made by transferring the higher-concentration mixtures to clean vessels followed by dilution, rather than diluting the mixture directly in its own vessel. While adsorption might still pose something of a problem, these early experiments were not designed for high accuracy but were more exploratory in nature.

The following observations were quite useful in defining the sensitivity limitations of the system.

c. Butane in Air. Mixtures of butane were prepared in both nitrogen and air. In order to prevent damage to the larger analytical instrument, mixtures with high pressures of air were analyzed on a Consolidated model 21-620 mass spectrometer where damage due to filament failure could be much more easily remedied. On this instrument, the smallest detectable quantity of butane, based on the (58) ion was 20 parts per million at an inlet pressure of 10.2 mm. Agreement with the data obtained mass spectrometrically and from the mixing data is shown in table 2.

Table 2. Detection of butane in air.

Butane Added	Butane Found
1.02 mole %	1.02 mole %
.10 mole %	.10 mole %
.010 mole %	.013 mole %
.002 mole %	.002 mole %

Earlier results with argon had suggested that the sensitivity* for the minor constituents followed changes in

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*The sensitivity is defined as the ion current in scale divisions, or other arbitrary units, per unit of pressure in the inlet system.

the sensitivity of the major constituent. Figure 1 shows the total ion yield for argon-40 and argon-36 as a function of pressure. While argon-36 is not a trace constituent, it is present at concentrations below 0.5 mole percent.

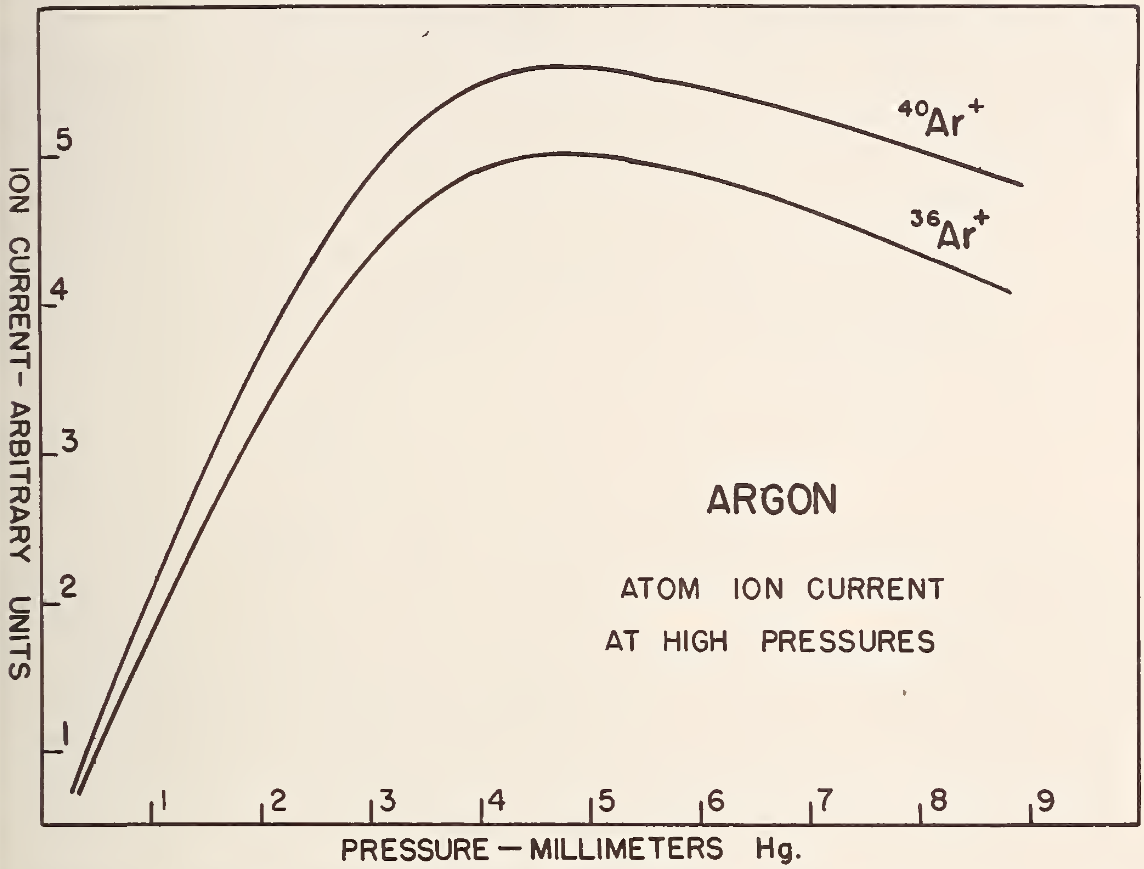

Figure 1. Effect of sample pressure on ion yield for argon.

From this data it was assumed that the sensitivity for the minor constituent would follow that of the major constituent. A comparison of the ratio of ion yield at (32) to that of (40), (43) and (58) in the air-butane system suggested that the sensitivity for the minor constituent did not in fact follow that of the major constituent but rather tended to increase relative to the major constituent as the pressure increased.

The low resolving power of the model 21-620 mass spectrometer made it difficult to measure the ions at mass 43 because of overlap both from atmospheric argon and carbon dioxide as well as a large peak at (42) due to N_3^+. It was necessary, therefore, to depend on the magnitude of the parent ion (58). The sensitivity used to calculate the pressure of butane from the parent ion was that determined at the 1% mixture level.

d. Benzene in Air. A detectable peak at (78) was found in the spectrum of a mixture of benzene in air calculated to have a benzene content of 2 ppm. The inlet pressure necessary to detect this concentration was 10.5 mm. Results are shown in table 3.

Table 3. Detection of benzene in air.

Benzene added	Benzene found
130 ppm	140 ppm
13 ppm	15 ppm
2 ppm	3 ppm

e. Sulfur Dioxide in Air. At an inlet pressure of 13 mm, a detectable peak was found at (64) in a mixture whose sulfur dioxide content was estimated to be 1.3 ppm. This system illustrates one of the problems which arises in high pressure mass spectrometry. The ion at (48) is quite unusual and occurs in a very limited number of spectra, consequently it is a valuable identifying ion. However, the ion molecule reaction $O_2 + O^+ \rightarrow O_3^+$ also has a mass of 48. This then could be a source of unpredictable error in the interpretation of any spectrum in which oxygen is a major component.

f. Propene in Carbon Dioxide. Another major problem in high pressure mass spectrometry is the tremendous broadening of peaks due to the major constituents. Thus far, no way has been found to reduce the broadening without simultaneously reducing the sensitivity. A brief study was made of the system CO_2-propene using both the model 21-620 and the model 21-103 mass spectrometers. With the model 21-103, the lowest concentration of propene that could be detected was about 180 ppm. Even this level of concentration was difficult to detect because the (42), $C_3H_6^+$, appears only as a dimple on the side of he rapidly rising (44). A situation such as this can be emedied to some extent by the use of other peaks in the spectra. or instance, while the (42) was difficult to detect, the (39) hich is prominent in propene was much easier to measure.

g. Oxygen in Nitrogen. The large number of requests or the determination of low concentrations of oxygen in nirogen and other gases prompted a brief study of the feasability f high pressure mass spectrometry for this analysis. The ajor peaks of both substances lie only 4 mass units apart and, s could be predicted, overlapping of the (28) on the (32) was he limiting factor. While mixtures of known concentration ere not prepared, it was still possible to see a peak due to xygen on the tail of the (28) at a pressure of 9 mm. This uggests that it may be possible to determine oxygen at conentrations near 10 ppm directly in nitrogen.

h. Summary. While this work is not yet considered omplete, the experience gained from the above and from work one before the period covered by this report has made it ossible to apply the knowledge gained to the solution of everal difficult service analyses as well as to a rather ineresting problem concerning the preparation of a gaseous ixture as a possible standard reference material. This work s reported in the following section.

2. Standard Reference Materials

a. Carbon Dioxide in Nitrogen. The increased nterest in possible long-term variations in the carbon dixide content of the atmosphere suggested the production of standard reference material consisting of a known concentraion of carbon dioxide in nitrogen at concentrations approxiately that of the atmosphere. Under normal operating conitions, the mass spectrometer would only be capable of deecting atmospheric concentrations of CO_2 (300 ppm) to an ccuracy of about 30%. Experience with high-pressure mass pectrometry suggested that an accuracy of better than 1% ight be possible within the range of inlet pressures previously used. Further, it suggested that a very rapid and precise method might evolve which would lend itself admirably to the production and analysis of such a gaseous standard reference material. However, such a method would depend completely on the availability of several mixtures of accurately known carbon dioxide content and it was felt that preparation of these was the logical first step.

A gas mixing manifold was constructed consisting of four pressure gages allowing pressures from 0 to 2000 psia to be measured with an accuracy greater than 1%. The gages for use above one atmosphere were calibrated over their entire ranges with a dead weight piston gage (see figure 2). The gage for pressures from 0 to 1 atmosphere was calibrated against a mercury manometer read with a cathetometer.

The equipment is shown in figure 3. Figure 4 shows schematically the arrangement of valves, gages and connections

Figure 2. Dead-weight piston gage.

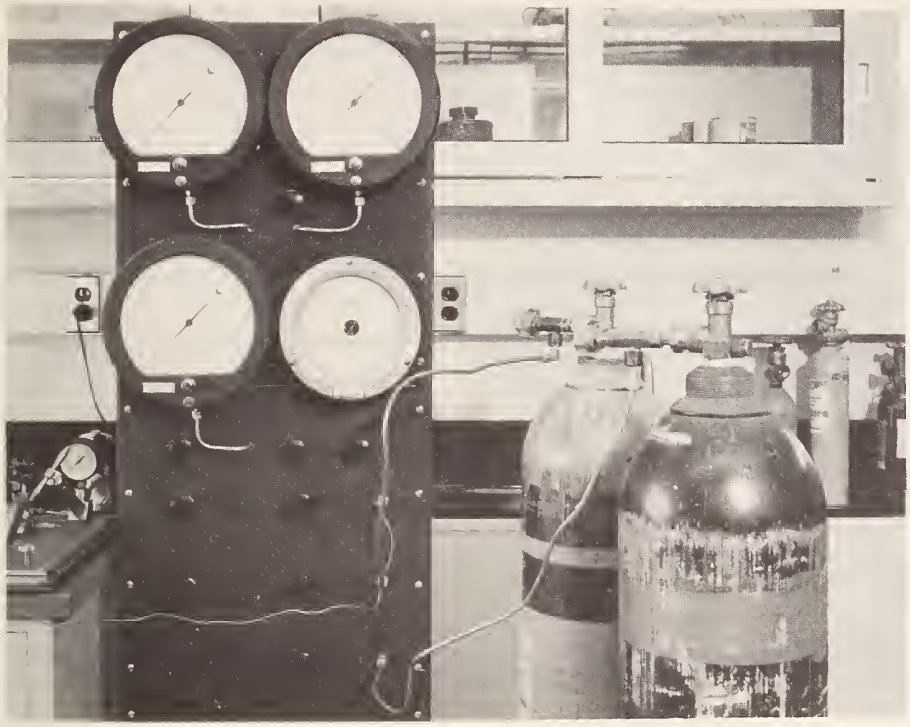

Figure 3. Gas-mixing manifold.

An initial mixture of carbon dioxide of approximately 5 ole percent was prepared from analyzed samples of nitrogen nd carbon dioxide. This was analyzed by mass spectrometry, y Orsat absorption analysis, and gravimetrically. The results ogether with the value calculated from the measured mixing ressures are shown in table 4.

Table 4. Analysis of carbon dioxide in nitrogen, mixture 1.

Analytical Method	CO_2 in Mole Percent
Mass Spectrometry	5.52 ± 0.07[a]
Orsat Analysis	5.5 ± .2[a]
Gravimetry	5.49 ± 0.05[a]
Calculated Value	5.60 ± 0.06[b]

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[a] Standard deviation.
[b] Estimate of the error involved in mixing.

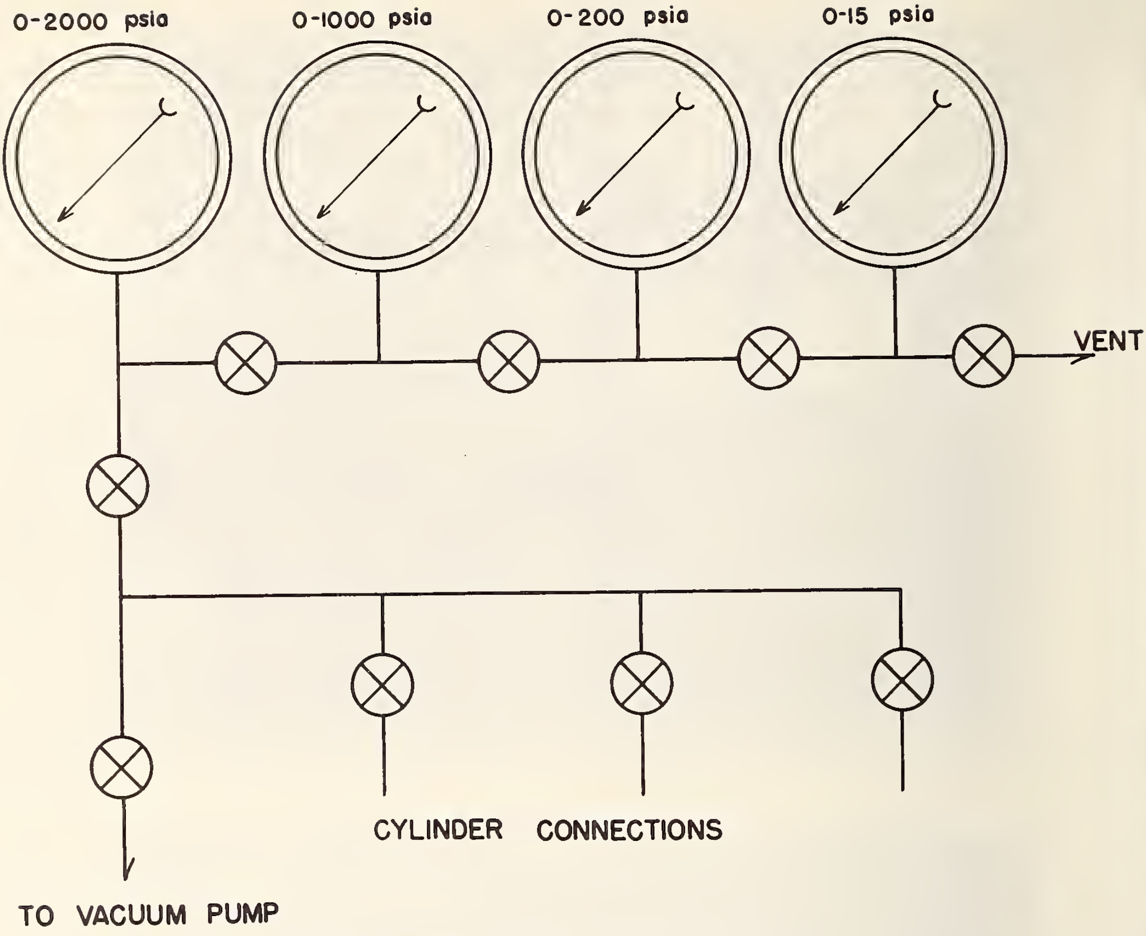

Figure 4. Schematic diagram of gas-mixing manifold.

This concentration region is ideal for accurate mass spectrometric and gravimetric analyses. Accordingly, the correct value for the mixture is taken as the average of these two methods. Some interaction between carbon dioxide and nitrogen has been reported at elevated pressures [3]. Since no data was available at the pressure of CO_2 at which the abov mixture was compounded, only a crude approximation of the magnitude of the effect was possible. This approximation amounts to 1.25% and reduced the calculated value from 5.67 to 5.60.

