STATES
ENT OF
ERCE
ATION

NBS TECHNICAL NOTE 583

Electrochemical Analysis Section:

Summary of Activities, July 1970 to June 1971

U.S.
RTMENT
OF
MMERCE
National
eau
of
ards

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] was established by an act of Congress March 3, 1901. The Bureau's overall goal is to strengthen and advance the Nation's science and technology and facilitate their effective application for public benefit. To this end, the Bureau conducts research and provides: (1) a basis for the Nation's physical measurement system, (2) scientific and technological services for industry and government, (3) a technical basis for equity in trade, and (4) technical services to promote public safety. The Bureau consists of the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Center for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of a Center for Radiation Research, an Office of Measurement Services and the following divisions:

> Applied Mathematics — Electricity — Mechanics — Heat — Optical Physics — Linac Radiation [2] — Nuclear Radiation [2] — Applied Radiation [2] — Quantum Electronics [3] — Electromagnetics [3] — Time and Frequency [3] — Laboratory Astrophysics [3] — Cryogenics [3].

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement, standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; provides advisory and research services to other Government agencies; and develops, produces, and distributes standard reference materials. The Institute consists of the Office of Standard Reference Materials and the following divisions:

> Analytical Chemistry—Polymers—Metallurgy—Inorganic Materials—Reactor Radiation—Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations leading to the development of technological standards (including mandatory safety standards), codes and methods of test; and provides technical advice and services to Government agencies upon request. The Institute also monitors NBS engineering standards activities and provides liaison between NBS and national and international engineering standards bodies. The Institute consists of a Center for Building Technology and the following divisions and offices:

> Engineering and Product Standards—Weights and Measures—Invention and Innovation—Product Evaluation Technology—Electronic Technology—Technical Analysis—Measurement Engineering—Building Standards and Code Services[4]—Housing Technology[4]—Federal Building Technology[4]—Structures, Materials and Life Safety[4]—Building Environment[4]—Technical Evaluation and Application[4]—Fire Technology.

THE INSTITUTE FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in improving cost effectiveness in the conduct of their programs through the selection, acquisition, and effective utilization of automatic data processing equipment; and serves as the principal focus within the executive branch for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

> Information Processing Standards—Computer Information—Computer Services —Systems Development—Information Processing Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal Government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System; provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world, and directs the public information activities of the Bureau. The Office consists of the following organizational units:

> Office of Standard Reference Data—Office of Technical Information and Publications—Library—Office of International Relations.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

[2] Part of the Center for Radiation Research.

[3] Located at Boulder, Colorado 80302.

[4] Part of the Center for Building Technology.

Electrochemical Analysis Section: Summary of Activities, July 1970 to June 1971

Richard A. Durst

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

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

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

Issued February 1973

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

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. We plan to issue these summaries for all of our sections. The following is the seventh annual report on progress of the Electrochemical Analysis Section:

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

This is the seventh annual progress report of the Electrochemical Analysis Section of the Analytical Chemistry Division. It covers the fiscal year 1971, which began on July 1, 1970 and ended on June 30, 1971. This report summarizes the total program of the Section, incomplete studies as well as finished work, and stresses its relationship to the missions of the Analytical Chemistry Division and the Institute for Materials Research.

This Section broadly concerns itself with studies of ionic processes in solution using electroanalytical and other related techniques. During this year, some redirection and reemphasis of effort were continued in order to bring the Section expertise to bear on important analytical problems in several areas of science, medicine, and technology. The special interests of the members of the Section lie for the most part in solution electrochemistry including the competence areas of potentiometry, electrometric titrations, coulometry, and polarography.

The Section staff in the past year maintained an overall scientific effort of about four man-years. The personnel and their competences are listed in section 8 of this report. Our most recent staff addition, Dr. Joseph R. Robinson, will develop a trace analysis competence in the area of anodic stripping voltammetry to complement the polarographic analysis competence.

Mrs. E. June Maienthal, who transferred to our Section this year from the Microchemical Analysis Section, was the recipient of the Department of Commerce Silver Medal for her outstanding success in providing novel, sensitive, and accurate methods for trace and major constituent determinations through polarographic measurement techniques. Contributions to over 200 Standard Reference Materials certificates, hundreds of analysis reports, and 15 research publications are indicative of Mrs. Maienthal's productivity.

In order to specify the procedures adequately, it has been necessary in certain instances 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.

The support of the Scientific Apparatus Makers Association (SAMA) for ionic activity studies is gratefully acknowledged.

The assistance of Mrs. Charlotte Wren and Mrs. Treva Monti in the preparation of this report is greatly appreciated.

Richard A. Durst, Chief
Electrochemical Analysis Section

TABLE OF CONTENTS

TABLE OF CONTENTS (CONT'D)

TABLE OF CONTENTS (CONT'D)

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES (CONT'D)

ELECTROCHEMICAL ANALYSIS SECTION: SUMMARY OF ACTIVITIES
JULY 1970 to JUNE 1971

Edited by Richard A. Durst

This survey of the activities of the Electrochemical Analysis Section, Analytical Chemistry Division, covers the period from July 1970 to June 1971. An attempt is made to briefly summarize a year's progress on the technical projects of the Section, to indicate the composition and capabilities of the unit as a whole, and to stress the Section's role in the mission of the Institute. Summaries of the work in each of the Section competences are given. In the area of acidity measurements, work was completed on the standardization of tris(hydroxymethyl)aminomethane for use as a biologic pH buffer material and standard for clinical pH measurements. High-precision coulometry is used to determine the atomic weight of zinc, the stoichiometry of gallium arsenide, and the purity of KCl and NaCl. Polarography is used to determine trace elements in a variety of environmental samples and Standard Reference Materials.

Key words: Acidity; coulometric analysis; electrochemical analysis; ionic activity; ion-selective electrodes; pH measurements; polarography; potentiometry; Standard Reference Materials.

1. INTRODUCTION

In last year's report on the activities of the Electrochemical Analysis Section [1], it was noted that the Section's expertise in the area of electroanalysis was being applied to a variety of analytical problems. Again this year, the work reported illustrates the diversity of interesting problems and materials, ranging from environmental samples to a redetermination of the atomic weight of zinc.

A. Facilities

Two additions to the facilities of the Section have been made this year. The transfer of the polarography competence from the Microchemical Analysis Section brought into the Section several pieces of equipment, including two cathode ray polarographs.

To supplement the polarographic work, an anodic stripping voltammetry system was added extending the voltammetric trace analysis capabilities to even lower concentration levels. The basic four-cell unit with its associated electronics is extended to eight-cell operation using the equipment shown in Figure 1. Each cell consists of a three-electrode system and nitrogen bubbler for deaeration and stirring. By the use of composite mercury graphite electrodes, trace analyses can be performed at the sub-ppb level.

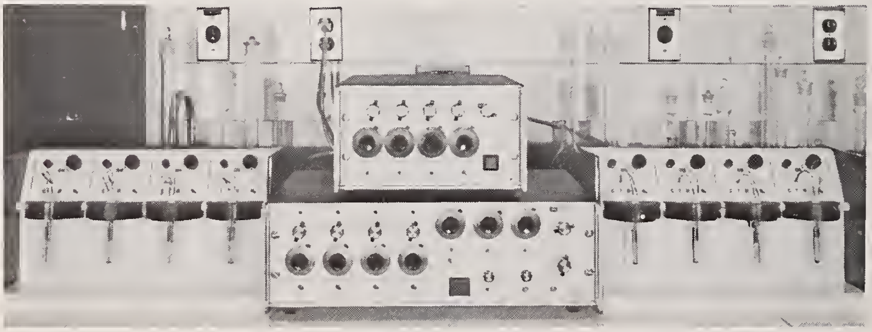


Figure 1. Anodic stripping voltammetric analysis system.

B. Activities

The laboratory is now organized into three major groups with personnel as listed in section 8 of this report. The groups are (1) potentiometry, (2) coulometry, and (3) voltammetry. The activities of the Section can be broadly divided into research, SRM certification, and service analyses for other NBS divisions and government and non-government agencies.

At the present time, automation of the pH and ionic activity measurement system is in the design stage. This system will ultimately control the various emf measurement and cell temperature parameters; perform emf, temperature, and barometric pressure data acquisition; and evaluate the pH and ionic activity functions from this data. This system should be operational by January 1972 and will be described in detail in next year's report.

NBS Special Publication 314, "Ion-Selective Electrodes" [2], which was published in January 1970 and reviews the state of the art of these sensors, has gone into its third printing after having sold more than 7000 copies in less than 18 months. This indicates the great interest in these sensors and the value of this monograph to this field.

Richard A. Durst

2. COULOMETRY

> "When you can express in numbers
> that of which you speak, you have
> the beginning of a science. Until
> that time your knowledge is meager
> and unsatisfactory."
>
> Lord Kelvin

A. Introduction

Today it is not sufficient to express the results of measurement in numbers. The requirement of today is for these numbers to be accurate.

Just as the accuracy of time, mass and length measurements throughout the United States depends on the accuracy of physical standards maintained by NBS, the accuracy of the chemical measurement depends on the chemical standards which NBS certifies and disseminates. In contrast to the physical standards, chemical standards are destroyed in the measurement process. The result is that chemical standards (though they are convenient as the medium for the transfer and dissemination) are depleted and periodically must be replenished, restandardized and reissued. The eminent need of today is to establish a permanent, nondestructable standard for chemical measurement of the stoichiometry of materials. In addition to permanence this standard should fulfill the requirements of a variety of chemical reactions that are used in the standardization process. The coulomb fulfills these criteria.

The essence of coulometric analysis, the measurement system and the consequences of the use of the coulomb will be briefly discussed as a model for absolute analytical measurement.

The coulometric method of analysis involves quantitative electrochemical conversion of the constituent which is being determined from some initial state to another well defined state and the measurement is simply the evaluation of charge necessary to perform this conversion. Below, two examples of the coulometric analysis processes are illustrated; a cyclic cathodic process and a unidirectional anodic process:

$$\begin{tikzcd}
3\,\mathrm{Fe(III)} + 3e \arrow[r] & 3\,\mathrm{Fe(II)} \arrow[d] \\
3\,\mathrm{Fe(III)} + \mathrm{Cr(III)} \arrow[u] & 3\,\mathrm{Fe(II)} + \mathrm{Cr(VI)} \arrow[l]
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{Ag} \arrow[r] & \mathrm{Ag}^{+} + 1e \arrow[d] & \\
 & \mathrm{Ag}^{+} + \mathrm{Cl}^{-} \arrow[r] & \mathrm{AgCl}
\end{tikzcd}$$

In the former case ferric ion is reduced to ferrous at a platinum cathode and the electric current which induces this reaction is measured in the external circuit. The ferrous ion thus generated in turn reacts with the hexavalent chromium, which is the species to be determined, reducing it to the trivalent state. Thus as long as the hexavalent chromium is present in the system ferric ion is regenerated. When all of the unknown has been consumed cycling ceases and the concentration of ferrous ion begins to increase. This point can be determined by a number of suitable indicator systems. In this reaction then one mole of chromium corresponds to three faradays of charge.

The determination of chloride is realized through the oxidation of silver from the solid phase. The soluble chloride is precipitated by the reaction product, Ag^{+}, into another solid phase, silver chloride. The measurement again involves the measurement of charge needed to carry out this conversion. When all of the soluble chloride, with the exception of the amount furnished by the solubility of AgCl in solution, has been consumed the concentration of silver ions in solution increases, and using a suitable indicator system the completion of reaction can be established.

The general configuration of the coulometric circuit is shown in Figure 2.

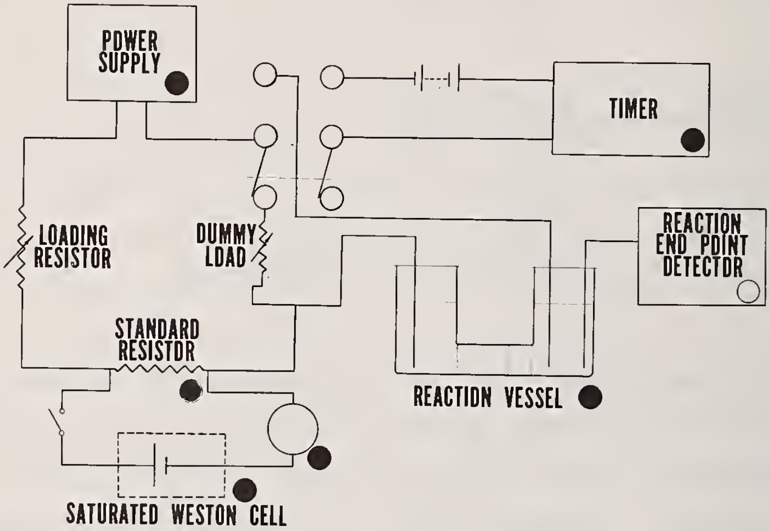


Figure 2. Coulometric circuit

The circuit consists of a high precision constant current power supply, an accurate current comparatory system, the necessary current stabilization resistors, the timing circuit, the coulometric electrolysis cell and the endpoint detector system. The general view of the coulometric facility is shown in Figure 3, and the close-up of the coulometric cell in Figure 4.

The design of the cell incorporates two significant features: (1) separation of the anode and cathode compartments in order to prevent the interference of the counter electrode reaction products with the analytical reactions conducted in the left hand side of the cell and (2) a provision for returning the unknown, which is invariably lost during the electrolysis period by diffusion and electromigration, back into the reaction compartment. Other features visible in the figure are the end-point detector probe, (glass electrode in this case for acidimetry) and a system for maintaining the inert atmosphere in the reaction vessel.

Figure 3. A general view of the coulometric facility.

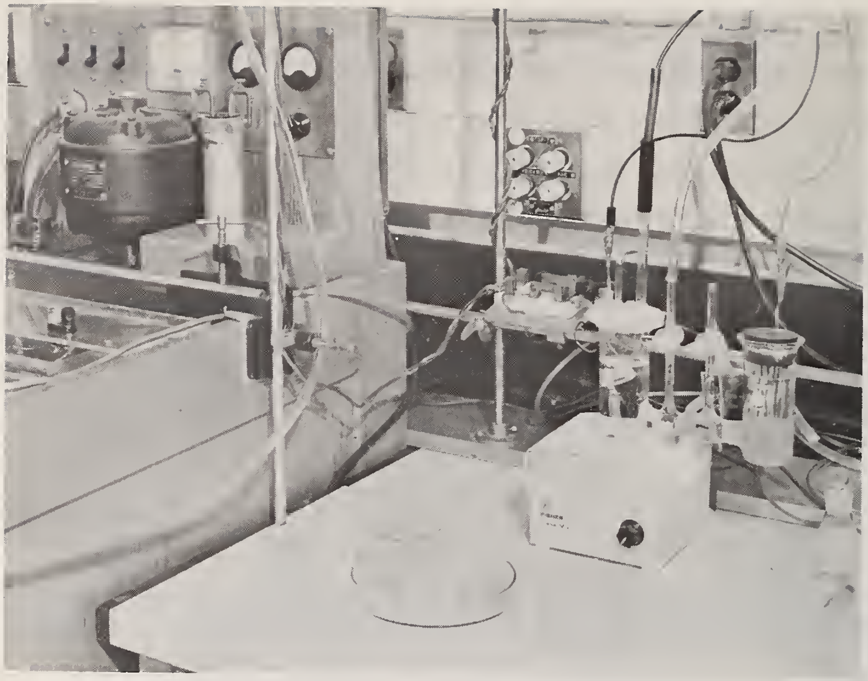


Figure 4. A close-up of the coulometric titration cell.

Figure 5 shows the typical amperometric end-point which one obtains in coulometric measurement. It has been established that in a coulometric titration the precision of a single measurement of 10 parts per million can be obtained. Thus, the system appears to be in a state of control and we "can express in numbers" that of which we speak. Let us examine the data which subjects the coulomb, as the absolute chemical standard, to a test; the test for accuracy.

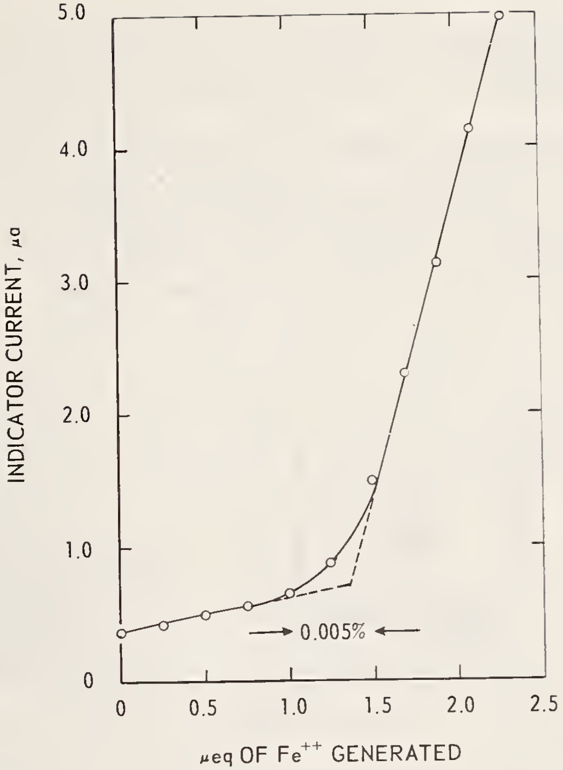
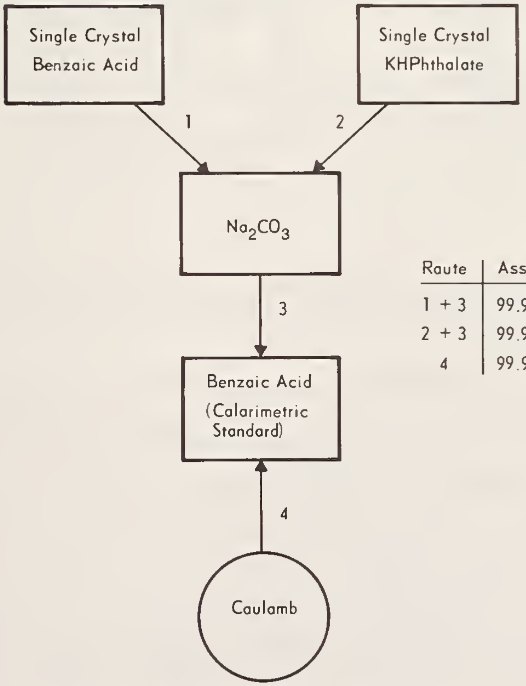


Figure 5. A typical amperometric end-point.

