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ANALYTICAL CHEMISTRY DIVISION

SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING OCTOBER 20, 1955

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ANALYTICAL CHEMISTRY DIVISION

SEMIANNUAL PROGRESS REPORT

For Period Ending October 20, 1955

M. T. Kelley, Director
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H. P. Raaen, Technical Editor

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ORNL-1788	Period Ending October 20, 1954
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ABSTRACT

ANALYTICAL CHEMISTRY DIVISION – X-10 SITE

The development of ionic methods for the determination of corrosion products in the highly radioactive Homogeneous Reactor (HR) fuels has been of major interest in the work of the Ionic Analyses Laboratory. Methods for the spectrophotometric determination of aluminum and for the polarographic determination of iron in HR fuels have been developed. The polarographic determination of molybdenum in uranyl sulfate solutions was studied. A polarographic method for the determination of zinc was developed. A fluorometric method for the determination of microgram amounts of fluoride was studied. Three organic reagents were investigated as precipitants for microgram quantities of zirconium in HR fuel. The automatic photometric titration technique was applied to the determination of thorium and of sulfate. A method was developed for the ion-exchange separation and potentiometric titration of cobalt. The ultraviolet absorption spectra of technetium and rhenium were studied.

The work of the Analytical Instrumentation Group has consisted primarily in instrument development for the High-Radiation-Level Analytical Facility. The first of three model Q-1673 polarographs with diode filters has been fabricated and is being evaluated. A pressurized polarographic cell was designed for operation by the Argonne model 8 master-slave manipulators and will be used with the new polarograph. A remotely controlled turret for the falling-drop densimeter has been fabricated. The turret and all other components of the falling-drop densimeter are being thoroughly tested as an entity. The remotely controlled servo pipets have been redesigned. A pipet of the new design was demonstrated at the Geneva Convention. Its precision is as good as that obtainable with careful hand pipeting. Five additional pipeters are being built for the High-Radiation-Level Analytical Facility. The screw-operated elevator has been improved by the addition of external guides. A prototype of the sample-bottle decapper has been completed. It is mounted on a movable carriage beneath the 1-ml pipet. A motorized Lab-Jack has been designed and tested, and several are being motorized. A model Q-1734 filter photometer for operation by master-slave manipulators has been designed; a prototype was tested, and three other photometers of the same design are being built. Plans have been made to adapt a commercial multiplier phototube that has good sensitivity in the region from 7,000 to 12,000 Å to the high-sensitivity recording flame photometer (model Q-1457).

The precision of the 3-ml remotely controlled dilution pipeter has been determined. The chronopotentiometric method of analysis has been investigated and has been compared with the polarographic method; a practical cell has been designed. Circuits for anticipatory automatic coulometric titrations have been investigated. The Analytical Instrumentation Group is participating in the ORNL in-line instrumentation assistance program with the Savannah River Plant; the purpose of the program is to develop in-line analyses of chemical process streams. A cell was built, equipped with instruments, and demonstrated at the International Conference on the Peaceful Uses of Atomic Energy, Geneva Exhibit, August 3–20, 1955. The demonstration was made in conjunction with the Uranium Processing Exhibit of the Chemical Technology Division. During the entire period of demonstration of these instruments, they all fulfilled design specifications and no malfunctioning was experienced. The cell and instruments are similar to those being built for use in the High-Radiation-Level Analytical Facility for the analysis of highly radioactive samples by remote control.

Studies of the decay schemes of Mg^{27} and of Sr^{89} have been made, and the cross section of Ba^{130} has been determined. The use of gamma spectrometric techniques has continued; useful applications of these techniques have been made in reactor and radioisotope analyses. The addition of new products to the isotopes catalog will require the development of new radiochemical methods; a survey has been made in order to determine possible methods. In electrodeposition of 0.1-mg quantities of plutonium, americium was observed to codeposit. Quantities of plutonium as great as 0.5 mg have been measured by a simple, nondestructive method that employs an alpha counter having approximately 0.005% counting yield. Studies of volatile fission products have been made for the General Electric Company and for the Metallurgy Division. Analyses of Thorex

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process samples for U^{232} and for Th^{228} have been made by two methods. Some research has been done in connection with the program of the Electronuclear Research Division. A promising liquid-liquid extraction method for cerium has been devised.

Neutron activation analysis has been applied to the determination of microgram or submicrogram quantities of the following: gold, copper, and nickel in petroleum; bromine in sea water; arsenic in low-boiling organic liquids; and nickel, iron, and tungsten in zirconium and in hafnium. Special studies included the use of activation analysis to determine milligram amounts of certain elements in milligram amounts of ion-exchange resins and in loop corrosion products. The elements determined included nickel, silicon, cobalt, manganese, potassium, sodium, aluminum, bromine, chlorine, and iodine. In addition to this work contaminant elements were identified in petroleum-cracking catalysts, in thorium oxide, and in ammonium thorium oxalate. Preirradiation separations of microgram and submicrogram amounts of nickel and of manganese, respectively, from elemental sodium were also made. The use of the discriminatory gamma counter in analysis has been extended. Also, the use of short-half-life radioisotopes of cobalt and of sulfur in analysis and a flux-monitoring method have been investigated. The activation analysis method for the determination of particle-size distributions has been studied further and has been applied to a large number of samples. Neutron activation–autoradiographic techniques have been used to determine the extent of segregation of cobalt in gold–cobalt wire. A preliminary investigation of an isotopic dilution method for the determination of niobium, as well as tantalum, in minerals has been made.

In spectrographic analyses, the uniformity of flow of powdered graphite or carbon samples through the sifter electrode was shown to be improved by storing the sample at 50 to 75% relative humidity before excitation. The nitrated cellulose–batch adsorption method can be applied to the separation of microgram quantities of rare earths from uranium, as well as from thorium. Microgram quantities of rare earths exert considerable influence on the intensities of each other's lines in the absence of foreign elements. A search is being made to find a material to swamp out this effect. A mechanism of the porous-cup discharge is suggested; it is based on information obtained from high-speed motion pictures.

Inorganic compounds prepared for the Chemistry Division included K_2ReCl_6 and large quantities of the halides of rubidium and cesium. Anhydrous ferrous and manganous bromides were prepared for the Physics Division, and the purification of materials used in the phosphor program and in other programs was continued.

Electron microscopy and particle-size studies of thorium oxide are discussed, and certain specific observations are illustrated. The ingredients of the films and corrosion products formed on type 304L stainless steel and on Inconel were observed in the electron microscope and were identified by electron diffraction. Other corrosion products that were investigated are listed. Materials studied by optical microscopy and by autoradiography are given. The new methods and techniques developed during the period are mentioned briefly. Preliminary observations were made regarding particle size–diffraction pattern relationships and regarding the use of high-frequency sounds waves to disperse particles; illustrations of the particles and of the diffraction patterns are included.

Eight new methods have been issued to the *ORNL Master Analytical Manual*; drafts of more than 45 other new methods have been edited. Thirteen new manuals were issued.

Analytical service analyses are summarized in tabular form; special problems are discussed briefly. Ionic analyses related primarily to phase and corrosion studies for the HRT. Radiochemical service analyses consisted mostly in the determination of cyclotron-produced activities, the nondestructive measurement of plutonium, and determinations of neutron flux. A summary is given of a large number of elements determined in a variety of materials by neutron-activation analysis. A bromination–carbon-reduction apparatus, additional pyrohydrolysis units, and an apparatus for determining water of crystallization in fluoride salts have been added to the General Analyses Laboratory. The determination of hydrogen, oxygen, and nitrogen in thorium, titanium, and zirconium by vacuum-fusion has been continued. A new vacuum-fusion apparatus and a low-pressure, carbon microcombustion apparatus have been constructed. Low-oxygen standard molybdenum samples from the Naval Research Advisory Committee have been analyzed by vacuum

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fusion, and the results were reported. Zinc, zirconium, and uranium were determined satisfactorily in a mixture of the oxides of these metals. A method for Np^{237} was evaluated initially preparatory to analytical service work for the Neptunium Recovery program. Plutonium determinations were made relative to HR blanket studies. Sodium, thorium, and chloride in amalgams and contaminants in thorium oxide were determined for the Metallex Process and Thorex Pilot Plant Groups. Equipment suitable for use in the High-Radiation-Level Analytical Facility was established; the status of other work for the facility is discussed.

ANALYTICAL CHEMISTRY DIVISION – Y-12 SITE

The major problems of the HRP Analytical Chemistry Laboratory have been the determination of corrosion products in solutions of uranyl sulfate and in slurries of thorium compounds. Methods were developed for the determination of stannite ion in the presence of uranium by derivative polarography, the amperometric titration of mercury(II) with tetraphenylarsonium chloride, the separation and polarographic determination of tin, the determination of carbonate in thorium oxide and of carbon dioxide in oxygen, the estimation of the particle-size distribution of thorium oxide, the spectrophotometric determination of silicon dioxide in thorium oxide, and the flame photometric determination of chloride.

The effects of several variables on the simultaneous determination of trivalent and hexavalent chromium in solutions of aluminum nitrate plus nitric acid and in solutions of nitric acid were established. Use of conductivity and pH measurements was continued for determining concentrations and characteristic behaviors of impurities in compounds of thorium. Optimum conditions were established for the spectrophotometric determination of ethylenediaminetetraacetic acid as the copper complex. The effects on the spectrophotometric determination of titanium of certain ions that cannot be separated from titanium by electrolysis were ascertained. Volumetric and gravimetric methods for the determination of sulfate in solutions of uranyl sulfate were evaluated.

The Raw Materials Group analyzed samples of kerosene from different sources by nine ASTM methods in an effort to determine the best test for identifying the source of kerosene.

The Methods Development Group has evaluated methods for the following: the determination of iron in titanium; the recovery of uranium from solids derived from monazite sand; the determination of the oxides of nitrogen in gas mixtures; determination of nitrite, nitrate, and other forms of nitrogen in sulfuric acid; and the determination of strontium by flame photometry. Work has also been continued on the determination of alkali metals and alkaline-earth elements by flame photometry; special consideration is being given to the interference of one element in the estimation of the others.

A review and a tabulated summary of the quality control data for the period are presented.

A tabulation of the 59,796 determinations reported by the service groups is included; the distribution of the work by divisions is given. Almost 90% of the service work was done for the Reactor Experimental Engineering and Materials Chemistry Divisions.

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PRESENTATIONS OF RESEARCH RESULTS

Several of the presentations listed below were made jointly with members of other divisions. In these cases, the member of the Analytical Chemistry Division is indicated by a single asterisk.

OPEN-LITERATURE PUBLICATIONS

Author(s)	Title	Publication
Cohen, B. L., E. Newman, T. H. Handley*	"(p,pn) + $(p,2n)$ and $(p,2p)$ Cross Sections in Medium Weight Elements"	*Phys. Rev.* 99, 723 (1955)
Handley, T. H., W. S. Lyon	"Long-Lived Isomer of Al^{26}"	*Phys. Rev.* 99, 755 (1955)
	"Neutron-Deficient Activities of Terbium"	*Phys. Rev.* 99, 1415 (1955)
Handley,* T. H., W. S. Lyon,* E. L. Olson	"Holmium-167"	*Phys. Rev.* 98, 688 (1955)
Jones, W. H., A. Timnick, J. H. Paehler, T. H. Handley*	"Bombardment Energy and Fission Product Yield Pattern for Protons on Natural Uranium and U^{235}"	*Phys. Rev.* 99, 184 (1955)
Kahn, B., W. S. Lyon*	"Decay of Y^{91}"	*Phys. Rev.* 98, 58 (1955)
Leddicotte,* G. W., H. A. Mahlman	"Determination of Microgram and Submicrogram Quantities of Thorium by Neutron Activation Analysis"	Paper No. A/Conf. 8/P/117, International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland; August 8–20, 1955
Lyon,* W. S., B. Kahn	"Decay of Sc^{47}"	*Phys. Rev.* 99, 728 (1955)
Lyon, W. S., S. A. Reynolds	"Radioactivity in Reactor Cooling Water"	*Nuclear Sci. Tech.* (TID-2017) 1, 197 (1955)
Mahlman, H. A., G. W. Leddicotte*	"Determination of Microgram and Submicrogram Quantities of Uranium by Neutron Activation Analysis"	*Anal. Chem.* 27, 823 (1955)
Manning, D. L., J. C. White	"Differential Spectrophotometric Determination of Zirconium"	*Anal. Chem.* 27, 1389 (1955)
McCown, J. J.	"Exploratory Cryoscopy of Complex Compounds"	A thesis submitted on July 15, 1955, to the University of Tennessee in partial fulfillment of the requirements for the Master of Science degree
Moore, F. L., G. W. Smith	"Electrodeposition of Plutonium"	*Nucleonics* 13(4), 66 (1955)
Raaen, H. P., P. F. Thomason	"Radioisotopic Study of Uranium Separations. Separations by Filter-Paper Partition Chromotography with 2-Methyltetrahydrofuran"	*Anal. Chem.* 27, 936 (1955)

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Author(s)	Title	Publication
Reynolds, S. A.	"Analytical Radiochemistry"	*Record Chem. Progr. (Detroit)* 16(2), 99 (1955)
Susano, C. D.	"Graphite- and Aluminum-Block Solution Evaporators"	*Anal. Chem.* 27, 1038 (1955)
Susano, C. D., J. C. White, J. E. Lee, Jr.	"Apparatus for the Pyrohydrolytic Determination of Fluoride and Other Halides"	*Anal. Chem.* 27, 453 (1955)
White, J. C., G. Goldberg	"Application of Volhard Titration to 2-Ethyl-1-Hexanol Separation Method for Determination of Lithium"	*Anal. Chem.* 27, 1188 (1955)

ORAL PRESENTATIONS

Author(s)	Title	Presented at
Feldman, C.	"Measurement of Temperature of Spark Discharges"	University of North Carolina, Chapel Hill; April 22, 1955
	"Special Spectrochemical Techniques of Interest to Chemists, Metallurgists, and Biologists"	Virginia Polytechnic Institute, Blacksburg; Oct. 13, 1955
Leddicotte, G. W.	"The Determination of Trace Elements in Titanium by Radioactivation Analysis"	128th National Meeting, American Chemical Society, Minneapolis, Minnesota, Sept. 12, 1955
Lyon, W. S., S. A. Reynolds[1]	"4 π-Coincidence Counting as a Technique for Absolute Measurements"	Meeting of National Research Council Subcommittee on Beta- and Gamma-Ray Measurements and Standards, Chalk River, Ontario, Canada; May 27, 1955
Reynolds, S. A.	"Analytical Radiochemistry"	Southern Research Institute, Birmingham, Ala.; April 18, 1955
		Florida State University, Tallahassee; April 20, 1955
		University of Florida, Gainesville; April 22, 1955

[1]Speaker.