This mixture was then used to prepare a second mixture with a calculated composition of 0.631 mole percent. In this concentration range, gravimetry is the only method capable of the desired degree of analytical accuracy. The results are shown in table 5.

Table 5. Analysis of carbon dioxide in nitrogen, mixture 2.

Analytical Method	CO_2 in Mole Percent
Gravimetry	0.628 ± .004[a]
Calculated from Measured Pressure	0.631 ± .006[b]
Mass Spectrometry	0.63 ± .01

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[a] Standard deviation.
[b] Estimate of the error involved in mixing.

The previously mentioned molecular interaction studied by Haney and Bliss has no significant effect at this concentration of carbon dioxide and the only deviation from ideality to be considered in the mixing data is the compressibility of nitrogen. Values of the compressibility factors for both nitrogen and carbon dioxide, accurate to better than 0.1%, are available [4].

Gravimetry at this level is satisfactory but large volumes of gas are necessary and unavoidable fluctuations in ambient temperature and barometric pressure can constitute significant sources of error. While these errors were minimized by careful observation of ambient conditions, it was not possible to eliminate the effect completely. For this reason, the concentration determined from the measured pressures is considered more valid than the gravimetric value. Accordingly, the value 0.631 mole percent is considered to be the concentration of carbon dioxide, in this mixture.

This latter mixture was next used to prepare 3 additional mixtures whose concentrations were determined both by gravimetry and by calculation from the measured mixing pressures. The results are shown in table 6.

Table 6. Analysis of carbon dioxide in nitrogen, mixtures 3,4, and 5.

Sample	CO_2 in Mole Percent	
	Gravimetry	Calculated from Measured Pressure
Mixture 3	0.0233 ± .0003[a]	0.0232 ± .0003[b]
Mixture 4	0.0308 ± .0010[a]	0.0312 ± .0003[b]
Mixture 5	0.0341 ± .0010[a]	0.0344 ± .0003[b]

---

[a] Standard deviation.
[b] Estimate of the error involved in mixing.

These latter three mixtures were those used to calibrate the mass spectrometer over a concentration range from 200 to 350 ppm. The three mixtures were analyzed at inlet pressures sufficiently high to allow the ion current at (44) due to carbon dioxide to be read to better than 1%. The ion current at (28) was measured under identical ionizing conditions to avoid complication arising from attempts to reproducibly vary the ionizing current. Consequently, it was necessary to replace the input resistor for the low sensitivity setting of the preamplifier ($5x10^{10}$) with a resistor of lower value ($1x10^9$). This arrangement allowed both mass numbers of interest to be recorded consecutively and rapidly at magnitudes so that each could be read to better than 1%.

A series of measurements were then made on two successive days. The ratio of the ion current at (44) to that of (28) was then calculated. The results are shown in table 7.

When the average of each set of ratios is plotted against the concentration of carbon dioxide calculated from the measured pressures, a straight line results as shown in figure 5.

Table 7. Ratio of $\frac{(44)}{(28)}$ for three mixtures determined on two successive days.

Date	Mixture No. 3	Mixture No. 4	Mixture No. 5
3/24	0.0131	0.0176	0.0196
	.0132	.0175	.0196
	.0129	.0177	.0195
	.0130	.0176	.0194
	.0131	.0177	.0195
		.0174	
		.0176	
		.0177	
Average	0.0131	0.0176	0.0195
3/25	0.0131	0.0177	0.0197
	.0132	.0177	.0197
	.0132	.0176	.0195
			.0195
Average	0.0132	0.0177	0.0195

The linearity indicates that the ratio of the ion current at (44) to that of (28) is directly proportional to the concentration of carbon dioxide. The inlet pressures for all samples reported in table 7 varied from 0.86 mm to 1.04 mm. The variation of the measured ratios with pressure are random and show no relation to the pressure, in the range of pressures measured.

This method will allow rapid determination of large numbers of samples of carbon dioxide in nitrogen on a routine basis. It will only be necessary to periodically affirm the calibration factor of the spectrometer to be certain that the ratio determined from the calibration standards has not changed.

b. Other Applications. The method for the determination of carbon dioxide in nitrogen described above is capable of a high degree of accuracy because it is based on a comparison of sample data with that obtained from standards of known composition. The pressures necessary to determine carbon dioxide accurately by this method are only 1 mm. This pressure could easily be increased from 5 to 10 times. Detection of ion currents 100 to 200 times smaller could also be achieved. Thus concentrations of carbon dioxide as much as one thousand times less could be detected, although with diminished accuracy.

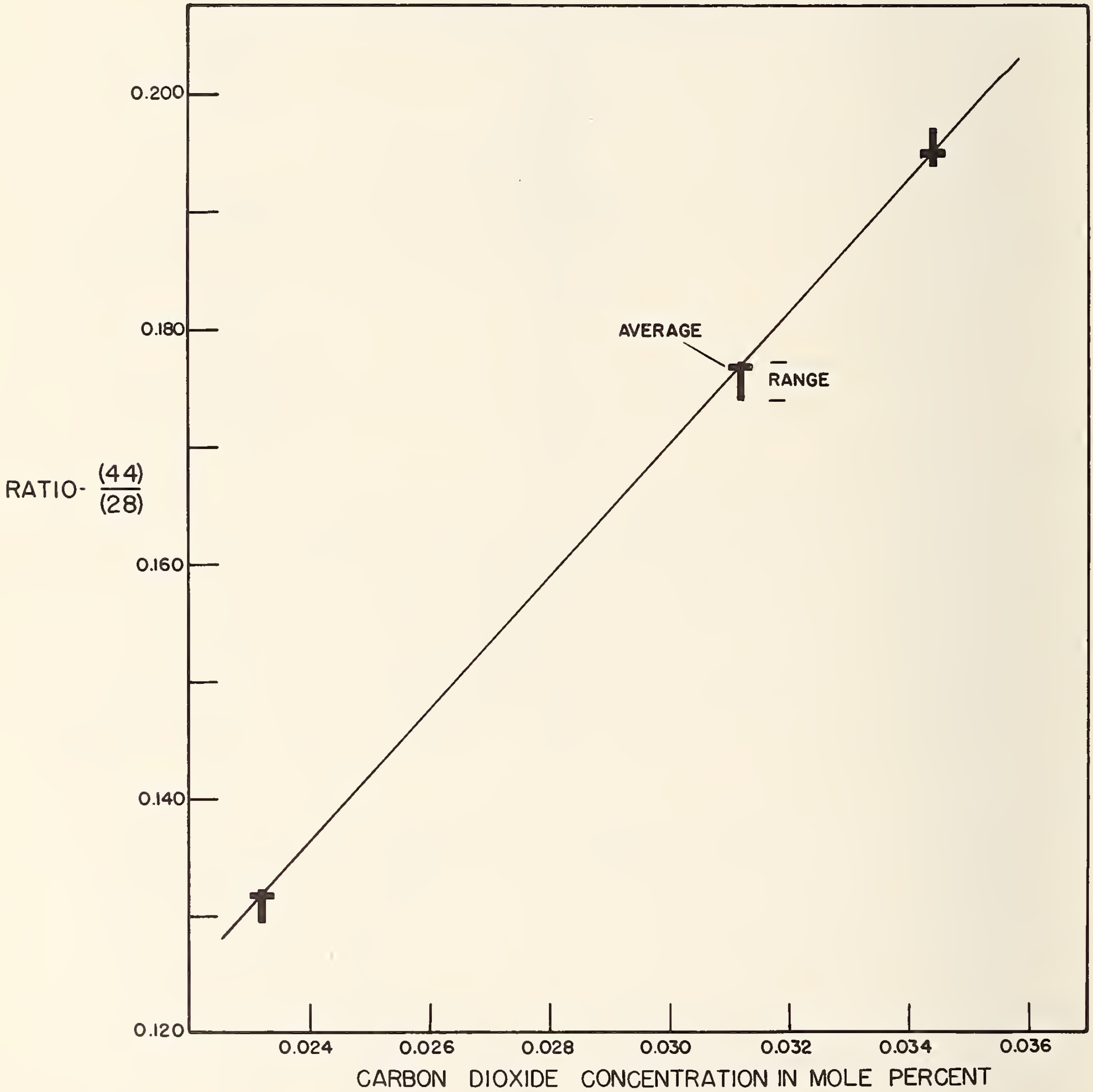

Figure 5. Relationship between the (44)/(28) ratio and the concentration of carbon dioxide.

Two gases presenting particularly difficult analytical problems in the region from 1 to 1000 ppm are carbon monoxide and oxygen. Carbon monoxide has a parent ion coincidental with that of nitrogen. Oxygen is an ever present background ion current in the mass spectrometer. Therefore, neither of these can be easily analyzed directly by mass spectrometry in the low concentration region. If, however, they were first converted to carbon dioxide, the analysis could be carried out as easily and as accurately as the previously described method.

Methods for the conversion of carbon monoxide and oxygen are readily available and no great difficulty with an analysis of this sort is anticipated.

D. Analytical Activities

1. Sample Pretreatment Prior to Mass Spectrometric Analysis

In many cases it is impossible to obtain quantitative results on analysis of certain samples by direct mass spectrometry. Some technique must be available by which the sample can be treated to alter its composition or nature in order to perform accurate analysis. A good illustration of this problem is a sample which contains deuterium and hydrogen in which exchange between the deuterium and hydrogen in the sample and that of water invariably present in the mass spectrometer can occur. Typical of this type of material is heavy water. It is impossible to directly measure the ratio of deuterium to hydrogen in water containing high concentrations of deuterium even with extensive pre-conditioning of the spectrometer.

The best method for this type of analysis is to first reduce the water or other compound to hydrogen and deuterium which can then be measured directly. Several methods have been suggested for this reduction but, in all cases, they are rather time consuming and do not lend themselves to the routine analysis of large numbers of samples, particularly those containing high concentrations of deuterium.

The system shown in figure 6 was found to work quite well for the rapid reduction of water containing as much as 99% deuterium. Liquid samples of less than 5µl volume are admitted through a heated silicone rubber septum into the evacuated system. The heated stainless steel septum holder is identical to that described in last year's report [ref. 1, p. 2]. The vaporized sample passes through the zinc column, heated to about 450°C, and ultimately the gaseous reaction products are collected in the small receiver (A). Any minor amounts of unreacted water are trapped in the small trap (B). The small size of the sample allows virtually complete reduction. Several samples were reduced without using the cold trap and no excess water was found in the reduced gases. Many samples can be reduced and analyzed after only a short period of conditioning with water of approximately the deuterium content as that of the sample.

Some further work is planned with this apparatus on a determination of the magnitude of the effect, if any, of preferential reduction of hydrogen especially as it may affect samples having high deuterium content.

Other samples in which the deuterium was determined with success were DCl and DBr, both of which were reduced over copper at 400°C. Deuteriated ammonium chloride was analyzed by reducing a solution consisting of a weighed quantity of water of known deuterium content in which had been dissolved a weighed portion of the ND_4Cl. The resulting solution was then reduced with hot zinc and the change in deuterium concentration was then used to calculate the deuterium content of the ND_4Cl.

The method and operation described above has the advantage that samples can be prepared for analysis with great rapidity and that many samples can be analyzed in a short time. However, it was found to lack precision. Results agreeing within 1% were possible but it is believed that isotope exchange effects preclude better precision.

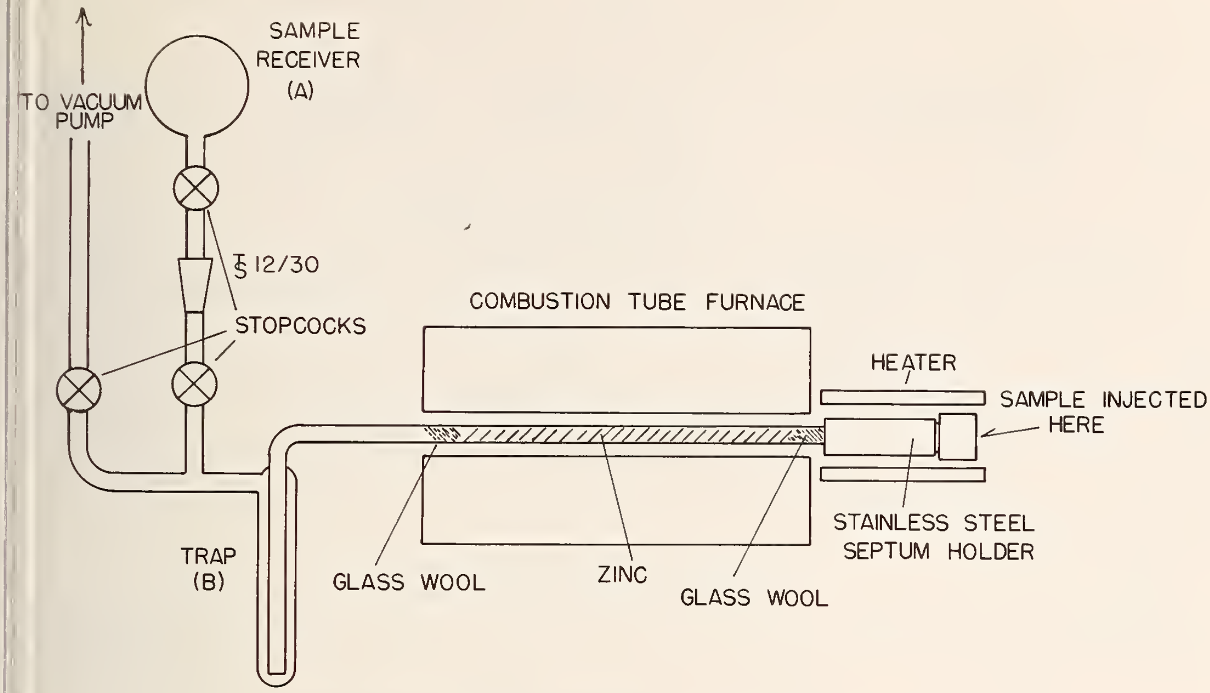

Figure 6. Apparatus for the rapid reduction of water samples.

2. General Applications

A large number of service analyses were performed, many of which included other methods of analysis such as nuclear magnetic resonance, gas-liquid chromatography, infra-red gas analysis, gravimetry and adsorption gas analysis. Also included was the compounding of several gas mixtures.

While some of the analytical services are of a routine nature, many presented a challenge due to lack of reference data or due to lack of knowledge of the system involved. A typical problem was that of developing a method for the determination of the presence of mixed boron halides resulting from the reaction of mixtures of boron halides. This work was performed in cooperation with members of the Inorganic Chemistry section of the Inorganic Chemistry Division.

The primary problem was the complete lack of reference spectra of the mixed boron halides and the existence of only a limited amount of information on the spectra of the boron halides. In spite of this, a method of analysis was developed which allowed not only the identification of the following species but allowed a reliable estimation of their concentration:

BF_2Cl $BFCl_2$ $F_2B\ BFCl$ $F_2B\ BCl_2$ $FClB\ BCl_2$

Other service analysis of some interest included the development of a rapid method for the testing of calibrated helium leaks, determination of ^{18}O enrichment of benzoic acid used in determinations of several organic reaction mechanisms analysis of high purity methane for use as a primary standard by the gas industry, and the chromatographic purification of cyanogen azide.

Table 8 gives a breakdown of typical service analysis indicating the type of analysis and the number in each category.

Table 8. Summary of mass spectrometric gas analysis services.