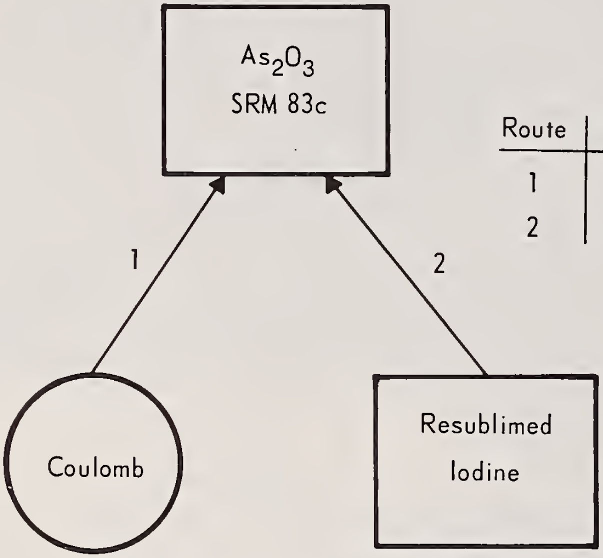


Route	Assay, %	$\bar{\sigma}$, %
1 + 3	99.9957	0.0006
2 + 3	99.9953	0.0006
4	99.9963*	0.0004

* Using F = 96,486.70 C mole^{-1} and U S legal volt of 1969

Figure 6. Comparison of benzoic acid assay by independent methods.

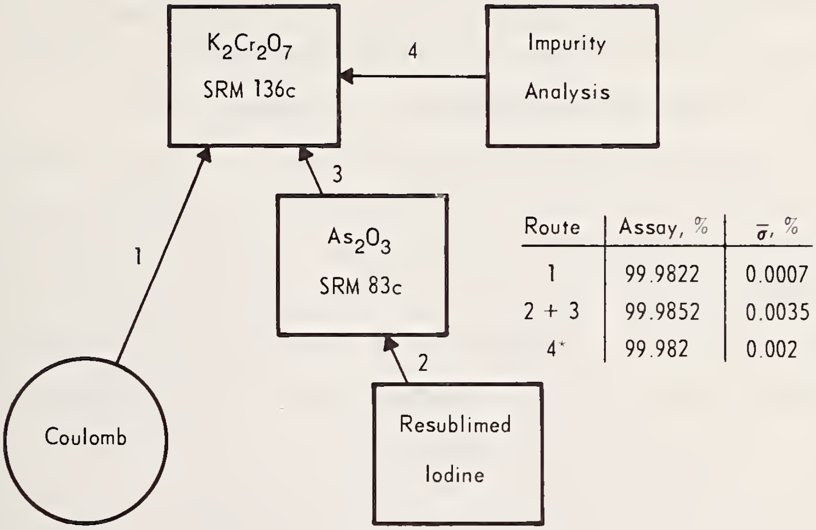
Standard Reference Material arsenious oxide was compared by Keith Sappenfield of the Analytical Chemistry Division to high-purity resublimed iodine via route 2 in Figure 7 and analyzed in our laboratory coulometrically via electrogenerated iodine (route 1). The agreement between these two independent methods is 5 parts per million.



Route	Assay, %	$\bar{\sigma}$, %
1	99.9873	0.0013
2	99.9878	0.0022

Figure 7. Comparison of arsenious oxide assay by independent methods.

Potassium dichromate (Standard Reference Material 136c) titrated coulometrically in our laboratory via route 1 in Figure 8, was compared to arsenious oxide by Sappenfield involving a two stage process, route 2+3, and analyzed for impurities (route 4). The results of these three independent determinations are again in agreement within 30 parts per million. Thus, on the basis of these three completely different coulometric reactions there is sufficiently convincing evidence that the coulomb fulfills two highly important requirements. Firstly, it unifies chemical measurements through the use of a single standard, the coulomb, and secondly, this standard is permanent and indestructible.



Route	Assay, %	$\bar{\sigma}$, %
1	99.9822	0.0007
2 + 3	99.9852	0.0035
4*	99.982	0.002

* The only significant impurity is 0.018% H_2O

Figure 8. Comparison of potassium dichromate assay by independent methods.

Accurate coulometric measurement of stoichiometry can be employed not only for the unification of chemical standardization but also in the determination of some important physical constants.

With the availability of high purity zinc (Standard Reference Material 682), the redetermination of the atomic weight of zinc by the coulometric method posed an unbearable challenge. In collaboration with Prof. Robert T. Foley of the American University this challenge was accepted.

To date only a small fraction of the data obtained on the redetermination of the atomic weight of zinc has been processed. However, even at this point it is possible to present a significantly improved value of the atomic weight of zinc.

B. Atomic Weight of Zinc

1. Research

The nature and experimental detail of some preliminary investigations will be discussed in future publications. Nevertheless, it is germane to the subject at hand to outline the results of these preliminary studies here.

(a) The presence of oxygen (air) in the electrolyte has a significant effect on the rate of spontaneous corrosion of zinc. This in turn affects the experimentally determined electrochemical equivalent and the atomic weight of zinc. For this reason air was removed from the electrolyte by purging with nitrogen. A nitrogen atmosphere was maintained in the coulometer in all final determinations of the electrochemical equivalent of zinc. In the absence of air the corrosion current density of zinc amalgam was found to be most significant (1.37×10^{-7} A cm^{-2}).

(b) Commercial grade zincs without any *a priori* processing yield a higher electrochemical equivalent (on the order of 0.01 percent) than the same materials subjected to vacuum fusion. This could easily be explained by the presence of gases (notably oxygen) in the commercial material which are removed under vacuum fusion conditions.

(c) Zinc anodes amalgamated on the surface undergo electrochemical dissolution without any detectable fall-off of material in the course of electrolysis.

(d) The difference between the free energies of the reaction

$$Zn(Hg) \rightarrow Zn^{++} + 2e \quad (U^0 = +0.799 \text{ V}) \qquad (1)$$

and the next conceivable reaction

$$Hg + 2OH^- \rightarrow HgO + H_2O + 2e \quad (U^0 = +0.098 \text{ v}) \qquad (2)$$

is sufficiently large that even at current densities as high as several amperes per square centimeter the former reaction proceeds at 100.000 percent current efficiency. This was verified experimentally by measurements of the working anode potentials at different current densities, using first pure mercury anode and then zinc amalgam anodes. Coulometric experiments conducted at current densities ranging from 10^{-5} to 1.0 A cm^{-2} substantiate this conclusion since no significant dependence between current density and the electrochemical equivalent of zinc could be found.

(e) Other parameters investigated include current (from 10^{-4} to 1.0 A), time of electrolysis (from 3 to 7×10^4 sec), electrode area (from 0.5 to 10 cm^2), total amount of charge passed through the cell (up to 3×10^4 C), purity of material, and mass of dissolved zinc (up to 10 g). Only the electrode area has a significant effect resulting from the dissolution of ZnO formed on the surface of the amalgam during handling of the electrode in air. The magnitude of this effect was evaluated (10.7 ± 1.5 μg cm^{-2}) and appropriate correction applied.

2. Method

The approach taken in this investigation is rather straightforward in its conception — to determine the mass of zinc dissolved anodically during the passage of a constant electrical current through the following electrochemical cell:

$$\text{Zn(Hg)} \mid \text{ZnCl}_2 \text{ (3 molal, aq), NH}_4\text{Cl (25 wt \%, aq)} \mid \text{Hg} \quad (3)$$

The quantitative reaction which is of specific interest here is

$$\text{Zn(Hg)} \rightarrow \text{Zn}^{++} + 2e \quad (4)$$

and the accompanying cathodic reaction is simply the reverse of reaction (4):

$$\text{Hg} + \text{Zn}^{++} + 2e \rightarrow \text{Zn(Hg)} \quad (5)$$

In such a cell the composition of electrolyte remains unaltered throughout the whole experiment.

The passage of two faradays of charge through the cell dissolves one mole of zinc from zinc amalgam. The coulometric circuit enabling passage of charge through the cell within an accuracy of 0.0002 percent has been described above. A weighed zinc amalgam anode is suspended at the top of the coulometer. The mercury pool cathode is located at the bottom of the coulometer. The ground glass flat joint in the coulometer is provided for insertion of a porous membrane filter which is used in some experiments to establish the existence or the absence of any significant fall-off of the material from the anode in the course of this electrochemical dissolution. The electrolyte is deaerated and a nitrogen atmosphere maintained in the coulometer throughout the experiment. Zinc amalgam anodes exhibited no significant material fall-off.

Zinc anodes are weighed by substitution on a 20-g capacity microbalance. The uncertainity of the mass measurement process (standard deviation) is 3×10^{-6} g. The smallest changes in the mass of Zn anodes roughly equivalent to the mass of a single weight in the calibrated set of weights (*e.g.* 2 g). After termination of electrolysis, the zinc anode is carefully removed from the coulometer, washed first in 0.1 molar NH_4Cl solution and then in hot distilled water and reweighed. Appropriate corrections for the effects of buoyancy of air are applied. Thus the charge-to-mass ratio can be readily computed.

3. Results

The results of experiments with metallic zinc samples of five different origins are summarized in Table 1. The first column in the table gives the original number of the experiment. Material code and the origin of material are given in columns two and three respectively. The last column, column four, gives the determined values of the atomic weight of zinc in each experiment.

The material designated as 1 is high purity zinc issued by the National Bureau of Standards as Standard Reference Material (SRM 682). The material was produced by Cominco American, Inc. from a special lot of high-grade electrolytic zinc. It was purified by vacuum distillation, zone-refining and degasification. The overall assessment of impurities indicates that the material is 99.9999 percent

Zn [4]. The material designated as 2 is a special high-grade metal (99.995 percent Zn) produced by the Electrolytic Zinc Company of Australasia Ltd. [5]. Materials 3, 4 and 5 were produced in Peru, Yugoslavia, and Italy respectively.

Table 1. Atomic weight of zinc determined by coulometry.

Experiment No.	Material Code	Origin of Material	Atomic Weight of Zinc
1$\overset{1}{3}$9	1	Canada	65.3759
140	1	Canada	65.3761
141	1	Canada	65.3782
142	2	Australia	65.3783
143	2	Australia	65.3778
144	3	Peru	65.3786
145	3	Peru	65.3764
146	4	Yugoslavia	65.3761
147	4	Yugoslavia	65.3751
148	5	Italy	65.3784
149	5	Italy	65.3783
150	1	Canada	65.3791
		Mean	65.3773_6

Pertinent Statistical Data:

Standard deviation of a single determination $s = 0.00134$

Standard deviation of mean $\frac{s}{\sqrt{n}} = 0.00039$

Two sided 95 percent confidences interval $\frac{ts}{\sqrt{n}} = \pm 0.00086$ for the mean based on 11 degrees of freedom.

The calculated values of the atomic weight of zinc in column four are based on the coulometrically determined electrochemical equivalent of zinc and adopted value of the faraday. For the determination of charge consumed in the electrochemical reaction, the value of electrical current is based on the NBS ohm and U. S. legal volt of 1969.

Time measurement is based on 100 kHz frequency maintained by NBS. Mass measurements were performed by substitution using a set of weights calibrated at NBS. The value of the faraday employed in these calculations is 96486.70 C mole^{-1} [6].

The mean value of the atomic weight of zinc based on coulometric data reported here is 65.37736. A two-sided 95 percent confidence interval for the mean, 0.00086, reflects adequately the uncertainty in this value due to the random sources of error. The accuracy of the result, however, depends not only on the random error of measurement, but also on the basis which could exist in the various stages on the measurement process and in the constants which are employed in calculation of the results.

The assessment of the uncertainties due to all known sources of possible systematic error (uncertainties in electrical standards, time, mass and the faraday) indicates that these sources can contribute as much as 0.002 percent (0.00131 amu) error. Thus, the sum of the components of error yields an uncertainty figure of 0.0022 in the atomic weight of zinc.

It is thus felt that on the basis of this work the atomic weight of zinc can be assigned the value

$$65.377 \pm 0.003. \qquad (6)$$

All the experimental values reported here lie well within the assigned uncertainty bounds. Further reduction in the uncertainty of this constant is anticipated when processing of all data is completed. Nevertheless, even the present uncertainty is an order of magnitude smaller than that of the presently accepted value.

On the basis of data presented here, there appears to be no significant difference between the values of atomic weight for materials of different origins even at the 10 percent level of significance. The published results of mass spectrometric investigations [7] also indicate no significant differences in the isotopic composition of zinc produced by electrolytic and chemical reduction processes. To insure that the value obtained in this research is truly representative of the terrestrial zinc, an experimental survey of primary zinc bearing minerals from world-wide sources is now in progress. This study is conducted on virgin minerals which have not been subjected to metallurgical processing (other than flotation), since this could produce isotope separation (isotope separation can conceivably occur in such processes as distillation which is commonly used in purification of zinc).

The equally challenging problem is the determination of the stoichiometry of a two component system — gallium arsenide. Coulometrically the number of moles of each component is directly determined independently of the atomic weight of the material and therefore the molar ratio of gallium to arsenic is directly extractable from the coulometric measurements. The results of this research will be discussed in a separate section of this report.

It is the aim here to give a varied picture of the challenging problems of accurate measurement of stoichiometry. It is attempted to consolidate these ideas as shown in Figure 9. The certification of Standard Reference Materials, the standardization of research materials such as separated isotope solutions for calibration of mass spectrometers, the determination of physical constants, such as the atomic weights and the faraday, the new area of the measurement of semiconductor stoichiometry can all be performed using a single standard, the coulomb. The long range goal of the coulometry program, to place chemical standardization on an absolute basis, has been achieved. Thus, through coulometry, the analytical measurement of the chemical composition of materials is placed on a firm foundation — The International System of Units (SI), and the standards for this measurement are the physical standards, maintained by NBS.

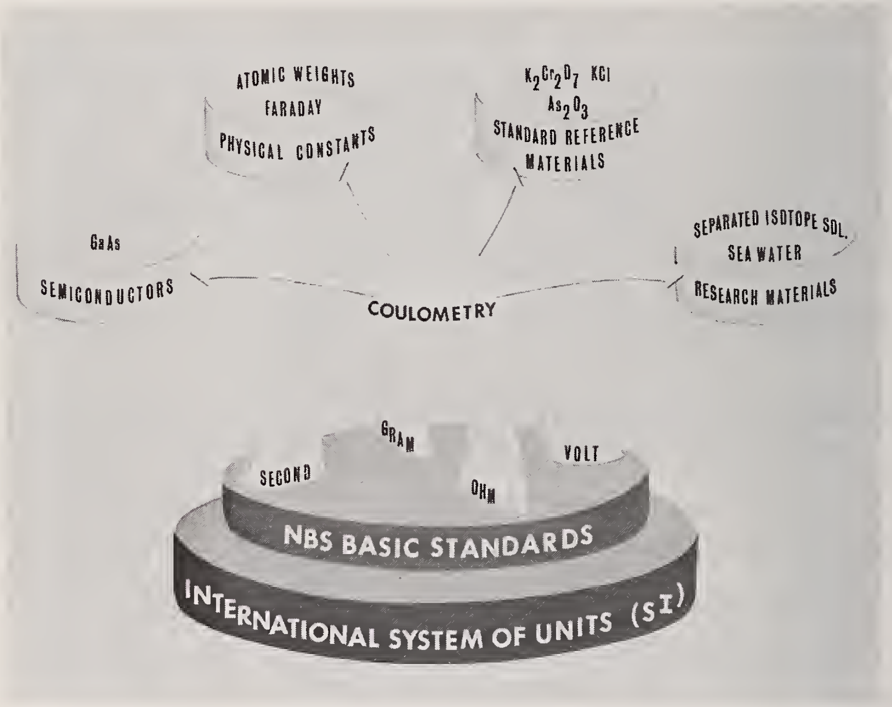


Figure 9. Foundation of versatility of coulometric measurement.

C. OECD Characterization Exchange Program

As part of a chemical characterization exchange program under the auspices of OECD (Organization for Economic Cooperation and Development) our coulometry laboratory participated in the determination of chloride in single crystal KCl and the determination of the stoichiometry of single crystal GaAs. In the following pages, the essence and the results of these studies summarized.

1. Single Crystal KCl

Samples of two designations were received from OECD for analysis: 5.5 and 7.5. Each crystal was removed from its plastic packaging with a pair of stainless steel tweezers, placed into a platinum boat without any preliminary treatment, weighed and delivered into a 125-ml Erlenmeyer flask by tipping the flask on its side, insertion of the Pt boat into the flask with tweezers and gentle emptying of the boat. The Erlenmeyer flasks were previously washed with fuming sulfuric acid, soaked in distilled water and dried at 110° C in a drying oven. Five milliliters of distilled water were added to the Erlenmeyer flask (containing the weighed KCl sample) by running it gently along the side of the inclined flask. The flask was covered with a small Petri dish. After dissolution, the KCl was ready for titration.

a. Method. In one sentence, the method could be classified as a constant-current coulometric-argentimetric titration with a biamperometric end-point determination. The details of procedure are given below.

Basically the method is similar to the one described earlier [8] with some modifications. The electrolyte was changed to 20 wt percent $HClO_4$. Coulometric generation of monovalent silver ion in 20 wt percent perchloric acid has been investigated in great detail by D. N. Craig *et al.* [9]. These investigators concluded that the $Ag \rightarrow Ag^+ + e$ reaction proceeds with 100 percent current efficiency for current densities as high as 150 mA/cm^2. In the titrations reported here the current density was 25 mA/cm^2 for the majority of the titration. One hundred milliliters of 20 wt percent perchloric acid were used for each titration. A small amount (*e.g.*, 20 μeq) of chloride was added to the electrolyte and pretitrated to saturate it with AgCl. Afterward, 99.9 percent of the calculated amount of silver required for titration were generated at 500 mA. Following pregeneration of silver ion, the sample was introduced into the cell via a syphon arrangement which is fitted into the flask containing the dissolved KCl sample. In this procedure the sample can be delivered and then electrolyte withdrawn from the cell back into the Erlenmeyer flask thus rinsing it as many times as desired and yet maintaining virtually constant volume of electrolyte in the cell.

At this point, the precipitate in the system is permitted to come to equilibrium (about one hour) in the dark. The titration is then completed at 0.643 mA.

b. Instrumentation. For constant-current coulometric titrations, three different instrumental facilities are required for measurements of current, time and end-point indicator signal.

Current: A Princeton Applied Research constant-current power supply Model TC602-CR was employed. Its maximum output is 60V and current rating of 2A. The power supply is operated in a constant-current mode. The current value is selected to be such that the IR drop across the standard resistor equals the voltage of the saturated standard cell. The standard resistor and standard cells are calibrated at NBS.

Time: A Beckman Model 3750 Universal EPUT and Timer was used for measuring the time interval between the start and the termination of the passage of current through the coulometric cell.

End-Point Determination: A Sargent Model XXI polarograph was used for application of the potential (0.05 V) between two polarizable silver electrodes and for recording the indicator current.

Mass Measurement: A Mettler Microbalance was used for weighing. The balance is a constant load type, 20-g capacity.