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Author(s)	Title	Presented at
Reynolds,[1] S. A., W. S. Lyon, E. I. Wyatt	"Radioisotope Assay Methods at Oak Ridge National Laboratory"	Meeting of National Research Council Subcommittee on Beta- and Gamma-Ray Measurements and Standards, Chalk River, Ontario, Canada; May 27, 1955
Van Artsdalen,[1] E. R., I. S. Yaffe, F. J. Miller*	"Electrical Conductance and Ionic Migration in Molten Salts"	107th Meeting of the Electrochemical Society, Cincinnati, Ohio; May 1–5, 1955
Willmarth, T. E.	"The Electron Microscope as a Research Tool in Colloid Chemistry"	Oak Ridge High School, Oak Ridge, Tenn.; May 19, 1955

TOPICAL REPORTS

Author(s)	Title	Report No.
Brooksbank, W. A., G. W. Leddicotte, J. H. Oliver	"Flux Measurement in Hole 10, ORNL Graphite Reactor"	ORNL CF-55-9-151 (Sept. 30, 1955)
Druschel, R. E., G. W. Leddicotte	"A Preliminary Study of the Effects of Sodium Pyrophosphate Concentration Upon Tharium Oxide Particle Dispersion in the Particle Size Assays by the Neutron Activation Analysis Method"	ORNL CF-55-6-181 (June 28, 1955)
Foster,[2] R. W., J. H. Cooper*	"Determination of Plutonium and Uranium in Scrup Dissolver Solutions"	ORNL-1854 (July 1, 1955)
Harmon, T. G., T. E. Willmarth	"To Determine the Changes Induced in Mild Steel by Contact with Molten Lithium at 750–800°C in a Reducing Atmosphere"	ORNL CF-55-6-58 (June 7, 1955)
Horton, A. D., P. F. Thomason	"Determination of Corrosion Products and Additives in Homogeneous Reactor Fuel. II. Polarographic Determination of Chromium"	ORNL-1887 (Sept. 13, 1955)
	"Determination of Corrosion Products and Additives in Homogeneous Reactor Fuels. III. Polarographic Determination of Iron(III)"	ORNL-1954 (Oct. 5, 1955)
McPherson,[3] W. L. (G. W. Leddicotte)	"Attempts to Apply an Isotope Dilution Technique to the Determination of Niobium and Tantalum in Minerals"	ORNL CF-55-9-142 (Sept. 30, 1955)

[2]Present address, E. I. du Pont de Nemours and Co., Inc., Savannah River Plant, Augusta, Georgia.
[3]Research participant from Virginia Polytechnic Institute.

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Author(s)	Title	Report No.
Powell, R. H.	"High Radiation Level Analytical Facility. Suggested Allocation of Work-Cell Space, Types of Analysis, and Equipment Within Cells"	ORNL CF-55-6-54 (June 8, 1955)
Reynolds, S. A.	"Calculations of Gamma Counting Rate of Thorium"	ORNL CF-55-6-43 (June 8, 1955)
Rogers, J. M.	"Nitrous Oxide: A Bibliography"	ORNL CF-55-9-169 (Sept. 13, 1955)
Stelzner, R. W., M. T. Kelley	"Radio-Frequency Oscillators for Determination of Alkali"	ORNL-1742 (June 9, 1955)
Surak,[4] J. G., P. F. Thomason	"Statistical Evaluation of Methods for the Analysis of Dibasic Aluminum Nitrate (Diban)"	ORNL-1931 (Sept. 1, 1955)
Toomer, F. M.	"Particle Size Distribution of Thorium Oxide Sample X-2"	ORNL CF-55-5-177 (May 27, 1955)
	"Electron Micrographs of Thorium Oxide Samples"	ORNL CF-55-8-89 (Aug. 11, 1955)
Vick,[5] M. M., G. W. Leddicotte	"Investigation of an Ion-Exchange Separation Procedure"	ORNL CF-55-9-152 (Sept. 30, 1955)
Willmarth, T. E.	"Examination of Material Removed from Walls of C-Loop"	ORNL CF-55-5-190 (May 27, 1955)
	"Identification of Constituents of Segment of FF in Line Scale"	ORNL CF-55-6-52 (June 9, 1955)
	"To Determine the Thickness of ThO_2 Particles in Relation to Precipitation Temperatures"	ORNL CF-55-7-21 (July 6, 1955)
	"To Compare the Particle Size of ThO_2 in the Presence of Additives, Irradiation for 700 Hours"	ORNL CF-55-7-22 (July 6, 1955)
	"Degradation of ThO_2 in C Loop"	ORNL CF-55-7-23 (July 6, 1955)
	"Determination of the Particle Size of Thorium Oxide Dispersed in 0.1 *N* HCl Solution"	ORNL CF-55-9-3 (Sept. 1, 1955)
Willmarth, T. E., T. G. Harmon	"Autoradiographs and Distribution of Active Particles Collected on Filters"	ORNL CF-55-4-188 (April 29, 1955)
Willmarth, T. E., F. M. Toomer	"Electron Diffraction and Electron Microscopy of Sample C-30-1300 W"	ORNL CF-55-4-107 (April 15, 1955)
	"Electron Microscopy of Thorium Oxide Samples"	ORNL CF-55-8-96 (Aug. 17, 1955)
	"Electron Micrographs of Thorium Oxide Samples Calcined at Varying Temperatures"	ORNL CF-55-8-126 (Aug. 23, 1955)
	"Electron Micrographs of ThO_2, Series CS-10"	ORNL CF-55-8-142 (Aug. 26, 1955)

[4]Summer employee from Marquette University.

[5]Summer employee from Louisiana State University.

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METHODS ISSUED TO *ORNL MASTER ANALYTICAL MANUAL*

Author(s)	Title	Number(s)	Date
Feldman, C.	"Separation of Rare Earths from Thorium by Adsorption on Activated Cellulose, Batch Method"	1 00705 9 00650	3-23-55
Koskela, U., C. E. Lamb	"Uranium, Spectrophotometric Ammonium Thiocyanate Method"	1 219210 9 00719210	11-12-53
Moore, F. L., G. W. Smith	"Preparation of Plutonium Deposits, Electroplating Method"	2 31629 9 008629	12-21-54
Parker, H. A.	"Trivalent Rare-Earth Activity in Aqueous or Organic Solutions"	2 21992	12-1-54
Ross, W. J., J. C. White	"Beryllium, Spectrophotometric *p*-Nitrobenzeneazo-orcinol Method"	1 211010 9 00711010	2-18-55
Surak,[4] J. G.	"Fluoride in the Presence of Nitrate, Pyrohydrolysis Method"	9 012207	3-30-55
White, J. C.	"Sulfur in Inorganic Compounds, Spectrophotometric Methylene Blue Method"	1 218110 9 00718110	3-15-55
Wyatt, E. I.	"Adsorption Capacity of Ion-Exchange Resins"	9 0732006	3-15-55

[redacted]

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ANALYTICAL CHEMISTRY DIVISION - X-10 SITE

RESEARCH AND DEVELOPMENT

IONIC ANALYSES

P. F. Thomason

Spectrophotometric Determination of Aluminum in Homogeneous Reactor Fuels

A. D. Horton P. F. Thomason

The development of an ion-exchange–spectrophotometric method for the determination of aluminum in Homogeneous Reactor (HR) fuels is nearly complete. Aluminum is separated from a 9 *M* hydrochloric acid solution of the fuel by ion exchange on a column of Dowex 1 resin in the chloride form. The effluent that contains aluminum(III), chromium(III), and nickel(II) is evaporated to dryness. The residue is dissolved in 6 *M* hydrochloric acid; pyridine is added to complex chromium(III) and nickel(II) in order to prevent their reaction with Aluminon reagent. Buffered Aluminon reagent[1] is added, and the color of the aluminum–Aluminon lake is developed at 100°C and is measured spectrophotometrically at a wavelength of 525 mμ; distilled water is used as the reference liquid.

A spectrophotometric calibration curve has been prepared for the range 0 to 50 μg of aluminum. Aluminum in several aliquots of a solution of Bureau of Standards aluminum bronze has been determined by this method. The average result obtained was 6.10% aluminum; the average result reported by the Bureau of Standards was 6.21%.

Polarographic Determination of Iron in Homogeneous Reactor Fuels

A. D. Horton P. F. Thomason

An ion-exchange–polarographic method was developed for the determination of iron in HR fuels. Copper is removed from the fuel by plating it out on a cadmium coil. Iron is oxidized to iron(III) by potassium permanganate, and the iron(III) is separated from interfering metal ions by ion exchange on a column of Dowex 1 resin in the sulfate form. The iron(III) in the effluent is determined polarographically in 0.5 *M* sodium citrate solution as a supporting electrolyte. A fairly well defined polarographic wave is obtained for the iron(III) → iron(II) reduction at an $E_{1/2}$ of approximately −0.15 v vs the S.C.E. The relative standard deviation of the data for 2 μg of iron(III) per milliliter was 6.5%; for 10 μg of iron(III) per milliliter, it was 0.6%. A topical report that describes this work has been issued.[2]

Polarographic Determination of Molybdenum in Uranyl Sulfate Solutions

P. F. Thomason

Microgram quantities of molybdenum are expected to be present in HR fuels because of the corrosion of reactor construction materials that contain this element and also because of the formation of fission-product molybdenum during the operation of the reactor. It will be desirable to know the total amount of molybdenum present in the fuel. Kolthoff and Lingane[3] describe a polarographic procedure for the determination of molybdenum in ores. This procedure was developed by Russian workers; they used 6 *M* phosphoric acid as the supporting electrolyte and obtained a well-defined double wave for the molybdenum(VI) → (V) and (V) → (IV) reductions, but they did not report the half-wave potentials or whether the diffusion current was linear with respect to molybdenum concentration. Preliminary work showed that 6 *M* phosphoric acid gave better waves than did either sulfuric acid or hydrochloric acid as supporting electrolytes.

A standard solution that contained 200 μg of molybdenum per milliliter was made by dissolving 0.3000 g of reagent-grade MoO_3 in a solution that

[1] C. L. Luke and K. C. Braun, "Photometric Determination of Aluminum in Manganese Bronze, Zinc Die Casting Alloys, and Magnesium Alloys," *Anal. Chem.* **24**, 1120 (1952).

[2] A. D. Horton and P. F. Thomason, *Determination of Corrosion Products and Additives in Homogeneous Reactor Fuel. III. Polarographic Determination of Iron (III)*, ORNL-1954 (Oct. 5, 1955).

[3] I. M. Kolthoff and J. J. Lingane, *Polarography*, vol 2, p 460, Interscience, New York, 1952.

[redacted]

contained 4.0 g of NaOH and by diluting the resulting solution to 1 liter with distilled water. Standard solutions that contained 10 to 140 μg of molybdenum per milliliter of 6 *M* phosphoric acid were prepared from this solution. Polarograms of these solutions were obtained by use of the ORNL model Q-1160 high-sensitivity polarograph. The diffusion currents were carefully measured and were found to be linear over this range; the $E_{1/2}$ was approximately –0.43 v vs the S.C.E.

Synthetic HR fuel samples prepared so as to contain 10 mg of uranium and 100 μg of molybdenum in 10 ml of 6 *M* phosphoric acid could not be polarographed directly because the uranium wave obscured the molybdenum wave. It was found that a single precipitation of the uranium as sodium diuranate by sodium hydroxide resulted in a loss of approximately 10% of the molybdenum. However, when the sodium diuranate precipitate was dissolved in hydrochloric acid, the precipitation of uranium with sodium hydroxide was repeated, and the filtrates were combined, the recovery of molybdenum was about 95%. The limit of detection of this method and also the effects of copper and nickel should be determined.

Polarographic Determination of Zinc

P. F. Thomason

The Laboratory and Semi-Works Control Group of the Analytical Chemistry Division requested a rapid and precise method for the determination of zinc. The polarographic method described by Kolthoff and Lingane[4] was found to be adequate for the samples to be analyzed. A supporting electrolyte that contained 1 *M* NH_4OH, 1 *M* NH_4Cl, and 0.005% gelatin gave well-defined waves at an $E_{1/2}$ of approximately –1.5 v vs the S.C.E. for the tetrammino-zinc ion.

Determination of Fluoride by Fluorescence Analysis

J. G. Surak[5] P. F. Thomason

The determination of 0- to 10-μg quantities of fluoride is of interest in the HR thorium oxide slurry program. Spectrophotometric methods have not been very successful for the determination of fluoride in this quantity range. A more successful method was developed that is based on the decrease in the fluorescence of an aluminum–morin complex by fluoride. It is a modification of the methods of Willard and Horton[6] and of Bouman.[7]

When morin (3,5,7,2′,4′-pentahydroxyflavone) is added to a solution of aluminum(III), the resulting complex will fluoresce when it is irradiated by ultraviolet light. Maximum fluorescence occurs at approximately 500 mμ. Fluorides in low microgram quantities, for which quantity range fluorometry is the most effective, form the AlF^{++} and AlF_2^+ ions, which diminish the fluorescence of the aluminum–morin complex. In the determination of fluoride, a solution of the aluminum–morin complex of known fluorescence is prepared. This is used in the preparation of fluoride standards, which are irradiated with ultraviolet light of the wavelength of maximum absorption. By comparison of the fluorescence of the fluoride standards with that of the solution of aluminum–morin complex, the diminution by fluoride of the fluorescence of the aluminum–morin complex can be determined; a calibration curve is then prepared that relates quantity of fluoride to diminution of fluorescence. In the ranges 0 to 1 μg and 0 to 10 μg, a linear relationship exists between the quantity of fluoride and the diminution of the fluorescence. In the fluoride quantity ranges indicated, a relative standard deviation of approximately 1% is obtained for data taken by this method. Interfering ions, whose presence tends to enhance, to diminish, or to extinguish the fluorescence, must be removed. This method is being prepared in tentative form for issue to the *ORNL Master Analytical Manual.*

Reagents for the Precipitation of Zirconium

H. R. Hunt, Jr.[8]

p-Bromomandelic acid,[9] phthalic acid,[10] and tetrabromophthalic acid were investigated as possible precipitants for microgram quantities of

[4] *Ibid.*, p 504–505.

[5] Summer employee from Marquette University.

[6] H. H. Willard and C. A. Horton, "Fluorometric Determinations of Traces of Fluoride," *Anal. Chem.* **24**, 862 (1952).

[7] J. Bouman, "Determination of Fluoride in Main Water," *Chem. Weekblad* **51**, 33 (1955).

[8] Summer employee from University of Chicago.

[9] R. E. Oesper and J. J. Klingenberg, "Use of Glycolic Acid Derivatives in Determination of Zirconium," *Anal. Chem.* **21**, 1509 (1949).