Material	Number of Samples	Sample Size	Determined
		Pure Chemicals	
N_2	2	500 ml STP	O_2, Ar
SF_6	1	Cylinder	Purity
CH_4	2	Cylinder	N_2, O_2, CO_2, C_2H_6, C_3H_8
He	1	Cylinder	N_2, O_2
$CH_3\text{-}C{\equiv}CH$	2	Cylinder	Methyl ether, 1-Butyne
N_2	1	Cylinder	O_2, H_2O
Morpholine	6	20 ml of each	Purity
Nitromethane	3	20 ml of each	Nitroethane, Nitropropane
C_2F_4	1	1 ml STP	C_2F_6

Table 8. (Continued)

Material	Number of Samples	Sample Size	Determined
		Organic Substances	
ethyl ethacrylate	3	20 ml of each	Comparison of mass spectra
enzoic acid	3	0.05 g	Amount of O^{18} enrichment
orpholine	2	20 ml	Compare mass spectra
		Inorganic Substances	
nknown Gas ixtures	2	100 ml STP	N_2, O_2, CO, CO_2, H_2
ixtures of $_2$ in N_2	5	Cylinder	O_2
ixtures of F_4 in air	12	100 ml STP	Total pressure of CF_4
ixtures of $_2$, O_2, CO_2	7	Cylinder	N_2, O_2, CO_2
e	4	300 ml STP	Rate of helium passage through various sized leaks
roducts of etonation	4	20 ml STP	N_2, O_2, CO_2, CO, H_2O
nknown in ealed Cell	1	10 ml STP	N_2 with normal isotope distribution
nknown Gas ixture	2	10 ml STP	H_2O, N_2, O_2, CO_2, CO
aseous Products of Reaction	5	0.1 ml STP	BF_3, BF_2Cl, $BFCl_2$, BCl_3, F_2BBFCl, F_2BBCl_2, $FClBBCl_2$, B_2F_4, B_2Cl_4

Table 8. (Continued)

Material	Number of Samples	Sample Size	Determined
Inorganic-Organic Mixtures			
Polluted Air	2	1000 ml STP	Chloroform, toluene
Air	12	10 to 300 ml STP	Possible hydrocarbon pollution, CO_2 and H_2
Flue Gas	2	500 ml STP	N_2, O_2, Ar, CO, CO_2, NO_2, SO_2
Products from Teflon Combustion	2	2 ml STP	N_2, O_2, CO_2, CF_4, SO_2F_2, SiF_4
Products from SiC Combustion	6	0.5 ml STP	CO_2, CF_4, SO_2F_2, SiF_4 C_2F_6, C_4F_8, C_3F_8, C_2F
Gaseous Products of Reaction	3	$3x10^{-7}$ moles	N_2O, C_2H_5Cl, C_2H_5OH, C_2H_4, C_2H_2, HCl, CO_2, Triethyl phosphate
Gaseous Products of Reaction	1	10^{-3} ml STP	H_2, CH_4
Gaseous Products of Reaction	2	0.01 ml STP	Hydrocarbons, boron compounds
Gaseous Products of Reaction	1	0.01 ml STP	Spectrum of compound $C_2H_3BCl_7Ge$
Gaseous Products of Reaction	1	$5x10^{-8}$ mole	N_2, O_2, H_2O, C_2H_4, C_2H_5OH, C_3H_8, C_2H_5Cl, Triethyl phosphate
Gaseous Product of Synthesis	4	0.5 ml STP	Purity of $C_2F_4H_2$
Gaseous Product of Synthesis	4	0.5 ml STP	$C_3F_4H_2$, $C_3F_5H_3$, CO_2
Gaseous Products of Polymer Combustion	6	0.5 to 1.0 ml STP	C_2F_4, $C_3F_3H_3$, $C_3F_5H_3$, cyclo-C_4F_8
Noncondensibles from Reaction	1	10^{-3} ml STP	H_2, Air, CH_4
Gaseous Products from Reaction	2	10^{-3} ml STP	BF_3, CH_3BF_2, $(CH_3)_2BF$

Table 8. (Continued)

Material	Number of Samples	Sample Size	Determined
	Deuterated Compounds		
$_2$	3	Cylinder	H/H+D ratio
Br	1	Cylinder	H/H+D ratio
cetic Acid-d_4	1	30 ml	H/H+D ratio
D_4Cl	3	0.05 g. crystal each	H/H+D ratio
$_2O$	1	10 ml	H/H+D ratio
D	1	10 ml STP	H_2, D_2

(E. E. Hughes and W. D. Dorko)

2. POLAROGRAPHIC ANALYSIS

A. Introduction

The polarographic research program has a two-fold objective. One aspect is the development of methods of increased precision and accuracy. The second is concerned with improvements in sensitivity in trace-level determinations. The use of micro-sized samples is a further aim in both program areas.

Success has been achieved in both of these directions during the past year. Considerable effort has been devoted to studies of differential polarography. A cell-reversal technique has been found to be highly advantageous in improvement of precision and accuracy. In addition, a number of methods have been developed for trace element determinations, particularly in standard reference materials and research materials used in investigations by other groups. The cathode-ray polarograph shown in figure 7 was used for all the work described, except for some determinations in the ultra-trace range. Anodic stripping voltametry has proved especially useful at this level of determination.

B. Facilities

The polarographic instrumentation is essentially the same as was described in the summary report of last year [ref. 1, p.8 However, the new facilities at the Gaithersburg laboratories permit a much more convenient arrangement of this equipment. The measurements laboratory has been divided into sub-modules by means of partial partitions allowing each type of instrument to be housed in a separate compartment.

A second thermostated bath and electrode synchronization device has been acquired for use with the cathode-ray polarograph. This makes it possible to use one electrode stand for single cell or for subtractive double-cell measurements and to keep a pair of well-matched capillaries in reserve, yet available for ready use for high-precision comparative measurements.

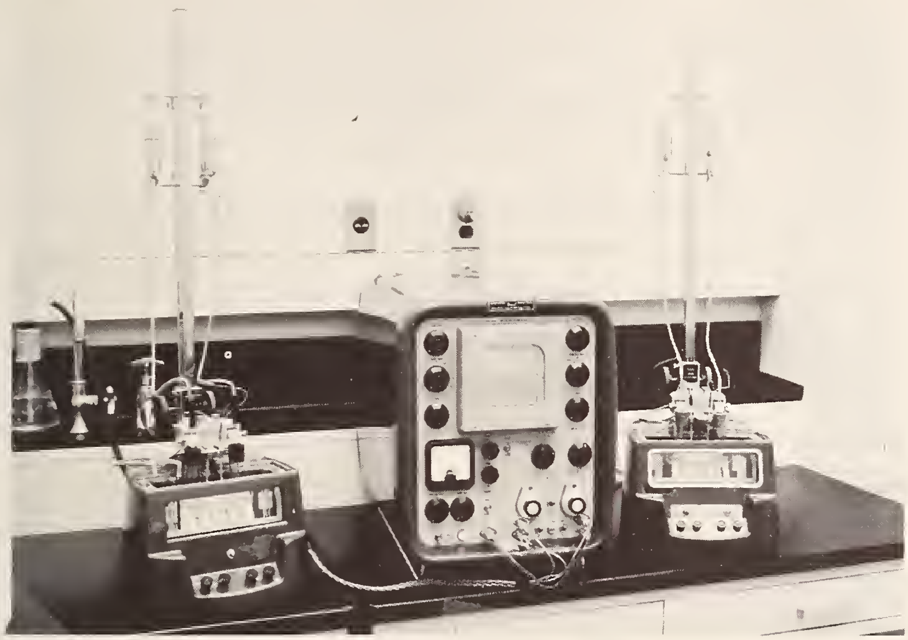

Figure 7. Cathode-ray polarograph equipped with dual electrode synchronizers.

C. Research Activities

1. High-Precision Polarography

Differential polarographic techniques have been developed in this laboratory which permit the determination of major constituents in brasses, alloys and other matrices with a precision of as good as 1.6 parts in 10,000. These techniques were described in a talk presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, February 21, 1966. A paper describing the work is being submitted for publication.

The precision of ordinary differential polarography is greatly limited by the matching of the capillaries and general electrode balance. The techniques developed here minimize this effect. To eliminate the constant bias owing to slight differences in capillary characteristics, resevoir heights, and general electrode balance, the differential signal from the sample is measured against that of an accurately known standard. The cells are then interchanged and the differential signal is remeasured. The average gives a result with minimum effect from electrode inequalities, since a positive unbalance in one position leads to an equal negative unbalance in the second position.

These techniques have been used for the determination of cadmium in metal-organic compounds and in lithium-cadmium alloys, copper and zinc in brass and manganese bronze, and iodine at the 0.1 ppm level. The most precise results, obtained for 10 determinations of cadmium in 1 N hydrochloric acid at the 100-ppm level, showed an average deviation of 0.016% of the amount present.

Copper and zinc were determined together in a solution of pyridine and pyridinium chloride. The metals were dissolved in dilute nitric acid, evaporated to dryness, after which the residues were dissolved in hydrochloric acid, pyridine and water, so that the final solutions were 0.5 M in pyridine and pyridinium chloride. Results for the analysis of standard reference materials, 62d (a manganese bronze), 37e (a sheet brass), and a copper-zinc solution are shown in table 9.

Table 9. Differential polarographic determination of copper and zinc.

Sample	Cu Present, %	Cu Found, %	Zn Present, %	Zn Found, %
Cu-Zn Solution	49.79	49.80	50.21	50.20
Brass, 37e	69.61	69.71	27.85	27.75
Bronze, 62d	59.07	59.03	37.14	37.06

This technique has the advantage that highly accurate and precise results are obtained on very small samples. The measurements of table 9 were made on 5 ml. of solution containing from 90 to 200 ppm of copper and zinc. This would be the equivalent of 90 to 200 micrograms of sample if a final volume of 1 ml had been used. The method is equally applicable to the determination of a number of other ions such as tin, lead, nickel, uranium, and chromium, many of which can also be determined when present together in the same solution.

Differential polarography may also be used to advantage in homogeneity and specification testing merely by comparing the unknown in one cell against a similar standard in another cell.

Certain anions may also be determined by this technique. For example, a research project in another government agency required that solutions containing about 0.1 ppm of iodide be analyzed with results accurate to within 2% of the true value. Iodide gives a poorly-shaped wave with cathode-ray polarography; however, the iodate wave is well-defined. The oxidation of very small amounts of iodide to iodate has been reported to be incomplete; therefore, it was necessary to investigate the optimum conditions. It was found that by adjustment of the pH to 3, addition of bromine, and gentle heating at steam bath temperatures to remove bromine, quantitative results could be obtained. The iodate may then be measured polarographically in a supporting electrolyte containing 10 g per liter each of sodium carbonate and potassium chloride.

Results on standard iodate solutions showed an average deviation of 5 parts in 1000 which is equivalent to an uncertainty of 0.5 ppb in the 0.1 ppm solution submitted for analysis.

2. High Sensitivity Polarography.

a. Determination of Tellurium in Selenium. A method developed in this laboratory [5] for the determination of trace amounts or greater of tellurium in cartridge brass and white cast iron standard reference materials has been extended to include its determination in intermediate purity selenium. The method, as originally developed, is extremely sensitive and selective and is applicable to the determination of nanogram quantities of tellurium in almost any matrix. For determination of tellurium in selenium, 2-g samples were dissolved in nitric acid and evaporated to dryness. Sulfuric acid was then added, the solutions were evaporated several times with nitric acid to remove selenium, and evaporated to dryness. The resulting residues were dissolved in 2 ml of 50% phosphoric acid, the solutions were diluted to 10 ml, and measured on a cathode ray polarograph at -1.2V vs. a mercury pool anode. Values of 0.33 and 0.35 ppm of tellurium were obtained. A limit of detection of 0.005 to .01 ppm in the final solution is possible. If a final volume of 5 ml is used, this would correspond to about 0.01 to 0.02 ppm in the original material. Larger sample weights would permit further lowering of the absolute detection limit.

The selenium also was examined for copper, cadmium, and lead. Two-gram samples were dissolved in a mixture of dilute nitric and hydrochloric acids and evaporated to dryness several times with hydrobromic acid to volitalize selenium. The residues were dissolved in 0.5 ml of 0.1 N hydrochloric acid, followed by the addition of 2.0 ml of 0.2 M oxalic acid and 2.0 ml of 0.06 M ammonium hydroxide, and examined polarographically. Polarographic examination of the resulting solution showed copper, cadmium, and lead each to be below the 0.5-ppm level.

b. Anodic Stripping Analysis. Both the high-purity zinc and reagent-purification programs have necessitated investigation of the determination of ultra-trace amounts of copper, cadmium, and lead. Extremely high instrumental sensitivity may be obtained by preconcentration by electrolysis (plating) onto a cathodic electrode for relatively short periods of time, generally about 5 to 15 minutes. The drop is then stripped anodically, and the enhanced peak current resulting from the oxidation of the metal accumulated in the drop is measured.

Several types of electrodes may be used including graphite, platinum, mercury-plated platinum, or a hanging mercury drop. The latter, the type that is commonly called a Kemula electrode, was used for the work described here. The electrode size is controlled by extrusion of a mercury drop through a glass capillary attached to a micrometer syringe.

There are many factors effecting the reproducibility of measurements with such an electrode, including temperature, plating potential, reproducibility of stirring rate during the preconcentration electrolysis, variation in drop size, completeness of oxygen removal, and capillary and cell positioning. Other problems, common to trace analysis in general, include adsorption on container walls and atmospheric and reagent contamination.

Since high-purity reagents are required for the analysis of high-purity zinc, several fractions of hydrochloric acid, purified and/or distilled by the Separation and Purification Section were submitted for evaluation of the effectiveness of the purification process. These were checked for copper, cadmium, and lead by the anodic stripping technique. The unpurified acid was found to contain about 3 ppb of cadmium, 13 ppb of lead, and 21 ppb of copper. Cadmium was not detected in any of the distillation fractions. In this particular case, the limit of detection was about 1 ppb; however, greater sensitivity could be obtained by such means as increasing the plating time and the electrode size. In the third fraction, the lead content was decreased to about 3 ppb and copper to about 4 ppb.

3. Ultra-Small Sample Analysis

As a result of studies by the Harry Diamond Laboratories on the vacuum-deposition of multi-component thin films which may be used in resistance circuits, analyses of microgram samples of nickel-chromium-copper-aluminum (75-20-2.5-2.5) films were required. Owing to the very small amounts of film usually involved, few analytical measurements of composition had been made by other workers in the thin-film field. The sensitivity and selectivity of the cathode ray polarograph appeared to offer a possible means of solution to the problem.

The films, weighing as little as 300 micrograms, had been deposited on glass plates weighing approximately 5 to 10 g. Obviously, the weighing errors for such samples are large. Fortunately the nickel-chromium-copper-aluminum ratios, and in some cases the nickel-chromium-copper ratios, give the required information. For convenience, the methods developed are based on the use of three separate aliquots from a solution of the film which has been stripped from the plate with aqua regia. However, if increased sensitivity is desired, as would be required for much smaller samples, all three may be done on the entire solution by making suitable separations. Chromium was determined in 1 *M* sodium hydroxide after oxidation with hydrogen peroxide. For the determination of copper and nickel, chromium was first reduced with sulfur dioxide, after which copper and nickel were measured in a pyridine-pyridinium sulfate supporting electrolyte. Aluminum was determined as the Solochrome Violet RS complex as described earlier [ref. 1, p. 13 after removal of copper and nickel by extraction with sodium diethyldithiocarbamate and extraction of the aluminum with cupferron. The precision of the results was generally about ± 2%. This can be improved, whenever more accurate results are required, by the use of differential polarography.

Other thin films submitted by Harry Diamond Laboratories were of nickel-chromium, which were analyzed as described above, and of antimony-bismuth, which were measured as described earlier [ref. 1, p. 13].