The standard deviation of the mass measurement process on this balance, established over a number of years, is 0.0003 mg. The samples were weighed in a platinum boat by the substitution method. NBS calibrated weights were used for this purpose. The weight of the samples was corrected to the mass in vacuum by applying appropriate corrections for the effect of air buoyancy.

Method of Calibration: The electrical and time measurements were performed against standards calibrated by the appropriate laboratories of the NBS. The accurate current measurement was based on the values of a standard resistor and the voltage of a saturated standard cell. In order to obtain a statistically larger sample SRM KCl was analyzed simultaneously with the samples issued by the OECD. Data obtained in this manner are useful in establishing whether or not the measurement process is in the state of control.

c. Standards

Physical Standards:

Molecular weight of KCl	:	74.555
Faraday	:	96,486.70 C mole $^{-1}$
Volt	:	U. S. legal volt of 1969
Frequency	:	Frequency standards maintained by NBS

Reference Material: As indicated earlier, NBS Standard Reference KCl was used in conjunction with OECD material as an independent check on the measurement process. SRM KCl is a polycrystalline material which requires drying at 500° C to release the entrapped mother liquor.

Table 2. Results of coulometric titration of KCl.

Titration Sequence	NBS Standard Reference Materials Assay, %	OECD Single crystal Assay, %	OECD Sample No.
1	99.9969	----	
2	99.9952	----	
3	99.9930	----	
4	99.9971	----	
5	99.9979	----	
6	----	99.9947	5.5
7	----	99.9961	5.5
8	----	99.9939	7.5
9	99.9961	----	
10	99.9991	----	
11	----	99.9988	5.5
12	99.9909	----	
13	99.9985	----	
14	99.9988	----	
15	99.9980	----	
16	99.9960	----	
Average	99.9965	99.9959	
Std. deviation	0.0025	0.0022	
$\frac{t_{95\%}S}{\sqrt{n}}$	0.0016	0.0035	

d. Error Analysis. Titrations of KCl samples issued by the Office of Standard Reference Materials and OECD were performed in an experiment which could be viewed as a "process control" experiment. Two different materials were analyzed in an interdispersed sequence as indicated in the data table. The standard deviations for each set are nearly the same. The sequential analyses of the differences between the individual values and the corresponding means are shown in Figure 10. The data in Table 2 were fitted three ways to an equation for straight line $\Delta = mx + b$, by the method of least squares, where Δ is (assay - mean assay) and X is the titration sequence. The first fit included all points, the second SRM KCl only the third excluded titration numbers 6, 7, 8, 11 and 12. On the basis of the analysis of these data there is no evidence to indicate that the measurement process is not in the state of control (the slope, m, is not significant even at the 10 percent level). Thus the measurement process is "in the state of control."

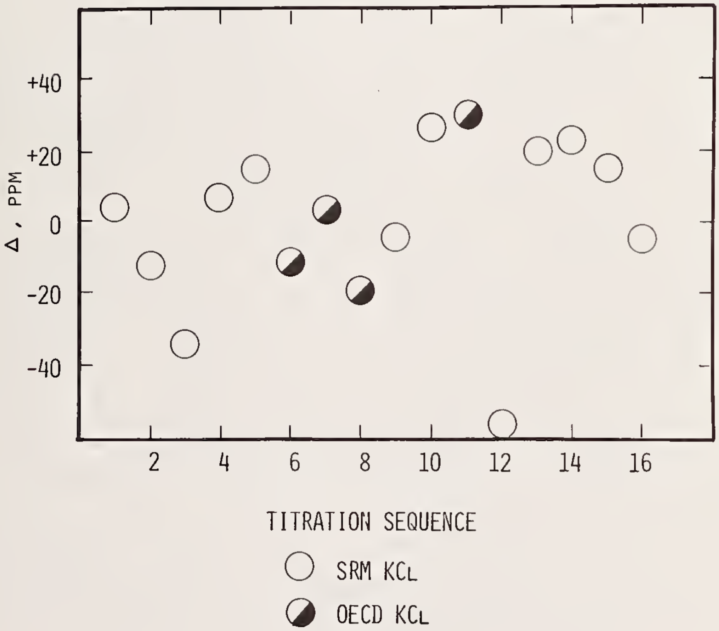


Figure 10. Differences between individual values and the corresponding means.

In addition to the random error component (standard deviation) one must also take into account possible sources of systematic error (due to uncertainties of mass, charge, faraday and molecular weight). Estimate of the magnitude of the systematic error is 0.0044 percent. The overall uncertainty (sum of systematic and random error estimates) is 0.0079 percent.

Three comments are in order:

1. It should be stressed that for large samples (*e.g.*, 11 meq) pregeneration of silver ion is a very important part of the procedure. Early attempts to deliver the chloride sample into the cell before generation of the major portion of silver ion yielded low results. Two factors could be responsible for this: a) high corrosion current of silver in the presence of chloride; b) loss of HCl from strongly acid (20 percent $HClO_4$) solution by volatilization.

2. KCl must be predissolved in water (5 ml) since potassium perchlorate is itself poorly soluble.

3. Before determining the end point, it is advisable to tap the indicator electrodes in order to remove the silver chloride precipitate which accumulates on them in the course of the prolonged equilibration period.

e. Conclusions. Determination of chloride by constant-current coulometric argentimetry can be performed with a precision on the order of 0.0025 percent. In addition to the random error, the uncertainty in the assay of KCl must also include the estimate of possible systematic errors. The estimate of the total systematic error is 0.0044 percent. The major part of the systematic error is contributed by the uncertainties in the atomic weights (0.0027 percent). Thus, the overall uncertainty in the assay is 0.0079 percent.

2. Gallium Arsenide Stoichiometry

Samples were removed from their plastic packaging, placed on a porcelain plate and divided approximately in half by applying moderate pressure with a steel knife along the cleavage plane of the crystal. Subsequently each piece was etched in a platinum crucible using ACS reagent-grade HF, washed in distilled water and vacuum dried in a desiccator as specified in the OECD instructions under deoxygenation procedure. Each piece was placed into a platinum boat, weighed and delivered carefully into a previously washed and dried 125-ml Erlenmeyer flask. Five milliliters of "Suprapure" nitric acid were delivered into the flask in a hood, the flask was inclined so that it was virtually horizontal, to prevent the loss of spray, and left in that position until dissolution of the sample was complete.

a. Method. Since this exercise involved the determination of GaAs stoichiometry obviously two methods were used: one for Ga and one for As. Gallium was determined via an EDTA complexation reaction and back titration of excess EDTA with zinc. In general, the analytical procedure of Reilley *et al.* [10] was adopted. These authors have already shown that gallium can be determined volumetrically with precision and accuracy better than 0.05 percent. The coulometric procedure was developed in our laboratory. The arsenic determination was based on our earlier work [11].

Reilley's procedure for the determination of gallium required standard EDTA and standard zinc solutions. Excess EDTA was added to complex the trivalent gallium (in acetate buffer solution), heated, and the excess EDTA was back titrated with standard zinc solution. A small amount of mercuric EDTA complex was added to the solution to act as a indicator ion, using a mercury indicator electrode.

In our method, EDTA was handled as a solid. It was standardized coulometrically with electrogenerated Zn^{++} and the end-point was determined amperometrically using a gold amalgam polarizable electrode, a standard calomel reference electrode and an applied potential of -1.20 V vs. SCE. This potential corresponds to the diffusion plateau of the Zn^{++} reduction wave.

b. Results. Two different materials were analyzed: OECD single crystall GaAs and a commercially available undoped polycrystalline material, which on the basis of impurity analysis was estimated by the manufacturer to be 99.999 percent pure.

The results of analysis are summarized in Tables 3 and 4. Since in the determination of stoichiometry it is the molar ratio of components which is of interest, the results are reported as moles of element (Ga or As) per gram of material.

Table 3. Coulometric analysis of GaAs.

Polycrystalline Material

Sample No.	Ga, mol/g GaAs	As, mol/g GaAs	Ga/As
1	6.91240	6.01202	
2	6.91264	6.91256	
3	6.91341	6.91208	
Average	6.91282	6.91222	
s =	0.00044	0.00029	1.000086
			± 0.000078

Table 4. Coulometric analysis of GaAs

Single Crystal Material (OECD)

Sample No.	Ga, mol/g GaAs	As, mol/g GaAs	Ga/As
18	6.91291	6.91325	
21	6.91324	6.91283	
22	6.91244	6.91276	
24	6.91269	6.91259	
Average	6.91280	6.91286	
s =	0.00035	0.00028	0.999994
			± 0.000065

c. Discussion. It is quite clear from the data in the above table that the OECD single crystal material is stoichiometric within 0.007 percent (*i.e.*, Ga/As = 1.000). In the polycrystalline material the Ga/As is about 0.01 percent greater than unity. The low value for the concentration of As appears to be responsible for this, since the concentration of Ga is approximately the same in both materials. This polycrystalline material is now under investigation to determine what element has replaced arsenic in the lattice (oxygen is one possibility).

The situation is quite disturbing when one attempts to perform mass balance calculations. The results of this exercise are summarized in Table 5.

Table 5. Mass balance for GaAs

Material	Element	At Wt of Ga[a] 69.72	At Wt of Ga[b] 69.733
Polycrystalline material	Ga	48.1962	48.2052
	As	51.7875	51.7875
		99.9837	99.9927
		± 0.0078	± 0.0078
Single Crystal Material (OECD)	Ga	48.1960	48.2050
	As	51.7922	51.7922
		99.9882	99.9972
		± 0.0065	± 0.0065

[a] Presently accepted value, *C & E News* 48, 39 (1970).

[b] G. E. F. Lundell and J. I. Hoffman, *J. Res NBS* 15, 409 (1935).

For both materials (disregarding the fact that the first material appears to be nonstoichiometric) the mass balance is low by over 0.01 percent. Since the impurity levels in these materials are such that they cannot possibly account for this material deficiency, two other alternate explanations are in order:

(1) Error in the method

(2) Error in the atomic weights

Since all experimental parameters are measured on an absolute basis, the only other possible way that the measurement method could be in error is if the determination of Ga and As were biased by the same amount and in the same direction due to unsuspected sources of error. The likelihood of this is rather remote.

In considering the errors in the atomic weights, arsenic can be ruled out as a possible suspect (mononuclidic element). When the report of the IUPAC Commission on Atomic Weights is examined, one finds that the value 69.72 for the atomic weight of gallium is based on three independent determinations: Richards and Craig (1923) 69.713 from $GaCl_3/3$ Ag (recalculated on the basis of Cl = 35.435; Au = 107.868); Lundell and Hoffman (1935) 69.7333, from 2 Ga/Ga_2O_3 ratio; and 69.72 value based on the mass spectrometric determination of Ga^{69}/Ga^{71} ratio by Inghram, *et al.* (1948).

Taking the atomic weight of gallium as 69.7333 (Lundell and Hoffman value) the mass balance is much more satisfactory as shown in the above Table.

Since the atomic weight of arsenic is well known, a more extensive study of GaAs stoichiometry could produce another independent value for the atomic weight of gallium on the basis of combining weight calculations. Further studies of the direct coulometric determination of the electrochemical equivalent and the atomic weight of Ga, using high-purity metal, are now in progress in this laboratory.

d. Error Analysis. In addition to the random errors of measurement there are the following two sources of possible systematic error: (1) the atomic weight of gallium is a suspect which might contribute as much as 0.01 percent error to the assay of GaAs; (2) other sources (measurement of current, time, mass and the faraday) amounting to about 0.002 percent.

The coulometric determination of the molar ratio in this two-component system, however, obviates these sources of the systematic error and thus only the random error component of the uncertainty is effective. For single crystal material, the uncertainty in the Ga/As is only 0.007 percent.

e. Conclusions. Both Ga and As in GaAs can be determined coulometrically with precision on the order of a few parts in 100,000.

The method appears promising for the determination of deviations from 1:1 stoichiometric balance.

The obtained data indicate that the accepted value for the atomic weight of gallium (69.72) is too low. The Lundell and Hoffman value (69.733) appears to be more accurate. Further work is in progress to test this conclusion.

The undoped polycrystalline material appears to be slightly nonstoichiometric (Ga/As = 1,000086). This material is still under the investigation to determine what element replaces As in the lattice.

D. Analysis of Standard Reference Materials

1. Tris-hydrochloride

Twelve samples of tris(hydroxymethyl)aminomethane hydrochloride were analyzed for their chloride content. The analyses were performed on an "as received" basis, *i.e.*, the material was taken for analysis from sample bottles without any pretreatment, such as crushing, drying, *etc.* The accurate mass of samples was obtained by applying appropriate buoyancy corrections to the weight in air. The chloride was precipitated by coulometrically generated Ag^+, and the results of analyses are summarized in the following table.

Table 6. Results of Analysis of Tris-hydrochloride

Sequence of Analysis	Sample No.	Chloride Assay % of theoretical
1	12	99.688
2	2	99.717
3	9	99.721
4	5	99.690
5	10	99.706
6	3	99.668
7	4	99.652
8	1	99.652
9	7	99.697
10	8	99.704
11	6	99.647
12	11	99.710
	Average	99.688
	$s = 0.027; \frac{s}{\sqrt{n}} =$	0.008

The coulometric determinations were shown earlier to be more than an order of magnitude more precise (0.003 percent) than the 0.027 percent, the random error estimate of the above set. On the basis of reasoning that the random error of a set of determinations is composed of the random error of measurement component, S_m, and the random distribution of impurity in the material (heterogeneity), S_h, one can state that

$$S_{total} = (S_h^2 + S_m^2)^{1/2} \qquad (7)$$

in the case at hand, S_{total} = 0.027 percent and S_m = 0.003 percent. Solving the above relationship for S_h one can conclude that heterogeneity of the sample is responsible for virtually all of the random error.

2. Standard Reference KCl

a. Preliminary Investigations. The purpose of the preliminary investigation of the material was to establish: the suitability of the material to be issued as primary standard in the form that it was obtained from the manufacturer; the need for such treatment as drying; the drying conditions; and the effect of relative humidity.

The preliminary investigations were conducted with two composite samples: Composite I was produced by mixing together equal weights of KCl from six bottles (Bottle Numbers 1-6) and Composite II consisted of equal weights of KCl from the remaining six bottles (Bottle Numbers 7-12).

The results of analysis of the above two composite samples and the corresponding changes of the conditions are summarized in Table 7.

From the above data it is quite apparent that the material in its original state contains nearly 0.1 percent water (assay on "as received" basis 99.91 percent). As such it does not meet the requirements for a primary standard, which must assay 99.98 percent or more. Moreover the occluded water is not distributed uniformly, as evidenced by the lower precision of the analytical results of untreated samples in comparison with other data.

Crushing and drying at 130° C apparently releases most of the occluded mother liquor as indicated by an increase in the assay of the material (99.97 percent), however not all of the water is released.

Table 7. Preliminary studies on SRM KCl

Treatment	Composite No.		Chloride assay, %
1. None:	1		99.915
"As received"	1		99.901
	11		99.912
		Average	99.909
2. Crushed and dried at	1		99.980
130 °C for 18 hours	1		99.981
	11		99.982
	11		99.975
		Average	99.979
3. Crushed and dried at	1		99.997
200 °C for 18 hours	1		99.996
	11		99.995
	11		99.995
		Average	99.996
4. Uncrushed; dried at	1		99.994
500 °C for 4 hours	1		99.990
		Average	99.992

Crushing and drying at 200° C appears to be highly satisfactory treatment of the material (assay = 99.996). From the standpoint of practical use crushing is a process which could cause contamination of the material, and for that reason a heat treatment at 500° C in Vycor crucibles without any crushing was attempted. Pyrex containers cannot be used for this process. A reaction between Pyrex and KCl occurs at this temperature. The material processed in this manner indicate that the material is converted to virtually stoichiometric KCl (assay = 99.992 percent). Material tested in this manner was also checked for decomposition (loss of KCl upon heating) by dissolving known amount of material in deserated distilled water and checking its pH. The pH of IM solution was very close to 7, indicating no appreciable decomposition.

The exposure of the material to relative humidities from "0" (P_2O_5) to 75 percent for four days indicates that it does not change significantly from its original state. The weight changes of KCl upon exposure to different environments are shown in Table 8.

Table 8. Exposure of KCl to various humidities.

Relative humidities	Percent change weight (4 day exposure)
"0" (P_2O_5)	-0.006
33%	-0.005
52%	-0.003
75%	+0.002

b. Final Determination of Chloride. It was thus decided that heating of the material at 500° C for at least four hours is a satisfactory treatment which insures virtually complete removal of occluded mother liquor. All work on final analysis of this material was conducted after such treatment.

The final analyses of the material were conducted on twelve samples, each sample representing approximately 8 weight percent of the material in the lot. The results of analysis are shown in Table 9. Column one represents the sequence of titrations, column two represents the number assigned to the sample bottle and column three gives the assay of material. The assay, 99.9965 percent, is consistent with the value obtained for composite samples (treatment 3 and 4 in Table 7), with the 95 percent confidence interval for the mean of 0.0016 percent, based on 11 degrees of freedom.

It should be pointed out that the assay is computed on the KCl basis. Any impurity which is precipitated by silver is also included in this value (*e.g.* Br^-, I^-, *etc.*). Moreover, corrections for cations other than potassium should also be applied. It is for these reasons that another value, the silver precipitation titer, can be useful: 0.0134124 ± 0.0000011 mol g^{-1}. The uncertainty figure represents the sum of the random error estimate (95 percent of confidence limits) and estimate of the possible systematic errors. Of all the sources of systematic error the uncertainities in the atomic weights of chlorine and potassium are by far the largest (total uncertainty 0.004 AMU or 0.005 percent). To reduce the systematic error contributions due to molecular weight uncertainty and the uncertainty of the faraday, another useful constant, the electrochemical equivalent, can be computed for this material. The value of the electrochemical equivalent for this material is 0.772724 ± 0.000019 mg C^{-1}.

Table 9. Final Analysis of SRM KCl.

Titration sequence	Sample No.	Assay, wt %
1	1	99.9969
2	2	99.9952
3	3	99.9930
4	4	99.9971
5	5	99.9979
9	11	99.9961
10	8	99.9991
12	12	99.9909
13	6	99.9985
14	9	99.9988
15	10	99.9980
16	7	99.9960
		99.9965

$S = 0.0025$

$$\frac{t_{95\%}S}{\sqrt{n}} = 0.0016$$

*In the titration sequence numbers 6, 7, 8, and 11 correspond to titrations of different material (OECD single crystal KCl), thus the results are not included in this data table.