[10] G. W. Leonard, Jr., D. E. Sellers, and L. E. Swim, "Turbidimetric Microdetermination of Zirconium," *Anal. Chem.* **26**, 1621 (1954).

zirconium in HR fuels. The amount of zirconium present in the precipitate was determined by the quercetin method.[11] *p*-Bromomandelic acid was found to be unsatisfactory, because a very large excess of the reagent was required to quantitatively remove the zirconium from solution, and the resulting precipitate could not be washed without loss of zirconium. Extraction of the zirconium–*p*-bromomandelate complex into nonaqueous solvents proved to be equally unsuccessful.

Two milliliters of 6% phthalic acid solution was found to precipitate approximately 80% of the zirconium from a 10-ml volume of hydrochloric acid solution at pH 1. The range studied was 10 to 50 μg of zirconium.

Tetrabromophthalic acid was found to be a better precipitant than phthalic acid for zirconium. Maximum precipitation occurs at pH 1; in more acidic solution, zirconium is not precipitated, and, in more basic solution, hydrolysis of the zirconium occurs. The precipitation must be performed under controlled conditions because only about 90% of the zirconium is removed from solution under these conditions. Quadruplicate determinations were made on 10- to 50-μg quantities of zirconium; the standard deviation was 2.8% in the best case and 21.4% in the worst. Further work will be required to improve the precision of this method.

Automatic Photometric Titrations

F. J. Miller

Sulfate ion has been determined by titration with barium perchlorate solution as described by Fritz and Yamamura.[12] This procedure has been introduced into the control laboratories. As an alternate to the manual titration and visual end-point detection, an automatic titration which uses photometric end-point detection and the ORNL model Q-945 automatic titrator has been developed. The titration assembly consists of a small radio chassis which contains batteries, a load resistor, light source, cell holder, and photocell. The assembly is mounted on a magnetic stirrer. This method is being written for issue to the *ORNL Master Analytical Manual.*

The automatic photometric titration has also been applied to the titration of fluoride[13] with thorium nitrate solution and to the titration of thorium with disodium dihydrogen ethylenediaminetetraacetate solution;[14,15] sodium alizarin sulfonate is used as the indicator in each case. The thorium titration gave excellent precision; the relative standard deviation was 0.18% for the determination of approximately 50 mg of thorium. The fluoride titration was characterized by indistinct conductometric type of titration curves, which resulted in poor precision; this titration needs further study.

Separation and Potentiometric Titration of Cobalt

F. J. Miller

A method was adapted for the rapid separation and precise determination of microgram (or smaller) quantities of cobalt. The cobalt is separated as cobaltous ion by ion exchange on a Dowex 1 resin column. The cobaltous ion is complexed by ammonia and is titrated as the complex by potassium ferricyanide solution. Potentiometric end-point detection is recommended. The method is being written for inclusion in the *ORNL Master Analytical Manual.*

Ultraviolet Spectrophotometry of Technetium and Rhenium

W. J. Wolkowitz

The ultraviolet absorption spectra of technetium and of rhenium were studied. Pertechnetate ion (TcO_4^-) in 1.1 *M* $HClO_4$ exhibits two absorption maxima in the ultraviolet. Molar absorbancy indices of 2363 and 6200 were found for the 288- and 244-mμ wavelengths, respectively. Perrhenate ion (ReO_4^-) in 1.1 *M* $HClO_4$ exhibits no sharp absorption maxima in the ultraviolet. The molar absorbancy index is 3575 at 235 mμ. Pertechnetate can be determined spectrophotometrically at either 288 or 244 mμ. Perrhenate can be determined spectrophotometrically at 235 mμ. Pertechnetate and perrhenate in solutions that contain both can be determined simultaneously by

[11] F. S. Grimaldi and C. E. White, "Quercetin as Colorimetric Reagent for Determination of Zirconium," *Anal. Chem.* **25**, 1886 (1953).

[12] J. S. Fritz and S. S. Yamamura, "Rapid Microtitration of Sulfate," *Anal. Chem.* **27**, 1461 (1955).

[13] M. L. Nichols and B. H. Kindt, "Titrations with a Photoelectric Titrimeter," *Anal. Chem.* **22**, 785 (1950).

[14] J. J. Fritz and J. J. Ford, "Titrimetric Determination of Thorium," *Anal. Chem.* **25**, 1640 (1953).

[15] C. V. Banks and R. E. Edwards, "Separation and Determination of Thorium and Aluminum," *Anal. Chem.* **27**, 947 (1955).

measuring the absorption of the solution spectrophotometrically at 288 and at 235 mμ. This study is described in detail elsewhere.[16]

ANALYTICAL INSTRUMENTATION

D. J. Fisher

Model Q-1673 Polarograph with Diode Filter

M. T. Kelley D. J. Fisher

The first of three model Q-1673 polarographs with diode filters[17] has been fabricated by the Instrument Department of the Instrumentation and Controls Division and is being tested. This type of polarograph will be used, together with the pressurized polarographic cell, described below, for remotely controlled analyses in the High-Radiation-Level Analytical Facility. Initial results obtained with this polarograph indicate that it will meet design specifications. A testing program to evaluate the instrument completely is being carried out. Polarographs of this type will also be used in other laboratories.

Pressurized Polarographic Cell

R. W. Stelzner D. J. Fisher
L. C. Bate[18]

A pressurized polarographic cell for remotely controlled operation by master-slave manipulators in the High-Radiation-Level Analytical Facility was designed and tested. The design is based upon Hanford in-line cell designs.[19] The drop time of the dropping-mercury electrode was controlled by varying the pressure of nitrogen gas above the mercury reservoir for the electrode. Satisfactory polarograms were obtained with and without the parallel-T filter. Plots of E_{de} vs $\log i/(i_d - i)$ for the pressurized cell and for an orthodox polarographic cell showed a slight disagreement, which was traced to a high-resistance salt bridge. A study of salt bridge parameters indicated that a more suitable resistance could be obtained by using a large-diameter porous glass, large-diameter Tygon tubing, and a short column of saturated potassium nitrate solution. The design of the polarographic cell was revised to take advantage of these findings. Bakelite C-8 epoxy casting resin is to be used. A cell is being fabricated according to the new design.

Turret for the Falling-Drop Densimeter

R. W. Stelzner

The construction of the remotely controlled turret[20] for the falling-drop densimeter[21] was completed by the Central Machine Shop, and preliminary testing of the turret has begun. Final testing of the densimeter awaits the construction of the 0.1-ml remotely controlled pipet. It is planned to test a derivative triggering circuit to determine whether its use can possibly eliminate an expensive VTVM monitor of the 2D21 bias.

Remotely Servo-Controlled Sampling Pipetters

M. T. Kelley D. J. Fisher

The 0.1- and 1-ml servo-controlled pipets[22] have been redesigned (Engineering Dept. Dwgs. Nos. D-21064-B and D-21065-B). The Central Machine Shop will fabricate five of these pipets for use in the High-Radiation-Level Analytical Facility. The Instrument Department of the Instrumentation and Controls Division is fabricating the Q-1348 control units for the pipets.

A 1-ml pipet (ORNL Photograph No. 14497) was used in the Analytical Cell Exhibit for the Geneva Convention. The tip of the pipet is a hypodermic needle of 0.020-in. bore. With this pipet, 100-μl aliquots of 9 N HNO_3 were delivered and were then titrated by use of a Beckman model K automatic titrator; the relative standard error of the results was ±0.15% at the 95% probability level. Under the same conditions, but by careful hand pipetting of the 100-μl aliquots, the relative standard error was ±0.14% at the 95% probability level.

A 1-ml pipet having a fluorothene liner has been built by the Central Machine Shop for pipetting

[16] W. J. Wolkowitz, *Ultraviolet Spectrophotometry of Technetium and Rhenium*, ORNL-1948 (to be issued).

[17] M. T. Kelley and D. J. Fisher, "Model Q-1673 Polarograph with Diode Filter," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 8.

[18] Activation Analyses Group.

[19] Hanford Atomic Product Operation Dwg. No. H-2-5022, *Unitized Polaromonitor Cell-Assembly*, sheet No. 2.

[20] R. W. Stelzner, "Remotely Controlled Turret Assembly for the Q-1551 Falling-Drop Densimeter," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 6–7.

[21] R. W. Stelzner *et al.*, "Remotely Controlled Falling-Drop Densimeter," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 6.

[22] M. T. Kelley and D. J. Fisher, "Remotely Controlled Sampling Pipets," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 8–9.

solutions that are corrosive to stainless steel. It is for use in the High-Radiation-Level Analytical Facility by the Spectrochemistry Group.

External Guides for Screw-Operated Elevator

M. T. Kelley D. J. Fisher

External guides have been designed and installed on a screw-operated elevator.[23] They provide for improved vertical guiding, takeup of wear, and reduced fabrication costs. These guides will be used on the six additional elevators to be built by the Central Machine Shop and by the Instrument Department of the Instrumentation and Controls Division. An elevator having the external guides (ORNL Photograph No. 14498) was built for the Analytical Cell Exhibit for the Geneva Convention. This elevator was demonstrated during the exhibit without malfunction.

Sample-Bottle Decapper for the High-Radiation-Level Analytical Facility

C. L. Burros L. C. Bate

The sample-bottle decapper of the original design[24] was built, tested, and found to perform satisfactorily with minor exceptions. A modification of the original sample-bottle decapper was built and was mounted on a movable carriage, on which was also mounted a magnetic stirrer. The carriage is aligned on a track. Two fixed positions are provided for the carriage; one fixes the sample bottle under the remotely controlled pipet so that the sample can be removed, and the other brings the magnetic stirrer under the pipet so that the sample can be delivered into a flask or beaker that rests on the magnetic stirrer. The 4-rpm reversible motor that drives the decapper has been shielded for protection in case of spills. The need for a separate bottle holder for pierce-sampling has been eliminated; this will reduce both cost and space requirements.

Motorized Lab-Jack

D. J. Fisher E. B. Wagner

A prototype motorized Lab-Jack[25] has been built and tested, and mechanical drawings of it have been made. Lab-Jacks are being motorized by the Central Machine Shop. These will be used in the High-Radiation-Level Analytical Facility for such purposes as positioning coulometric cell assemblies and also for positioning titration vessels below the titrant delivery unit of the automatic velocity-servo titrator.

Model Q-1734 Filter Photometer for Operation by Master-Slave Manipulators

M. T. Kelley D. J. Fisher
E. B. Wagner

A prototype filter photometer, designed to be operated remotely by means of master-slave manipulators,[26] has been built and tested. Mechanical drawings of the photometer have been made. Three of these photometers for use in the High-Radiation-Level Analytical Facility are being constructed by the Instrument Department of the Instrumentation and Controls Division and by the Central Machine Shop.

High-Sensitivity Recording Flame Photometer

M. T. Kelley D. J. Fisher

It is planned to extend the useful spectral range of the model Q-1457 flame photometers well into the infrared region by the use of Farnsworth type 16PM1 multiplier phototubes. This newly developed tube is said to be the only commercially available multiplier phototube that will function in the wavelength region from 7,000 to 12,000 Å. A mount for the phototube will be built so that this tube can be tested with the Bausch & Lomb grating monochromator.

The 3-ml Remote Control Dilution Pipetter

L. C. Bate

The 3-ml remotely controlled dilution pipetter was modified to permit the pipet to be raised and lowered by a screw-type elevator rather than by a hydraulic lift. The connection between the Brown motor and the dial indicator of the plunger is similar to that shown in Engineering Dept. Dwg. No. 542-21-C-2042-A, and the dial indicator is

[23] M. T. Kelley and D. J. Fisher, "Pipet Elevator," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 9.

[24] C. L. Burros, "Sample-Bottle Decapper for the High-Radiation-Level Analytical Facility," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 8.

[25] M. T. Kelley and D. J. Fisher, "Motorized Lab-Jack," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 8.

[26] M. T. Kelley, D. J. Fisher, and E. B. Wagner, "New Filter Photometer for Operation by Master-Slave Manipulators," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 9.

similar to that shown in Engineering Dept. Dwg. No. D-9476. The modified pipetter was found to have good linearity throughout the range of the piston displacement. The precision of the 3-ml remotely controlled dilution pipetter was found to be improved by changing the 12AU7 tubes and related circuitry of the Brown amplifier to use 12BH7 tubes. The improved precision is shown by the following results:

Volume Delivered by the Pipetter (μl)	Relative Standard Deviation (%)	
	12AU7 Tubes	12BH7 Tubes
9	8.10	7.69
30	3.82	2.81
90	1.00	0.96

Investigation of the Chronopotentiometric Method of Analysis

A. F. Schram[27]

In the chronopotentiometric method the concentration of a particular ion is determined by measuring the time lag (transition time) in the polarization of a quiet-mercury-pool cathode when the electrolyzing current through the solution is held constant. This time lag results from the partial depolarization of the cathode by the discharge of the ion in question. The present investigation was undertaken with the idea of applying the technique to routine analyses, particularily at low concentrations. Solutions that contained 10^{-2} to 10^{-5} M cadmium(II) in a supporting electrolyte that was 1 M in both NH_4Cl and NH_4OH and solutions that contained from 5 to 200 μg of uranium(VI) per milliliter of 0.1 M HNO_3 were analyzed.

A satisfactory cell was designed (ORNL Photograph No. 15318), which permits samples to be changed easily and which also maintains a constant cathode surface area from sample to sample. For work at concentrations of about 10^{-4} M or less, the best results are obtained with a relatively large cathode and a relatively large anode bridge of low resistance. For work at these low concentrations it is not practical to select a single fixed current and then prepare a standard curve for the current that relates transition time to concentration, because there is a limited range over which transition times can be measured accurately. This limitation of concentration range that can be determined for a particular constant current is the result of the capacity effect of the ionic double layer at the cathode surface. A suitable procedure has been developed and is described elsewhere.[28]

Anticipatory Automatic Coulometric Titrations

R. W. Stelzner

In order to avoid titrating beyond the end point in certain coulometric titrations, it would be desirable to slow down the rate of addition of titrant as the end point is approached. Inasmuch as current must remain constant unless a current integrator is used, time is the only variable which can be used for anticipatory control. The Beckman model K automatic titrator was modified for anticipatory automatic coulometric titrations, but the results were not satisfactory because a large number of false cutoffs obscured the end point. A gating circuit having an "on" time of 1 sec and an "off" time of 6 sec and based upon an asymmetrical multivibrator was also tried. The performance of the gating circuit was much better than that of the modified Beckman model K titrator, but it was still not satisfactory for micro coulometric titrations. Evaluation for macro titrations was not made.