D. Analytical Development Activities

1. Standard Reference Materials

Many of the methods used for the analysis of standard reference materials, while very accurate, are time-consuming, tedious, and/or often require large sample weights. Polarography has been applied in this laboratory to many of these materials in an attempt to improve the methods, for confirmatory analysis, and to provide results by more than one technique to evaluate reliability of analytical results. During the past year, procedures have been developed for the polarographic determination of 6 elements in various standard reference materials and for the determination of about 12 other elements in a variety of matrices. Values obtained by polarography on standard reference materials are shown in table 10 and are compared with those obtained by other analysts using different techniques.

a. Stainless Steels. Polarographic procedures were investigated for the determination of aluminum, lead, and tin in stainless steel spectrographic standards 1152 and 1154. Aluminum was determined in 1152 on 0.2-g samples which were dissolved in aqua regia. Most of the copper, iron, nickel, cobalt, manganese, vanadium, and titanium was extracted as diethyldithiocarbamate complexes with chloroform. Aluminum was then extracted with cupferron and chloroform at a pH of 4.5, followed by destruction of the organic material by fuming to dryness with nitric acid and perchloric acid. To remove residual amounts of iron and titanium, an additional acid cupferron extraction was made. Aluminum was then separated from residual amounts of chromium by extraction of the cupferrate complex at a pH of 4.5. The organic material was destroyed as above, the residue was dissolved in 1 ml of 5 M perchloric acid, 5 ml of 2 M sodium acetate, and 2 ml of 0.05 percent Solochrome Violet RS, diluted to 50 ml, and heated 5 minutes at 55-70°C to form the aluminum-dye complex. The complex was measured polarographically at -0.7 V vs. a mercury pool anode.

Samples of 1154 weighing 0.5 g were dissolved in 50 percent hydrochloric acid, diluted, filtered, and the residue ignited at 800°C. After evaporation to dryness with sulfuric acid and hydrofluoric acid, the residue was fused with 0.20 g sodium carbonate and added to the original filtrate which was then diluted to 50 ml. Aluminum was then determined as described

Table 10. Analysis of Standard Reference Materials by Polarographic and Other Techniques

SRM	Element	NBS (Polaro- graphic)	NBS (Other Tech- niques)	A	B	C	D	E	F	G	H	I	Final Certified Value
1152	Pb	.001	.003[a]						.003[a]				.001
	Sn	.004	.004[a]						.004[b]				.004
	Al	.003											.003
1154	Pb	.012	.014[a]						.014[a]				.012
	Sn	.023	.030[a]						.020[b]				.023
	Al	.034	.039[a]						.039[a]				.035
73c	Cu	.082		.081[c]	.077[d]						.082[c]		.080
	Ni	.245	.248[c]	.248	.241[e]						.251[c]		.246
1156	Al	.047			.044	.050	.046						.047
	Ti	.208			.207	.205	.21 [c]						.21
82b	Ti	.028						.027[b]		.025[c]		.027[c]	.027

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[a] Spectrographic

[b] Titrimetric

[c] Photometric

[d] Gravimetric, 10 g sample

[e] Electrogravimetric, 5 g sample

[f] Photometric, 5 g sample

above, using 10-ml aliquots.

Lead was determined polarographically in stainless steel standards 1152 and 1154 after making some separations. The samples, weighing from 0.2 to 0.5 g, were dissolved in dilute aqua regia and evaporated to dryness. The resulting residues were dissolved in 2 ml of 50% hydrochloric acid, and evaporated to dryness again. Iron was extracted with isobutyl acetate from a hydrochloric acid solution of the residue. Chromium was volatilized as chromyl chloride by fuming to dryness with perchloric and hydrochloric acids. Residual iron was reduced with ascorbic acid and lead was extracted as the sodium diethylidithiocarbamate complex with chloroform from an ammoniacal solution containing potassium cyanide and sodium tartrate. After destruction of the organic material, lead was measured polarographically in a sodium tartrate-nitric acid supporting electrolyte at -0.7 V vs. a mercury pool anode. Spectrographic standard 444 was used as a reference standard and duplicate values of 0.0038% of lead were obtained. The standard is certified to contain 0.0037% of lead, based on chemical and spectrographic analyses.

Tin was determined in sample 1152 by two methods using 1-g samples. In one set, the samples were dissolved in 30% hydrochloric acid, oxidized with nitric acid, heated to boiling, gassed with hydrogen sulfide, and filtered. After oxidation of sulfide and organic material, tin was precipitated with ammonium hydroxide using aluminum as a carrier. The precipitates were dissolved in hydrochloric acid and diluted to 25 ml in a supporting electrolyte whose final concentration was 1 *M* in hydrochloric acid and 4 *M* in ammonium chloride. Tin was measured on the cathode-ray polarograph at about -0.45 V vs. a mercury pool anode. In the second set, tin was extracted as the thiocyanate complex from a hydrochloric acid solution. After oxidation of the thiocyanate and organic material, tin was precipitated with ammonium hydroxide using iron as a carrier and finished as described above.

Tin was determined using 0.5-g samples of 1154 by thiocyanate extraction-ammonia precipitation using iron as a carrier, and finished as for 1152. Individual results are given in table 11.

Table 11. Polarographic determination of tin.

Method	1152	1154
	Percent	
Hydrogen sulfide precipitation	0.0041	
	.0045	
Thiocyanate extraction	.0043	0.0238
	.0042	.0245
	.0045	.0224

A value of 0.021% of tin was found for reference standard 101e, which is certified to contain 0.020% tin and 0.015% for reference standard 444 which is certified to contain 0.014% of this element.

The thiocyanate separation would seem to be quicker and more convenient than the hydrogen sulfide precipitation. Both methods, however, offer considerable advantages over the traditional method consisting of hydrogen sulfide separation, ammonium hydroxide precipitation, reduction of tin(IV) to tin(II) by prolonged boiling with lead, and maintenence of an oxygen-free atmosphere during the subsequent titration with standardized iodate. A value of 0.020% of tin in a 10-g sample of 101e was obtained earlier by the author using this latter method.

For the certification of stainless steel 73c, attempts to determine both copper and nickel in the same ammonium hydroxide-ammonium chloride supporting electrolyte with no prior separations gave reasonably good results. However, for the more accurate work needed for the certification of a standard reference material, copper and nickel were determined together in 0.2-g samples in pyridine-pyridinium sulfate media after extraction of iron with isobutyl acetate and volatalization of chromium as chromyl chloride. Values of 0.129% of copper and

.199% of nickel were obtained on the reference standard 73b which is certified to contain 0.125 and 0.197% respectively. Copper was also checked by another direct determination in the following manner. The iron was reduced with hydrazine hydrochloride and copper measured in a starch-sodium formate supporting electrolyte (pH 2-3) at -0.25 V vs. a mercury pool anode. Nickel was not determined in this media; however, lead could be measured at about -0.5 volts in the same solution. A value of 0.124% of copper was obtained for 73b by this procedure.

The direct determination of copper and nickel in ammonium hydroxide-ammonium chloride media should be adequate for many purposes. It is quite rapid, requiring only the sample dissolution, neutralization, dilution to volume, and polarographic measurement. The results would generally be slightly low, owing to adsorption on the bulky hydroxide precipitate. Ascorbic acid is unsuitable as a reductant for iron in this case, because the copper may be partially reduced to the metal. Results obtained by this direct method are shown in table 12.

Table 12. Direct polarographic determination of Cu and Ni in stainless steel.

Sample	Copper found, Percent	Nickel found, Percent
73b	0.119	0.195
73c	.084	.230
	.085	.237
	.085	.221
	.083	.225

b. Maraging Steel. Polarographic determinations of aluminum and titanium in maraging steel, standard reference material 1156, were also investigated. The procedure for aluminum utilized the method described above. Titanium was determined in a sodium acetate-EDTA supporting electrolyte after cupferron and ammonium hydroxide separations. Sample weights of 0.2 g were used in both determinations. Standard reference material 170a was used as a reference standard in both determinations. A value of 0.277% was obtained for titanium, whereas the certified value is 0.281%. The polarographic result, however, may be compared with a value of 0.278% titanium obtained earlier by the author using the conventional hydrogen peroxide-photometric method, after separation of all interferences. At the same time, a value of 0.282% was obtained by a gravimetric procedure using a 5-g sample. The polarographic determination yielded a value of 0.043% for aluminum in 170a, which is certified to contain 0.046%. However, an earlier determination by the author gave the value 0.042% using the conventional ASTM sodium bicarbonate-sodium hydroxide-aluminum oxide method, with a 10-g sample.

c. Nickel-Chromium Cast Iron. Titanium was determined in nickel-chromium cast iron 82b with 0.5-g samples by essentially the same procedure as used for 1156, with the exception that the ammonium hydroxide separation was omitted. A value of 0.047% was obtained on reference standard 82, which is certified to contain 0.048% titanium.

2. Research Materials

The versatility of polarography has made it very useful in the analysis of a wide variety of research materials, as well as in many "trouble shooting" situations in which chemical analyses have been needed. A few of the more interesting problems and the methods developed for their analysis by cathode ray polarography are described in the following sections.

a. Lubricating Oils. Three lubricating oils containing 1, 50, and 500 ppm respectively of each of copper, iron, aluminum, lead, chromium, nickel, tin, silver, and magnesium were prepared by another NBS group as standards to monitor engine wear and predict possible engine failure. Because of difficulties in preparation and mixing of the sample, homogeneity and possible segregation on standing were of major interest. Samples, taken under a planned program, were submitted for analysis. Polarography was found to be especially convenient for the determination of copper, nickel, lead, iron, and aluminum by the methods described below.

In all cases, it was necessary to ash the samples, which had been prepared from relatively non-volatile metal-organic standard reference materials as described in an NBS Monograph [6]. Samples weighing from 1 to 18 g were very slowly dry-ashed to a temperature of 500°C and the residues dissolved. Copper and nickel were measured polarographically in pyridine-pyridinium sulfate supporting electrolyte.

The method used for the determination of iron depended upon the amount present. At the 1-ppm level, iron was extracted with cupferron from an acid solution and determined by the polarographic reduction of the Solochrome Violet RS complex. In the 50- and 500-ppm samples, iron was determined directly on a solution of the residue in a sodium acetate-EDTA supporting electrolyte. Aluminum was reduced polarographically as the Solochrome Violet RS complex after its extraction as aluminum cupferrate. Lead was measured in 1 M sodium hydroxide. The determination of chromium was investigated concurrently with that of lead. It appeared possible to determine both in the same sodium hydroxide solution, although other workers had found merging lead-chromium peaks at the sodium hydroxide concentrations used. Solutions containing 100 and 200 micrograms each of lead and chromium were evaporated to dryness, after which the residues were dissolved in 3 drops of hydrochloric acid and 10 ml of water. Two ml of 30% hydrogen peroxide was added, followed by sufficient 10 M sodium hydroxide to give final alkali concentrations of 0.1, 0.2, 0.5 and 0.8 M respectively. The solutions were boiled 10 minutes to oxidize chromium and diluted to 50.0 ml, before measuring lead and chromium polarographically. The solutions which were 0.5 and 0.8 M in sodium hydroxide gave peaks which were poorly resolved. In the remaining two solutions, the peaks were well-defined and sufficiently separated for individual measurement. The results are shown in table 13.

Table 13. Effect of sodium hydroxide concentration on Cr-Pb peak potential.

Sample	$E_{Cr} - E_{Pb}$ (volts) 0.1M	0.2M	0.5M	0.8M
2 ppm	-0.22	-0.17	-0.15	-0.10
4 ppm	- .27	- .19	- .16	- .14

Thus it appears that lead and chromium may both be determined in a supporting electrolyte which is not more than 0.2M in sodium hydroxide.

b. Chromium in Various Matrices. The determination of chromium as a minor constituent is illustrated by the following examples for a non-metallic and metallic matrix, respectively.

A synthetic sapphire, also containing about 1% of yttria, was pulverized, after which 0.5-g portions were dissolved by heating with 10 ml of hydrochloric acid in a sealed tube at 270°C [7]. The resulting solution was diluted to 100 ml and portions equivalent to 10 mg of sample were aliquoted. The chromium was then oxidized with hydrogen peroxide in 1M sodium hydroxide and measured polarographically. Replicate values of 0.661, 0.668 and 0.664% of chromium illustrate the precision of the method.

Two nickel-chromium powders containing about 93 and 97% of the former were analyzed for their chromium content. Fifty-mg samples were used and the solutions for the calibration curve were prepared to contain the same amount of nickel as the samples to correct for possible adsorption losses on the nickel precipitate. Chromium was determined as described above and duplicate values of 2.96 and 2.95% were obtained for one sample and 4.67 and 4.72% for the other. The time required for each determination is approximately 20 minutes.

c. Lithium-Cadmium Alloys. The differential polarographic techniques discussed earlier were used to good advantage in the case of two lithium-cadmium alloys, received from the Alloy Physics Section, containing about 90 and 95% cadmium respectively. Since these alloys react rapidly with air, it is necessary to keep then in an inert atmosphere. Accordingly, the rod-shaped samples, which had been stored in oil, were transferred to a glove bag containing an atmosphere of helium. Samples weighing 0.7 to 1.5 g were prepared in the following manner. The rods were cut with diagonal cutters, cleaned in benzene, dried, weighed, removed from the glove bag, and dissolved in hydrochloric acid and water. After dilution to 500 or 1000 ml, 10-ml aliquots were diluted to 100 ml with 1N HCl. These were then measured comparatively with reference to standard cadmium solutions of similar composition and results of 94.10 and 92.45% of cadmium, respectively, were obtained for the two specimens. The values of lithium by difference were then 5.90 and 7.55%. In order to determine the extent of oxidation, and also for an independent measurement of the lithium content, aliquots of the original solutions were given to the Analytical Coordination Chemistry Section for determination by atomic absorption. Values of 5.88 and 7.45% of lithium were obtained which show excellent agreement with those obtained by difference.

d. Indium-Thallium Alloys. Other samples received from the Alloy Physics Section were six indium-thallium alloys, ranging in composition from about 5 to 70% indium, for the determination of either constituent. The suitability of several supporting electrolytes was investigated. A sulfuric acid-potassium chloride medium had previously been used very successfully in this laboratory for the determination of indium. However, for the present samples, the reduction of thallium was found to be too close to that of indium for good peak resolution. A 2 M acetic acid-2 M ammonium acetate mixture was tried and two well-defined peaks were obtained, that for thallium occurring at approximately -0.7 volts and for indium at -0.9 volts. The calibration curve for indium was linear, for both anodic and cathodic scan in the region of concentration checked (40-200 ppm). For thallium, the calibration curve was linear by cathodic scan between 60 and 180 ppm, but not at 300 ppm. It seems probable that the region of linearity would be extended by a more thorough investigation of the polarographi conditions.

The method developed for the determination of indium was as follows: Samples, weighing from 0.1 to 0.2 g, were dissolved in dilute nitric acid and diluted to 100 ml. Ten-ml aliquots were taken and 5.5 ml of acetic acid and 3.9 g of ammonium acetate were added. The pH at this stage was about 4.6 to 4.8. The solutions were diluted to 50 ml and measured polarographically at -0.9 V as indicated above.

e. Bismuth in Bismuth-Tin Alloys. As a result of some phase-diagram studies by the Metallurgy Division, analyses of a large number of binary alloys of bismuth and tin were required, ranging in composition from 0 to 100% bismuth. In order to remove tin, the samples were dissolved and evaporated with a hydrobromic acid-bromine mixture, as described earlier for aluminum-tin alloys [ref. 1, p. 13]. Although evaporations to dryness were done at approximately 100°C, some loss of bismuth in standard solutions occurred. The addition of sulfuric acid before subsequent evaporation to sulfuric acid fumes was found to eliminate this loss.

Several supporting electrolytes were investigated, including nitric acid-sodium tartrate at a pH of 4.5 and a sulfuric-hydrochloric acid mixture. The latter gave better defined peaks in the concentration ranges covered, although the calibration curve was somewhat non-linear. In some cases, relatively large amounts of sample were used in order to minimize the effect of inhomogeneities. However, aliquots were chosen so that the final bismuth concentration was approximately 2 to 10 mg per 100 ml. Results on standard solutions of bismuth showed an average recovery of 99.8 ± 1.3%.

f. Metal Organic Complexes. Polarography has been very useful in the determination of copper, nickel, and zinc in a variety of metal organic complexes which have been of interest in connection with EPR studies of their structures. These compounds are of a relatively rare type, the copper ions in the lattice being very close together and reacting strongly in a magnetic field.