Here again the uncertainty figure is the sum of the 95 percent limits of random error (0.0016 percent) and the estimate of possible sources of systematic error (mass, electrical and time measurements: 0.0009 percent).

c. Analytical Procedure. After drying the KCl samples at 500° C for four hours they were placed into a P_2O_5 desiccator and stored there until needed. For each titration a 2-g sample was weighed out in a Pt boat and delivered into 125-ml Erlenmeyer flask. Five ml of distilled water were added to the flask and the sample was dissolved. The titrations were performed by electrogenerated silver ion. The method was similar to the one described earlier [12]. The electrolyte was changed to 20 wt percent $HClO_4$, which was used by Craig and co-workers at the NBS in their determination of the value of the faraday. Thus the electrochemical parameters of this system (corrosion current density, current efficiency, dissolution of silver oxide, *etc.*) are well known. Secondly, this electrolyte has lower specific resistance than the electrolyte used earlier. Consequently, the power dissipation (heating) in the cell is reduced accordingly. Following pregeneration at 500 mA of about 99.95 percent of Ag^+ which is needed to precipitate all of the chloride in the sample, the sample is delivered into the cell via a syphon arrangement and permitted to equilibrate 1 hour in the dark. The titration is finally completed at 0.6 mA current.

d. Conclusions. The material is homogeneous and perfectly suitable as a primary standard, provided it is dried at 500° C for four hours, and can be certified as 99.9965 ± 0.0025 percent based on chloride (halide) assay. This value is based on 74.555 as the molecular weight of KCl and 96486.70 C mol^{-1} for the faraday.

Based on chloride assay two other useful constants should be given: silver precipitation titer 0.0134124 ±

.0000011 mol g^{-1} and the electrochemical equivalent 0.772724 ± 0.000014 mg C^{-1}.

3. Standard Reference NaCl

Preliminary evaluation of this lot of NaCl indicated that this material, as received, does not meet the specifications for a primary standard. The assay is 99.92 percent (NBS Tech. Note 505, pp. 65-67). Crushing and drying the material at 200° C improves its assay to 99.99 percent.

The determination of halides in this material was performed by the earlier published method [8].

As in the case of KCl crushing and drying at 200° C is a satisfactory treatment for the material. Crushing however could cause contamination of the material. For that reason a heat treatment at 500° C without any crushing was carried out in Vycor crucibles.

The results of analyses of samples from eight different locations in the lot are summarized below (Table 10) in the sequence in which analyses were performed.

The original design of experiment (as proposed by Dr. John Mandel, Statistical Consultant, NBS) required duplicate analysis on each sample, thus enabling separation of variations in the results into two components: (1) those caused by random errors of the method, and (2) those caused by the variability of the material in the log (heterogeneity). Since in the certification of this material for the purpose at hand (clinical standard) an uncertainty of 0.01 percent can be considered negligible, it appears that separation of the two error components is not warranted. The total error (both due to the random error component of the method and to the heterogeneity) is much less than 0.01 percent and one can thus safely make a statement that the lot is homogenous at the 0.01 percent level.

In summary, halide titrations show that this lot of material conforms to NaCl stoichiometry to the extent of

99.9950 ± 0.0035 percent, where the uncertainty figure represents the 95 percent confidence interval for the mean.

Table 10. Coulometric determination of halides in SRM NaCl

Sample No.	Assay as NaCl, %
3C	99.9912
3A	99.9939
1A	99.9946
4D	99.9927
4B	99.9975
1C	100.0002
2B	99.9905
2D	99.9998
Mean	99.9950
standard deviation	0.0037
S.D. of the mean	0.0013
95% confidence interval for the mean	0.0031

George Marinenko

3. POLAROGRAPHY

A. Introduction

During the past year most of the analytical efforts of the polarographic laboratory have been devoted to trace analysis and have been greatly concerned with heavy metals in environmental samples and Standard Reference Materials. Considerable effort has also been spent in the analysis of major constituents, particularly those in copper-base alloys. A few of the more interesting of these activities are described in the following sections of this chapter. The polarographic facilities have been transferred to the Electrochemical Analysis Section during the past year and part of the equipment in the new facilities is shown in Figure 11.

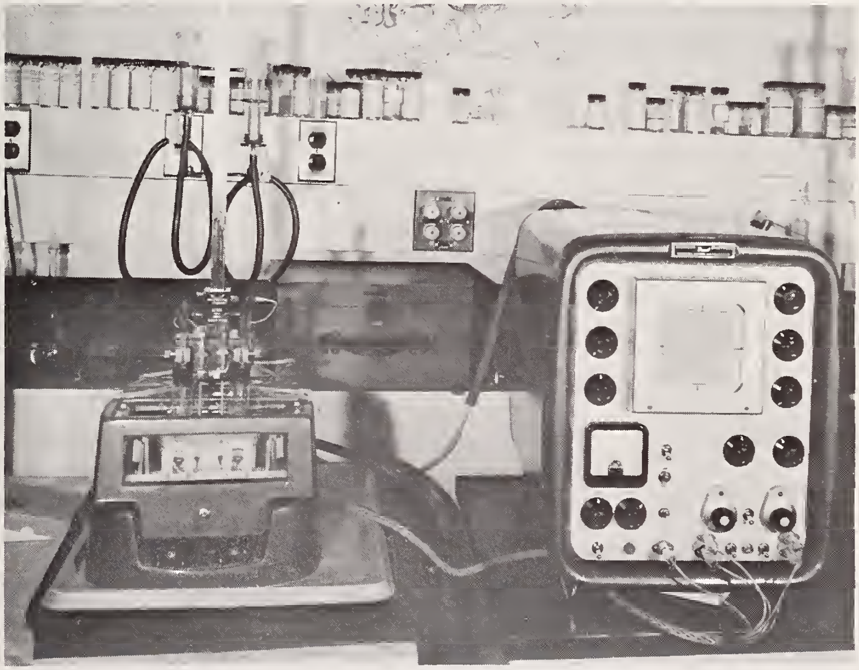


Figure 11. Cathode ray polarograph.

B. Trace Analysis

1. Reagent and Environment Blanks

In an effort to increase the quality of the reagents used in the trace analysis program of the Analytical Chemistry Division, a number of acids have been redistilled in sub-boiling quartz stills by Section 310.06 and made available to other members of the Division. Samples of these acids weighing from 160 to 290 g as well as a sample of the Division distilled water were taken for analysis. The samples, which had been evaporated to dryness in quartz beakers in laminar-flow hoods, were treated with 5 drops of nitric acid (purified by 310.06) to destroy residual amounts of organic material and again evaporated to dryness. One-half ml of hydrochloric acid was added and the samples were again evaporated to dryness on low heat. The residues were dissolved in 2.0 ml of 15 percent hydroxylamine hydrochloride, heated 60 seconds, and measured polarographically. The results are shown in Table 11.

Table 11. Cu, Pb, Cd, and Zn in acids and distilled water.

Sample	Cu, ppb	Pb, ppb	Cd, ppb	Zn, ppb
distilled H_2O	4	0.4	0.03	0.6
HNO_3	<0.1	<0.5	<0.1	<0.1
HCl (6M)	<0.1	<0.5	<0.1	<0.1
$HClO_4$	<0.1	<1	<0.1	<0.1

Iron was also of interest since iron is to be determined polarographically in lunar samples taken on the Apollo flights. Additional samples of the acids were evaporated to dryness and the residues were dissolved in dilute perchloric acid. Sodium acetate and Solochrome Violet RS were added and iron was determined polarographically. The results are given in Table 12.

Table 12. Iron in redistilled acids.

	Fe	
Sample	μg, total	ng/g sample
HCl (9M)	0.62	2.6
HNO_3	0.41	1.4

Since the iron content of the samples to be analyzed is expected to be about 10 percent, these acids are sufficiently pure for use.

The iron fall-out in the laminar-flow hoods discussed in last year's annual report [13] was also measured. Some of the metal in the interior showed corrosion and it was probable that the iron fallout had increased. An uncovered 50-ml beaker was allowed to stand in the hood 24 hours then treated with acid and measured polarographically. A value of 0.55 μg of iron was obtained, which represents about a 10-fold increase from last year.

It was necessary also, in connection with the analyses of lunar samples, to determine the iron contamination which would occur if the sample were broken in a diamond mortar. A piece of a pure quartz container was taken as well as a sample of the same quartz container, crushed to a fine powder in an agate mortar, after having been first broken into smaller pieces in an iron mortar. One-gram samples were dissolved in hydrofluoric acid and fumed to dryness several times with perchloric acid to remove fluoride. The residues were dissolved in 1 ml of 9M HCl, transferred to a separatory funnel, diluted to about 10 ml and iron was extracted with cupferron and chloroform. After evaporation of chloroform and destruction of the organic material by fuming with nitric and perchloric acids, iron was determined polarographically as the Solochrome Violet RS complex. Values of 2.6 ppm of iron were obtained for the uncrushed quartz, and 81.7 ppm for the crushed quartz, showing that considerable iron contamination arises from the mortar.

2. Environmental Analysis

NTA in water -- The purpose of this project was to investigate the feasibility of using cathode ray polarography for the determination of trace amounts of NTA after its separation from interfering constituents in natural water and sewage.

A number of polarographic methods for the determination of NTA have been reported, most of them involving the addition of an excess of metal ion and measuring the reduction peak of the metal-NTA complex. Daniel and LeBlanc utilized the addition of excess cadmium ion at a pH of 7-10 to determine NTA in EDTA by conventional d.c. polarography [14, 15]. Farrow and Hill modified the method somewhat using standard additions of the Cd-NTA complex and single cell cathode ray polarography [16]. Haberman determined traces of NTA in river water and sewage by the addition of excess indium and measurement of the In-NTA reduction peak [17]. To increase the sensitivity and reduce interferences, he used both cation and anion exchange column separations. Afghan and Goulden have developed methods for the determination of traces of NTA in water by measurement of either the Pb-NTA complex or the Bi-NTA complex [18, 19]. The method using the Bi-NTA complex has been adapted by Gahler of the Water Quality Office, Pacific Northwest Laboratory, Corvallis, Oregon, for the determination of NTA in seawater [20] and by the Inland Waters Branch, Department of Energy, Mines and Resources, Ottawa, Canada, for the determination of NTA in water [21].

Preliminary studies were conducted involving the lead, cadmium and bismuth complexes to determine which gave the best defined polarographic peaks. Indium was not considered as Afghan [19] reports that very high concentrations of indium are necessary for complete NTA recovery and at a mole ratio of 5:1 of In:NTA, the polarographic peak of the indium-NTA complex is extremely difficult to measure owing to its proximity to the indium reduction peak. The Pb-NTA complex was investigated in 3 different buffer systems: tris hydrochloride-ammonium hydroxide, glycine-ammonium hydroxide, and ammonium chloride-ammonium hydroxide around pH 7-8. The Cd-NTA complex was also measured in an ammonium chloride-ammonium hydroxide buffer system at pH about 9. The Bi-NTA complex was then investigated in NaCl media at pH 2 and appeared to give the best-defined peaks and the greatest peak height for a given concentration of NTA.

Aliquots of the supernatant liquid of several solutions of NTA, which had been equilibrated with river bottom mud for about a month to give final concentrations of 10 and 20 ppm of NTA, were then analyzed. The river bottom mud solution contained about 5 percent solids. Values of 5.2 and 10.3 ppm of NTA were obtained showing recoveries of only about 50 percent. The original NTA solutions used to prepare the sludge mixtures were then analyzed to determine if the solution composition had changed. Values of 9.6 and 18.9 ppm were obtained showing good agreement with the 10 and 20 ppm starting compositions.

The recommended procedure for the preparation of the calibration curves which was essentially that developed by Afghan and Goulden [18, 19] and recommended by Traversy [21], utilizing a differential cathode ray polarograph in the subtractive mode of operation is given below. Aliquot 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of standard NTA solution (10 mg/l) into 50-ml beakers. Add 5 ml of 1N HCl to the blank. Add 4.5 ml of 1N HCl to each of the other solutions. Add 1 ml of 1 percent hydroxylamine hydrochloride to each beaker to reduce iron, then add 0.5 ml of bismuth solution (0.2 mg Bi/ml in 1M HCl). Add 25 ml of distilled water to each, adjust the pH to 2.0 with ammonium hydroxide and dilute the solutions to 50.0 ml in a volumetric flask. Add about 1 ml of mercury to each polarographic cell and transfer the solutions to the cells. The blank solution is placed in the right hand cell position and the sample solutions in the left hand cell position. Deaerate with nitrogen for 10 min., then measure the Bi-NTA polarographic peak at about -0.25V vs. a mercury pool anode.

Several calibration curves in the region from 0.2 to 1.0 ppm of NTA were then run on different days. The results are shown in Figure 12.

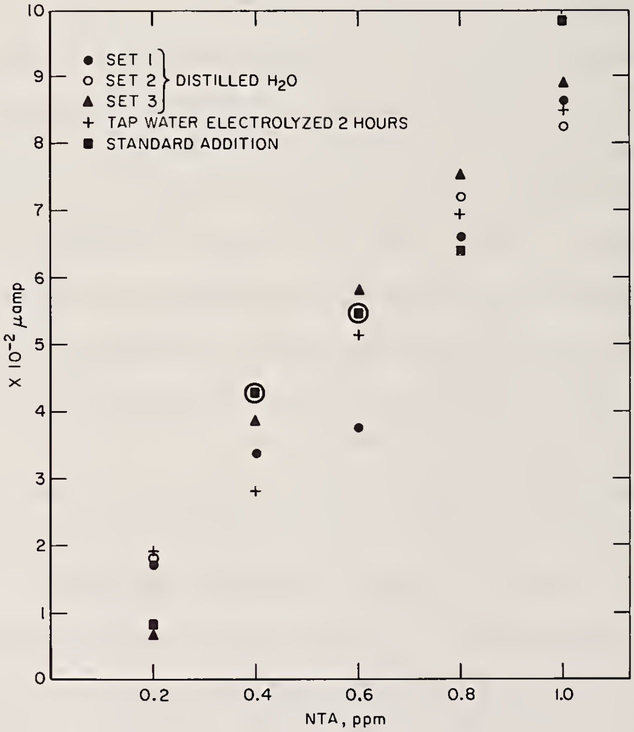


Figure 12. NTA calibration curves.

Some tap waters were also measured, but generally erratic and incomplete NTA recovery was obtained. An interfering peak believed to be copper or ferric ion which had not been successfully reduced appeared close to the rising portion of the Bi-NTA peak making reproducible measurement of the Bi-NTA difficult. Although the solutions were measured subtractively with a tap water blank in the second cell, it was not possible to balance out the base lines.

Gahler [20] found that as little as 2 ppm of copper in water causes very high results. At first this seemed to be inconsistent with the above findings. Then it was realized that he was using a low resolution conventional polarograph which would present the Cu-Bi-NTA peak as a single peak. The cathode ray polarograph separates the two peaks, but the Bi-NTA peak follows the interfering peak so closely that a diffusion level plateau from which to measure the base line is is not reached.

In view of the fact that the chromatographic separation of NTA might not be feasible, it seemed possible that interfering metal ions could be separated by electrolysis of an acidified solution of the tap water for several hours at -0.9V. Preliminary efforts showed this to be feasible. The results are also given in Figure 12 showing good recovery except for the 0.4 ppm point.

Although NTA is reported to form complexes with few metal ions, except bismuth, commonly present in tap water at pH 2, the possibility exists that incomplete NTA recovery from tap water could result from its reacting with some other species in the water. This effect could probably be overcome by a standard addition technique. A set of tap water samples was taken through the procedure as described above except 4 ml of additional NTA was added to each solution including the blank. The results are also shown in Figure 12. It is seen that the recovery is quantitative except for the 0.2 ppm point.

Sufficient instrumental sensitivity is available so that as little as 0.05 ppm of NTA in the final solution could be readily determined. Although this is the equivalent of 0.1 ppm in the original water sample, usually sufficient water sample is available for preconcentration making possible the determination of even lower levels of NTA.

In conclusion, it appears that the polarographic determination of NTA as the Bi-NTA complex is a suitable method. However, if the chromatographic separation of the NTA is not performed, a pre-electrolysis step and/or the standard addition technique may be necessary.

C. Lead in Paint

A variety of types of paint was submitted for lead determinations by the National Commission on Product Safety. The pigments of the individual samples included lead-base, titanium-base and others. Approximately 100 mg of the dried paint samples were slowly ashed in Vycor crucibles to 500° C and sent for spectrographic analysis which showed no significant amounts of lead present. The filtrates were evaporated to dryness and diluted with dilute hydrochloric acid to an appropriate volume in a volumetric flask. Aliquots were taken and lead was extracted with sodium diethyldithiocarbamate and chloroform. After destruction of organic material and evaporation to dryness, the residues were dissolved in 0.1N hydrochloric acid containing ascorbic acid and measured polarographically. The results are given in Table 13, as well as values obtained in another laboratory.

Aliquots of samples 2 through 6 were also run directly with no separations and the results showed good agreement with those obtained above. The results for samples 2 through 6 were 4.20, 0.37, 0.48, 9.50, and 0.46 percent lead, respectively.

Table 13. Lead in paint.

Sample designation	Lead, Percent Polarography	Atomic absorption
1	0.11	0.12
2	4.18	4.6
3	.34	.40
4	.48	.54
5	9.63	9.5
6	.44	.43
7	.13	.15

D. Lead in Industrial Air

Polarography has again proved to be a very helpful technique in the monitoring of the safety of a lead-glass preparation process (13). The NBS Glass Section collected a number of particulate samples on Metricil filters at various steps of the process. The maximum permissible limit of lead exposure is set at 0.2 mg/m^3/8-hr day/5-day week. The samples were collected at the rate of 0.035 m^3/min and from 0.017 to 41 m^3 of air was sampled.

The papers were wet-ashed with nitric, hydrochloric and perchloric acids. After evaporation to dryness, the residues were dissolved in 0.1N hydrochloric acid and the lead reduction peak measured polarographically. The results are shown in Table 14 and are blank corrected. Only one sample, #789, was above the permissible limit.

E. Copper, Lead, Cadmium and Zinc in a Particulate Standard Reference Material.

In the consideration of methods appropriate for the analysis of a proposed particulate Standard Reference Material, cathode ray polarography seemed to offer many advantages. Owing to the selectivity of the method, a variety of elements may be determined concurrently. The sensitivities obtainable are such that less than 0.1 µg of the element in question can be determined, making the use of small samples possible. Previous experience in this laboratory in the polarographic determination of iron, copper, lead and cadmium in particulate material collected on Millipore filters and in dust fall-out has proved the usefulness and reliability of the technique [13].

Table 14. Lead in air.

Sample designation	Pb, micrograms	Sample size, m^3
781	3.8	13.65
782	0.13	.035
783	9.5	33.25
784	8.9	.052
785	.75	.087
786	.49	5.25
787	2.9	15.61
788	4.9	17.75
789	22.9	.070
790	.20	.017
791	3.2	41.3
792	2.9	11.9
793	.09	blank paper

Although the work described was done with no chemical separations, it appeared that more accurate results, such as would be required for SRM's, could be obtained by the use of some separations. Also other supporting electrolytes which might give improved peak definition could be investigated. Comparisons of oxalic acid, EDTA-sodium acetate, and hydroxylamine hydrochloride supporting electrolytes showed that the latter gave the best-defined peaks for the amounts and ratios of copper, lead, cadmium and zinc probably present in the sample.