The ORNL In-Line Assistance Program

R. W. Stelzner

The Savannah River Plant has requested assistance from ORNL in the development of a program for in-line analyses of chemical process streams. A committee consisting of J. W. Landry of the Chemical Technology Division, M. J. Kelly of the Instrumentation and Controls Division, and R. W. Stelzner has been appointed to investigate the scope of ORNL assistance.

Instrumentation for the Analytical Cell Exhibit for the Geneva Convention

M. T. Kelley, C. L. Burros, D. J. Fisher, R. W. Stelzner, E. B. Wagner

An analytical cell was built, equipped with instruments developed for the purpose, and demonstrated at the International Conference on the

[27] Research participant from Texas A & M College.

[28] A. F. Schram, *Investigation of the Chronopotentiometric Method of Analysis*, ORNL CF-55-10-38 (in press).

Peaceful Uses of Atomic Energy, Geneva Exhibit, August 3–20, 1955. The demonstration was made in conjunction with the Uranium Processing Exhibit of the Chemical Technology Division. The cell is described by Engineering Dept. Dwg. No. D-22930. Two Argonne model 8 master-slave manipulators are installed in the cell. The cell is similar to the ones built in the High-Radiation-Level Analytical Facility, in which highly radioactive samples will be analyzed by remote control. For this reason, development work done for this exhibit was directly applicable to instrumentation for the High-Radiation-Level Analytical Facility. Prior to its shipment to Geneva, the cell was operated and tested, as was the remainder of the exhibit. During this test period a movie was made of the exhibit in operation; also, still shots were taken – for example, the photograph of the colorimetric determination of uranium by remote control (ORNL Photograph No. 14573).

A close-up view of the interior of the cell is shown in Fig. 1. The instruments within the cell include the following: a delivery unit of the Beckman model K automatic titrator modified so that it can be operated easily with the manipulators; a Bausch & Lomb Spectronic 20 colorimeter modified for master-slave manipulation; and a 1-ml servo pipetter mounted on a screw-operated elevator. Apparatus that was designed and supplied with the cell included carriers for a beaker, for a flask, and for a reagent bottle; a sample-bottle holder; a special ring stand and clamp; and a stopcock adapter. An 8-power 30-mm-dia-objective monocular was modified so that it could be focused down to 6 ft; a mount (ORNL Photograph No. 14574) for it was designed and was built. With the exception of the Spectronic 20 and the magnetic stirrer, all panels for the instrument controls and adjustment knobs were located outside the cell in the instrument chase. The hard-rubber surfaces of the slave fingers, supplied by the manufacturer, were replaced by sponge-rubber surfaces in order to achieve positive gripping of rounded glass surfaces.

The Beckman model K automatic titrator was used either for the titration of acidity as such or for the determination of nitrate after it was converted to nitric acid by ion exchange on a resin column mounted inside the cell. The buret regularly supplied with the titrator was replaced by one having an automatic filling device so designed that the buret could be filled remotely to the zero mark by use of a rubber bulb at the end of rubber tubing that led to the reservoir of standard base reagent. The delivery unit was mounted on a ring stand built for the purpose. A clamp was built to hold the buret in position. The beaker platform was modified to increase its vertical travel, and special knobs were added so that the master-slave manipulators could readily position a beaker under the electrodes. The control unit of the titrator was mounted in the instrument chase and was connected to the delivery unit by means of 20-ft cables. No difficulty was experienced with the operation of the modified titrator.

The Bausch & Lomb Spectronic 20 was placed on a platform in order to facilitate the positioning of cuvettes in the instrument by means of the manipulators. The standard amplifier and light-control knobs were removed, and crank knobs were fabricated and were substituted to make easy their operation by the manipulators.

The modified, 8-power 30-mm-dia-objective monocular was used to read the scales of the Spectronic 20 and of the buret on the Beckman automatic titrator. The modification that makes possible its use at short viewing distances is simple and does not impair the optical quality of the monocular. The flexible mount designed and built for the monocular positions it in front of the cell window at any location required for easy viewing.

All controls for the 1-ml servo pipetter and for the screw-operated elevator (Engineering Dept. Dwg. No. E-19550) are on the panel of the Q-1348 remote pipetter control unit, which was mounted on the instrument chase. The vacuum equipment used for filling and cleaning the pipet (Engineering Dept. Dwg. No. D-21065) was located beneath the cell floor. The pipet tip was a hypodermic needle. Sample bottles from the pulse column of the Uranium Processing Exhibit were conveyed inside the cell on a carrier. By means of the manipulators, the bottles were removed from the conveyer and were positioned and clamped in a special bottle holder mounted on the base of the elevator. The rubber diaphragm covers were pierced by the needle tip of the descending pipet, and the pipet could then be filled with sample. The elevator and the pipetter worked satisfactorily during the exhibit.

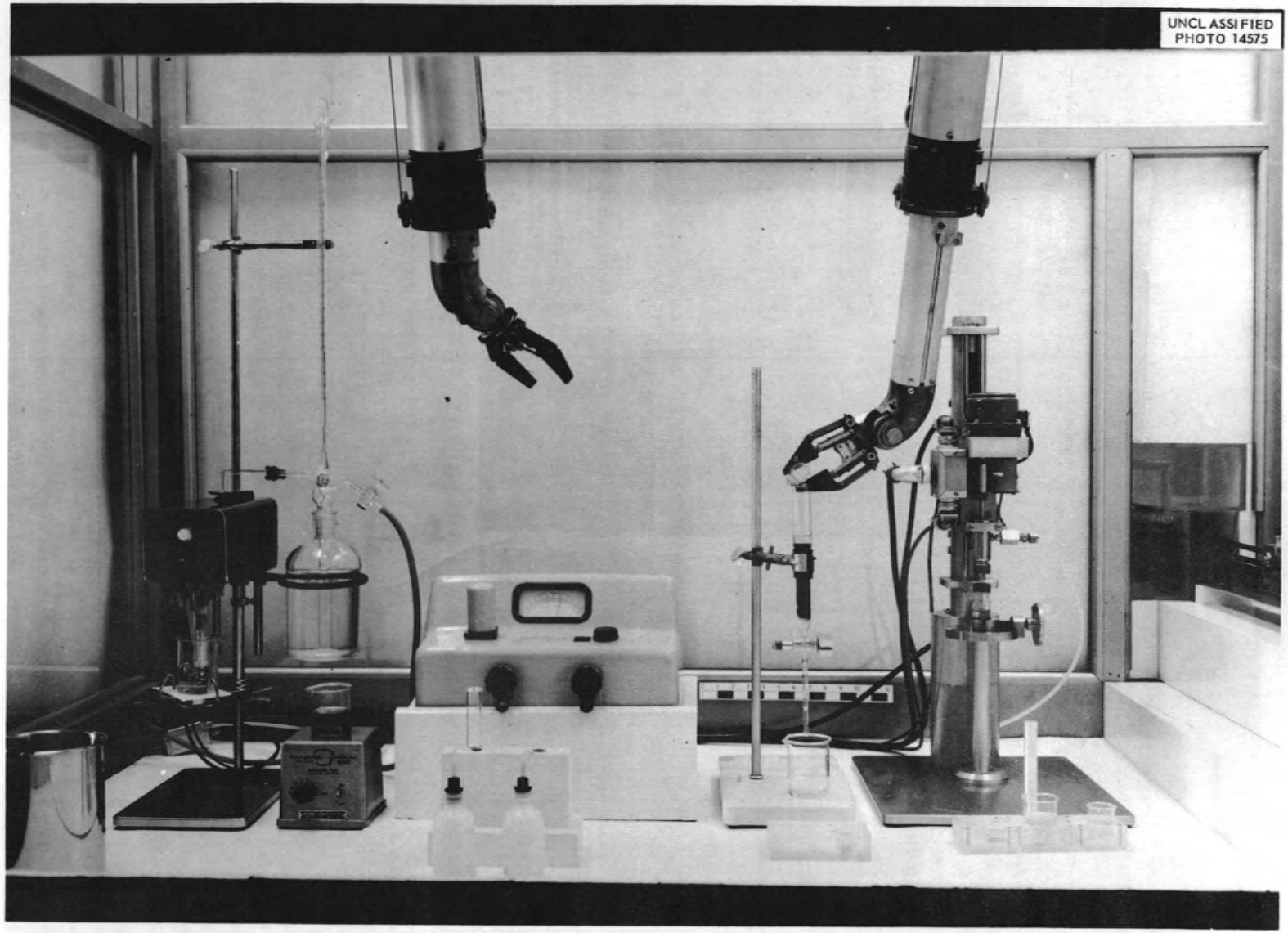

Fig. 1. Analytical Cell Exhibit for the Geneva Convention.

RADIOCHEMICAL ANALYSES

S. A. Reynolds

Nuclear Properties

Mg^{27} (W. S. Lyon, N. H. Lazar[29]). – A publication resulting from work on the decay scheme of Mg^{27} will be submitted to *The Physical Review.*

Activation Cross Section of Ba^{130} (W. S. Lyon, W. L. McPherson[30]). – The thermal-neutron activation cross section for the reaction $Ba^{130}(n,\gamma)Ba^{131}$ has been determined. The method used was to irradiate barium nitrate in the ORNL Graphite Reactor, free it from cesium, allow the daughter Cs^{131} to grow in, separate the Cs^{131} from a known amount of barium, and measure the Cs^{131} activity by x-ray counting. The yield of cesium and the amount of barium were determined by flame spectrometric analysis. The amount of Ba^{131} parent was calculated from the amount of Cs^{131} daughter by use of the known growth time of Cs^{131} and of the half lives of Ba^{131} and Cs^{131}. The cross section found for the reaction is 10 barns.

Gamma-Ray Branching in Sr^{89} (W. S. Lyon, R. R. Rickard[31]). – A description of the gamma-ray branching in Sr^{89} will be submitted for publication in *The Physical Review.*

Instrumental Methods

Reactor and Radioisotope Analyses Using Gamma-Ray Counting and Spectrometry (W. S. Lyon, T. H. Handley, H. W. Wright). – A large number and variety of special analytical problems have been solved by use of gamma counting and spectrometry. Induced activities in reactor materials have been measured, and the results were used to determine the neutron flux "seen" by the material (see "Reactor Analyses," this report). Unknown activities in a variety of samples have been identified. Samples examined have included air and smear samples submitted by the Health Physics Division; residues, adsorbed activities, and solutions from both process and research units of the Chemical Technology Division; piping and sodium residues from the ANP project; and a large number of radioisotope solutions from the Operations Division. Radioisotopes of more than routine interest encountered during the past six months have included Lu^{177}, Sb^{122}, As^{76}, I^{129}, and Cd^{109}.

Radioisotope Analysis

Survey of Tentative Methods for Radioisotopes (T. H. Handley, W. S. Lyon). – A survey of the literature was made for the best decay-scheme data on 29 radioisotopes that are to be added to the isotopes catalog of the Operations Division. Tentative methods for the determination of disintegration rates have been proposed. In order to routinize the measurements, the ion chamber will be calibrated by use of 4π and 4π-coincidence counting so that it can be used to measure these isotopes. This method is also necessary in some cases because of the complexity of the decay schemes, which prohibits calculation of ion-chamber efficiency factors.

Heavy Elements

Electrodeposition of Plutonium (F. L. Moore, G. W. Smith). – A series of plutonium electrodeposits with a density of approximately 100 μg per square centimeter of surface area on 0.5-in.-dia, 2-mil nickel foils has been prepared for the Physics Division. The technique[32] used has been found to give electrodeposits of adequate uniformity and adherence. During the course of this work it was observed that Am^{241} coplated with approximately 100 μg of plutonium. Previously it had been found that less than 1% Am^{241} plated alone under the conditions of the procedure. Therefore any americium or curium present should be removed before the electrodeposition of the plutonium is performed.

Assay of High-Level Plutonium (T. H. Handley). – Samples of plutonium deposited on metal disks have been assayed for plutonium by counting on a low-geometry alpha counter. A "low, low-geometry" (approximately 0.005%) alpha chamber was built for use on the hotter samples (as much as 0.5 mg). Factors were established for the comparison of results from the two chambers. An attempt to correlate alpha counting with gamma spectrometry by measurement of the approximately

[29] Physics Division.

[30] Research participant from Virginia Polytechnic Institute.

[31] Radioisotope Production Analyses Group.

[32] F. L. Moore and G. W. Smith, "Preparation of Plutonium Deposits, Electroplating Method," Method Nos. 2 31629 and 9 008629 (12-21-54), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols I, II, and III.

100-kev peak associated with plutonium decay was unsuccessful. Because the work has become routine, it will be done in the future by the Plutonium Isolation Laboratory. Results of this work will be reported in detail by R. H. Rainey of the Chemical Technology Division.

Reactor Analyses

Determination of Volatile Fission Products from Fuel Elements (G. W. Smith, T. H. Handley). – In continuation of the work for the General Electric Company that was reported previously,[33] samples of charcoal were examined for fission-product radioactivities. The ion-exchange scanner proved to be useful for locating bands of activity on charcoal in tubes. An attempt was made to develop an oxygen condensation method for the collection of radioactivity, but the handling of the closed tubes of liquid oxygen in Dewar flasks proved to be cumbersome and created an explosion hazard. Xenon-133 was collected from iodine production off-gas and, after decay and transfer by heating, was found to be pure. Laboratory bench tests were carried out to determine the extent of I^{131} and Xe^{133} adsorption in traps and lines. A proposed method for the extraction of iodine from charcoal by leaching the charcoal with a solution of hydrogen sulfide proved inefficient when evaluated on iodine activity produced by the irradiation of fuel elements in the LITR. A 20-channel scintillation spectrometer will be available in the future for sample analysis.

By request of the Ceramics Laboratory of the Metallurgy Division, analyses are continuing[34] to be made on volatilized activities from fuel elements. The same techniques of measurement as described before[34] are being used. Findings of the earlier investigation were reported.[35] Results will again be reported in detail by the Metallurgy Division.

[33] G. W. Smith, "Determination of Volatile Fission Products from Fuel Elements," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 12.

[34] S. A. Reynolds, "Activities Volatilized from Reactor Elements," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 13.

[35] W. E. Moody, Jr., A. J. Taylor, and J. R. Johnson, *Preliminary Investigation of the Fission Product Retention Ability of Cermet Compacts*, ORNL-1778 (June 23, 1955).

Neutron-Flux Determinations (H. W. Wright). – A number of neutron-flux determinations have been made by the radiochemical analyses of Cr^{51} and of Zr^{95}. The technique employed was to expose samples of known composition in an unknown neutron flux and then to compare the gamma photopeaks with those of a known sample that had been exposed to a known neutron flux. These gamma photopeaks were measured with a gamma spectrometer. Conversely, Cr^{51} and Zr^{95} have been determined in samples of unknown composition.