For the determination of zinc in crystals of zinc-doped copper complexes, 0.1-g samples were measured polarographically in a pyridine-pyridinium chloride supporting electrolyte after dissolving in dilute hydrochloric acid. A typical determination gave results of 0.21% for the zinc content of the crystals.

Nickel was determined directly on a one-mg sample of a nickel complex after dissolution in 0.1 ml of 50% perchloric acid, addition of water, 0.1 ml of pyridine and dilution to 5 ml. The nickel content of this material was found to be 14.5%.

Zinc and copper were determined in 10-mg samples of a zinc-copper phenanthroline complex after destruction of the organic material by treatment with sulfuric and nitric acids, evaporation to dryness, dissolution of the residue in 0.2 ml of 50% perchloric acid, addition of 0.2 ml of pyridine, and dilution to 10 ml. Zinc was found to be 17.6% and copper 0.17%, which illustrates the nature of the analytical problem.

Other samples of this nature were nickel- or zinc-doped copper complexes. Four to 9 mg samples were wet-ashed, then ignited, and dissolved in 1 ml of 50% hydrochloric acid. One ml of pyridine was added, the solutions diluted to 10 ml and measured polarographically. Copper in the copper-nickel mixture was found to be 24.8% and nickel 0.53%. Copper in the copper-zinc mixture was found to be 24.5% and zinc to be less than 0.1%.

3. Identification of Metals.

This laboratory has been called upon occasionally to make qualitative or semiquantitative examinations of small amounts of samples, especially of metals. For example, a water filter housing, suspected to be brass, was quickly identified as such by cathode ray polarography. Minute scrapings taken from the interior were measured in a supporting electrolyte containing 0.4 ml of 50% hydrochloric acid, 0.4 ml of pyridine and 4 ml of water. The scrapings were found to contain approximately 65% of copper and 35% of zinc. Such a determination requires about 5 minutes and provides positive identification of the alloy used.

A fragment from the radiator of an antique aircraft, suspected of being either copper or brass was treated in a similar manner and found to contain about 61% copper and 17% zinc.

(E. J. Maienthal)

3. COULOMETRIC ANALYSIS

A. Introduction

The program in coulometric analysis was initiated nine years ago at the National Bureau of Standards. Its primary objective was to develop absolute methods of analysis based upon physical standards, rather than upon standards of chemical purity. The program has been very successful in that it has provided methods for the assay of standard reference materials that are reliable to a few parts in one hundred thousand and are accordingly the most precise and accurate primary standardization procedures available.

During the past year, coulometry has been extended by the development of an iodometric method of precision comparable to the earlier methods. This has been used to establish the reductimetric equivalency of arsenious oxide intended as a chemical primary standard. Coulometric methods already developed have been used in the analysis of several research materials as described in a following section. In addition, preliminary work has been initiated on precise methods of controlled-potential coulometry.

B. Facilities

The general facilities and equipment for coulometric analysis were described in detail in the previous report [ref. 1, p. 14]. In brief, they consist of a power supply capable of maintaining a selected level of current within a few parts in a million over a period of 8 hours. A quartz-crystal controlled time-interval meter permits the duration of electrolysis to be determined within a part in a million.

The move to the new laboratories in Gaithersburg, Maryland provided the opportunity to rearrange the laboratory equipment in what appears to be a very satisfactory layout, shown in figure 8. The electrical measurement equipment is located in one module, while chemical operations are carried out in a separate room. The laboratory furniture, consisting of a combination of tables and benches, is arranged in a F shape, the vertical portion of which is parallel to one of the walls of the room on which the services are located. This arrangement provides 28 linear feet of bench-front perimeter with nine directions of approach so that considerable flexibility in the placement of equipment is possible.

Figure 8. General lay-out of coulometric laboratory.

Two standard relay racks on casters are used to mount the equipment employed in constant current coulometry and controlled potential coulometry, respectively, as shown in figure 9. The mobility thus provided, together with the flexibility resulting from the arrangement already described, should greatly facilitate both the research and analytical aspects of the coulometric laboratory.

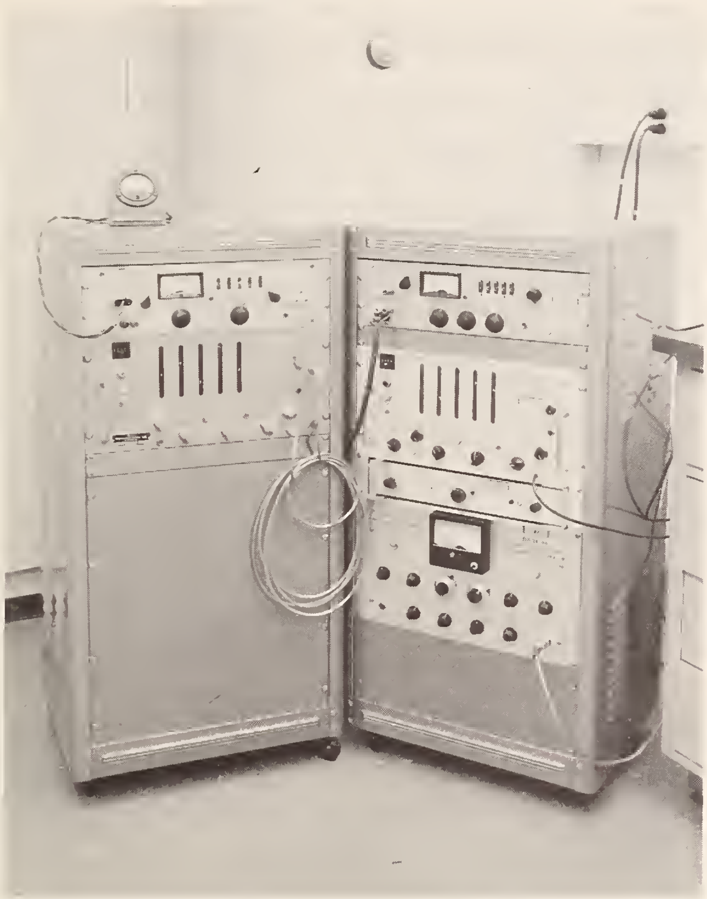

Figure 9. Coulometric electronic equipment mounted on relay racks.

C. Research Activities

1. Coulometric Iodimetry

a. Efficiency of Generation of Iodine. A prime requirement for accurate constant-current coulometry is the establishment of conditions to insure efficient electrode reactions. The electrolytic oxidation of iodide to produce iodine has been studied as early as 1890, independently by Herroun [8] and by Kreider [9]. However, their investigations as well as those of subsequent workers have not been of sufficient accuracy to establish conditions for reagent generation within the requirements of the present program (0.001% or better).

Accordingly, an intensive study of the electro-oxidation of iodide was undertaken.

A series of precise measurements was made over a wide rang of two varying parameters, namely current density and concentration of iodide in the electrolyte. The complete results will b described in a forthcoming publication. In brief, it was established that in a phosphate buffer at pH 7, when the iodide concentration is 0.1 molar, the current efficiency is 100.0000 percent for current densities between 1.2 and 3.0 mA/cm^2. For a current density of 3.8 mA/cm^2 in this electrolyte, the curren efficiency falls to 99.9998 percent, while for 5.0 mA/cm^2 it becomes 99.9985 percent. Since the composition of the electrolyte does not change significantly during a titration, these values based on electrochemical measurements represent the titration efficiency that can be expected under the conditions specified.

b. Summary of Procedure. On the basis of the measur ments described above, a supporting electrolyte composed of a 0.1 M solution of potassium iodide in a pH 7 phosphate buffer (0.05 M KH_2PO_4-0.05 M Na_2HPO_4) was chosen. The current density used was 2.5 mA/cm^2. An amperometric end-point system was used consisting of two platinum indicator electrodes with areas of 1 cm^2 with 150 mV impressed between them. The electrolysis cell was of the design developed in this laboratory. Current and time measurements were made in the manner described in earlier publications from this laboratory.

c. Iodimetric Analysis of As_2O_3. Portions of arsenious oxide, NBS Standard Sample 83c, varying in size from about 2 to 15 meq were titrated. The differences between the number of microequivalents calculated to be present and that found by titration were plotted with respect to size of sample and the result is shown in figure 10.

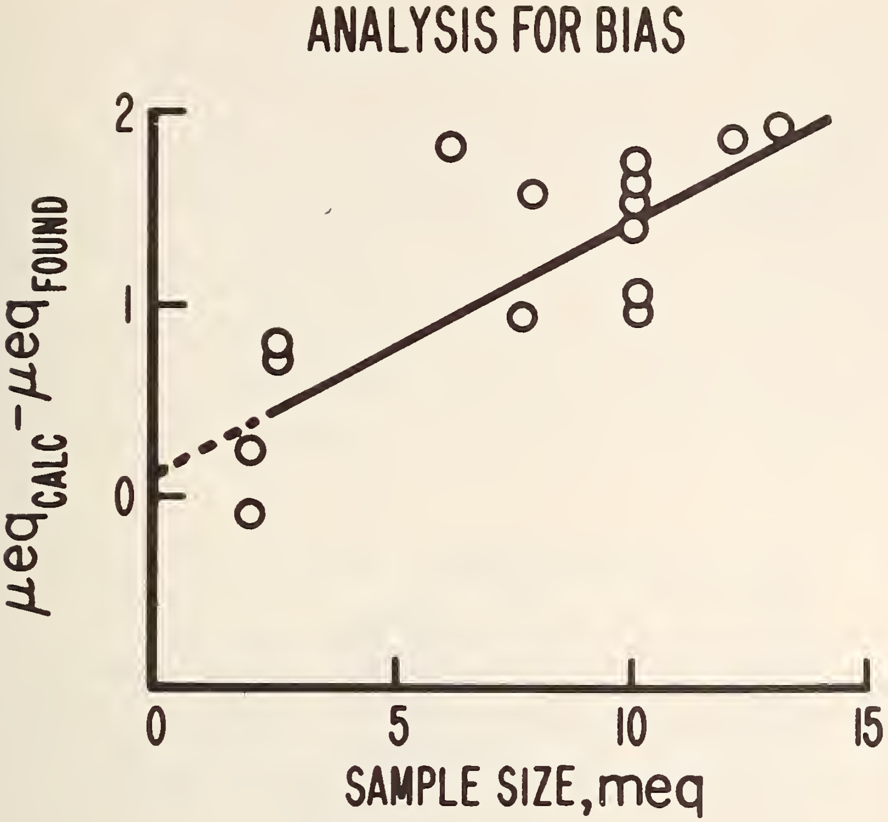

Figure 10. Analysis of coulometric titration data for bias.

Such a plot is a convenient and sensitive means to indicate any analytical bias which is evidenced by an intercept for a sample size of zero. The deviation of the material from either stoichiometry or absolute purity is reflected in the slope of such a curve. In the present case it can be seen that the intercept corresponds to approximately 0.04 μeq which is in good agreement with the intercept. Independent determinations of the blank correction on the same amount of reagents as used in the sample preparation gave a value of 0.05 μeq.

The assay of two lots of arsenious oxide, using 0.5 g samples, is given in table 14. The standard deviation of this determination was found to be 32 ppm. This oxide was also assayed by titration with iodine purified by sublimation from a $KI-I_2$ mixture, and a result of 99.98_7 percent was obtained (K. Sappenfield, private communication). The excellent agreement of these two results confirms the electrochemical conclusion that the coulometric method is both accurate and precise.

Table 14. Analysis of arsenic trioxide.

Number	Assay, percent
1	99.985_9
2	99.983_4
3	99.984_4
4	99.989_6
5	99.983_0
6	99.990_4
Average	99.986_1 $S = 0.003_2$

2. High Precision Controlled-Potential Coulometry

a. Amalgam Stripping Coulometry. A new method for the coulometric analysis of metals which form amalgams is being investigated. A weighed sample of the metal is dissolved in mercury and subsequently stripped from it coulometrically under controlled-potential conditions whereby only the desired constituent will be anodically dissolved into the electrolyte. The current-time function is integrated by converting the resulting voltage drop across a standard resistor in series with the coulometric cell to frequency, by means of a voltage-to-frequency converter, using a scaler for read-out.

Amalgam stripping offers several advantages over conventional coulometry. The time of analysis is decreased because diffusion coefficients of metals are significantly larger in amalgams than those of the corresponding metal ions in solution. Mechanically, the amalgam method does not require careful handling of solutions nor is there the danger of loss of sample into the auxiliary electrode compartment. Indeed, the fact that the sample is confined in a separate phase eliminates the need for separation of the electrode compartments, since the phase oundary provides the separation of reactants and products of he electrode reaction.

b. Cell Design and Construction. A cell has been designed and constructed for use in controlled-potential stripping-coulometry, which incorporates the following features. The cell, shown in figure 11, is constructed of Teflon to take advantage of its hydrophobic properties. It may be completely disassembled for cleaning. The anode compartment is located centrally, thus providing a uniform electrical field distribution with a consequent more uniform current density distribution.

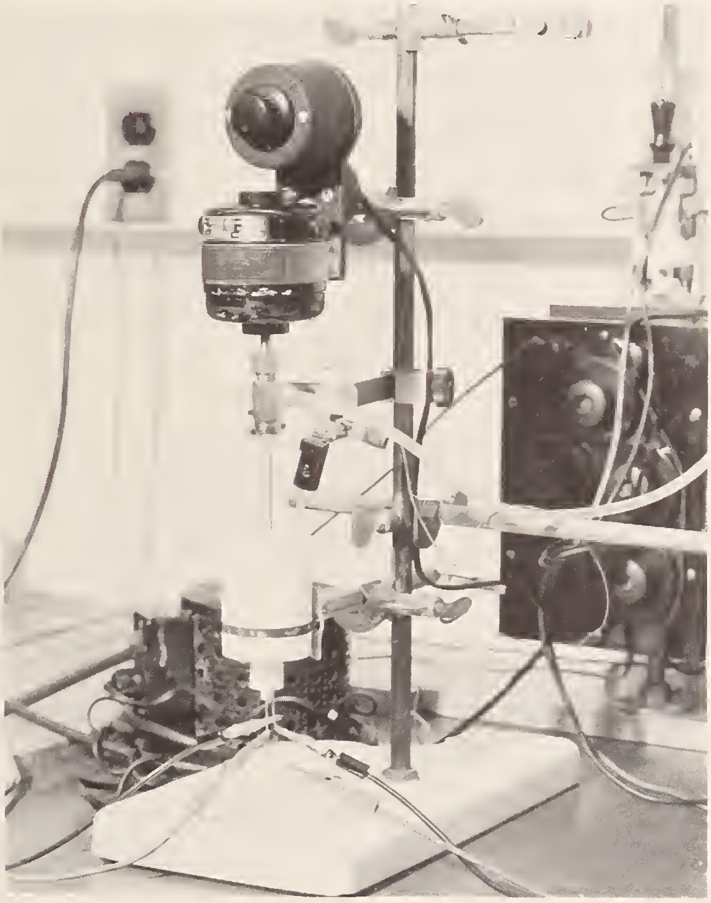

Figure 11. Teflon cell for use in amalgam-stripping coulometry.

The contact with the mercury anode is inserted through a hole drilled in the Teflon body of the cell. It may be a rod of platinum or other suitable metal. However, pyrolytic graphi is prefereed since it is not wetted by mercury and thus will no trap portions of the amalgam under analysis. The cell top is made of Lucite to permit viewing of the cell interior during assembly and also during the electrolysis.

c. Evaluation of Performance. Preliminary studies for the evaluation of the method and equipment are presently in progress. Samples of Melting Point Zinc, Standard Sample 43g, weighing 7 to 8 mg have been analyzed with a precision of about 0.01 percent. This precision is within the limit attributable to weighing errors and other uncertainties of the experiments. Further refinements in technique are planned to exploit the full potentialities of this new method. Studies are also planned to apply this procedure to the assay of lead, cadmium and other amalgam-forming metals. Modification of technique to permit successive stripping of metallic constituent should also make possible the analysis of metallic mixtures.