Separation of the copper, lead, cadmium and zinc could probably be accomplished by extractions with either dithizone or sodium diethyldithiocarbamate and chloroform. Preliminary attempts at dithizone extraction were unsuccessful, possibly because of the interference of large amounts of iron. Large amounts of iron would also interfere with the extraction by carbamate so it was decided to remove the bulk of the iron by extraction with isobutyl acetate prior to the carbamate extraction [22]. The conditions used for the extraction of copper, lead, cadmium, and zinc with carbamate were as given by Bode [23]. Complete recoveries were obtained to within about ±5%. The possible interference of residual amounts of iron or manganese could be eliminated by brief, gentle heating of the hydroxylamine hydrochloride supporting electrolyte, reducing the iron and manganese to their non-interfering lower valence states.

Some problems were experienced in the acid dissolution of the particulate sample. After repeated fumings with nitric and perchloric acids, several small black particles remained undissolved. The procedure used is given below.

Duplicate 100-mg samples were dissolved and organic material was oxidized by fuming with nitric and perchloric acids. The soluble residues were dissolved in hydrochloric acid and iron was extracted with isobutyl acetate. The acid layer was evaporated to dryness and the residues dissolved in hydrochloric acid. Ascorbic acid was added to reduce residual iron. Sodium citrate and ammonium hydroxide were added to adjust the pH to about 9, and copper, lead, cadmium and zinc were extracted with sodium diethyldithiocarbamate and chloroform. After evaporation of chloroform and destruction of organic material by fuming with nitric and perchloric acids, copper, lead, cadmium and zinc were determined polarographically in a hydroxylamine hydrochloride supporting electrolyte which had been heated for 2 minutes at slightly below 100° C.

A blank solution and two reference solutions, one containing 81 µg of copper, 406 µg of lead, 6.1 µg of cadmium, and 200 µg of zinc, and the other containing 121 µg of copper, 812 µg of lead, 10 µg of cadmium and 401 µg of zinc, were also carried through the procedure.

The results obtained by the above procedure are shown below in Table 15.

Table 15. Determination of copper, lead, cadmium, and zinc in proposed particulate standard reference material.

Cu, %	Pb, %	Cd, %	Zn, %
0.0926	0.709	0.00674	0.368
0.0928	0.713	0.00676	0.339

Except for zinc, it is felt that the results show excellent agreement and are well within the 2-5 percent measuring error commonly encountered in polarography. The inconsistency of the zinc results have not been satisfactorily explained. A possible, but unlikely, explanation could be that erratic zinc contamination occurred. However, even the zinc results are still well within the precision generally encountered in this type of measurement.

Bismuth and thallium could probably have been determined at the same time on the same sample by use of a slightly larger sample weight. A larger sample weight might also allow accumulation of sufficient weight of the undissolved particles for a semi-qualitative spectrographic analysis.

Iron, aluminum, and probably nickel could also be readily determined on the same sample.

F. Iron in 1-ppm Glass

The analysis of the trace elements in glass standards was discussed in detail in last year's report [13]. The possibility existed that the iron value might be slightly high in the 1-ppm glass owing to the omission of the ammonium hydroxide precipitation, so six more samples were taken through the procedure including the ammonium hydroxide separation. The supporting electrolyte contained 0.2 ml of 1 + 1 sulfuric acid, 0.5 ml of saturated sodium pyrophosphate and sufficient ammonium hydroxide to reach a pH of 2. The solutions were then diluted to 10.0 ml. The oxygen interference in this supporting electrolyte was found to be somewhat less than with the EDTA or oxalic acid solutions. Two or three separate measurements were made on portions of the same solution of each sample and the average of the results is given in Table 16.

Table 16. Determination of iron in 1-ppm glass.

Sample No.	Fe, ppm
2	13.3
36	13.8
40	12.6
69	13.3
76	13.7
114	12.8
Average =	13.3
s, ppm =	0.48
s, % =	3.6

These values are in good agreement with the 13.5 ppm value obtained earlier.

G. Aluminum, Lead, Bismuth, Tellurium and Titanium in Special Steels.

The work discussed in last year's annual report [13] on the determination of several trace elements in special steels has continued with the determination of aluminum, lead, bismuth, tellurium and titanium in SRM's 1262, 1263, 363, and 1264.

For the determination of aluminum in 1263 and 363, duplicate samples of each weighing 0.5 g were dissolved in dilute hydrochloric acid, filtered and washed with dilute hydrochloric acid. The filter papers were ignited and the residues treated with sulfuric and hydrofluoric acids and evaporated to dryness. The residues were fused with sodium carbonate, the fusion products dissolved in water, neutralized with hydrochloric acid and added to the main filtrate. Ten-ml aliquots were transferred to a separatory funnel. After buffering with acetic acid and sodium acetate, iron, copper, manganese, *etc.* were extracted with chloroform and sodium diethyldithocarbamate. Aluminum was then extracted from the aqueous layer with chloroform and cupferron. After destruction of organic material, aluminum was measured polarographically as the Solochrome Violet RS complex. A value of 0.045 percent aluminum was obtained on SRM 170a, which was carried through the procedure at the same time. The certified value is 0.046 percent. The results are given in Table 17.

Lead in SRM 1264 was separated from the bulk of the iron by extraction of the iron from 1-g samples with isobutyl acetate. Lead was then extracted with sodium diethyldithiocarbamate and chloroform. The extracts were evaporated to dryness, organic material was destroyed with nitric and perchloric acids, and lead was determined polarographically in a nitric acid-sodium tartrate supporting electrolyte. The results for six separate determinations are shown in Table 19.

Table 17. Aluminum in SRM 1263 and 363.

Sample Designation	Al, %	Average
1263 (composite 2A + 2C)	0.234, .233	0.234
363 (composite)	0.231, .232	0.232

Aluminum in SRM 1264 was determined as just described except 1/10 aliquots of solutions from four 1-g samples were taken. The reduction peaks were somewhat ill-defined, owing to the close proximity of some more easily reduced substance. If additional determinations are made, an acid-cupferron extraction will also be made. The results are given in Table 18.

Table 18. Aluminum in SRM 1264

Sample Designation		Al, %
1264 (composite 1A + 1C)		0.0081
		.0084
		.0084
		.0079
	Average	0.0082

Table 19. Lead in SRM 1264

Sample Designation		Pb, %
1264 (composite 1A + 1C)		0.0190
		.0195
		.0174
		.0189
		.0197
		.0200
	Average	.0191
	s =	0.0009%

Lead and bismuth were determined in SRM 1263 and 363 polarographically on aliquots equivalent to 0.2-g samples after separation of iron with isobutyl acetate and separation of lead and bismuth with sodium diethyldithiocarbamate. A blank equivalent to 2 ppm of lead was obtained. Tellurium was determined polarographically after precipitation with SO_2 using selenium carrier. The results are shown in Table 20.

Table 20. Lead, bismuth and tellurium in SRM 1263 and 363.

Sample Designation	Pb, %	Bi, %	Te, %
1263 (composite 2A + 2C)	0.0016	0.00076	0.0022
n	3	3	2
s	.0001	.0001	.0003
363 (composite)	.0018	.00060	.0023
n	3	3	2
s	.0001	.0001	.0001

For the determination of titanium in SRM 1262 and 1263, triplicate 0.5-g samples were dissolved in dilute hydrochloric acid. Ascorbic acid was added to reduce iron to the ferrous state, titanium was precipitated with cupferron, filtered, washed, dried, and ignited in platinum at 550° C. The residues were treated with hydrofluoric, perchloric and hydrochloric acids and fumed to perchloric fumes. The solutions were then transferred to beakers, titanium was precipitated with ammonium hydroxide, filtered and washed. After destruction of organic material with nitric and perchloric acids, titanium was determined polarographically in sulfuric acid-EDTA-sodium acetate supporting electrolyte. The results are given in Table 21.

Table 21. Titanium in SRMs 1262 and 1263.

Sample designation	Ti, %	s, %
1262 (composite 2A + 2C) coarse and fines	0.084	0.004
1263 (composite 2A + 2C)	.049	.002

Titanium in SRM 1264 was determined as just described except that quadruplicate samples weighing 0.2 g each were taken. The results are given in Table 22.

Table 22. Titanium in SRM 1264

Sample designation		Ti, %
1264 (composite 1A + 1C)		0.237
		.238
		.238
		.249
	Average	.240
	s =	0.006

H. Orchard Leaves (SRM 1571)

The need for certified botanical standards both in research and in industrial and field applications is leading to the development and production of number of new Standard Reference Materials by the National Bureau of Standards. The first of these to be produced and certified is an orchard leaf standard. The determination of a number of important trace elements by cathode ray polarography was investigated and found to offer considerable advantages in sensitivity and accuracy over many other techniques. In addition several elements may be done simultaneously on the same solution. The methods were developed and applied to the analysis and certification of nickel, lead, bismuth, copper and iron in the orchard leaves. Results were also obtained for aluminum and cadmium which have not yet been certified.

For the determination of nickel, the samples were dried for 24 hours at 90° C and 1-g portions were taken. Organic material was oxidized with hydrochloric, nitric, and perchloric acids. The samples were fumed almost to dryness, diluted with water and transferred to a separatory funnel. After addition of solutions of sodium citrate, hydroxylamine hydrochloride, and dimethylglyoxime, and adjustment of the pH with ammonium hydroxide, the nickel dimethylglyoxime complex was extracted with chloroform. The chloroform extracts were then evaporated to dryness and organic material was destroyed by fuming to dryness with nitric and perchloric acids. The residues were dissolved in dilute sulfuric acid; pyridine and water were added and the nickel reduction peak was measured polarographically at about -0.9V vs. a mercury pool anode. Solutions for the establishment of a calibration curve were carried through each step of the procedure. The results are shown in Table 23.

Table 23. Determination of nickel in orchard leaves.

Sample designation		Nickel, ppm
2		1.4
9		1.5
10		1.2
11		1.5
12		1.3
15		1.5
19		1.5
	Average	1.4
	s, ppm =	0.1

An average value of 1.2 ppm was obtained by another technique, isotope-dilution spark-source mass spectrometry. The nickel was then certified at 1.3 ppm.

For lead and bismuth, one-gram samples of the dried material were weighed and organic material destroyed as described above for nickel. The residues were treated with dilute hydrochloric acid and water and iron was reduced with ascorbic acid. Lead and bismuth were then extracted with chloroform as the sodium diethyldithiocarbamate complexes from an ammoniacal solution using sodium tartrate and potassium cyanide to complex interferences. The chloroform extracts were evaporated to dryness and the organic material destroyed as already described. The residues were then dissolved in dilute nitric acid and a sodium tartrate solution. The lead and bismuth reduction peaks were then measured at about -0.7 and -0.5V vs. a mercury pool anode, respectively. Solutions for the establishment of a calibration curve were also carried through each step of the procedure. The results are shown in Table 24.

An average value of 43 ppm was obtained by isotope-dilution spark-source mass spectrometry and 45 ppm by photon activation analysis. In view of the fact that the sample contained a small amount of siliceous material which could possibly contain a small amount of lead, unattacked by the acids used, it was decided to include hydrofluoric acid in the sample dissolution. The procedure was repeated on the last four samples with the addition of hydrofluoric acid and an average value of 44.0 ppm was obtained. Again #15 showed significantly higher values for lead.

Table 24. Determination of bismuth and lead in orchard leaves.

Sample designation	Bi, ppm	Pb, ppm
2	0.11	44.2
	.10	41.8
9	.10	46.3
10	.13	44.2
	.15	44.8
11	.11	44.2
12	.11	43.6
	.11	44.2
13	.12	43.0
15	.09	47.9
	.10	47.9
19	.09	43.6
	.10	44.2
Average	0.11	44.6
s, ppm	.02	1.7

For the determination of iron and aluminum, quarter-gram samples of the dried material were weighed and organic matter destroyed as described above. The residues were treated with 1 ml of dilute perchloric acid and the solution transferred to a separatory funnel. Iron was then extracted with chloroform as the cupferron complex. The extracts were evaporated to dryness and organic material destroyed by evaporation to dryness with nitric and perchloric acids. Hydrochloric acid was added and the solution evaporated to dryness on low heat. The residues were then taken into solution with dilute sulfuric acid and diluted to volume with a sodium acetate-EDTA suppor supporting electrolyte. The iron reduction peak was measured at about -0.2V vs. a mercury pool anode. Solutions for the establishment of a calibration curve were carried through each step of the procedure. The results on the first set (not reported) showed a variation of iron content of 195 to 359 ppm which is far more than has previously occurred through inherent procedure or measurement errors and could only be ascribed to either gross environmental contamination or sample inhomogeneity. Subsequent sets of samples by this same procedure did not show this variation. The results are shown in Table 25.

Table 25. Determination of iron (acid-soluble)[a] in orchard leaves.

Sample designation		Fe, ppm	
		Set II	Set III
2		260	258
9		257	282
10		263	272
11		257	259
12		257	255
13		254	253
15		258	282
19		262	267
	Average	259	266
	s, ppm	3.0	11.7
	Pooled Average	262	
	Pooled s	8.8	

[a] $HCl\text{-}HNO_3\text{-}HClO_4$

An average value of 278 ppm was obtained by isotope-dilution spark-source mass spectrometry.

Aluminum was separated from the aqueous layer remaining after the iron extraction by addition of cupferron, then sodium acetate was added to raise the pH to 4.5 to 5, followed by extraction of the aluminum cupferrate complex with chloroform. The organic material was destroyed as already described, the residues dissolved in 1 ml of 6N perchloric acid and 5 ml of 2M sodium acetate. Five ml of 0.1% Solochrome Violet RS were added, and the solutions were diluted to 50 ml and transferred to polyethylene bottles. The solutions were heated in a water bath at 55-70° C for 5 minutes, cooled, and the aluminum-Solochrome Violet RS complex reduction peak was measured at about -0.7V vs. a mercury pool anode. Solutions for the establishment of a calibration curve were carried through each step of the procedure. The results are shown in Table 26.

Table 26. Determination of aluminum (acid-soluble)[a] in orchard leaves.

Sample	Al, ppm		
	Set I	Set II	Set III
2	226	lost	218
9	226	222	211
10	228	241	224
11	225	223	225
12	220	226	204
13	225	229	222
18	223	226	222
19	230	228	225
Average	225	228	219
s, ppm	3.0	6.3	7.6
Pooled average		224	
Pooled s		6.7	

[a] $HCl-HNO_3-HClO_4$

A small amount of adventitious siliceous residue was always present after the hydrochloric-nitric-perchloric acid dissolution of the orchard leaves. It seemed of interest then to determine the contribution to the total iron and aluminum content this residue would make if dissolved by HF and sodium carbonate fusion. The aluminum content of the silica-like material would undoubtedly be greater than that of iron, but some iron would also be expected to be present. The procedures outlined above for iron and aluminum were followed with the following variations:

After sample dissolution and destruction of organic material, the residues were treated with dilute hydrochloric acid and the resulting solutions were filtered through Whatman #42 filter paper and the residues policed into the papers. The papers were ignited in platinum crucibles and the residues were evaporated to dryness with hydrofluoric acid and perchloric acid to remove silicon. The remaining residues were fused in sodium carbonate, the fusion dissolved in dilute hydrochloric acid, and added to the main filtrate. Iron and aluminum were then extracted with cupferron and the procedure completed as already described. The results are shown in Tables 26 and 27. From comparison with Tables 24 and 25 it is seen that the iron and aluminum content of siliceous residue is 50 and 123 ppm, respectively. These results were qualitatively confirmed by independent work on the residues by the Spectrochemical Analysis Section.

Again, one set of iron determinations (not reported) showed extreme variations of from 263 to 333 ppm. These variations also could only be attributed to gross environmental contamination or sample inhomogeneity.

Cadmium in the orchard leaves was also of special interest. Cadmium is also extracted with sodium diethyldithiocarbamate along with the lead and bismuth; however the peaks were small and not too well defined but gave approximate values of 0.1 ppm. Larger samples were taken and cadmium, as well as additional values for copper, lead, and bismuth were determined as described below.

Table 27. Determination of iron (total)[a] in orchard leaves.

Sample designation	Iron, ppm	
	Set I	Set III
2	322	297
9	323	314
10	336	295
11	317	310
12	320	310
13	305	295
15	318	317
19	316	300
Average	320	305
s, ppm	8.7	9.0
Pooled average	312	
Pooled s	11.4	

---

[a] HCl-HNO_3-$HClO_4$-HF, Na_2CO_3 fusion

Table 28. Determination of aluminum (total)[a] in orchard leaves.

Sample designation	Al, ppm	
	Set II	Set III
2	359	344
9	340	349
10	340	341
11	340	348
12	345	348
13	341	350
15	346	350
19	350	368
Average	345	350
s, ppm	6.7	8.0
Pooled average	347	
Pooled s	7.5	

---

[a] HCl-HNO_3-$HClO_4$-HF, Na_2CO_3 fusion

Duplicate 5-g samples were dissolved and organic material destroyed by fuming to dryness with nitric and perchloric acids. The residues were dissolved in hydrochloric acid, and iron was extracted with isobutyl acetate. The acid layer was evaporated to dryness, dissolved in 1 ml of hydrochloric acid and water and residual iron was reduced with ascorbic acid. Cadmium, copper, lead, and bismuth were then extracted from a buffered solution with sodium diethyldithiocarbamate and chloroform. After evaporation to dryness and destruction of organic material, cadmium, copper, lead and bismuth were measured polarographically in a hydroxylamine hydrochloride supporting electrolyte. Values of 0.108 and 0.098 ppm of cadmium were obtained, which gave an average of 0.103 ppm. Average values obtained at the same time for the other elements are: Bi, 0.11 ppm; Cu, 11.5 ppm; Pb, 44.5 ppm. These values are in good agreement with those already submitted by polarography for lead and bismuth and with the 12 ppm value for copper obtained by isotope-dilution spark-source mass spectrometry.

I. Major Constituent Analysis

Cathode ray polarography has also been very useful for the rapid determination of major constituents. In cases where errors of ± 2% are permissible, single cell polarography has sufficed; where greater accuracies are needed, double cell comparative methods have been used [24].