LITR Cooling Water (W. S. Lyon, T. H. Handley). – The amount of Na^{24} and Mg^{27} remaining in LITR cooling water as a function of demineralization rate is of interest in calculations relative to long-range planning for reactors. The method used has been to analyze the water for Na^{24} (15.1 h) by the usual radiochemical method. The Mg^{27} (9.5 m) has been assayed by first adding magnesium carrier, carrying out a quick chemical separation to free the magnesium from Na^{24}, Mn^{56}, and other contaminants, and then following the decay of the Mg^{27} on a calibrated well-type scintillation counter. The magnesium radiochemical yield is found later by flame photometric analysis. The results obtained thus far are shown below:

Demineralization Rate (gpm)	Na^{24} (d/min/ml $\times 10^{-4}$)	Mg^{27} (d/min/ml $\times 10^{-4}$)
15	4.80	4.31
5	7.05	4.91
3	8.55	4.89

Process Analyses

U^{232} and Th^{228} Determinations (T. H. Handley, S. A. Reynolds). – Analysis of Thorex process solutions for U^{232} and Th^{228} was made by two methods:[36] (1) separating and counting the Ra^{224} member of the decay chain and (2) making an alpha-pulse analysis of the gross sample. In each instance the first method gave results approximately 25% lower than those of the second method. Traces of sulfate in the solution could explain this difference. Analysis of these solutions was requested by members of the Chemical Technology Division in order to explain and to

[36] T. H. Handley and S. A. Reynolds, *Thorium-228 Analyses*, ORNL CF-55-7-50 (July 12, 1955).

determine the source of high gamma activity of uranium and thorium products.

Gamma Scintillation Spectrometry Studies of Thorex Streams (H. W. Wright). – The radiochemical determination of protactinium, cerium, ruthenium, and zirconium–niobium in Thorex process streams by use of a gamma spectrometer[37] was attempted. It was desired to hold chemical treatment of the sample to a minimum and to determine the individual nuclides by use of a suitable portion of the sample just as it was received from the pilot plant. Inability, at present, to duplicate the radiochemical values that were determined by E. I. Wyatt led to the postponement of these studies.

Cyclotron Research

T. H. Handley

A survey of (n,α) cross sections is being conducted by H. G. Blosser and others of the Electronuclear Research Division. Radiochemical analyses of target materials were made after the targets were bombarded by fast neutrons. Two series of experiments have been completed and a third is planned. It was necessary to use modifications of standard radiochemical procedures because of the large quantities (i.e., as much as 5 g) of target materials used.

Members of the Electronuclear Research Division have submitted a series of metal-foil stacks to be analyzed for activities produced by proton bombardment. They wish to determine excitation functions and cross sections for the proton reactions of interest. Assay was made by the gamma spectrometry technique of Kahn and Lyon.[38] The results of these investigations will be reported in the open literature by members of the Electronuclear Research Division.

Solvent Extraction Methods

Liquid-Liquid Extraction Method for Cerium (G. W. Smith, F. L. Moore). – A study was made of a thenoyltrifluoroacetone (TTA) extraction method[39–41] for radiocerium in fission-product solutions. The method consists in extracting the cerium(IV) into TTA,[41] washing the TTA with water, and stripping the cerium into 10 *M* HNO_3. Since radiocerium may be in the trivalent state, it must be oxidized. Oxidation to cerium(IV) is easily carried out in a solution 0.1 *M* in $K_2Cr_2O_7$ and 1.0 *M* in HNO_3 at room temperature. High-speed stirring of the sample with the TTA for 10 min was found necessary in order to attain equilibrium. The presence of sulfate (0.1 *M* H_2SO_4) in the original aqueous phase and in the aqueous wash solutions results in an extraction efficiency of 99% and losses of cerium during the washing procedure of less than 0.1%. A 10-min agitation with approximately 10 *M* HNO_3 strips out the cerium quantitatively. The tentative procedure gives satisfactory decontamination of the cerium from trivalent rare earths, ruthenium, zirconium, and niobium radioactivities.

Electrolytic Methods

H. W. Wright S. A. Reynolds

An investigation is being carried out to ascertain which elements can be determined radiochemically by carrier techniques used in conjunction with electroplating. To date, copper tracer has been electroplated and has been demonstrated to be proportional to the copper carrier plated.

The circuit in use in the electrolysis is essentially that described by Willard *et al.*[42] A Fisher electroanalyzer is used as the power source, and a Leeds & Northrop pH meter is used to measure the negative cathode potential vs an S.C.E. A platinum gauze cathode small enough to be inserted in a well-type scintillation counter is employed. A 60-ml platinum crucible serves as both the plating vessel and the anode. Magnetic stirring is utilized, and provisions have been made for temperature control (25 to 100°C) of the bath.

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[37] H. W. Wright, "Analysis of Thorex Solutions by Gamma Spectrometry," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 11.

[38] B. Kahn and W. S. Lyon, "Use of a Scintillation Spectrometer in Radiochemical Analysis," *Nucleonics* 11(11), 61 (1953).

[39] J. R. Thomas and H. W. Crandall, *The Chelate Process*, CN-3733 (Oct. 10, 1946).

[40] F. L. Moore and J. E. Hudgens, Jr., *A Solvent Extraction Method for Plutonium Analysis*, ORNL-153 (Aug. 23, 1949).

[41] F. L. Moore, "Separation of Zirconium from Other Elements by Liquid-Liquid Extraction," submitted for publication in *Analytical Chemistry*.

[42] H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, *Instrumental Methods of Analysis*, 2d ed., p 246, Van Nostrand, New York, 1951.

ACTIVATION ANALYSES

G. W. Leddicotte

Use of Discriminatory Gamma Counting

W. A. Brooksbank S. A. Reynolds
G. W. Leddicotte

Sometimes radiochemical procedures do not provide sufficient decontamination to ensure radiochemical purity of the radioelements finally isolated. The measurement of the radioactivity therefore becomes a problem. If the matrix material has a low-neutron-capture cross section, it may contribute sufficient activity to make difficult the direct measurement of the activity of the contaminant element. For these reasons the method of discriminatory gamma counting was investigated.

Instrumentation for discriminatory gamma counting was described previously.[43] The comparator sample is scanned manually at an appropriate gain setting and at a window, or slit, width of 1.00 v. The most intense photopeak in the spectrum is used in the analysis. The photopeak is scanned at a wide slit by use of the motor-driven potentiometer; the energy–slit-width relationships used in discriminatory gamma counting are listed below:

Slit Width (v)	Pulse Height Setting, PHS Units (v)
1.00	4.0–100.0 (used in manual scan of comparator sample)
1.00	4.0–10.0
2.00	10.0–20.0
3.00	20.0–35.0
5.00	35.0–70.0
8.00	Over 70.0

The pulse height is then set for the mid-point of the photopeak, and the radioactivity of the sample is counted. The comparator samples are counted after all the unknown samples have been counted. Counting is continued until 10,000 counts have been recorded or until 10 min have elapsed, whichever occurs sooner. Instrumental conditions for the measurement of certain radioisotopes by discriminatory gamma counting are given in Table 1.

To date, discriminatory gamma counting has been compared with three other methods of gamma counting, namely, gamma scintillation counting in a well-type crystal,[44] photopeak-area measurement,[45] and integral counting above a certain gamma energy.[45] The results of a study in which Br^{82} (35.7 h) was used are shown in Table 2. The data of Table 2 show that the reproducibility of discriminatory gamma counting is as good as, or better than, that of other methods of counting at counting rates above 2000 counts/min. However, discriminatory counting decreases the sensitivity of activation analysis methods because the sensitivity is proportional to the ratio of the number of photons in the peak being measured to the total number of photons observed in the over-all spectrum. This can be a serious drawback.

[43] W. A. Brooksbank, S. A. Reynolds, and G. W. Leddicotte, "Discriminatory Gamma Counter," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 13.

[44] C. J. Borkowski, "Instruments for Measuring Radioactivity," *Anal. Chem.* **21**, 348 (1949).

[45] W. S. Lyon, "Single-Channel Gamma Scintillation Spectrometer," Method Nos. 2 00367, 5 00367, and 9 00367 (9-26-55), *ORNL Master Analytical Manual.*

TABLE 1. INSTRUMENTAL CONDITIONS FOR DISCRIMINATORY GAMMA COUNTING

Radioisotope	Degree of Amplification (Gain)	PHS, PHS Units (v)	Slit Width (v)	Photopeak Energy (Mev)
Np^{239}	32	18.5	2.00	0.090
Br^{82}	8	37.0	3.00	0.766
As^{76}	8	27.0	3.00	0.55
Ti^{51}	16	30.5	2.00	0.32
Al^{28}	8	85.0	8.00	1.80
Mg^{27}	8	41.3	4.00	0.84

TABLE 2. COMPARISON OF GAMMA DISCRIMINATORY COUNTING WITH OTHER METHODS OF GAMMA COUNTING

Gamma Counting Method	Instrumental Conditions			Gamma Activity of Br^{82} (counts/min/mg)	Mean Deviation	
	Degree of Amplification (Gain)	Pulse Height Setting, PHS Units (v)	Slit Width (v)		Counts/min/mg	Per Cent
Discriminatory	8	37.0	3.0	1.16×10^6	$\pm 0.02 \times 10^6$	1.7
Scintillation				9.11×10^7	$\pm 0.34 \times 10^7$	3.7
Integral	8	Integral over 31.0		6.81×10^6	$\pm 0.23 \times 10^6$	3.4
Photopeak-area measurement	8	20.0 to 40.0		$8.63 \times 10^{3*}$	$\pm 0.23 \times 10^{6*}$	7.1

*Determined, in counts/min/unit area, by plainimeter measurement.

Discriminatory gamma counting has the advantages of selecting the radioisotope being determined from among extraneous activities and giving low background counts. The reproducibility of data taken by the method is good. In instances of complex radiation spectra, it will sometimes be necessary to narrow the recommended slit opening in order to ensure that only one photopeak is being counted. In those cases where a contaminant photopeak is very close to the main peak under study, it is very often possible to measure a secondary photopeak of the radioisotope being determined.

In practice, discriminatory gamma counting has proved to be a valuable measurement method. Many analyses that would otherwise have to have been repeated because of contamination have been completed successfully by use of this new counting technique. The method will be used for all gamma measurements.

Neutron-Flux Determination

J. H. Oliver W. A. Brooksbank
G. W. Leddicotte

A new method for the determination of thermal neutron flux in Hole 10 of the ORNL Graphite Reactor has been devised.[46] Hole 10 is a vertical, water-cooled irradiation facility in the top face of the ORNL Graphite Reactor. It is sometimes expedient to measure the flux of this facility as a function of distance from the bottom of the hole in order to know the flux at which a series of samples for activation analysis has been irradiated. Typical data from an investigation in which dilute solutions of manganese were used are reported elsewhere.[46] Studies are being made on solutions of other metallic elements in order to confirm the results obtained.

Use of Short-Half-Life Radioisotopes in Analysis

W. A. Brooksbank J. H. Oliver

The previous report[47] described briefly the use of short-half-life radioelements in activation analysis. This work was extended to include studies of the usefulness of the short-half-life radioisotopes of cobalt and sulfur in quantitative activation analysis.

Determination of Cobalt. – The nuclear reaction $Co^{59}(n,\gamma)Co^{60m}$ (10.1 m) can be utilized in assays for microgram and submicrogram amounts of cobalt. Cobalt-60*m* is an isomeric state, and its transition to Co^{60} (5.3 y) is accompanied by gamma radiation of 0.059-Mev energy, which can be measured by discriminatory gamma counting.[43] Under the conditions of 10-min irradiation in the ORNL Graphite Reactor and measurement of the radiation 5 min after discharge of the sample from the reactor, the limit of detection of the method for cobalt is 0.09 μg. This limit can be extended downward by use of longer irradiation periods in the ORNL Graphite Reactor, after which the

[46] W. A. Brooksbank, J. H. Oliver, and G. W. Leddicotte, *Flux Measurement in Hole 10, ORNL Graphite Reactor*, ORNL CF-55-9-151 (Sept. 30, 1955).

[47] W. A. Brooksbank, "Determination of Microgram and Submicrogram Amounts of Aluminum, Magnesium, and Titanium in Nickel Oxide," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 14.

radiation induced in Co^{60} (5.3 y) is measured, or by irradiating the sample in the LITR.

Determination of Sulfur. – The nuclear reaction $S^{36}(n,\gamma)S^{37}$ (5.0 m) has been evaluated for use in the determination of microgram amounts of sulfur. This reaction was considered to be favorable, because it has a short saturation, or growth, factor and a gamma energy (2.75 Mev) suitable for measurement by gamma discriminatory counting.[43] Under the conditions of 50-min saturation irradiation in the ORNL Graphite Reactor and direct measurement of the irradiated sample 5 min after its discharge from the reactor, the limit of detection was no better than 250 μg. The small natural abundance of S^{36} (0.017%) and the small activation cross section for the reaction make this method less sensitive than those methods based upon the nuclear reactions $S^{34}(n,\gamma)S^{35}$ (87.0 d) and $S^{32}(n,p)P^{32}$ (14.3 d). Although the $S^{34}(n,\gamma)S^{35}$ reaction has the disadvantages that the induced radionuclide has a long half life (i.e., small growth factor during irradiation) and emits very weak beta radiations, it is possible to determine as little as 1.0 μg of sulfur after a one-week irradiation period. Likewise, as little as 1.0 μg of sulfur can be determined by the (n,p) reaction after a one-week irradiation, although the yield of epithermal neutrons in the ORNL Graphite Reactor is about 3%. The limits of detection of the above neutron reactions can be extended downward by irradiating the sample in the LITR.

Preirradiation Separation Methods in Activation Analysis

W. T. Mullins

Microgram amounts of manganese and of nickel in metallic sodium have been determined by methods similar to the one described previously.[48] The small amount of the element to be determined is separated from the sodium *before* the neutron irradiation by "carrying" it on a known amount of some element into which very little, if any, radioactivity is induced during the irradiation.

In the assay for manganese in sodium, iron(III) is added to the solution of the sodium sample and is precipitated as FeS, which carries the manganese. The FeS is dissolved, the solution is irradiated in the ORNL Graphite Reactor, and, after discharge of the solution from the reactor, the radioactive Mn^{56} (2.59 h), produced by the reaction $Mn^{55}(n,\gamma)Mn^{56}$, is separated by an isotopic-carrier procedure. The separated radioactivity is measured by gamma counting. In the assay for nickel the nickel is carried from a solution of the sodium on a Tl_2S precipitate. The precipitate is dissolved, and the solution is irradiated in the ORNL Graphite Reactor. The radioactive Ni^{65} (2.6 h), produced by the reaction $Ni^{64}(n,\gamma)Ni^{65}$, is separated by means of an isotopic-carrier procedure and is counted in a Geiger-Mueller counter. In each method of analysis, comparator samples are used. Also, blanks of the reagents used in making the preirradiation separations are irradiated and processed in a similar manner. By this method it has been possible to estimate concentrations of manganese and of nickel as small as 0.02 and 1.0 μg per gram of sodium, respectively. A factor for radioactivity "recovery" had to be applied in the final estimation of the nickel content of a sample because no more than 88% of the Ni^{65} tracer was carried by the Tl_2S precipitate. It is planned to investigate other carriers for nickel.