D. Analytical Activities

1. Analysis of Uranium Oxide.

The highly precise coulometric method for the determination of uranium developed earlier in this laboratory [ref. 1, p. 16,1 has been used for analyses related to the uranium isotopic standards program. Oxides of several isotopic compositions were subjected to thermal treatment, converted to uranyl sulfate and titrated coulometrically with electro-generated titanous sulfate as previously described.

The results of analyses of these oxides are summarized in table 15. All oxides were prepared by the same thermal treatment, consisting of ignition in air, followed by ignition in oxygen. This work was done by L. A. Machlan (Section 310.04) and is described in the Annual Report of the Analytical Coordination Chemistry Section [10]. Sample 950a is of normal ranium and is issued by NBS as a chemical standard for the nalysis of uranium. The other materials are for use in the reparation or calibration of uranium isotopic standards. The erms "depleted" and "enriched" refer to the U_{235} isotopic ontent. The atomic weights were calculated from the isotopic abundances of all of the uranium atoms in the various samples. All materials were "pure" in that the total metallic impurities are believed to be less than 100 ppm.

Table 15. Analysis of uranium oxide from several sources.

Material	Assay, percent	s^a	Atomic Weight of U in Sample
950a	99.923	0.023	238.03
Depleted Secondary	99.929	0.027	238.050
Depleted Primary	99.921	0.009	238.051
Enriched Primary	99.922	0.006	235.047

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[a] Standard deviation for a single determination.

The average assay values of these materials are in close agreement with each other. It may therefore be concluded that the thermal treatment was reproducible and leads to the same U/U_3O_8 ratio, independent of the isotopic composition of the samples. In order to establish an uncertainty limit for the compliance with U_3O_8 stoichiometry, all of the analytical results were pooled to provide an average assay value of 99.924 ± 0.011 percent, where the uncertainty figure represents the 95 percent confidence interval for the mean, based on 11 degrees of freedom. This is in excellent agreement with a value of 99.925 ± 0.013 percent, based on 16 degrees of freedom, found in some earlier assays in this laboratory for sample 950a subjected to the same thermal treatment.

Previous work in this laboratory has involved extensive assay of uranium metal "dingot", for which a value of 99.977 ± 0.004 percent was obtained. Samples of this metal were converted to oxide by the thermal treatment described. The U_3O_8

so prepared gave an assay value of 99.906 percent. When this is corrected to reflect the uranium content of the original metal, the U_3O_8 assay value is calculated to be 99.928 percent which is in close agreement with the composition obtained for the other four oxides.

In summary, it may be concluded that the thermal treatment used in these experiments produces an oxide which is within 99.928 percent of theoretical stoichiometry. The empirical stoichiometry may be considered to be $U_3O_{8.0058}$.

2. Iodide Content of Tracer Solutions.

Two independent methods of analysis were required to insure an accurate, unbiased analysis of the iodide content of a tracer solution containing about 17 mg I/ml. Three samples of the solution were provided for analysis, each containing about 1 mg of iodine. One of the methods chosen for this purpose was the conversion of iodide to iodate by oxidation with bromine water, followed by polarographic measurement of the diffusion current resulting from the reduction of iodate. The second method involved coulometric titration of iodide with electrogenerated silver ion.

In coulometric analysis, to minimize dilution effects, it was necessary to evaporate all solutions prior to analysis. Accordingly, a study was made of conditions of evaporation. Eight 2-ml aliquots of a solution of potassium iodide, each containing 2.845 µeq of iodide, together with additional materials in several cases, were evaporated to dryness at 100°C in an oven and analyzed coulometrically. The results obtained are given in table 16.

It is evident that significant losses occur on evaporation of neutral potassium iodide solutions with or without addition of bisulfite (samples 1, 2, 4 and 5). This is attributed to air oxidation. Addition of sodium carbonate minimizes such losses. Accordingly, all evaporations were made under this condition.

Table 16. Conditions for evaporation of iodide solutions.

Sample		Recovery, percent
1	2 ml KI soln	98.4
2	2 ml KI soln	96.7
3	2 ml KI soln + 250 mg Na_2CO_3	99.4
4	2 ml KI soln + 5 mg $K_2S_2O_5$	87.7
5	2 ml KI soln + 5 mg $K_2S_2O_5$	62.6
6	2 ml KI soln + 5 mg $K_2S_2O_5$ + 25 mg Na_2CO_3	99.1
7	2 ml KI soln + 5 mg $K_2S_2O_5$ + 25 mg Na_2CO_3	101.9
8	2 ml KI soln + 5 mg $K_2S_2O_5$ + 250 mg Na_2CO_3	99.2

The oxidation of iodide to iodate was verified for solutions approximating the composition of the tracer solution. Solutions of KI were oxidized with bromine water and the excess bromine was expelled by boiling. The solutions were diluted with supporting electrolyte (final concentration 10 mg/ml Na_2CO_3; 0.1 N KCl; 0.001% Triton X-100) and determined polarographically. For comparison, iodate solutions were prepared, from the reagent grade KIO_3, aliquoted, diluted to volume with supporting electrolyte and measured polarographically.

The results presented in figure 12 show good agreement between the two types of calibration and consequently verify the conditions for oxidation of iodide. The comparison of the results of the analysis of the solution by the two methods is given in table 17.

The agreement of the results obtained is very satisfactory, when it is considered that some determinations were made on samples as dilute as 6 ppm. The independence of the two methods provides considerable confidence in the accuracy of the results. The polarographic method is not subject to interference from other halogens or elements titratable by silver. On the other

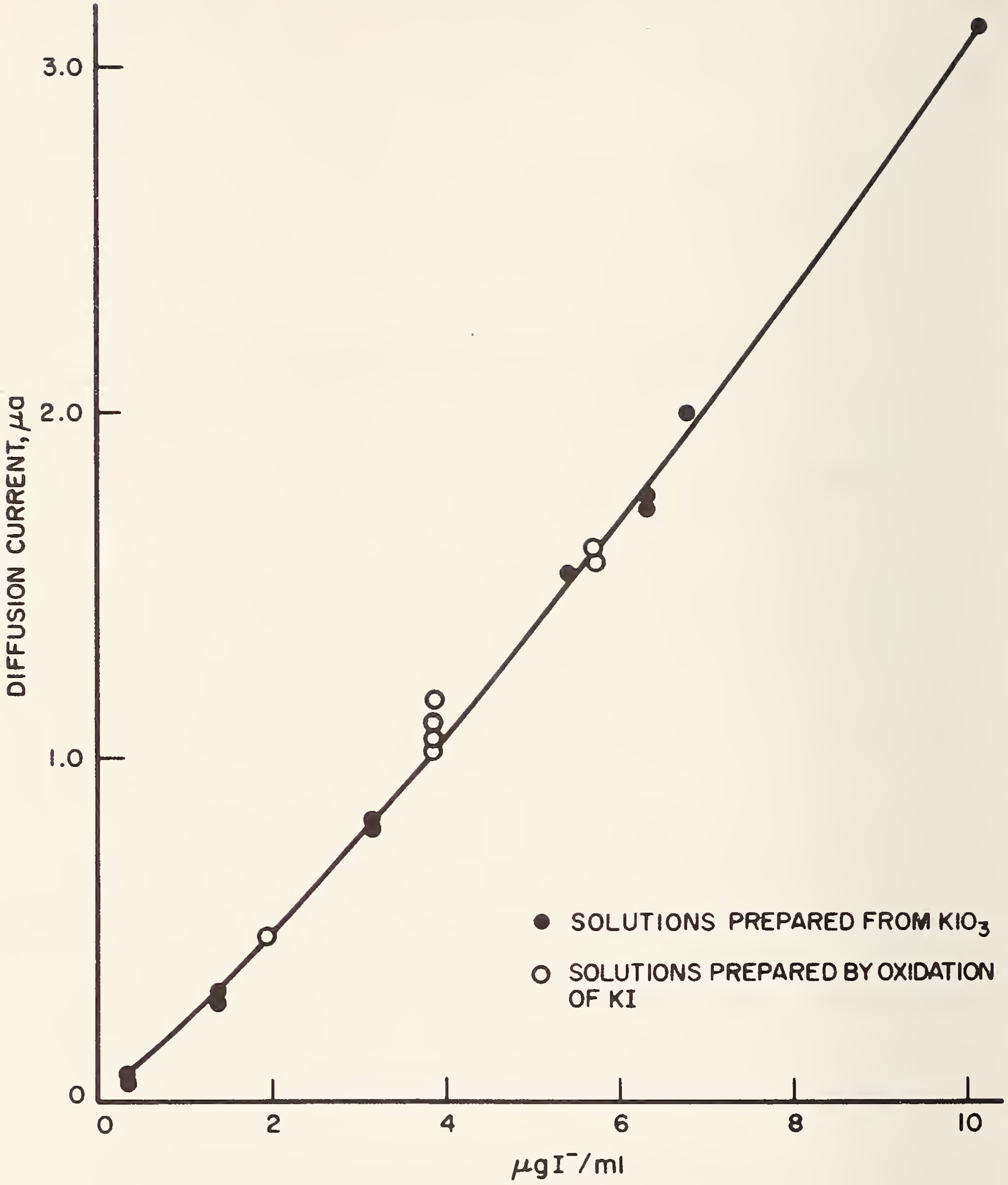

Figure 12. Polarographic calibration curve for reduction of iodate.

hand, these are the only elements that would interfere in the coulometric procedure under the conditions of the analysis.

Table 17. Analysis of iodide tracer solution.

Polarographic

Flask No.		mg I/ml
1		17.42
2		17.42
3		17.20
	Average	17.35 s = ± 0.13 mg I/ml[a]

Coulometric

Flask No.		mg I/ml
1		17.36
2		17.02
3		17.30
	Average	17.23 s = ± 0.18 mg I/ml[a]

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[a] s represents standard deviation of individual measurement.

3. General Applications

The method developed in this laboratory for precise argentimetric analysis of halides has been used on several occasions to verify the compositions of solutions used in other research programs. In all cases, a reliability of 0.01 percent or better was required. Primary standardizations of alkaline earth chloride solutions have been made in conjunction with the isopiestic research project. Accurate determinations of chloride have also been made for the program concerned with the establishment of the pD scale.

(G. Marinenko)

4. STOICHIOMETRY

A. Introduction

Deviations from ideal composition, nonstoichiometry, occu in many chemical compounds. In many cases these deviations ar too small to be detected chemically but in many other cases they are large enough to be detected by precise and accurate chemical analysis. Because of this possibility of departure from the law of constant proportions, stoichiometric considerations are necessary whenever highly precise chemical analyses are undertaken. For example, in gravimetric analysis in which a precipitated compound of an element is ignited or converted to a weighable compound, the stoichiometry of the compound weighed is of the utmost importance. Whenever a compound is used as a standard for an element, the stoichiometry of the compound is again of prime importance.

Most of the classical methods of analysis have not been proven better than 0.1%. Only a few methods have been reporte with a proven precision and accuracy of 0.01% or better. Work in this laboratory has been concerned with the development of methods of this precision and accuracy so that the stoichiometr of a compound can be verified to 0.01%.

Emphasis has been given to the Division's program for the mass spectrometric determination of atomic weights in which it is necessary to quantitatively blend the separated isotopes of an element with a precision of about 0.01 percent. Since the amounts of separated isotopes available for this use ordinarily are relatively small, the methods developed for their determination should require only small samples. This small sample requirement is also consistant with the mission of this section that is, obtaining the largest amount of information from the smallest possible sample.

Precise and accurate methods of analysis have previously been described for chlorine, bromine, copper, and chromium in last year's "Summary of Activities"[ref. 1, p. 26]. Using thes thods, it should be possible to prove the stoichiometry of mpounds of these elements to about 0.01%.

It is anticipated that future work will be focused on oichiometric problems arising from the program for the mass ectrometric determination of atomic weights, but attention ll also be given to stoichiometric problems elsewhere within e Bureau.

Research and Development

1. Magnesium

a. Non-Stoichiometry of MgO. Attempts to prepare oichiometric magnesium oxide from magnesium metal were not ccessful. The MgO/Mg ratios so obtained were at least 0.2% gher than theoretical. This high ratio is probably due ther to occlusion of gases by magnesium oxide, the amount of ich depends in a large degree upon the method and throughness ignition, or to a higher oxygen content than theoretical. nce oxides of many metals are known to exhibit both phenomena, was decided to abandon the attempts to prepare stoichiometric gO.

b. Stoichiometry of Magnesium Sulfate. An investigaion of the stoichiometry of magnesium sulfate showed that it s possible to prepare stoichiometric magnesium sulfate. This as shown by converting pure magnesium metal crystals, shown contain less than 20 ppm of detected metallic impurities by pectrographic analysis, to magnesium sulfate by dissolution in urified sulfuric acid and evaporation of the resulting solution ollowed by ignition at 600°C. The $MgSO_4/Mg$ ratio was found to e 4.9514 which is in good agreement with the calculated ratio sing 1962 atomic weights of 4.9512.

Because of the hygroscopic nature of magnesium sulfate, t was necessary to resort to a special weighing technique to btain valid results. The platinum crucible which contained he magnesium sulfate was covered with a small piece of latinum foil before the final ignition at 600°C. After the furnace had cooled to 500°C, the crucible was transferred to a special individual desiccator which was kept in an oven at 150°C to lessen the thermal shock on transfer. The individual desiccator was constructed by sealing a small glass drying bulb to a 70 ml glass weighing bottle, as shown in figure 13. The drying bulb was packed with P_2O_5 and closed with a rubber stoppe when cool. The desiccator containing the crucible was transferred from the oven, cooled, stoppered, and allowed to stand at room temperature for about four hours to attain thermal equilibrium. The covered crucible was then weighed against time on a micro-balance. Weighings were recorded each minute for five minutes. The weight at "zero time" was determined from a weight vs. time plot. The weight of the magnesium sulfate was determined from this weight less the weight of the crucible and cover.

c. Concentration of Magnesium Solutions. A method has been developed for the precise assay of magnesium solutions (as nitrate, chloride, or sulfate) based on weighing the magnesi sulfate produced on evaporation of weighed portions of the solution and conversion to magnesium sulfate by repeated evaporation after the addition of purified sulfuric acid. The precision and accuracy of this method has been determined by applying the method to solutions containing known amounts of magnesium. Four solutions prepared from the high purity magnesium metal crystals were assayed by withdrawing four weighed portions from each solution and determining the magnesiu as described. The results of these determinations are shown in table 18.

Comparison of the known and found concentrations showed that: (a) the determined concentration of magnesium agreed to about 0.01% with the calculated magnesium concentration, (b) systematic errors were negligible, and (c) the analysis of the four solutions were of equal (within limits) precision.