1. Single Cell Polarography

Duplicate solutions of a low-melting alloy, probably of the Woods' metal type, were submitted for determination of lead, bismuth, and cadmium. Tin had already been determined by another technique in portions of the solution. For lead and cadmium, aliquots of the solution equivalent to 100 mg of sample were evaporated to dryness with hydrobromic and perchloric acids. The residues were dissolved in 2 ml of hydrochloric acid, diluted to 250 ml with water and measured polarographically. Values of 25.3 percent lead and 8.9 percent cadmium were obtained. Bismuth was determined on aliquots equivalent to 20 mg of sample in a nitric acid-sodium tartrate supporting electrolyte. An average value of 43.8 percent was obtained. Smaller samples could have been used with equal convenience.

A segment of metal tube was submitted for a rapid copper and zinc analysis to determine if the composition was consistent with Admiralty Brass specifications. The sample was dissolved in dilute nitric acid and taken to dryness. The residue was dissolved in 20 ml of hydrochloric acid, 40 ml of pyridine was added and the solution was diluted to 2 liters. Copper and zinc were then determined polarographically and found to be 71 percent and 27 percent, respectively.

A sample of a portion of a bronze statue was submitted for polarographic analysis of copper, lead and zinc. This was readily done on 50-mg samples by a method similar to that just described after removal of tin. All three elements could be determined concurrently. Values of 90 percent copper, 2.6 percent lead and 2.3 percent zinc were obtained, and the bulk of the remainder was assumed to be tin.

2. Comparative Polarography

Some work in the Corrosion Section of the Metallurgy Division required that the zinc composition of a magnesium-zinc crystalline mixture be known to 0.1 percent. This was readily accomplished by the comparative polarographic method after dissolution of the sample and measurement in a dilute hydrochloric acid supporting electrolyte. The reference standard solutions were prepared from melting-point zinc, SRM 43e. Duplicate results of 84.16 percent and 84.08 percent were obtained giving an average of 84.12 percent zinc with a standard deviation of 0.06 percent.

The comparative polarographic technique recently enabled us to participate in a program on the comparative analysis of archaeological materials. The objectives of the program were to find how well analyses by different laboratories using different methods compare and whether standards made from archaeological specimens are needed or if synthetic standards would suffice. The Freer Gallery contributed the two pieces to be studied. One was a fragment of a Shang Dynasty (1766-1122 B.C.) bronze ku, a ceremonial vessel, and the other a Luristan spear point. The samples were prepared from these two bronzes in the form of chips and were sent out to the cooperating analysis in 500-mg portions. The first polarographic determinations were to be of copper, requiring only a few mg of sample. The samples as received were very heterogeneous; therefore a much larger sample was taken, hopefully to minimize the inhomogeneity.

The samples, in a small glass vial, were mixed by rotating rapidly for about 5 minutes, then 100-mg portions were tapped into a weighing pan and weighed. The samples were dissolved in 20 ml of dilute HCl and 1 ml of HNO_3 and evaporated to dryness several times with perchloric acid, hydrobromic acid, and bromine added to remove tin. The residues were dissolved in 10 ml of hydrochloric acid, 20 ml of pyridine was added and the solutions were diluted to 1 liter. The reference standard solutions were prepared from melting-point copper, SRM 45d, and taken through the procedure along with the samples. Copper was then measured comparatively on several portions of the solutions and the values obtained are shown in Table 29.

These results are in good agreement with the general average of the results turned in so far by the cooperating analysts.

Table 29. Copper in archaeological specimens.

Sample	Cu, %	Average
ku	81.06	81.09
	81.11	81.09
	81.10	81.09
spear point	95.61	95.59
	95.56	95.59

E. June Maienthal

4. pH AND IONIC ACTIVITY STANDARDS

A. Tris(hydroxymethyl)aminomethane/tris(hydroxymethyl)-aminomethane·hydrochloride in Aqueous Solution

A new buffer has been added as a standard for the pH(S) scale based upon previous investigations of suitability. The buffer tris(hydroxymethyl)aminomethane/tris(hydroxymethyl) aminomethane·hydrochloride(tris/tris·HCl) in a ratio of 1:3 was chosen as a new Standard Reference Material for use primarily in the field of biological pH measurements. The tris molality chosen was 0.01667 molal and the tris·HCl is then 0.0500 molal. This new reference buffer has several advantages over reference buffers previously available. For example, the tris buffer will not complex ionic species, such as calcium and magnesium, present in body fluids. This compatibility with biologic systems has been a primary consideration in the selection of this buffer material. Other considerations have included the desirability of matching the pH of the tris buffer solution as closely as possible with the blood acidity range while choosing a buffer having a sufficient buffer capacity. Another advantage of the new buffer is the temperature coefficient (-0.026pH/°C) which more closely approximates that of whole blood (-0.015pH/°C) and plasma (-0.01pH/°C) [25] than does the phosphate buffer (-0.0015pH/°C).

Measurements of the potential of the cell without liquid junction

$$\mathrm{Pt;H_2(g)\ |\ tris{\cdot}HCl\ (0.0500m),\ tris\ (0.01667m)\ |\ AgCl;Ag}$$

were made at 5° C intervals from 0 to 50° C. The buffer solutions were prepared by dissolving the crystalline salts in carbon dioxide-free water.

The acidity function $p(a_H\gamma_{Cl})$ was derived from the measured emf of the cell according to the equation

$$p(a_H\gamma_{Cl}) = \frac{E-E°}{k} + \log m_{Cl} \qquad (1)$$

where E° is the standard emf of the cell [26] and k is (RT ln 10)/F. Conventional pa_H values for each buffer solution were computed by the equation

$$pa_H = p(a_H\gamma_{Cl}) + \log \gamma_{Cl} \qquad (2)$$

where the single ion activity coefficient for the chloride ion was evaluated by the Bates-Guggenheim convention [27]:

$$-\log \gamma_{Cl} = \frac{A\sqrt{I}}{1+1.5\sqrt{I}} \qquad (3)$$

where A is the Debye-Hückel limiting slope and I the total ionic strength. The total ionic strength is calculated by the equation

$$I = 1/2\ \Sigma\ m_i Z_i^2 \qquad (4)$$

where m_i and Z_i are the molality and charge of each ionic species and the summation is made for all the ionic species present in the solution. In this system the only ionic species present is tris·HCl, therefore the value of I is 0.05 m. This procedure is similar to that used in the assignment of pH(S) values to the NBS standard buffer solutions comprising the National pH scale [28].

The tris and tris·HCl were obtained from the Sigma Chemical Company of St. Louis, Missouri. The salts were coulometrically assayed and the tris was found to be of 99.99 ± 0.02 mole percent purity after drying in a vacuum oven at 70 °C for 24 hours. Coulometric assay of the tris·HCl as received was 99.96 ± 0.05 mole percent. The tris·HCl material should not be heated above 40 °C due to the risk of decomposition. Further, it is recommended that reference electrodes containing linen-fiber junctions not be used with this buffer. Such junctions produce large liquid-junction potentials, drift, and long equilibrium times [29].

The emf values for six determinations, corrected to a hydrogen partial pressure of 1 atmosphere, are shown in Table 30. The corresponding pH(S) values are illustrated as a function of temperature in Figure 13.

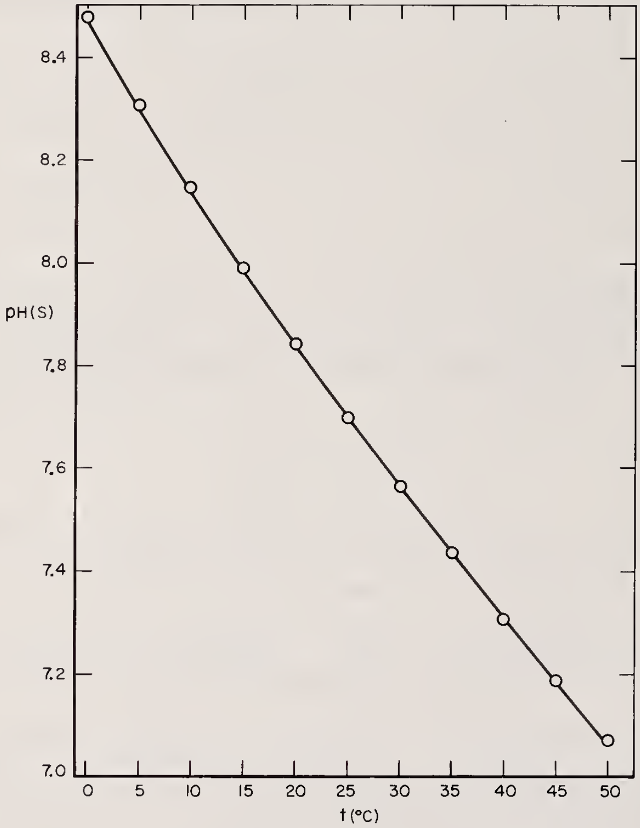


Figure 13. pH(S) as a function of temperature.

Table 30. Average emf values for the standard buffer containing 0.01667 mol of Tris and 0.0500 mol of Tris·HCl per Kg, from 0° to 50°C.

Temp, °C	Av. emf, mV[a]
0	770.68
5	768.70
10	766.62
15	764.47
20	762.21
25	759.87
30	757.46
35	754.98
40	752.38
45	749.73
50	746.95

[a] Average of six emf determinations at each temperature.

The pH(S) is described as a function of temperature by the equation

$$pH(S) = -12.4746 + 3833.17/T + 0.0336811T - 0.0655 \times 10^{-5} T^2 \quad (5)$$

where T is the temperature in kelvins. The standard deviation of this fit is 0.0005 pH unit.

The maximum difference in emf was 0.09 mV for the six measurements. Such a difference corresponds to less than 0.002 pH units. The values tabulated apply only to the lots specified on the SRM certificate. The materials are available as SRM 922 and SRM 923, for preparation of the standard buffer solution.

B. Comparison of Procedures

As matter of interest in determining the suitability of the extrapolation to obtain $p(a_H\gamma_{Cl})^\circ$ for buffer solutions, which in turn allows calculation of the conventional pH(S), the emf of the tris buffer was measured with varied amounts of KCl. The same procedure described [28] was followed. The added concentrations of KCl were 0.015, 0.010 and 0.005 m, and these were used in the extrapolation. In the calculation of log γ_{Cl} from equation 3, the total ionic strength was calculated for the solution containing no added KCl, *i.e.*, the extrapolated solution composition in which the tris·HCl alone contributed to the ionic strength (I = 0.05m).

The encouraging results are shown in Table 31. One should note that the last column is the actual difference given to four decimal places. This average difference is seen to be less than 0.001 pH unit, or somewhat less than the actual experimental error involved in the measurement of the emf.

Table 31. Comparison of extrapolated pH values with pH determined directly.

t, (°C)	pH(S) (from extrapolation procedure with added chloride)	pH(S) (without extrapolation, no added chloride)	ΔpH
0	8.472_1	8.471_2	0.000_9
5	8.303_8	8.303_1	0.000_7
10	8.142_7	8.142_2	0.000_5
15	7.988_5	7.988_2	0.000_3
20	7.841_3	7.840_2	0.001_1
25	7.699_6	7.698_2	0.001_4
30	7.564_1	7.563_1	0.001_4
35	7.433_4	7.432_9	0.000_5
40	7.308_0	7.307_2	0.000_8
45	7.187_3	7.186_7	0.000_6
50	7.071_3	7.069_9	0.001_4

C. Borax

Preliminary measurements for the certification of SRM 187b, borax ($Na_2B_4O_7 \cdot 10H_2O$) buffer were discussed in the preceding NBS Technical Note 543 [1]. An example of the data obtained is given in Table 32 which shows emf and $p(a_H \gamma C_1)$ at various KCl molalities for 25 °C.

Table 32. Acidity function and emf with varying KCl molalities.

m KCl	Emf (corrected to 1 atm H_2)	$p(a_H \gamma_{Cl})$
0.015	0.87717	9.2438
.015	17	.2438
.015	12	.2429
.015	06	.2419
0.010	0.88762	9.2422
.010	59	.2438
.010	54	.2430
.010	53	.2428
0.005	0.90530	9.2422
.005	42	.2442
.005	33	.2427
.005	19	.2403

From the data in Table 32, the limiting acidity function $p(a_H \gamma_{Cl})^\circ$ is obtained by extrapolation to zero chloride concentration. Then pH(S) is calculated from the relationship

$$pH(S) \equiv pa_H = p(a_H \gamma_{CL})^\circ - \log \gamma_{Cl} \qquad (6)$$

using equation   to obtain $\log \gamma_{Cl}$.

The pH(S) for the 0.01 m borax buffer solution as a function of temperature is given by

$$pH(S) = 5723.31 - 38.1774/T + 0.032942T - 1.2906x10^{4}T^{2} \qquad (7)$$

where T is the temperature in kelvins. The standard deviation of pH(S) from this equation is 0.0002 pH unit.

D. Future pH Buffer for Clinical Use

As previously reported [1], electrochemical studies of five buffer systems have been made in isotonic saline. This medium, 0.16 m NaCl in water, was chosen for some of its characteristics which match those of blood, namely, its osmotic pressure and ionic strength.

In conjunction with the certification of the tris/tris•HCl in water, the determination of pH(S) for this same buffer in isotonic saline is now underway. This new buffer will consist of tris (0.01667 m), tris•HCl (0.0500 m) and enough NaCl to produce a total ionic strength of 0.16 m. The new ampouled standard will be available in solution form, designed specificially for the calibration of clinical pH meters.

E. Ion-Selective Electrodes

The details of the procedure employed to obtain the required single ion activities of unassociated chlorides for certification of Standard Reference Materials has been presented [1, 30]. In brief, the Stokes-Robinson hydration theory [31] is used to evaluate the hydration number of the cation assuming that the chloride ion is not hydrated [32]. If the cation is hydrated with h molecules of water and m' is its molality in moles per kilogram of unbound water, then

$$m' = \frac{m}{1 - 0.018hm} \qquad (8)$$

The activity of chloride ion is the same on the two scales $m\gamma_{Cl^-} = m'\gamma'_{Cl^-}$. Then

$$\ln \gamma_{M^+} = \ln \gamma'_{M^+} - h \ln a_w - \ln (1 - 0.018hm) \qquad (9)$$

$$\ln \gamma'_{M^+} = \ln f'_{DH} - \ln [1 - 0.018(2)m'] \qquad (10)$$

where f_{DH} is the electrostatic contribution expressed as an activity coefficient on the mole fraction scale, and it follows that

$$\ln \gamma_{M^+} = \ln f_{DH} - h \ln a_w - \ln [1 - 0.018(2-h)m] \qquad (11)$$

With the definition of the osmotic coefficient ϕ

$$\phi = \frac{-\ln a_w}{0.018\nu m} \qquad (12)$$

the expressions of the activity coefficients become

$$\log \gamma_{M^+} = \log \gamma_{\pm} + 0.00782\ hm\phi \qquad (13)$$

and

$$\log \gamma_{Cl^-} = \log \gamma_{\pm} - 0.00782hm\phi \qquad (14)$$

Using the same procedure one derives the equations applicable to an unassociated salt MCl_2,

$$\log \gamma_{M^{++}} = 2 \log \gamma_{\pm} + 0.00782hm\phi + \log [1 + 0.018(3-h)m] \qquad (15$$

and

$$2 \log \gamma_{Cl^-} = \log \gamma_{\pm} - 0.00782hm\phi - \log [1+0.018(3-h)m] \qquad (16)$$

1. Equipment

An interim measuring system has been adopted pending completion of an automated system. A digital voltmeter, DVM, accurate to 0.01 mV is being used to directly measure the potential of most of the electrode systems except those of very high impedance, such as the glass electrodes. In cases involving high impedance, the DVM is used to measure the output of a vibrating reed electrometer.

The DVM has been equipped with a plug-in unit for binary-coded decimal (BCD) input-output and is compatible with the Analytical Division computer. Programs are being written to aid in the future automation of the measuring functions involving both ion-selective electrodes and pH measurement.

2. Standards for Sodium, Potassium and Chloride Activities

A major practical accomplishment in the area of ion-selective electrodes during the past year was the certification of and the actual issuance of NaCl and KCl as Standard Reference Materials 2201 and 2202 respectively.

The values of the ionic activities for these lots of materials have appeared in the previous Technical Note 543 [1].

3. Solution Standards for Calcium Ion Activity

The reference materials for the calcium ion activity standards will be made available in ampouled solution form. Solutions will be prepared by dissolving the presently available calcium carbonate (SRM 915) in a slight excess of purified hydrochloric acid.

Solutions of calcium chloride have been prepared from the SRM using this procedure. About 5 grams of calcium carbonate were dissolved in an excess of 1 molal HCl obtained from constant boiling HCl. The solution of about 200 ml was evaporated to dryness in a 500 ml Erlenmeyer flask. The

$CaCl_2$ was redissolved in a small amount of H_2O and again evaporated to dryness. A weighed amount of H_2O was added to the weighed flask to obtain a solution 0.1 molal in $CaCl_2$. The distilled water was purged with pure nitrogen to remove dissolved carbon dioxide.

Other solutions were prepared by serial dilutions of 25 ml to 250 ml in volumetric flasks. The molalities used were 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4}. The emf as a function of activity at 25° C is illustrated in figure 14 for a typical commercially available calcium-selective electrode. The observed response slope is 31 mV compared to the theoretical Nernstian slope of 29.6 mV. Further work is in progress to elucidate the behavior of calcium-selective electrodes in these solutions.

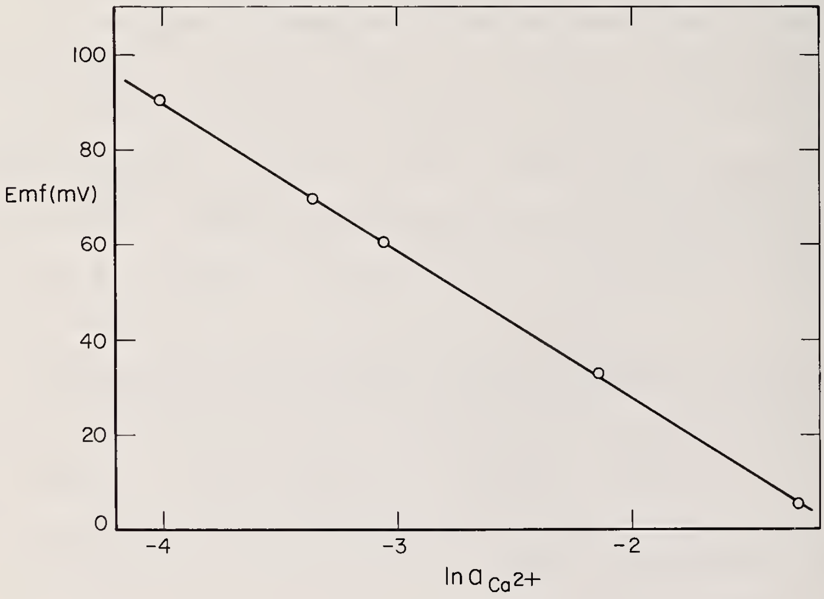


Figure 14. Emf as a function of calcium activity.