Use of preirradiation separation techniques in the assay of samples of high-cross-section elements almost entirely eliminates radiation hazards to personnel, which can arise if the sample is exposed to a high flux of neutrons. Also, these techniques increase the usefulness of activation analysis for the determination of those elements, such as nickel, for which activation analysis is not a sensitive method. In these instances, increased sensitivity could be obtained by evaporating the solution of the carrier element to dryness and irradiating the residue in the LITR. Such carriers as iron and thallium are useful in the determination of short-half-life radioelements because very little radioactivity is induced into them in the short irradiation times required.

Activation Analysis as a Qualitative or Semiquantitative Method

J. H. Oliver, M. M. Vick[49]
W. A. Brooksbank, G. W. Leddicotte

The progress of the investigation of activation analysis as a qualitative method has been re-

[48] J. E. Strain and G. W. Leddicotte, "Determination of Microgram and Submicrogram Quantities of Europium in Lithium Iodide by Neutron-Activation Analysis," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 15–16.

[49] Summer employee from Louisiana State University.

ported previously;[50,51] a brief description of the extension of this work follows.

Ion-Exchange Methods. – A qualitative identification scheme based upon the results of studies by Hicks *et al.*[52] of anionic complexes with HCl and Dowex 1 resin has been investigated further.[53] Solutions of irradiated material are placed on a Dowex 1 resin column, and the adsorbed ions are eluted with definite volumes of hydrochloric acid solutions of various molarities. Assays of cracking catalysts have been made. The contaminant elements cadmium, cobalt, chromium, iron, gallium, hafnium, indium, sodium, nickel, phosphorus, platinum, sulfur, antimony, scandium, silicon, strontium, tungsten, zirconium, and zinc were identified. At present, this particular scheme is considered unsatisfactory, because the ions do not separate out sharply into the various HCl eluates. The 12 *M* HCl eluate contained so many different activities that it was necessary to employ carrier separations to separate them further. This analysis scheme could possibly be used if the distribution of elements throughout the different eluates was known more definitely. Also, anionic complexes with such acids as hydrobromic and hydroiodic should be studied.

Precipitation Method. – An adaptation of Handley's precipitation method[54] has given the best results in the use of activation analysis as a qualitative method. Studies have been made on carriers or combinations of carriers that contained from 1 to 3 mg of the carrier element. These carriers are added to a solution of the irradiated sample; each carrier, together with those radioelements that are selectively precipitated with it, is separated by precipitation. The separated radioactivities are then measured by counting. The carriers usually employed are silver, copper, arsenic, cobalt, zinc, manganese, iron, yttrium, barium, and sodium. They are precipitated finally as AgCl; CuS; As_2S_3; a mixture of CoS, ZnS, and MnS; $Fe(OH)_3$; $Y_2(C_2O_4)_3$; and a mixture of $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$. The sodium remains in solution as a carrier for the soluble ions.

This particular procedure has been applied to the assay of thorium oxide for contaminant elements; copper, phosphorus, sodium, tungsten, rare earths, and fission products have been detected. The rare earths probably came from either fission or (n,γ) reactions on stable rare-earth isotopes. The fission products could be the result either of slow-neutron fission of Pa^{239}, U^{233}, or U^{235}, or of fast-neutron fission of Th^{232}. Also, copper, phosphorus, lanthanum, manganese, and sodium, and possibly gallium, holium, and dysprosium, were detected in samples of ammonium thorium oxalate by this method.

Determination of Metals in Petroleum

L. C. Bate J. H. Oliver
W. A. Brooksbank M. M. Vick
G. W. Leddicotte

Determination of Gold. – The nuclear reaction $Au^{197}(n,\gamma)Au^{198}$ (2.69 d) was used to determine microgram and submicrogram amounts of gold in petroleum. The irradiated samples were assayed by a direct-measurement method, which employed the discriminatory gamma counter;[55] comparator samples were used. The Au^{198} radioactivity was identified by half-life measurements and by gamma spectral analysis. As little as 0.04 μg of gold can be determined by this method. This limit could be extended downward by use of a radiochemical separation.

Determination of Copper. – The nuclear reaction $Cu^{63}(n,\gamma)Cu^{64}$ (12.8 h) has been used to determine microgram and submicrogram amounts of copper in petroleum. The irradiated samples were assayed by a direct-measurement method, which employed the discriminatory gamma counter.[55] The comparator-sample technique was used. The Cu^{64} radioactivity was identified by half-life measure-

[50] H. A. Mahlman and G. W. Leddicotte, "Use of Radioactivation Analysis as a Qualitative or Semiquantitative Analytical Method," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 16.

[51] M. M. Vick, H. A. Mahlman, and G. W. Leddicotte, "Use of Radioactivation Analysis as a Qualitative or Semiquantitative Analytical Method," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 18.

[52] H. G. Hicks *et. al.*, *The Qualitative Anionic Behavior of a Number of Metals with an Ion Exchange Resin, "Dowex 2,"* LRL-65 (Dec. 1953).

[53] M. M. Vick and G. W. Leddicotte, *Investigation of an Ion-Exchange Separation Procedure*, ORNL CF-55-9-152 (Sept. 30, 1955).

[54] T. H. Handley, "Qualitative Analysis Scheme," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1951*, ORNL-955, p 47.

[55] W. A. Brooksbank, S. A. Reynolds, and G. W. Leddicotte, "Discriminatory Gamma Counter," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 13.

ments. As little as 0.8 μg of copper can be determined by this method. The limit of detection of the method can be extended downward by use of a radiochemical separation procedure.

Determination of Nickel. – The loss of volatile nickel compounds during the ashing process used in the assay of petroleum for microgram amounts of nickel is of considerable interest.[56] It is generally agreed that nickel appears in petroleum as porphyrin compounds; therefore synthetic blends of tetraphenyl nickel porphyrin in mineral oil, in which the nickel content was known, were used in this investigation. Gross quantities of the oils were ashed by heating with sulfuric acid; the resulting ash was dissolved and the solution was irradiated. Also, the original oil samples were irradiated and then ashed. The amount of nickel recovered ranged from 22 to 30% of the amount known to be present. The loss is approximately the same when ashing included prolonged heating in a muffle furnace and when a sulfuric–nitric acid mixture was used on the activated oils. These treatments have one operation in common, namely, boiling with sulfuric acid. Therefore it appears that volatilization of the tetraphenyl nickel porphyrin occurs during this step. The possibility of trapping the volatile nickel compounds is being considered.

The possible determination of nickel in petroleums by means of the neutron reaction $Ni^{58}(n,p)Co^{58}$ (72.0 d) was also considered.[56] In preliminary studies it was found feasible to irradiate a sample of oil in the ORNL Graphite Reactor and, after the irradiation, to measure the gamma radioactivity associated with Co^{58}. This work is to be extended in order to determine the limit of detection of the method.

Determination of Arsenic in Low-Boiling Organic Liquids

W. A. Brooksbank J. H. Oliver

As previously reported,[57] arsenic can be determined by the nuclear reaction $As^{75}(n,\gamma)As^{76}$ (26.8 h); however, Br^{82} (35.7 h) interferes. In the determination of submicrogram amounts of arsenic in light oils and in acetone, this interference was almost entirely eliminated by a Parr bomb ignition of the irradiated sample, followed by a radiochemical separation involving distillation and final precipitation of the isotopic carrier as $MgAsO_4$. The results of a series of assays of light oil and of acetone samples showed a range of arsenic concentration from 1 to 35 ppb.

Determination of Iron in Hafnium and in Zirconium

W. T. Mullins

Microgram amounts of iron were determined in zirconium, in hafnium, and in their alloys by the nuclear reaction $Fe^{58}(n,\gamma)Fe^{59}$ (47.1 d). The samples were irradiated in either the ORNL Graphite Reactor or the LITR for at least one week and were then processed by an isotopic-carrier procedure. The Fe^{59} radioactivity was measured by gamma counting. The comparator-sample procedure was used. As little as 0.25 μg of iron can be determined by this method.

In these determinations, the decontamination of radioactive zirconium (or hafnium) from the small amount of induced Fe^{59} was a problem; also, it was difficult to establish which compound of iron was most suitable for counting. Table 3 shows the results of decontamination studies in which Zr^{95} (65.0 d) tracer and an isotopic-carrier procedure were used. From these studies it was concluded that decontamination could be achieved best by two or three isopropyl ether extractions of the iron, precipitation of the iron as $Fe(OH)_3$, and ignition of the final $Fe(OH)_3$ precipitate to Fe_2O_3. Contaminant amounts of other iron compounds, such as Fe_3O_4, in the Fe_2O_3 residue were shown to have little, if any, effect on the iron assay. Iron can be determined in other materials by this same method.

Determination of Tungsten in Hafnium and in Zirconium

W. T. Mullins

Microgram amounts of tungsten were determined in hafnium, in zirconium, and in zirconium alloys by the nuclear reaction $W^{186}(n,\gamma)W^{187}$ (24.1 h). The samples were irradiated in the ORNL Graphite Reactor for at least 16.0 hr and were then processed by an isotopic-carrier procedure. The comparator-sample technique was used. The separated W^{187} can be measured by either gamma

[56] M. M. Vick and G. W. Leddicotte, *The Use of Activation Analysis in Determining Volatility Losses of Nickel in Petroleums*, ORNL CF-55-9-153 (Sept. 30, 1955).

[57] J. E. Strain, W. A. Brooksbank, and L. C. Bate, "Determination of Nonmetals in Petroleum," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 15.

TABLE 3. RESULTS OF DECONTAMINATION OF RADIOACTIVE ZIRCONIUM FROM RADIOACTIVE IRON

Separation Method[a]	Number of Determinations	Zr^{95} Carried on Fe_2O_3[b] (% of total Zr^{95} added)
Mercury cathode	3	0.2, 2.4, 1.0
Three ferrous oxalate precipitations	2	0.2, 0.3
Two zirconium mandelate precipitations	2	0.2, 0.02
One isopropyl ether extraction	3	0.5, 0.05, 0.005
Two isopropyl ether extractions	3	None[c]
Three isopropyl ether extractions	3	None[c]

[a]Following each separation procedure, iron wos precipitated as $Fe(OH)_3$, which was ignited to Fe_2O_3.

[b]Zr^{95} was determined by gamma counting.

[c]Equivalent to complete decontamination.

scintillation or discriminatory gamma counting.[55] Typical results are shown below (the sample was prepared by the Metallurgy Division; the estimated tungsten concentration was 25.0 μg/g):

Sample	Number of Determinations	Tungsten Concentration (μg/g)
Zr standard	12	30.5 ± 1.5
Zr getter	4	3.0 ± 0.1

In the assay of samples other than zirconium, tungsten was determined in concentrations as small as 2 μg/g. However, there appeared to be a wide range in the results obtained for various portions from the same sample. From the activity data obtained in the analyses reported above, it is estimated that as little as 0.04 μg of tungsten can be determined by this method. This limit can be extended downward by the use of irradiation facilities in the LITR. The nuclear reaction $W^{184}(n,\gamma)W^{185}$ (73.2 d) can also be used in this analysis.

Determination of Bromine in Sea Water

J. H. Oliver W. A. Brooksbank

Microgram and submicrogram quantities of bromine in samples of water from the Pacific Ocean and from the Sacramento River estuary have been determined by the nuclear reaction $Br^{81}(n,\gamma)Br^{82}$ (35.9 h). In preliminary analyses, gamma-ray spectroscopy[58] was used in an attempt to measure directly the radioactivity in the irradiated sample. Sodium-24 (15.0 h), induced into the Na^{23} of the sea water, interfered. Two ion-exchange methods were evaluated for the elimination of this interference. One employed a cation-exchange resin, Dowex 50, to separate the Na^{24} from the Br^{82} by elution of the Br^{82} with H_2O; the other employed the anion-exchange resin, Dowex 1, to retain the Br^{82} on the column. In each procedure, the radiochemical purity of the separated activity was confirmed by gamma spectral analysis. Results obtained in the assay of a large number of samples by both procedures confirmed results obtained by chemical analysis; the bromine content of the samples ranged from 0.08 to 13 μg/ml.

Determination of Milligram Amounts of Certain Elements in Milligram-Sized Samples

L. C. Bate J. E. Strain[59]
W. A. Brooksbank G. W. Leddicotte

The feasibility of using activation analysis to assay small amounts (milligrams or, at most, fractions of a gram) of a sample for milligram amounts of an element has been demonstrated. The assays reported herein would have required

[58]B. Kahn and W. S. Lyon, "Use of a Scintillation Spectrometer in Radiochemical Analysis," *Nucleonics* 11(11), 61 (1953).

[59]U.S. Navy.

micro or semimicro procedures if made by conventional chemical methods. Also, activation analysis permitted the qualitative detection of contaminant elements, which are not always easily detected by conventional methods.

Loop Corrosion Products. – Milligram amounts of a corrosion product, Fe_3O_4, from a circulatory loop were assayed for nickel, silicon, cobalt, and manganese. All analyses of the neutron-irradiated material were made by isotopic-carrier separations. Activity measurements for the separated Ni^{65} (2.6 h) and Si^{31} (2.7 h) were made by means of a Geiger-Mueller counter, for Mn^{56} (2.59 h) by a gamma scintillation counter, and for Co^{60} (5.3 y) by the gamma discriminatory counter.[60] The comparator-sample technique was used in all assays. Typical results showed that the sample contained 0.003 mg of manganese, 0.011 mg of nickel, 0.005 mg of silicon, and 2.0×10^{-3} μg of cobalt per milligram. Iron was determined colorimetrically, and the concentration was of the order of 0.60 mg/g.

Ion-Exchange Resins. – Macro amounts of manganese, cobalt, potassium, sodium, aluminum, nickel, copper, bromine, chlorine, and iodine were determined in ion-exchange resins that were of interest in a study of the ionic selectivity of cross-linked ion exchangers (submitted by G. E. Myers and G. E. Boyd, Chemistry Division). The end products of the respective neutron reactions, that is, Mn^{56} (2.59 h), Co^{60} (5.3 y), K^{42} (12.4 h), Na^{24} (15.0 h), Al^{28} (2.3 m), Ni^{65} (2.6 h), Cu^{64} (12.8 h), Br^{82} (34.7 h), Cl^{38} (38.5 m), and I^{128} (25.0 m), were favorable for an assay by direct measurement of the irradiated sample in the discriminatory counter.[60] The comparator-sample technique was used. The results showed that these elements were present in concentrations ranging from 0.009 to 0.30 mg/g.