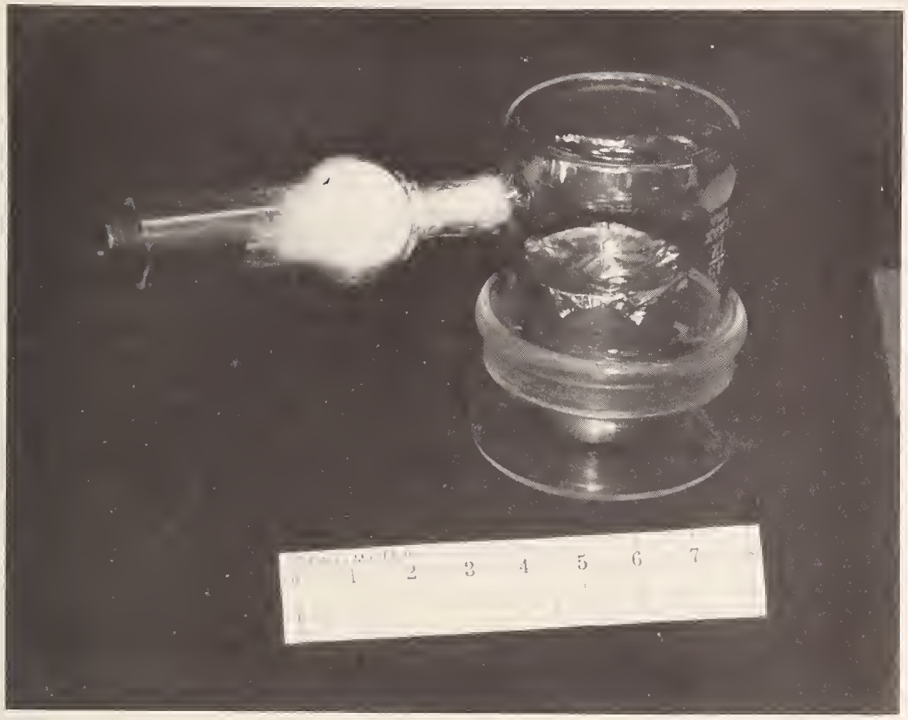

Figure 13. Individual desiccator for drying magnesium sulfate samples.

Statistical analysis of the data resulting from these alysis and from the analysis of solutions prepared from parated magnesium isotopes showed that the standard deviation an individual determination of the concentration of a gnesium solution is 0.0001334 millimole (mM) Mg/g sol with degrees of freedom. The standard error of the average of ur determinations is $\frac{0.0001334}{\sqrt{4}}$ or 0.0000667 mM Mg/g sol. The certainty of the concentration at the 95% confidence is .110X0.0000667 or 0.000142 mM Mg/g sol. This corresponds to uncertainty of 0.02% for solutions containing 0.7 mM Mg/g l.

Table 18. Analysis of solutions containing known amounts of magnesium.

Sol'n No.	Wt Sol'n g	Mg Found mM		Conc. Sol'n mM Mg/g Sol'
A	6.61027	4.368086		0.660803
	6.49334	4.292734		0.661098
	6.61881	4.376424		0.661210
	6.66686	4.408895		0.0661315
			Avg.	0.661107
			Calc.	0.661056
B	7.51133	5.471140		0.728385
	7.49563	5.460829		0.728535
	7.11456	5.182303		0.728408
	6.93171	5.048420		0.728308
			Avg.	0.728409
			Calc.	0.728410
C	7.31937	5.000183		0.683144
	7.26266	4.961524		0.683155
	7.15365	4.887438		0.683209
	7.52151	5.138688		0.683199
			Avg.	0.683177
			Calc.	0.683072
D	6.79383	4.148876		6.610683
	6.98897	4.265132		0.610266
	6.20624	3.790209		0.610709
	6.69536	4.088852		0.610699
			Avg.	0.610589
			Calc.	0.610559

This method for the determination of the concentration of
agnesium solution was adopted after deciding that none of
e conventional methods for magnesium were capable of yielding
ecise results. It is a valid method so long as the purity
the magnesium sulfate is known since magnesium sulfate has
ready been shown to be a stoichiometric compound. The
gnesium sulfate should be examined by emission spectrography
other techniques to determine the cationic impurity concen-
ation and a correction made if necessary. The repeated
eatments with sulfuric acid would remove most of the common
ionic impurities such as chloride, bromide, or nitrate with
e exception of phosphate which would cause erroneous results.

d. Purification of Magnesium Compounds. A procedure
s been developed for the purification of water soluble
gnesium compounds. This method which is based on the pre-
pitation of the magnesium salt of (ethylenedinitrilo)-
tracetic acid (EDTA) has proven effective in reducing most
purities to the low parts-per-million level or less.

The magnesium salt is dissolved in water, an excess of
ammonical solution of EDTA is added, and the pH is adjusted
4.0. After about 2 days, the precipitation of the Mg-EDTA
substantially complete (better than 98%). Magnesium is the
ly known element to form a relatively insoluble precipitate
ith EDTA. After recovering the Mg-EDTA by filtration through
rous glass, the salt was dissolved in dilute NH_4OH and re-
recipitated by adjusting the pH to 4.0. The Mg-EDTA was then
gnited to MgO. The MgO can be dissolved in the appropriate
cid (nitric, hydrochloric, etc.) to produce the desired solution
s salt.

The effectiveness of this method was shown by adding 50
lements at the 0.1% level to a solution of magnesium and
recipitating the magnesium by this method. The purified MgO
as then examined by qualtitative emission spectrography. The

results of this analysis are shown in table 19. With the exceptions of tungsten, molybdenum, palladium and rhodium, elements which do not form complexes with EDTA, the impurity elements were either eliminated or reduced to the low parts-per-million level. Since W, Mo, Pd, and Rh and not likely impurities in magnesium compounds, the purity of most magnesiu compounds can be greatly increased by this method.

e. Preparation of Calibration Mixtures for the Mass Spectrometric Determination of the Atomic Weight of Magnesium. The previously described work has been applied to the preparation of calibration mixtures of separated magnesium isotopes for the mass spectrometric determination of the atomic weight of magnesium. Separated magnesium isotopes in the form of $Mg^{24}O$ and $Mg^{26}O$ containing about 0.2% Cu and up to 0.05% of several other elements were purified by the EDTA method. Samples of this purified $Mg^{24}O$ and $Mg^{26}O$ were analyzed by quantitative emission spectrography. The results of this analysis showed that the $Mg^{24}O$ and the $Mg^{26}O$ contained about 25 ppm and 17 ppm total detected cationic impurities, respectively.

The purified oxides were taken into solution with dilute nitric acid and solutions of each of the separated isotopes were prepared. The magnesium content of each separated isotop solution was determined by converting weighed portions to the sulfate as described. The calibration mixtures were then prepared by mixing weighed portions of each separated isotope solution. These were then used as standards by the Analytical Mass Spectrometry Section to obtain the absolute abundance ratios of magnesium and the atomic weight was calculated.

Table 19. Analysis of purified magnesium oxide.

ement[a]	Concentration Range Percentage	Element	Concentration Range Percentage
Ag	-	Mn	-
Al	-	Mo	0.001-01
As	-	Na	-
Au	-	Nb	-
B	-	Ni	-
Ba	-	Os	-
Be	0.0001-0.001	P	-
Bi	-	Pb	-
Ca	0.0001-0.001	Pd	0.001-0.01
Cd	-	Pt	-
Ce	-	Rh	0.001-0.01
Co	-	Ru	-
Cr	< 0.0001	Sb	-
Cs	-	Si	0.0001-0.001
Cu	0.0001-0.001	Sn	-
Fe	0.0001-0.001	Sr	-
Ga	-	Ta	-
Ge	-	Te	-
Hf	-	Th	-
Hg	-	Ti	-
In	-	U	-
Ir	-	V	-
K	-	W	0.01-0.1
La	-	Zn	-
Li	-	Zr	-

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[a] The initial concentration of each element before purification was 0.1%.

Note: - not detected

< less than

2. Lead

A search of the chemical literature has shown that ther is a need for a high precision-high accuracy method for lead Initial work on the development of such a method based on th precipitation of lead chromate with a small excess of potass dichromate and determination of the excess chromate has been encouraging. This method takes advantage of the precise analysis of standard reference material 136b, potassium dichromate, which has been shown to be 99.977 ± 0.003% [11]. A weighed amount of this $K_2Cr_2O_7$ is reacted with less than the stoichiometric amount of lead and the excess chromate is determined spectrophotometrically. Preliminary results indicate that a precision and accuracy of 0.01% should be possible with this method.

(T. J. Murphy)

5. CLASSICAL MICROCHEMICAL ANALYSIS

A. Introduction

Activities of this laboratory are for the most part, conerned with the elemental analysis of small samples. Microchemical methods are economical of sample, a necessity when amounts of materials available are very small. Frequently they are relatively rapid to perform compared with macro determinations. The aim is to obtain more and more information from smaller and smaller samples through more sensitive methods and by determining more than one element in a single sample. For organic analysis which is still the largest part of the work, this means using instrumental methods instead of the traditional Pregl gravimetric and volumetric methods.

B. Facilities

Most of the equipment in this laboratory was described in the report of last year [ref. 1, p. 20]. In addition, an F and M Carbon-Hydrogen-Nitrogen Analyzer, shown in figure 14, has been obtained. With this instrument, carbon, hydrogen and nitrogen are determined simultaneously through gas chromatographic separation and thermal conductivity detection of the combustion products. The weight of sample used is approximately 0.6 mg.

The newly established microscopical laboratory is equipped with a binocular polarizing microscope, shown in figure 15. It is equipped to view samples with either transmitted or incident light, and photographs may be made with a 35 mm camera attachment. The low power micromanipulators are available for microchemical work.

This equipment is presently installed in a small laboratory module used exclusively for this purpose. Such an arrangement is suitable for many purposes. However, for work with extremely small particles, a clean-bench facility will be set up to minimize contamination from the laboratory atmosphere.

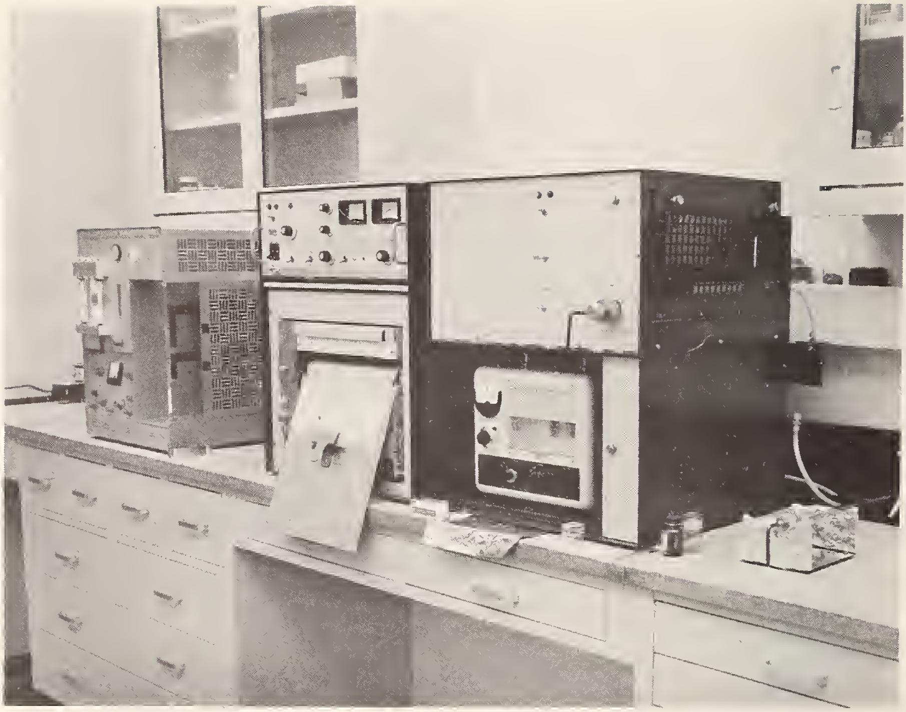

Figure 14. Carbon-hydrogen-nitrogen analyzer.

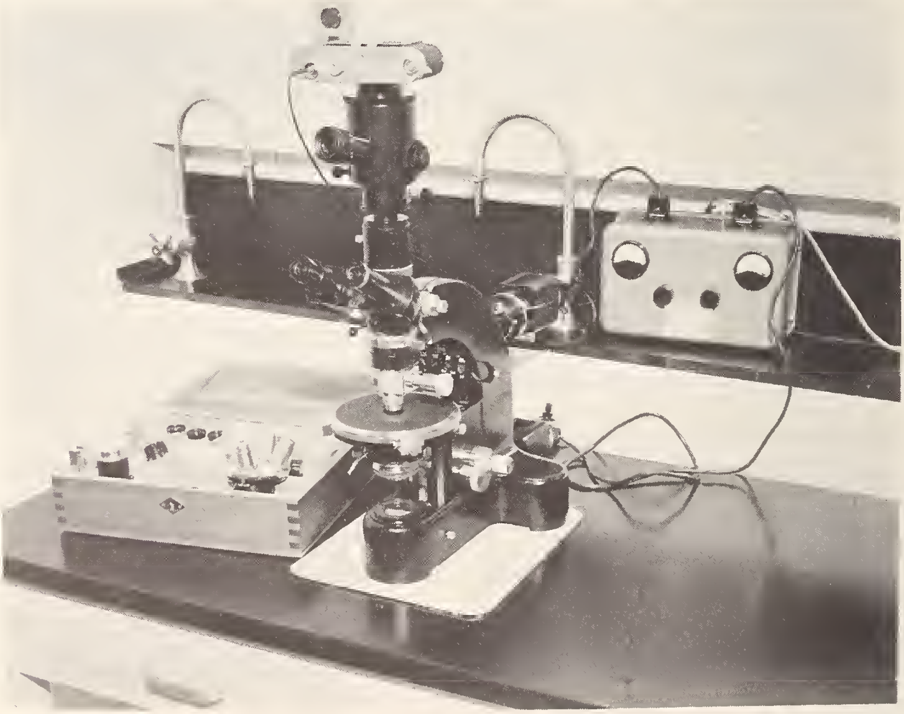

Figure 15. Microscopic equipment.

The microchemical laboratory in the new NBS facilities at Gaithersburg, Md., consists of two adjoining modules with an interconnecting balance room at the rear. One module contains most of the larger equipment, such as the carbon, hydrogen and nitrogen combustion equipment. The other module is used for chemical operations and contains such equipment as a pH meter, chloride titrator, Kjeldahl apparatus, oxygen flask combustion apparatus, microburettes, oven, furnace, etc. Each module has a four-foot fume hood and a desk, as well as storage space under the lab benches.

The balance room has two microchemical balances and a semimicro balance mounted on a marble slab supported on concrete piers. An electrobalance is also available for certain weighing operations.

C. Research Activities

Two research problems have been under investigation during the past year. Since both are still in progress, it is only possible to summarize the results obtained up to the present time.

1. Elemental Analysis of Small Samples

A study has been made of the use of the C-H-N Analyzer for small samples. The usual size of samples for this instrument is 0.5 to 0.7 mg. because the peak height linearity is best in this range. However, the instrument has a considerable reserve of sensitivity and samples of 0.1 mg. can be used if samples having about the same amounts of nitrogen, carbon and hydrogen are used for calibration. The limiting factors are the magnitude of the blanks and the weighing of sample; but it would appear that the carbon, hydrogen and nitrogen could be determined within 1% absolute with a sample of this size.

The determination of carbon in highly fluorinated fluorocarbons with the C-H-N Analyzer was studied. Samples of copolymers of C_2F_4 and $C_3F_3H_3$ with fluorine contents of 60% to 75% were used. The normal combustion tube packings of copper oxide and copper metal were used. These samples were also analyzed with a conventional combustion train with a special packing of magnesium oxide to remove fluorine. This has been used here for many years. Table 20 gives the results obtained.

Table 20. Determination of carbon in fluorocarbons.

Sample	By Conventional Combustion	By C-H-N Analyzer
	Carbon, percent	Carbon, percent
A	30.78	30.70 31.16
B	28.90	28.80 28.65
C	25.33	25.48 25.31
D	30.23	30.28 30.50
E	32.45	32.43 32.16
F	34.71	34.50 34.35

The results agree within the acceptable limits of microchemical analysis. The advantage of the C-H-N Analyzer is tha is requires about 10 minutes for a determination using a 0.6 mg. sample. The conventional combustion furnace requires an hour using a 4 to 5 mg. sample. If hydrogen is to be determined also, the copper reduction tube in the C-H-N Analyzer must be repacked each day since a peak, probably from HF, begins to form just before the water peak, affecting the heigh of the latter. Also, the C-H-N Analyzer should be calibrated with standards every five or six runs to check the correction constants.