B. R. Staples

5. POTENTIOMETRY

A. Chromatographic Detector for NTA and Other Complexing Agents using a Cupric Electrode Flow-Through Cell

An electrochemical detector based on the cupric ion-selective electrode has been developed for the determination of complexing agents, such as NTA, EDTA, *etc.*, after separation by ion-exchange chromatography. This detector was developed independently of the separation methods, and the evaluation of its response to NTA in the final system must await completion of the chromatographic method.

The detector system, shown in figures 15 and 16 and diagrammed in figure 17, is based on the response of a cupric ion-selective electrode to electrochemically generated cupric ion in a continuous, flow-through cell arrangement. In principle, the detector system operates in this way: (1) cupric ion is generated coulometrically at constant rate upstream from the detector, *i.e.*, between the chromatographic column and the detector; (2) the rate of generation is continuously variable to obtain optimum response at the detector depending upon the concentration of the complexing agents; (3) the detector assembly, described in detail below, produces a constant emf output until the cupric ion level is perturbed by complexation with NTA or other ligand; (4) since the electrode only responds to the uncomplexed cupric ions, the magnitude of the emf change can be related to the degree of complexation and consequently to the amount of complexing agent present.

The detector assembly consists of a flow chamber machined from Teflon into which are mounted the cupric ion-selective electrode and a reference electrode designed for use in flow assemblies. The indicator electrode is held securely in place by the aluminum holder attached to the Teflon assembly as shown in figures 15, 16, and 17. This holder permits the electrode to be seated tightly against the flow chamber lip, thus preventing solution leakage around the electrode tip. The cupric ion indicator electrode is mounted 60° from the vertical to avoid bubble entrapment in the flow chamber which could cause spurious electrode response.

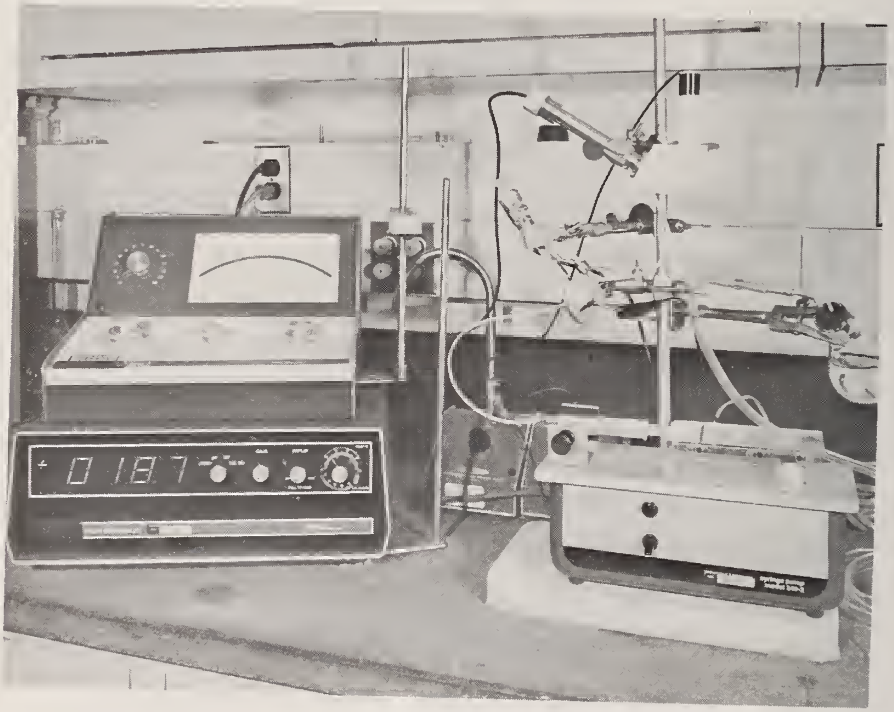


Figure 15. Cupric electrode/NTA detector system.

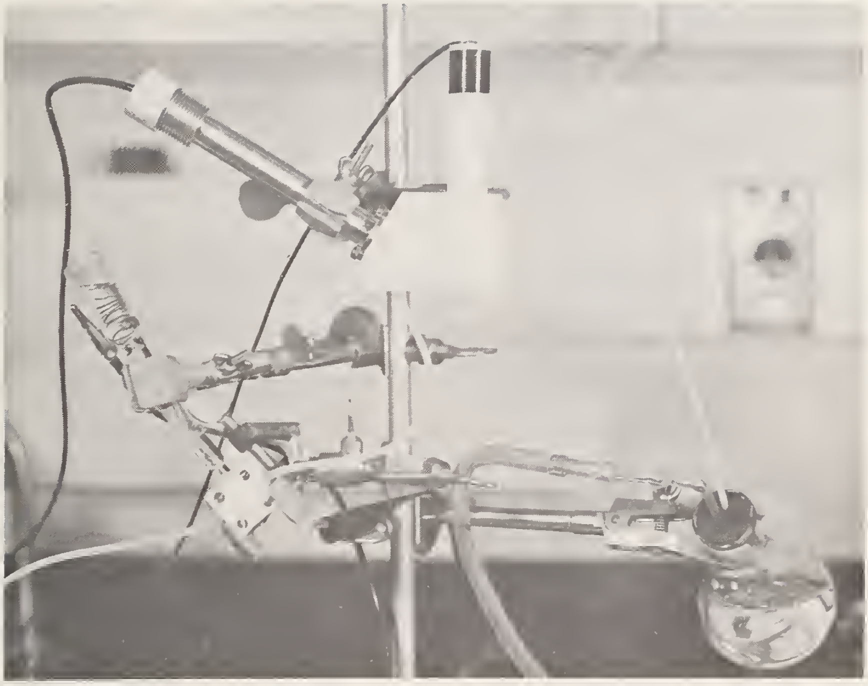


Figure 16. Close-up of the cupric electrode flow-through cell.

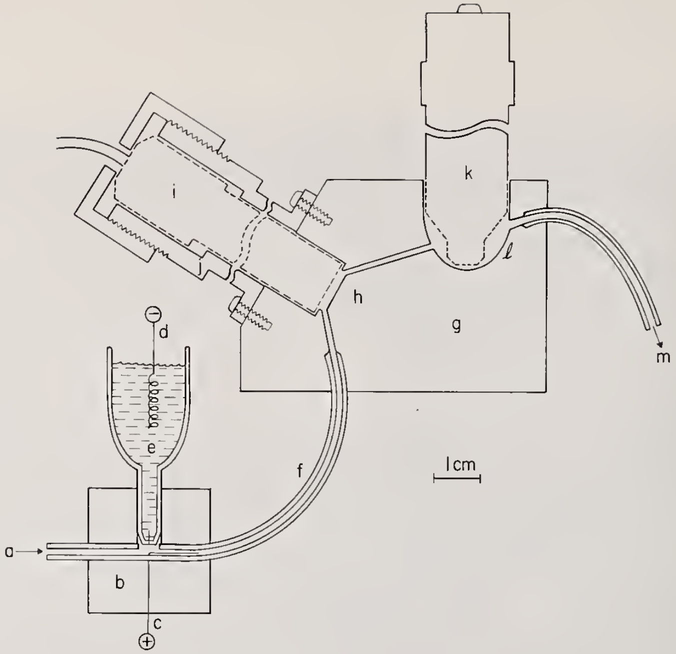


Figure 17. Diagram of flow-through cell and coulometric cupric ion generator.

a) Sample inlet
b) Teflon assembly for electrochemical generation of cupric ion
c) Copper wire anode (cupric ion generation)
d) Copper wire cathode
e) Cathode compartment: Cath olyte - 0.01 M KNO_3, fiber wick junction to sample stream
f) Teflon tubing connection between generator and detector assemblies
g) Teflon detector assembly
h) Detector cavity - volume: 50 μl
i) Cupric ion-selective electrode
j) Aluminum electrode holder
k) Reference electrode
l) Reference electrode cavity
m) Overflow to waste

In order to test the response characteristics of this system, an electrolyte solution (0.01 M KNO_3) was flowed through the generator and detector assemblies at constant rate (0.4 ml/min) using a syringe pump (figure 15). A constant current was applied to the coulometric cupric ion generator. From a knowledge of the flow rate and current, the concentration of cupric ion generated could be calculated and a working curve established for the electrode system. This curve, shown in figure 18, is linear from 5 ppm to about 0.2 ppm with a response slope of approximately 21 mV/pCu (theoretical: 29.5 mV/pCu). The response time of the electrode system to achieve a stable emf reading was measured for step changes in the generator current, *i.e.*, the cupric ion activity. In general, at the very dilute cupric ion levels generated (0.1 to 5 ppm), the time required to establish an equilibrium emf was about 3-4 minutes. Calibration of the electrode system in stirred standard solutions showed similar behavior, *i.e.*, equilibration times of several minutes and a sub-Nernstian response slope of approximately 23 mV/pCu. At higher cupric ion concentrations, the electrode response is faster and more Nernstian.

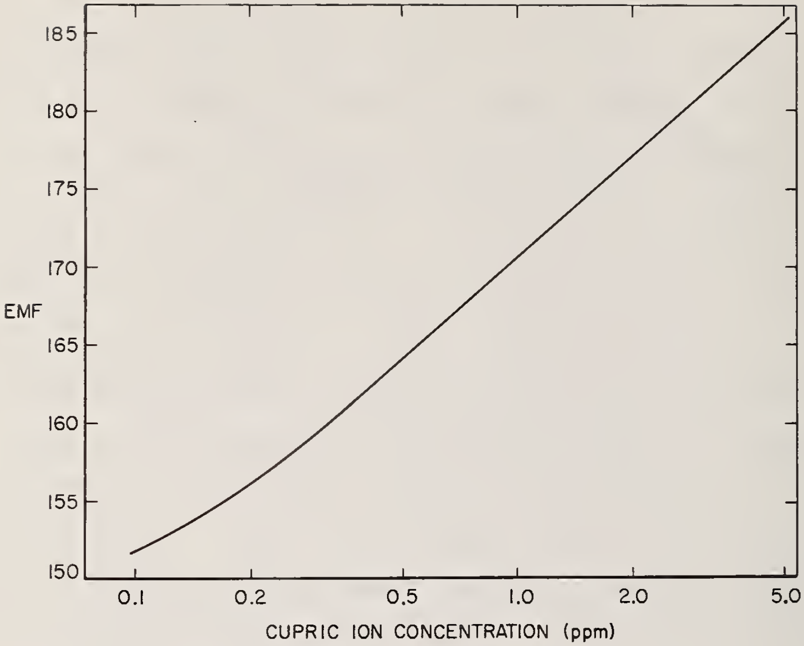


Figure 18. Emf response in mV of the cupric ion flow-through cell.

The chromatographic procedure will require the removal of divalent cations from the complexing ligands, perhaps using a cation exchanger in the hydrogen ion form, followed by conversion of the acid-form ligands to their sodium salts by passage through another cation exchanger in the sodium form. This procedure would result in a sample of the proper characteristics to be determined by the cupric ion electrode detector.

B. Potentiometric Determination of Total Calcium

A potentiometric titration method has been developed for the determination of total calcium in samples provided as part of the NBS-clinical chemistry interaction exercise. In anticipation of analyses on actual serum samples, the procedure developed minimizes potential interferences from other blood electrolytes, especially magnesium ion.

The method consists of titrating the sample ($\sim$10 ml) with the tetrasodium form of EGTA [Ethyleneglycol bis(2-aminoethyether)tetraacetic acid] using a calcium ion-selective electrode as the end-point detector. EGTA was chosen as the titrant ligand because it selectivity complexes calcium in the presence of magnesium as demonstrated by Schmid and Reilley [33]. The Na_4EGTA titrant was prepared according to the procedure of van't Riet and Wynn [34]. The EGTA is dissolved by the addition of an accurately measured volume of sodium hydroxide solution and adjusted to pH 7. The tetrasodium salt is prepared by the addition of another identical volume of the NaOH solution.

Since EGTA does not form as strong a complex with calcium as does EDTA (which also binds magnesium strongly), the chemical equilibration beyond the end point is rather slow and results in a somewhat drawn-out sigmoidal titration curve. For this reason, evaluation of the titration data was accomplished by a graphical procedure devised by Gran [35] in which data points before the end point are plotted as an exponential function of the emf vs. milliliters of titrant and results in a linear extrapolation to the end point volume.

Using this method, three sets of the samples where run on three separate days. The results of the titrations, which were performed in a random manner according to exercise directions, are given in Table 33. The calculated calcium values, based on the preparation of solutions from standard reference calcium carbonate (SRM 915), were 8.182 (solutions 2 and 103), 10.391 (solutions 26, 37, and 63), and 11.758 (solutions 42 and 82). All values are expressed as mg Ca^{++}/100 ml of solution.

Table 33.

Total Calcium in NBS Test Solutions as Determined by Potentiometric Titration
(Results given as mg Ca^{++}/100 ml of solution.)

	Solution 2	Solution 103	Solution 42	Solution 82
Set A	8.04	8.36	11.57	11.74
Set B	8.39	8.24	11.99	11.75
Set C	8.15	8.14	11.66	11.81
Average	9.19	8.25	11.74	11.77
Pooled Average	8.22		11.75	

	Solution 26	Solution 37	Solution 63
Set A	10.49	10.42	10.36
Set B	10.39	10.41	10.43
Set C	10.48	10.47	10.58
Average	10.45	10.43	10.46
Pooled Average		10.45	

6. DISSOLVED OXYGEN IN SEAWATER

A. Introduction

Dissolved oxygen plays a vital role in biological processes in natural water systems. The measurement of the amount of oxygen present in these natural waters is of particular importance in the fields of oceanography and marine chemistry as well as environmental pollution studies.

The calibration of a wide variety of oxygen-measuring devices depends on a few absolute measurements. The National Oceanographic Instrumentation Center (NOIC) of the National Oceanic and Atmospheric Administration (NOAA) had a requirement for reference standards and data for calibrating such instruments, and a program to determine dissolved oxygen in a number of saturated solutions of seawater has been initiated.

The program was designed to determine dissolved oxygen in seawater samples saturated with each of five different gas mixtures of varying oxygen content. The mixtures prepared are of the following compositions of oxygen in nitrogen: 0, 4, 8, 12, 16, and 20.94 mole-percent oxygen. The determinations were to cover five temperatures: 0, 10, 20, 30 and 40 °C.

Many methods have been employed to measure dissolved oxygen in aqueous systems. There are few absolute methods available; the most widely known being the Winkler method [36]. The Winkler titration method is tedious, cumbersome and time-consuming. The Winkler (1888) method and numerous modifications still remain the most accurate procedure for routine use. The method depends upon the reaction of dissolved oxygen with freshly precipitated manganese hydroxide. A concentrated solution of manganous chloride or sulfate is added to the water sample and an excess of a solution of sodium hydroxide and potassium iodide introduced. The precipitated manganese hydroxide is allowed to settle and is then dissolved by acid. Iodine is liberated and titrated with standard thiosulfate using starch as the indicator. The reactions are as follows:

$$Mn(OH)_2 + 1/2\ O_2 \rightarrow MnO(OH)_2$$

$$MnO(OH)_2 + 4H^+ + 3I^- \rightarrow Mn^{2+} + I_3^- + 3H_2O$$

$$I_3^- + 2S_2O_3^= \rightarrow 3I^- + S_4O_6^=$$

Even at the lowest extreme of concentrations of dissolved oxygen (*e.g.* 1 ppb), the assumption always made is that the oxidation and reduction of the manganese precipitate is quantitative under the imposed conditions.

A number of physical methods based on coulometric, gasometric, polarographic, or amperometric principles are also in use for determining dissolved oxygen. Most of these methods require standardization. In 1952, Hersch [37] demonstrated the applicability of galvanic cells for the determination of low concentrations of oxygen in gas-flow systems. The Hersch cell contains an alkali hydroxide electrolyte with a lead anode and an inert cathode of silver or platinum. The half-cell reactions

$$1/2\ O_2 + H_2O + 2e^- \rightarrow 2\ OH^- \text{ (cathode)}$$

$$Pb + 4OH^- - 2e^- \rightarrow PbO_2^= + 2H_2O \text{ (anode)}$$

produce a flow of current when oxygen is present. A few modifications have appeared in the literature [38, 39, 40].

Recently, Ives, *et al.* [41] have developed a technique to measure absolute values of oxygen in inert gases over the range of 1 to 1,000 ppm oxygen. The method involves a flow of the gas through a series of galvanic cells similar to Hersch cells. The current outputs of the cells allows calculation of the absolute concentration of oxygen. These same cells were used to attempt a determination of the total amount of oxygen swept out of gas-saturated solutions by a stream of high purity nitrogen, which then passed through the cells.

B. Experimental

The cells and procedure have been described in detail [41, 42] and only a few modifications were made for the present purpose. Since the amount of oxygen present is proportional to the integrated current, the voltage produced by the galvanic cell was measured across a standard 20-ohm resistor, then a voltage-to-frequency converter was used to accumulate counts on an electronic counter-timer. The apparatus is illustrated in Figure 19. The cells are shown to the left of the picture with the standard resistor in the foreground. To the right is the V-to-F converter and counter.

A U-shaped apparatus with a double rubber septum injection port was used to receive the sample. The purging of the sample was accomplished with nitrogen bubbling through the medium porosity glass frit in the U-tube.

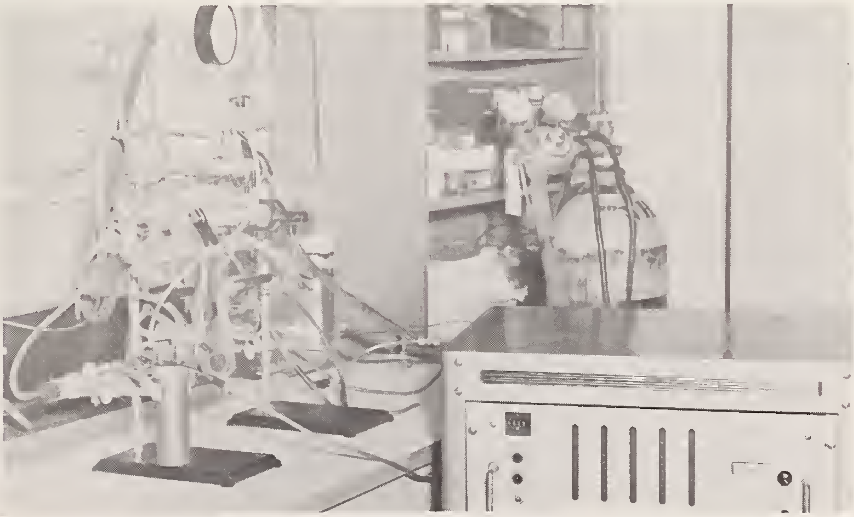


Figure 19. Hersch cell.