Determination of Nickel in Zirconium

G. W. Leddicotte

By the neutron reaction $Ni^{64}(n,\gamma)Ni^{65}$ (2.59 h), microgram and submicrogram amounts of nickel were determined in 0.30-g, or smaller, samples of zirconium metal that originated from a zone-melt study by the Metallurgy Division. The samples were irradiated in the LITR and were then dissolved in acid in the presence of inactive nickel carrier. Portions of the solutions were analyzed by a radiochemical separation method. The comparator-sample technique was used, and the separated radioactivity was measured by means of a Geiger-Mueller counter. As little as 0.2 μg of nickel was determined, with a relative standard deviation of 5%.

Particle-Size Distribution

R. E. Druschel J. H. Davidson
G. W. Leddicotte

Several points in question regarding the proposed method for the determination of particle-size distribution in thorium oxide–water slurries[61] have been clarified. For samples of submicrogram particle size it has been shown that the amount of radioactivity remaining in the solution after the determination is so small (less than 1% of the total activity) that the results of the determination are not affected. Dispersion of the particles by air sparging was found to be equivalent to the dispersion resulting from 25 manual inversions. A suitable procedure was developed for determining the particle-size distribution at zero time (start of sedimentation).

Another method for the determination of particle-size distribution, which is rapid and precise, has been developed. It is similar to the method proposed earlier;[61] however, the apparatus has been modified to permit the vertical movement of the counter up and down the sedimentation tube. Approximately 2 hr is required for the completion of a single determination as compared with about 62 hr for six determinations by the first method proposed.[61]

The activation analysis–sedimentation method of determining particle-size distribution is being compared with optical methods and with the Andreasen pipet method; glass beads, aluminum oxide, and cerium oxide are used to make the comparisons.

[60] W. A. Brooksbank, S. A. Reynolds, and G. W. Leddicotte, "Discriminatory Gamma Counter," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 13.

[61] G. W. Leddicotte and H. H. Miller, "Particle-Size Distribution," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 21.

Detection of Cobalt Segregation in Gold–Cobalt Wire by Neutron Activation–Autoradiography

W. A. Brooksbank J. H. Oliver
G. W. Leddicotte

By the neutron activation–autoradiographic technique described earlier,[62] gold–cobalt wire was inspected qualitatively for segregation of cobalt. The Au^{198} (2.69 d), produced by the reaction $Au^{197}(n,\gamma)Au^{198}$, was allowed to decay out so that Co^{60} (5.3 y), the product of the reaction $Co^{59}(n,\gamma)Co^{60}$, would be the radionuclide autoradiographed. The results confirmed the existence of cobalt segregation, which had been indicated by activation analysis.

New Applications of Activation Analysis

G. W. Leddicotte

Inquiries were received regarding the suitability of activation analysis for the determination of contaminant elements in the following: titanium metal, ceramics, coffee beans, biological specimens, tin metal, and thorium oxide. Samples have been accepted for the determination of contaminant amounts of gadolinium, samarium, and dysprosium in yttrium oxide; copper and nickel in chromium; tantalum in silicon; and halogens in low-boiling organic liquids. Information was requested regarding the use of activation analysis to determine krypton, xenon, and argon in mixtures of gases.

Determination of Niobium and Tantalum in Minerals by Isotope Dilution

W. L. McPherson

An isotopic dilution method was evaluated for the determination of microgram amounts of niobium in minerals.[63] This method would supplement activation analysis methods, which are not particularly sensitive. Tantalum can also be determined by the same method. Radioactive tracers of these elements are mixed with ilmenite or with ilmenorutile, and the mineral is decomposed. The niobium and tantalum are separated by means of a sulfuric acid–hydrofluoric acid–organic extractant. The lack of suitable equipment for handling the solvent system, as well as information concerning the separation of titanium, caused the precision of results obtained by this method to be poor.

SPECTROCHEMICAL ANALYSES

C. Feldman

Sifter Electrode Procedure: Improvement in Uniformity of Feed Rate

J. Y. Ellenburg C. Feldman

The rate of flow of particles through the sifter electrode[64,65] should be uniform if precise and accurate analytical results are to be obtained. Batches of carbon and graphite occasionally became compacted in the electrode and flowed erratically, if at all. Tests showed this behavior to be caused by insufficient atmospheric humidity. Carbon and graphite samples that had been dried by ignition always flowed irregularly, whereas the samples, if stored overnight at 50 to 75% relative humidity, flowed uniformly.

Rapid Separation of Microgram Quantities of Rare Earths from Gram Quantities of Uranium Present in Homogeneous Reactor Fuels (Nitrated Cellulose – Batch Adsorption Method)

J. Y. Ellenburg

The procedure previously developed for separating microgram quantities of rare earths from thorium[66] was found to be applicable to the separation of rare earths from uranium if the uranium was present as the nitrate, but not if it was present as the sulfate. In order to collect rare earths from HR fuels by this procedure, it is therefore necessary to separate them from the sulfate ions.

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[62] G. W. Leddicotte, T. C. Rains, and T. Willmarth, "Use of Autoradiography in Activation Analysis," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1953*, ORNL-1639, p 13.

[63] W. L. McPherson (G. W. Leddicotte), *Attempts to Apply an Isotope Dilution Technique to the Determination of Niobium and Tantalum in Minerals*, ORNL CF-55-9-142 (Sept. 30, 1955).

[64] C. Feldman and J. Y. Ellenburg, "The 'Sifter' Electrode and Its Application to the Determination of Boron in Graphite and Carbon," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 21.

[65] J. Y. Ellenburg and C. Feldman, "Determination of Boron in Carbon and Graphite," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 26.

[66] C. Feldman, "Separation of Rare Earths from Thorium by Adsorption on Activated Cellulose, Batch Method," Method No. 1 00705 and 9 00650 (3-23-55), *ORNL Master Analytical Manual.*

Determination of Microgram Quantities of Rare Earths in Rare-Earth Mixtures: Spark Method

J. Y. Ellenburg C. Feldman

The best sensitivity and precision for the spectrographic determination of gadolinium, dysprosium, and samarium were obtained by evaporating solutions on the ends of waterproofed graphite rods and sparking the rods in an argon–oxygen atmosphere. Since one component of a mixture of rare earths often caused a shift in the working curve of another when the sample size was small, attempts were made to swamp out this effect by the addition of a foreign element (swamping agent). Because 5 μg of lanthanum was found to affect the intensities of Sc 3372, Gd 3422, Dy 3531, and Sm 3624 lines markedly and in various degrees, the efficacies of several swamping agents were tested by noting the effect on line intensity of adding 5 μg of lanthanum when the swamping agent was already present. The ratio f_x, describing the effect of swamping element x on a given line, is defined as

$$f_x = \frac{\text{Intensity of line in presence of 30 } \mu\text{g of } x + 5\ \mu\text{g of lanthanum}}{\text{Intensity of line in presence of 30 } \mu\text{g of } x} .$$

The ideal swamping element is one which gives f_x values which are high and identical for all the rare-earth lines tested. Experimental values of f_x for several elements are given in Table 4. Zinc appears to be the most promising swamping agent; however, quantities of the swamping agent other than 30 μg are yet to be considered.

The present limits of detection for gadolinium, dysprosium, and samarium, when each is alone on the electrode, are as follows: Gd, 0.1 μg; Dy, 0.1 μg; and Sm, 0.3 μg. The intensity ratios Gd 3422/Sc 3372, Dy 3531/Sc 3372, and Sm 3624/Sc 3372 are reproducible to within ±2%.

Mechanism of the Porous-Cup Discharge

C. Feldman

High-speed, color motion pictures have shown that when a porous-cup discharge is excited by a triggered, d-c pulsed discharge [porous-cup electrode (PCE) = anode], the sequence of events is as follows: Soon after the trigger-spark breakdown occurs, a jet of incandescent aqueous vapor is emitted from the PCE surface, and a jet of carbon vapor is emitted from the counter electrode surface. The jet from the PCE seldom originates at the point of impact of the trigger spark; the counter jet usually, but not always, does. As the power stored in the main condenser begins to pour through the gap, "feelers" from the spark channel find their way to these jets, and the discharge channel thenceforth coincides with the axes of these jets. The PCE jet advances into the gap at a velocity equal to or less than 3.4 m/sec when the current pulse is 11 amp high and lasts for 940 μsec. The counter (i.e., cathode) jet is much more rapid; it can deflect or repress the PCE jet, depending upon the angle of the encounter. The geometry of the encounters between these jets probably has an important influence on the precision of line-intensity ratios in spectrochemical analysis.

TABLE 4. VALUES OF SWAMPING FACTOR f_x FOR RARE-EARTH LINES

Spectral Line	Value of f_x for						
	Cu	Zn	Au	Ga	Ge	Ag	Li
Sc 3372	0.46	0.69	1.23	1.51	0.91	1.08	1.45
Gd 3422	0.57	0.69	0.63	0.78	0.50	0.50	0.73
Dy 3531	0.59	0.72	0.97	1.08	0.78	0.83	1.03
Sm 3624	0.66	0.92	<0.1	1.00	0.67	0.54	0.84

INORGANIC PREPARATIONS

D. E. LaValle

Special Preparations

D. E. LaValle

For the Nuclear Chemistry Group of the Chemistry Division, 100 g of potassium perrhenate ($KReO_4$) was converted to potassium chlororhenite (K_2ReCl_6)[67] and 100 g of RbI to $RbBrO_3$. For the Fused Salts Group of the Chemistry Division, a total of about 700 g of the chlorides, sulfates, and bromates of rubidium was converted to RbI. A quantity of 480 g of CsCl was converted to CsI, which, after use, was converted to CsBr.

For the Nuclear Physics and Neutron Diffraction Group of the Physics Division, 200 g of anhydrous $FeBr_2$ (ref. 68) and 100 g of anhydrous $MnBr_2$ were prepared. Also, for the same group, numerous attempts were made to produce $SrFeO_3$ (strontium perferrite) with 100% quadrivalent iron (ref. 69), but 90% was the maximum yield achieved.

For the Special Projects Group of the Solid State Division, 10 g of high-purity Li_3N was prepared.

Miscellaneous Preparations and Purifications

R. H. Sampley

The materials listed below were either prepared or purified in pound quantities, except as indicated otherwise, for the Physics Division.

Purified	Prepared
LiCl	LiCl, g
$Th(NO_3)_2$, 100 g	$MgCl_2$, g
$(NH_4)_2CO_3$	Li_2CO_3
Tri-*m*-tolyl phosphate, 500 ml	TlI, g
Pb (metal), 100 g	Li_2S, g
HI, liter amounts	$InCl_3$, g
Ca (metal), 100 g	In_2S_3, g
Phenyl clyclohexane, 250 ml	$Pb(ClO_4)_2 \cdot 3H_2O$, 500 ml of saturated solution
	HI
	LI (anhydrous)
	Phosphors: Activators:
	LiF $In_2O_3 + Li_2S$
	LiF $In_2S_3 + Li_2S$

Various other inorganic chemical work was done for the Physics Division. A solution of Li^6Cl was analyzed for Li^6 content. The weight loss of ferrite on ignition at 1000°C was determined. Baths for electroplating gold, silver, nickel, and copper were prepared, and small parts were electroplated by use of them. Various alloys used in the fabrication of apparatus were identified.

OPTICAL AND ELECTRON MICROSCOPY

T. E. Willmarth

T. G. Harmon F. Toomer

Electron Microscopy and Particle-Size Determination of Thorium Oxide

The microscopy of thorium oxide has continued to be of interest not only relative to particle-size determinations but also to changes in the shape and in other physical characteristics of thorium oxide that result from the methods of preparation and from the length of loop runs. A large number and variety of samples were examined. A few of the studies made are discussed below.

A series of electron micrographs were taken to show how the size, shape, and uniformity of thorium oxide particles are related to the temperatures. Figure 2 shows four thorium oxide samples prepared at a calcination temperature of 400°C and at precipitation temperatures in the range 10 to 100°C. Note the uniformity of particle size and shape of the material precipitated at 10°C.

Electron micrographs (Fig. 3) were made of thorium oxide from dried slurry that was scraped from the walls of a loop after an extended run. The results indicated that the thorium oxide agglomerates of irregular shape and nonuniform size, which were used as starting material, became spheroidal or ellipsoidal agglomerates of uniform size by movement in the flow stream and that they plated out on the walls in this shape.[70]

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[67] H. S. Booth (ed.-in-chief), *Inorganic Synthesis*, vol 1, p 178–179, McGraw-Hill, New York, 1939.

[68] G. P. Baxter, T. Thorvaldson, and V. Cobb, "A Revision of the Atomic Weight of Iron," *J. Am. Chem. Soc.* **33**, 319 (1911), esp pp 319, 328, 335.

[69] R. Scholder and W. Klemm, "Über neue Metallate mit Sauerstoff und Fluor als Liganden," *Angew. Chem.* **66**, 461 (1954), esp p 465.

[70] T. E. Willmarth, *Examination of Material Removed from Wall of C-Loop*, ORNL CF-55-5-190 (May 27, 1955).