2. Reversed Phase Chromatography

Some work was performed on the separation of traces of ron from high purity zinc by reversed phase chromatography. n this method, a solution of the zinc in 5 ml of 8 M hydrohloric acid is passed through a small column containing 7 cm^3 f Teflon-6 powder coated with 2-octanone. The iron is retained n the column while the zinc is eluted with 6 M hydrochloric cid. Four 3-ml washings is sufficient to remove all the zinc. he iron and the 2-octanone are stripped from the column with ethyl alcohol and ethyl ether after which the iron is determined spectrophotometrically with o-phenanthroline reagent. y this method, a sample of reagent grade mossy zinc was found o contain 34 ppm of iron, while a sample of high purity zinc as found to contain 1 ppm of iron. The limiting factor is he magnitude of the blanks obtained. With a partial cleanp of reagents and the column resin, the blank amounted to 1 µg. ith this small column it was possible to separate as much as 0.4 mg of iron from a gram of zinc.

A program which is just starting involves the examination and identification of particulate matter in the size range of 1 to 10 µg. Identification will be made by microscopical study of the morphological and optical properties of the material, and also, where feasible, by ultra microchemical tests.

D. Analytical Activities

The analytical activities include determinations on a wide variety of materials received from other NBS research projects, from the NBS Standard Reference Material program, and also from other government agencies. Samples were received from seven other government agencies during the past year. The samples are often "problem" materials which require special treatment or the development of methods or the modification of existing methods. Some of these are described below.

1. Alumina Boules

Samples of alumina boules containing about 0.1% each of yttrium and thorium and 1% chromium were analyzed. Solution of this material was very difficult and required five days of digestion in concentrated hydrochloric acid at 270°C in a sealed glass tube [7] to complete the solution of 0.5 g samples. Chromium was determined polarographically (see p. 36 of this report), yttrium was determined by flame photometry (section 310.04) and thorium was determined spectrophotometrically on an aliquot of the solution using thoron reagent. It was found that the presence of 25 mg of aluminum increased the apparent thorium color by approximately 15%, so it was necessary to add a like amount of aluminum to the thorium standards. The results on three separate samples were 0.133, 0.116 and 0.122% thorium.

2. <u>Linac Cooling Water System</u>

The appearance of a brown sludge on a plastic sight tower and the apparent corrosion of a filter holder led to an investigation of a recirculatory cooling water system in the NBS Linac facility. The system contained fiber filters and a demineralizer to remove particles and metal salts from the water as they might form. Analyses were made for metals in the water, filters and demineralizer resin using micro electrodeposition for copper and lead in the resin, spectrophotometry for iron, copper and nickel in the water and filters, and spectrochemistry for other metals on the resin. The brown sludge apparently was iron from the make up water, and the filter holder which was brass had lost a thin nickel plating allowing a tarnish to appear. Although the water was quite pure, a number of metals had been retained by the demineralizer. Copper was present in the largest amount due to solubility of the copper pipes. After analyzing several layers of resin, it was calculated that 5.5 grams of copper had dissolved but this is negligable compared to the large amount of copper metal in the system. Also found were lead and tin from soldered joints, nickel and zinc from the filter holder and alkaline earth metals from the make up water.

3. Beryllium Carbide

A special sample of beryllium carbide was analyzed for ne NBS Heat Measurements Section who must know the composition f their materials very exactly in order that their measurements f specific heats may be interpreted properly. The beryllium arbide, total beryllium, total carbon, uncombined carbon and itrogen were determined by methods described in an earlier eport [ref. 1, p. 24]. In addition, beryllium oxide and ater were determined directly. Beryllium oxide was determined y heating a 100 mg sample in a stream of dry hydrogen chloride t 700°C. The residue was ignited in air to remove free carbon eaving a residue of beryllium oxide which was weighed or etermined spectrophotometrically.

Beryllium metal was determined by collecting all the gases ormed when a 10 mg sample was dissolved in a potassium hyroxide solution. These gases were analyzed in the mass pectrometer and beryllium metal was calculated from the ydrogen. The water present was determined by heating a 100 g sample in a stream of oxygen in a combustion train. The ater reacts with the beryllium carbide to form methane which s oxidized to form an equivalent amount of water which is bsorbed and weighed. The results of a typical analysis are iven in table 21.

Table 21. Composition of a typical sample of beryllium carbide.

Component	Percent
Beryllium carbide	92.6
Beryllium oxide	2.0
Beryllium metal	2.6
Free carbon	2.8
Water	0.4
Beryllium nitride	0.02
Total beryllium	59.6
Total carbon	39.8

4. Iodide in Photographic Fixing Baths

The concentration of iodide present in used photographic solutions, and especially in fixing baths, is of interest today because of its possible relation to the stability of microfilms. The analysis is complicated by silver and by the large amounts of sodium thiosulfate and other sulfur compounds present. In the method of analysis used, the fixing baths are made strongly alkaline with sodium hydroxide, after which the silver is precipitated as silver sulfide with sodium sulfide solution. After filtration, an aliquot is treated with 30% hydrogen peroxide to oxidize sulfur compounds. The iodide is oxidized to iodate with bromine in acetic acid and then titrated with 0.01 N sodium thiosulfate.

The method was checked by adding weighed amounts of silver iodide to new and used fixing baths. The results are shown in table 22.

Table 22. Determination of iodide in photographic fixing baths.

Iodide added (mg KI/ml)	Iodide Recovered (mg KI/ml)
2.072	2.088
1.568	1.516
0.904	0.888
0.084	0.083
0.058	0.053

5. Standard Reference Materials

Standard reference materials analyzed included the acetanilide microchemical standard No. 141b which is a standard for carbon, hydrogen and nitrogen and was checked for those elements. A number of organic fluorine compounds, of possible use as reference materials, were analyzed for carbon and hydrogen. Sodium nitroprusside crystals which are used as a Mössbauer spectroscopy standard were analyzed for carbon, drogen and nitrogen with the C-H-N Analyzer and for iron by tration with potassium dichromate.

Intermediate purity selenium was analyzed for trace ounts of chloride and sulfur. For chloride, a two-gram mple was dissolved in nitric acid in the presence of silver trate. After coagulating overnight, the silver chloride s collected on a Selas filter. It was dissolved in a few of ammonium hydroxide and reprecipitated in a Nessler tube th nitric acid. The chloride was determined nephlometrically comparison with known solutions. One ppm and three ppm of loride were found in two samples of selenium. The sensitivity the test, as outlined, is one ppm chloride.

For the determination of sulfur, two-gram samples of lenium were dissolved in nitric acid and the selenium com- etely vaporized by repeated evaporations as selenium bromide th hydrobromic acid. This step was necessary since earlier ests had shown that selenium inhibited the precipitation of arium sulfate. The sulfur was precipitated as barium sulfate n a Nessler tube and determined nephlometrically by comparison ith standard solutions. Ten ppm of sulfur were found. A good ecovery of sulfur added to selenium was obtained.

In addition, carbon, sulfur and phosphorus have been etermined in a large number of iron base standard reference aterials.

6. Miscellaneous Analyses

A brief mention is given of a number of analyses performed o show the variety which is encountered. A chromium-osmium lloy, which was of special interest because of its unusual lectrical properties at low temperatures, was received from he Dental Research Section. A 100 mg sample of this alloy as fused with sodium peroxide in a nickel crucible and then issolved in nitric acid. The osmium was volatilized as smium tetroxide by boiling. The chromium was reduced with ulfurous acid, reoxidized to chromate with ammonium persulfate nd titrated potentiometrically with ferrous iron solution which had been previously standardized with dichromate.

A method of analysis of fluoboric acid was evaluated for the Harry Diamond Laboratories of the Department of Defense by analyzing known mixtures of fluoboric acid and boric acid. Analyses performed on the electrolyte in small capacitors from NASA showed that changes took place during environmental testi Six samples of graphite and diamond dust from the Naval Researc Laboratory were checked for purity by microcombustion methods. A referee microanalysis for bromine and sulfur was made on a purine compound for the National Institutes of Health by the oxygen flask combustion method.

Scandium oxide and boric oxide were determined in materia used in phase diagram studies by the High Temperature Chemistr Section. Samples of 30 to 100 mg were dissolved by sealed tub method. Boric oxide was then determined in the same solution by titration with sodium hydroxide in the presence of mannitol.

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

6. INTERNATIONAL RESEARCH GRANTS PROGRAM

The National Bureau of Standards awarded a grant to the hnion-Research and Development Foundation, Haifa, Israel, December 1, 1965, to investigate "Trace Analysis by Anodic ripping Voltammetry". Professor Magda Ariel, Chemistry partment, Technion, Israel Institute of Technology, is incipal investigator. Dr. John K. Taylor, Section 310.05, the NBS project monitor.

Professor Ariel and her students will investigate anodic ripping voltammetry including its application to media con-ining varying proportions of organic solvents. Problems sed by adsorbtion, solution resistance, and the effect of ectrodes, permitting the analysis of non-amalgam forming tals will be given special consideration. The knowledge tained from this work will be applied to practical analytical tuations.

The determination of trace amounts of zinc in silicates d other insoluble substances of a kindred nature has been itially investigated. An analytical method has been developed ich is sensitive and unaffected by interferences resulting om varying sample composition.

In the method, which has been submitted for publication 2], the sample of rock is fused in a boric acid-lithium uoride flux or decomposed by direct acid attack, as required. either case, a final acid solution is passed through an ion exchange column under conditions to retain zinc while iron, ckel, vanadium, titanium, manganese, etc., pass through. Zinc eluted with de-ionized water, directly into the electrolysis ll where it is determined by anodic stripping polarography.

The method has been applied to the analysis of three stand-rd samples, ranging in zinc content from 47 to 500 parts per illion with standard deviations of 5 to 10 relative percent.

(J. K. Taylor)

7. SUPPORTING SERVICES

The section does a limited amount of work in the areas of gas chromatography, nuclear magnetic resonance, infrared spectroscopy, and fluorescence measurements. Activities have been confined largely to the use of these techniques for the analysis or identification of certain research materials.

Several of the above techniques find considerable use in connection with other analytical competences. In particular, gas chromatography has been used as an adjunct to mass spectrometry, both as a preseparation or preconcentration technique and for confirmatory analyses. Infrared spectrometr has been used in the identification of gas chromatographic fractions. Nuclear magnetic resonance spectra are furnished a an analytical service to other research projects.

The section is responsible for the maintenance of the equipment mentioned above and makes it available to qualified users in other sections of the Bureau. This arrangement is advantageous to those chemists who have only occasional need for specialized equipment. In a similar situation, the sectio also provides occasional chemical services to non-chemical groups at NBS, such as preparation of unusual solutions or handling of materials under special conditions, for example.

(J. K. Taylor)

8. PERSONNEL AND ACTIVITIES

Personnel Listing

John K. Taylor, Section Chief
Carolyn E. Smith, Secretary

ss Spectrometric Gas Analysis --

Ernest E. Hughes
William D. Dorko

larography --

E. June Maienthal

ulometry --

George Marinenko
Robert A. Martin

oichiometry --

Thomas J. Murphy

assical Microchemistry --

Rolf A. Paulson
John R. Baldwin
William P. Schmidt

. Publications

1. E. J. Maienthal and J. K. Taylor, Determination of ellurium by Cathode Ray Polarography, Anal. Chem. 37, 1516 1965).

2. J. K. Taylor, E. J. Maienthal and G. Marinenko, lectrochemical Methods, Trace Analysis, Interscience, N.Y., 1965).

3. G. Marinenko and J. K. Taylor, Coulometric Calibration f Microvolumetric Apparatus, J. Research NBS, 70C, 1 (1966).

4. R. A. Durst and J. K. Taylor, Photopolarographic ehavior of Inorganic Depolarizers, J. Research NBS, 69A, 517 1965).

5. J. K. Taylor, Density and Specific Gravity, Encyclopedia f Industrial Analysis, Vol. 1, Interscience, N.Y., (1965).

C. Talks

1. J. K. Taylor, "The Science of Measurement" North Bethesda Junior High School, Bethesda, Maryland, September 1965.

2. J. K. Taylor, "Panel Discussion of Preparation, Preservation, and Use of Ultra-Pure Materials", 1965 Eastern Analytical Symposium, New York, N. Y., November 1965.

3. J. K. Taylor, "The Science of Measurement", Dunbar High School, Washington, D. C., December 1965.

4. E. J. Maienthal and J. K. Taylor, "Improvement of Precision of Comparative Polarography", American Chemical Society, Winter Meeting, Phoenix, Arizona, January 1966.

5. G. Marinenko and J. K. Taylor, "High-Precision Coulometric Iodimetry", American Chemical Society, Winter Meeting, Phoenix, Arizona, January 1966.

6. E. J. Maienthal and J. K. Taylor, "Applications of Differential Polarography", Pittsburgh Conference on Analytica Chemistry and Applied Spectroscopy, Pittsburgh, Pennsylvania, February 1966.

7. J. K. Taylor, "Careers in Chemistry", Walter Johnson High School, Bethesda, Maryland, March 1966.

8. J. K. Taylor, "Modern Chemical Analysis", Georgetown University, Washington, D. C., April 1966.

9. J. K. Taylor, "Careers in Chemistry", Crossland High School, Camp Springs, Maryland, April 1966.

D. Committee Activities

J. K. Taylor

Service Analysis Coordinator, Analytical Chemistry Division
Member, Analytical Standards Committee
Chairman, Panel on Chemistry, Civil Service Board of Examiners
Vice-Chairman, Civil Service Board of Examiners

nber, Review Board, Science Book List, American Association
'or the Advancement of Science
esident, Washington Academy of Sciences (WAS)
airman, Committee on Science Education, WAS
nber, Joint Board on Science Education
Director of Science Projects
ected member, Council of the American Chemical Society (ACS)
airman, Canvassing Committee for the ACS Award in Pure Chemistry
airman-Elect, ACS Division of Analytical Chemistry
nber, Board of Managers, Chemical Society of Washington
mber, Professional Relations Committee, Chemical Society of
Washington
ssion Chairman, 1965 Eastern Analytical Symposium
airman, Arrangements Committee, IMR Symposium on Trace
Characterization
fety Officer, Analytical Chemistry Division

June Maienthal

S Reporter for Capital Chemist, Chemical Society of Washington
ected member, Board of Managers, Chemical Society of
Washington

J. Murphy

mber, Civil Service Board of Examiners
mber, Committee on Meeting Arrangements, Chemical Society of
Washington
mber, Arrangements Committee, IMR Symposium on Trace
Characterization
mber, Committee on Annual Report of Atomic Weights, American
Chemical Society.

A. Paulson

mber, Service Analysis Committee, Analytical Chemistry
Division
llaborator, Committee for Study of Microchemical Methods,
Association of Official Agricultural Chemists

Member, Arrangements Committee, IMR Symposium on Trace
Characterization

W. D. Dorko

Member, Arrangements Committee, IMR Symposium on Trace
Characterization

9. REFERENCES

J. K. Taylor, Editor, NBS Technical Note 273, October 1, 1965.

E. T. Suttle, D. E. Emerson, B. W. Burfield, Anal. Chem. 38, 51 (1966).

R. E. D. Haney, H. Bliss, Ind. Eng. Chem. 36, 985 (1944).

J. Hilsenrath et al, Tables of Thermal Properties of Gases, NBS Circular 564, November 1, 1965.

E. J. Maienthal, J. K. Taylor, Anal. Chem. 37, 1516 (1965).

H. S. Isbell et al, Analytical Standards for Trace Elements in Petroleum Products, NBS Monograph 54, October 1962.

C. L. Gordon, W. G. Schlecht, E. Wichers, J. Research NBS 33, 451 (1944).

D. A. Kreider, Am. J. Sci. [4] 20, 1 (1905).

E. F. Herroun, Phil. Mag. [5] 40, 91 (1895).

O. Menis, Editor, NBS Technical Note 402 (1966)

G. Marinenko, J. K. Taylor, J. Research NBS 67A, 453 (1963).

G. Koster, U. Eisner, M. Ariel, J. Electroanalytical Chem. (In press).

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