C. Results

1. Efficiency of the Measuring System. To determine the efficiency of the measuring system a coulometric analyzer was used to electrolyze distilled water containing Na_2SO_4. The theoretical number of counts was obtained by generating a known number of microequivalents directly to the counting system, across a 20.0-ohm resistor. For example, at 6.43 ma, 10.00 meq registered 19.384×10^6 counts (100 mV scale) and 1.000 μeq registered 1.9375×10^6 counts. Then the percentage recovery of oxygen could be calculated from the current obtained (counts) after purging of the electrolyzed solution with nitrogen. Efficiencies of the system thus determined are given in Table 34.

The efficiency of the counting system by direct generation was found to be 100.4 percent as calculated below. The 100 mV scale and 20.0-ohm resistor gives a current of

$$I = \frac{V}{R} = \frac{100\text{mV}}{20\Omega} = 5 \text{ ma}$$

The rate of counting is 10^5 counts s^{-1} and hence for a 5 ma current, there are 0.2×10^5 counts s^{-1} ma^{-1} (counts mC^{-1}). Converting this to 5×10^{-5} mC $count^{-1}$ or 5×10^{-2} mC $count^{-1}$, the μeq recovered may be obtained by

$$\frac{19.384 \times 10^{-6} \text{ counts} \times 5 \times 10^{-2} \ \mu\text{C count}^{-1}}{96487 \ \mu\text{C} \ \mu\text{eq}^{-1}} = 10.04 \ \mu\text{eq}$$

The output of the coulometric analyzer was shown to be 100 percent by measuring the voltage drop across a 10.0-ohm standard resistor in series with the electrolysis cell. The emf was 6.435 ± 0.001 mV which gave a current of 0.643 ma, the nominal rating of the coulometric analyzer.

Table 34. Cell efficiencies for oxygen determinations.

μeq	Percent recovery
10	88.0
10	81.1
10	78.3
(electrode surfaces cleaned and new electrolyte added)	
10	45.8
1	54.2
10	75.7
5	63.6
10.5	74.3
2	70.2
2	81.9
5	71.0

2. Discussion and Summary

As observed in Table 34, erratic and unpredictable results were obtained for numerous determinations. Cleaning and preparing fresh cells as indicated brought little improvement.

With a slow flow rate (~2 cc min^{-1}), a second cell in series showed no change in potential, indicating that all the O_2 was being consumed in the first cell, and that there were no leaks of O_2 into the system.

A steady-state generation of O_2 (and H_2) by electrolysis using platinum electrodes gave about 95-98 percent efficiency indicating that the method was satisfactory as a flow system but apparently not as a disolete sample method.

Actual samples of air-saturated distilled water were used to estimate the reproducibility of the method. Using Mancy's [43] values for O_2 solubility (1.00 μeq ml^{-1}) the results can be compared in Table 34 for selected sample sizes.

Table 35. Comparison of dissolved oxygen determined by the system with literature data.

ml distilled H_2O	$\mu eq\ ml^{-1}$ recovered
10	0.62
10	0.53
5	0.47
5	0.56
5	0.44
5	0.46
10	0.41
10	0.43
10	0.38
10	0.42

air-sat'd. H_2O contains 1.00 $\mu eq\ ml^{-1}$ of O_2

D. New Frontiers

Although the method seems to be unsuitable for discreet solution samples, it has stimulated interest in using a number of other approaches for solving this important problem. Experiments are now underway to investigate the feasibility of using coulometric determinations in systems such as ferrous sulfate, chromous chloride, and modified Hersch cells containing large amounts of electrolyte.

The method involving chromous ion and its rapid and quantitative reaction with O_2 looks promising. Other preliminary results on cells containing different metal electrodes in $Ca(OH)_2$ solutions as well as KOH solutions, seem to point to a two-electron reduction of O_2 as suggested by G. Marinenko. It is anticipated that publication of these results will be forthcoming.

B. R. Staples

7. FOREIGN-CURRENCY PROGRAM

A research project on the measurement of ionic activities in multicomponent systems and biologic fluids has been initiated under the direction of Dr. J. Padova of the Soreq Nuclear Research Center in Yavne, Israel. This project, funded under Public Law 480, will involve the measurement of electrolyte activities by two independent techniques: (1) a gravimetric isopiestic method using an improved apparatus developed in Dr. Padova's laboratory and (2) an electrometric method using ion-selective electrodes in cells without liquid junctions.

The isopiestic method is very convenient for deriving the activity of electrolytes in multicomponent systems from measurements of the activity of the solvent and calculations involving the Gibbs-Duhem equation. Ion-selective electrodes will be used to measure ionic activities directly in cells without transference and these results will be correlated with the isopiestic data.

The proposed investigation is aimed at gathering activity data for ions in solutions of increasing complexity with an ultimate view to producing standards for ions which are important in physiological processes. The systems to be studied will consist of mixed solutions of such ions as sodium, potassium, calcium, magnesium, chloride, bicarbonate, phosphate, organic acids, and proteins as are found in biologic fluids.

Richard A. Durst

8. PERSONNEL AND ACTIVITIES

A. Personnel Listing

Richard A. Durst, Section Chief

Charlotte P. Wren, Section Secretary

pH and Ionic Activity--
Bert R. Staples

Coulometry--
George Marinenko
Dale Friend (part time)

Polarography--
E. J. Maienthal

Anodic Stripping--
Joseph R. Robinson (EOD 6/14/71)

Potentiometry--
Richard A. Durst
Benjamin T. Duhart (part time)

B. Publications and Manuscripts

1. Bates, R. G., Staples, B. R., and Robinson, R. A., "Ionic Hydration and Single Ion Activities in Unassociated Chlorides at High Ionic Strengths," *Anal. Chem.* 42, 867-71 (1970).

2. Robinson, R. A., "The Dissociation Constant of m-Nitroanilinium Ion in Water-Tetrahydrofuran Solvents at 25° C," *J. Res. NBS*, 74A, 4, 495-97 (1970).

3. Champion, C. E., Marinenko, G., Schmidt, W. E., and Taylor, J. K., "Determination of Submicrogram Amounts of Chromium by Coulometric Titrimetry," *Anal. Chem.* 42, 11, 1210-13 (1970).

4. Cantanzaro, E. J., Champion C. C., Garner, E. L., Marinenko, G., Sappenfield, K. M., and Shields, W. R., "Boric Acid -- Isotopic and Assay -- Standard Reference Material," NBS Special Publication 260-17, U. S. Government Printing Office, Washington, D. C. 20402, (1970).

5. Durst, R. A., and Duhart, B. T., "Ion-Selective Electrode Study of Trace Silver Adsorption on Selected Surfaces," *Anal. Chem.* 42, 1002 (1970).

6. Thun, H. P., Staples, B. R., and Bates, R. G., "Thermodynamics of Hydrochloric Acid in 80 Weight Percent 2-Methoxyethanol and 20 Weight Percent Water from 10 to 50° C," *J. Res. NBS* 74A, 641-45 (September-October 1970).

7. Paabo, J., and Bates, R. G., "Acidic Dissociation of Diprotonated Piperazine in Methanol-Water Solvents from 10 to 40° C," *J. Res. NBS* 74A, 667-71 (September-October 1970).

8. Durst, R. A., "Pick an Ion, Any Ion," *Ind. Res.* 36-9 (1970).

9. Davis, M. M., "Bronsted Acid-Base Behavior in Inert Organic Solvents" in the *Chemistry of Nonaqueous Solvents*, J. J. Lagowski, Editor, Vol. III, Chapter 1, 1-135, Academic Press, Inc., New York (1970).

10. Durst, R. A., Editor, "Electrochemical Analysis Section: Summary of Activities July 1969 to June 1970," U. S. National Bureau of Standards Technical Note 543, 1-81, U. S. Government Printing Office, Washington, D. C. 20402, (1970).

11. Bates, R. G., "Measurement of pH" in *Handbook of Biochemistry*, Sober, H. A., Editor, 190-95, Chemical Rubber Co., Cleveland, Ohio (1971).

12. Durst, R. A., "Ion-Selective Electrodes in Science, Medicine, and Technology," *American Scientist* 59, 3, 353-61 (1971).

13. Marinenko, G., and Foley, R. T., "A New Determination of the Atomic Weight of Zinc," *Phys. and Chem.* (In press).

14. Durst, R. A., and Staples, B. T., "Tris/Tris·HCl: A Standard Buffer for Use in the Physiologic pH Range," *Clinical Chemistry* (In press).

15. Durst, R. A., "Ion-Selective Electrodes," Proceedings International Conference on Localized Corrosion (In press).

C. Talks

1. B. R. Staples, "Dissociation of Protonated Tris(hydroxymethyl) aminomethane in Aqueous Alcohol Solvents," 160th National Meeting American Chemical Society, Chicago, Illinois, September 1970.

2. G. Marinenko, "Coulometric Determination of GaAs Stoichiometry," Third International Symposium on Gallium Arsenide and Related Compounds, Aachen, Germany, October 3-9, 1970.

3. E. J. Maienthal, "Polarographic Analysis," NBS Activation Analysis Section Seminar, October 5, 1970.

4. R. A. Durst, "Ion-Selective Electrode Potentiometry," NIH/NBS Conference on Meaningful Clinical Analysis Standardization, Gaithersburg, Maryland, October 9, 1970.

5. R. A. Durst, "Ion-Selective Electrode Monitoring of Environmental Pollutants," 14th Conference on Analytical Chemistry in Nuclear Technology, Oak Ridge National Laboratory, Gatlinburg, Tennessee, October 14, 1970.

6. G. Marinenko, "Coulomb -- The Absolute Chemcial Standard," 1970 Eastern Analytical Symposium, Statler-Hilton Hotel, New York City, November 1970.

7. B. R. Staples, "Activity Standards for Ion-Selective Electrodes," Combined Southeast - Southwest Regional Meeting, American Chemical Society, New Orleans, Louisiana, December 1970.

8. R. A. Durst, "Ion-Selective Electrodes - Mechanisms and New Directions," (Discussion Leader), Gordon Research Conference on Electrochemistry, Santa Barbara, California, January 18, 1971.

9. R. A. Durst, "Ion-Selective Electrodes - Theory, Characteristics, and Methodology," University of Maryland Seminar, College Park, Maryland, February 19, 1971.

10. R. A. Durst, "Ion-Selective Electrodes," Some Current Research in IMR, NBS/IMR Conference, Gaithersburg, Maryland, February 23, 1971.

11. G. Marinenko, "Accurate Measurement of Stoichiometry," Some Current Research in IMR, NBS/IMR Conference, Gaithersburg, Maryland, February 23, 1971.

12. G. Marinenko, "Accurate Measurement of Stoichiometry," Bell Telephone Laboratories, March 11, 1971.

13. R. A. Durst, "Ion-Selective Electrodes," Detroit Section of the American Chemical Society, Detroit, Michigan, March 16, 1971.

14. R. A. Durst, "Ion-Selective Electrodes," Chemistry Department Seminar, Renssalaer Polytechnic Institute, Troy, New York, March 18, 1971.

15. E. J. Mainethal, "Polarographic Analysis of Trace Elements in Glass," ASTM Committee C-14 and E-2, NBS, April 13, 1971.

16. R. A. Durst, "Recent Developments in Ion-Selective Electrodes and Coulometry," Frontiers in Chemistry Lecture Series, State University College, New Paltz, New York, May 6, 1971.

17. R. A. Durst, "Activity Standards for Ion-Selective Electrodes," Instituto Superiore di Sanita and C.I.T.C.E. Symposium on the Biological Aspects of Electrochemistry, Rome, Italy, June 4, 1971.

9. REFERENCES

[1] Durst, R. A., Editor, Electrochemical Analysis Section: Summary of Activities, July 1969 to June 1970, NBS Technical Note 543, U. S. Government Printing Office, Washington, D. C. 20402, 81 pages, (1970).

[2] Durst, R. A., Editor, Ion-Selective Electrodes, NBS Special Publication 314, U. S. Government Printing Office, Washington, D. C. 20402, 452 pages (1969).

[3] Bates, R. G., Wichers, E., *J. Res NBS* 59, 9 (1957).

[4] This high purity Standard Reference Material, SRM No. 682 is available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D. C. 20234, along with the "Certificate of Analysis" at a unit price of $90.00.

[5] Gill, A. S., Acting General Superintendent of Electrolytic Zinc Company of Australasia Ltd., Private Communication.

[6] Taylor, B. N., Parker, W. H., and Langenberg, D. N., *Revs. Mod. Phys.* 41, 375 (1969).

[7] Hess, D. C., Inghram, M. G., and Hayden, R. J., *Phys. Rev.* 74, 1531 (1948).

[8] Marinenko, G., Taylor, J. K., *J. Res. NBS* 67A, 31 (1963).

[9] Craig, D. N., Hoffman, I. I., Law, C. A., and Hamer, W. J., *J. Res. NBS* 64A, (Phys. & Chem.) 381 (1960).

[10] Reilley, C. N., Schmidt, R. W., and Lomson, D. W., *Anal. Chem.* 30, 835 (1953).

[11] Marinenko, G., Taylor, J. K., *Anal. Chem.* 39, 1569 (1967).

[12] Marinenko, G., Taylor, J. K., *J. Res NBS* 67A, (Phys. & Chem.) 31, (1963).

[13] Maienthal, E. J., "Polarographic Analysis" in Microchemical Analysis Section, Summary of Activities, July 1969 to June 1970, NBS Technical Note 545, U. S. Government Printing Office, Washington, D. C. 20402, 114 pages (1971).

[14] Daniel, R. L., LeBlanc, R. B., *Anal. Chem.* 31, 1221 (1959).

[15] LeBlanc, R. B., *Anal. Chem.* 31, 1840 (1959).

[16] Farrow, R. N. P., Hill, A. G., *Analyst* 90, 241 (1965).

[17] Haberman, J. P., *Anal. Chem.* 43, 63 (1971).

[18] Afghan, B. K., Goulden, P. D., *Journal of Environmental Science and Technology*, 5, 601 (1971).

[19] Afghan, B. K., "Differential Cathode Ray Polarography for Trace Analysis with Special Reference to NTA and Its Complexes with Heavy Metals," a talk presented at the International Symposium on Identification and Measurement of Environmental Pollutants, Ottawa, Canada, June 15, 1971.

[20] Gahler, A. R., private communication.

[21] Traversy, W. J., "Methods for Chemical Analysis of Waters and Waste Waters in Use in Water Quality Division Laboratories," Inland Waters Branch, Department of Energy, Mines and Resources, Ottawa, Canada (1971).

[22] Rooney, R. C., *Analyst* 83, 83 (1958).

[23] Bode, H., *Anal. Chem.* 144, 165 (1955).

[24] Maienthal, E. J., Taylor, J. K., *Microchim. Acta* 1967, 939.

[25] Rosenthal, T. B., *J. Biol. Chem.* 173, 25 (1948).

[26] Bates, R. G., Bower, V. E., *J. Res. NBS* 53, 283 (1954).

[27] Bates, R. G., Guggenheim, E. A., *Pure Appl. Chem.* 1, 163 (1960).

[28] Staples, B. R., Bates, R. G., *J. Res. NBS* 73A, 37 (1969).

[29] Westcott, C. C., Johns, T., Appl. Res. Technical Report No. 542, Beckman Instruments, Inc., Fullerton, California.

[30] Bates, R. G., Staples, B. R., and Robins, R. A., *Anal. Chem.* 42, 867 (1970).

[31] Stokes, R. H., Robinson, R. A., *J. Amer. Chem. Soc.* 70, 1870 (1948).

[32] Glueckauf, E., *Trans. Faraday Soc.* 51, 1235 (1955).

[33] Schmidt, R. W., Reilley, C. N., *Anal. Chem.* 29, 264 (1957).

[34] Van't Riet, B., Wynne, J. E., *Anal. Chem.* 41, 158 (1969).

[35] Gran, G., *Acta Chem. Scand.* 4, 559 (1950); also *Analyst* 77, 661 (1952).

[36] Winkler, L. W., *Ber. dtsch. chem. Ges.* 21, 2843 (1888).

[37] Hersch, P., *Nature* 169, 792 (1952).

[38] Hersch, P., *Anal. Chem.* 32, 1030 (1960).

[39] Waclawik, J., Waszak, S., *Chem. Anal.* (Warsaw) 8, 865 (1963).

[40] Keidl, F. A., *Ind. Eng. Chem.* 52, 491 (1960).

[41] Ives, J. M., Hughes, E. E., and Taylor, J. K., *Anal. Chem.* 40, 1853 (1968).

[42] Taylor, J. K., Editor, Microchemical Analysis Section: Summary of Activities, July 1967 to June 1968, NBS Technical Note 455, U. S. Government Printing Office, Washington, D. C. 20402, 132 pages (1968).

[43] Mancy, K. H., Editor, Instrumental Analysis for Water Pollution Control, Ann Arbor Science Publishers, Inc., Michigan (1971).

☆ U. S. GOVERNMENT PRINTING OFFICE : 1973—511-323/168

M NBS-114A (1-71)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBS TN-583	2. Gov't Accession No.	3. Recipient's Accession No.

TITLE AND SUBTITLE
LECTROCHEMICAL ANALYSIS SECTION: SUMMARY OF ACTIVITIES,
uly 1970 to June 1971

5. Publication Date
February 1973

6. Performing Organization Code

AUTHOR(S)
Durst, Richard A.

8. Performing Organization

PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.

11. Contract/Grant No.

Sponsoring Organization Name and Address

Same as No. 9

13. Type of Report & Period Covered
Final

14. Sponsoring Agency Code

SUPPLEMENTARY NOTES

ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

This survey of the activities of the Electrochemical Analysis
ection, Analytical Chemistry Division, covers the period from July 1970
o June 1971. An attempt is made to briefly summarize a year's progress
n the technical projects of the Section, to indicate the composition
nd capabilities of the unit as a whole, and to stress the Section's
ole in the mission of the Institute. Summaries of the work in each of
he Section competences are given. In the area of acidity measurements,
ork was completed on the standardization of tris(hydroxymethyl)amino-
ethane for use as a biologic pH buffer material and standard for
linical pH measurements. High-precision coulometry is used to determine
he atomic weight of zinc, the stoichiometry of gallium arsenide, and
he purity of KCl and NaCl. Polarography is used to determine trace
lements in a variety of environmental samples and Standard Reference
aterials.

KEY WORDS (Alphabetical order, separated by semicolons) Acidity; coulometric analysis; electro-
emical analysis; ionic activity; ion-selective electrodes; pH measurements; polarog-
phy; potentiometry; Standard Reference Materials.

AVAILABILITY STATEMENT ☒ UNLIMITED. ☐ FOR OFFICIAL DISTRIBUTION. DO NOT RELEASE TO NTIS.	19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED	21. NO. OF PAGES 113
	20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED	22. Price $.75 Domestic Postpaid $.50 GPO Bookstore

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234