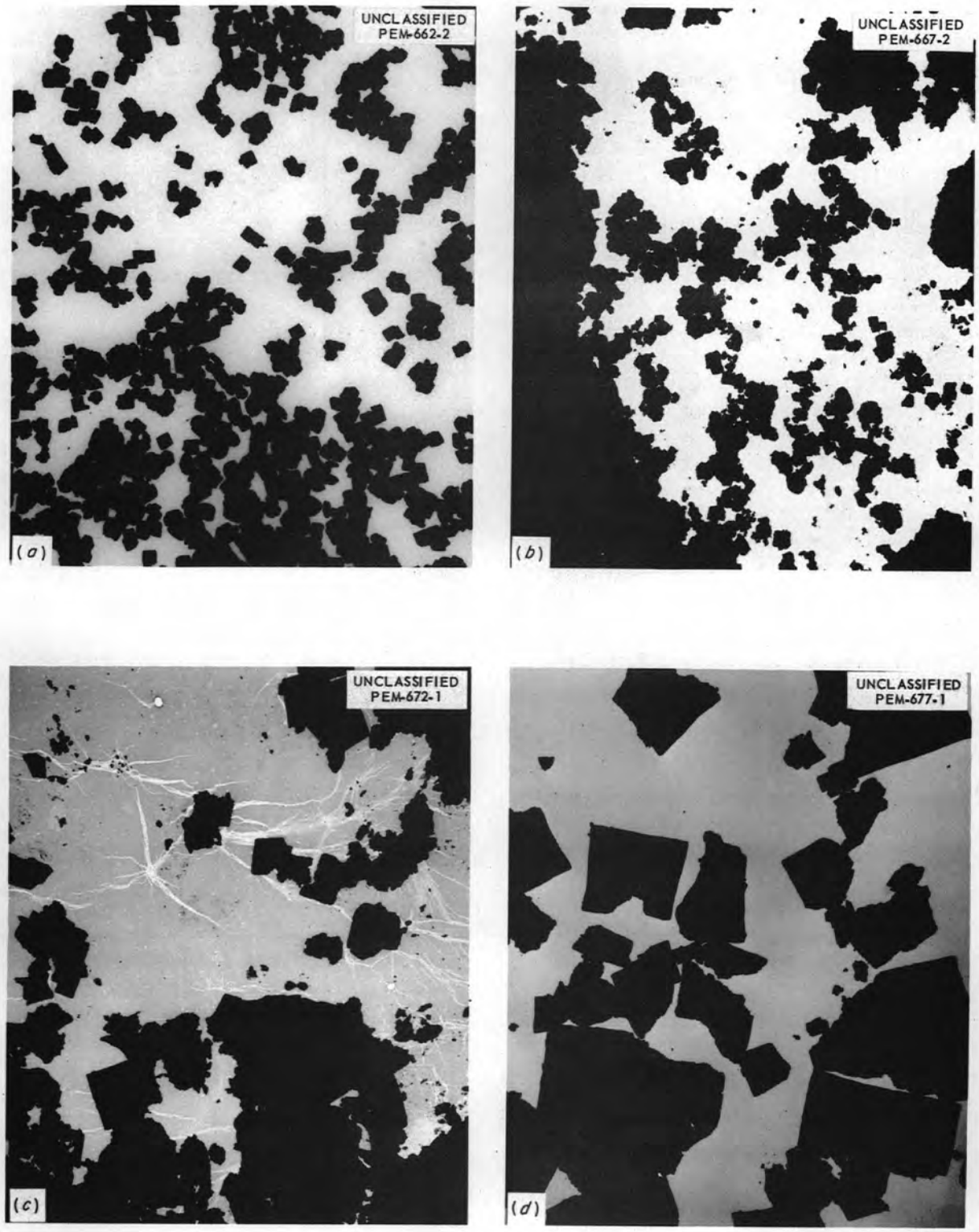

Fig. 2. Effect of Precipitation Temperature on Particle Size of Thorium Oxide Calcined at 400°C (4000 X). (*a*) Precipitated at 10°C. (*b*) Precipitated at 40°C. (*c*) Precipitated at 70°C. (*d*) Precipitated at 100°C.

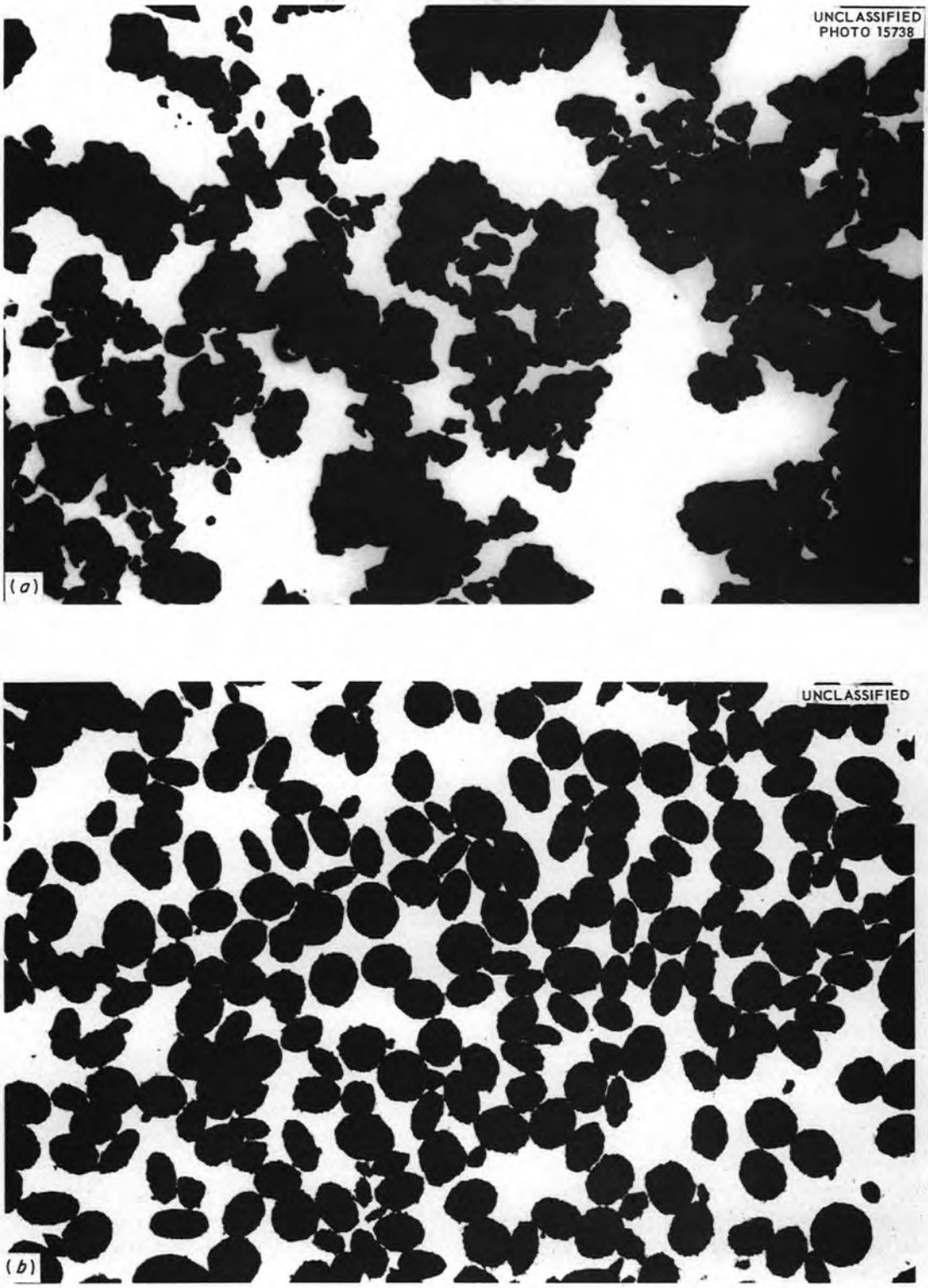

Fig. 3. Changes in Particle Size and in Shape of Thorium Oxide During a Loop Run (9000 X). (*a*) Unpumped ThO_2 starting material used in C loop. (*b*) Pumped ThO_2 from C loop.

A series of samples was micrographed to determine the size degradation of thorium oxide as a function of time of the thorium oxide in the loop. Pronounced degradation in particle size was shown to occur during a run. When the thorium oxide particles of particle-size range 0.3 to 7.0 μ were inserted in the loop, they were broken down to secondary particles of approximately 150-Å particle size. It appears that a pronounced breakdown starts after about 23 hr and continues thereafter.[71]

The mechanics of the growth of uniformly shaped thorium oxide agglomerates was studied. Figure 4 shows typical electron micrographs, obtained by the shadowcasting technique, that were used to determine the ratio between the growth of the particles in the horizontal direction and that in the vertical direction.[72]

Studies of Oxide Films and Corrosion Products

Study of oxide films and corrosion products formed on metals of interest in reactor technology was continued. Electron diffraction examination of a bulk oxide formed on a coupon of type 304L stainless steel that had been exposed to a uranyl sulfate solution in the presence of Li_2SO_4 at 300°C indicated that the bulk oxide was chiefly 1:1 $Cr_2O_3 \cdot Fe_2O_3$. The films on Inconel pins before and after the pins were heated to 1750°F in a hydrogen atmosphere were examined. The thin oxide film formed on the unheated Inconel pins was identified as Fe_2O_3, together with small amounts of Cr_2O_3 and Fe_3O_4, whereas the film on the heated pins was principally Fe_3O_4.

Other corrosion products examined included nickel anodes, crystalline material from the walls of the HRT mockup pressurizer, material from the walls of thorium oxide slurry loops, and the bulk oxide formed on Zircaloy in-pile test coupons.

Optical Microscopy and Autoradiography

Various materials were examined with the optical microscope. These included ion-exchange resins, glass beads, polystyrene spheres, specimens of Zircaloy, titanium, stainless steel, mild steel, Inconel, nickel–beryllium alloy, nickel, copper, rare-earth crystals, crystals of a uranium sulfate–copper sulfate complex ascertained to be johannite, titanium oxide, and glass capillary tubes.

Autoradiographs were made of Inconel and gold that had been irradiated, of plutonium oxide that was deposited on the walls of a metal liner, and of air filters from hot cells.

New Methods and Techniques

Optical and electron microscopy is concerned with obtaining information about micro- and submicroquantities of a great variety of unrelated materials. New techniques to meet specific problems and improvements to existing methods are being sought constantly. Development work has been done on the following:

1. the production of thin carbon films able to withstand the temperatures reached at the sample plane when the electron beam is brought to sharp focus by the microscope condenser lens,
2. a method of stripping oxide films from Zircaloy,
3. a modification of the technique for stripping oxide film from stainless steel and Inconel,
4. an electron etch to reveal the grain structure of Zircaloy,
5. an electron microscope screen holder for use in shadowcasting and in making silica replicas,
6. a meter for use with the Philips electron microscope to establish accurately the input voltage,
7. the replacement of the 45-v dry bias battery in the Philips electron microscope by a 45-v cadmium–mercury battery in a shielded and grounded case, mounted outside the microscope, to ensure better instrument stability,
8. preliminary work on a method of correlating apparent crystallite size with the line-broadening in electron diffraction patterns; Fig. 5 shows four sizes of submicro thallous chloride crystallites, evaporated in the electron microscope from thallic chloride, and the electron diffraction patterns of these areas,
9. preliminary work with the use of ultrasonics to disperse particles for electron microscopy observation, some of the effects already noted being: (1) the dispersion of thorium oxide particles in high-frequency sound fields tends to reduce the movement of the suspended particles; (2) hydrogen peroxide is apparently formed in the distilled water that is used as a suspension medium; and (3) the temperature of the liquid suspension medium is appreciably increased with prolonged exposure in the sound field.

[71] T. E. Willmarth, *Degradation of ThO2 in C Loop*, ORNL CF-55-7-23 (July 6, 1955).

[72] T. E. Willmarth, *To Determine the Thickness of ThO2 Particles in Relation to Precipitation Temperatures*, ORNL CF-55-7-21 (July 6, 1955).

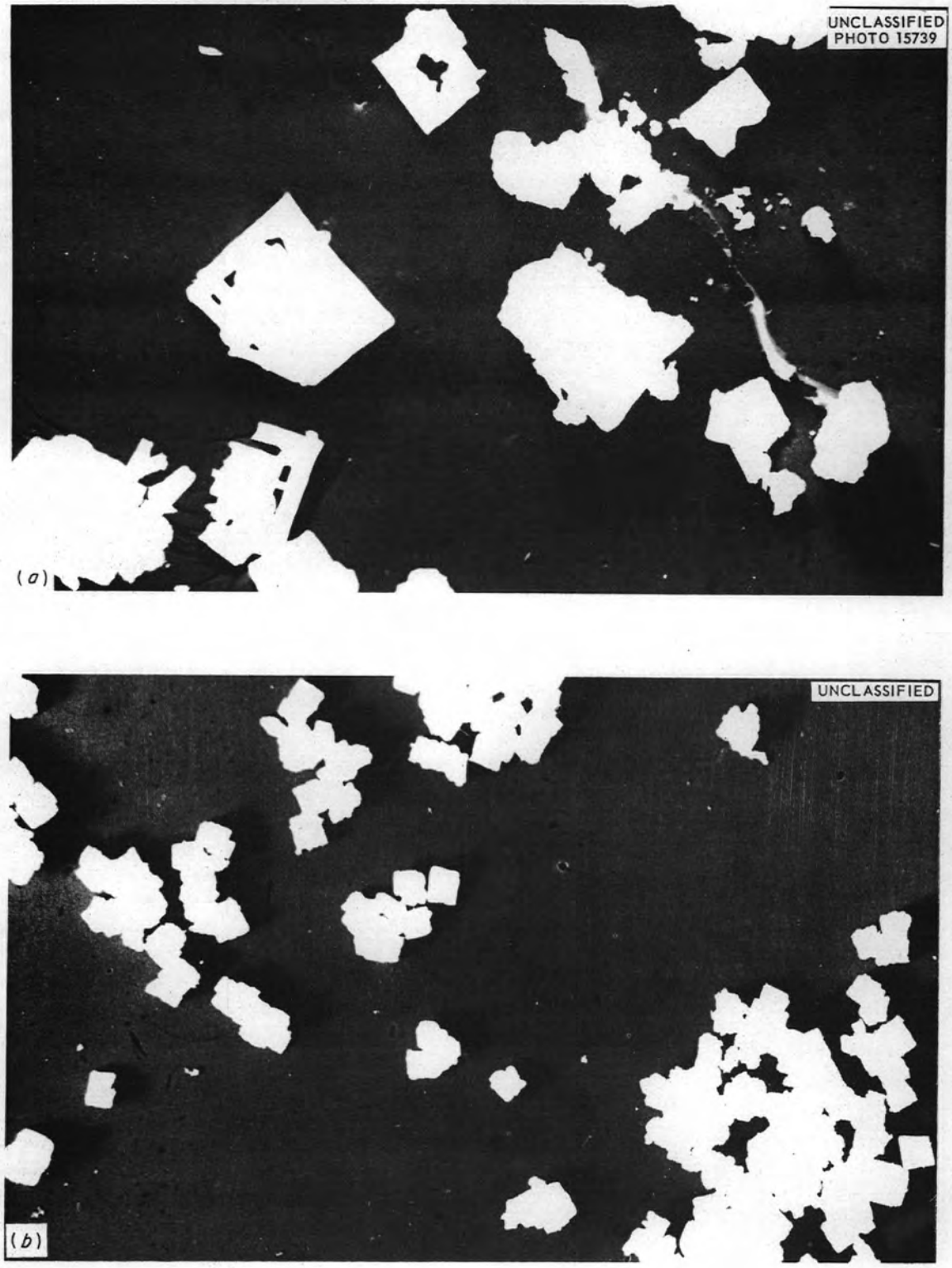

Fig. 4. Thorium Oxide Particles Shadowcast with Gold-Manganin for Thickness Determinations (9300 X). (*a*) ThO_2 precipitated at 70°C, calcined at 400°C. (*b*) ThO_2 precipitated at 10°C, calcined at 400°C.

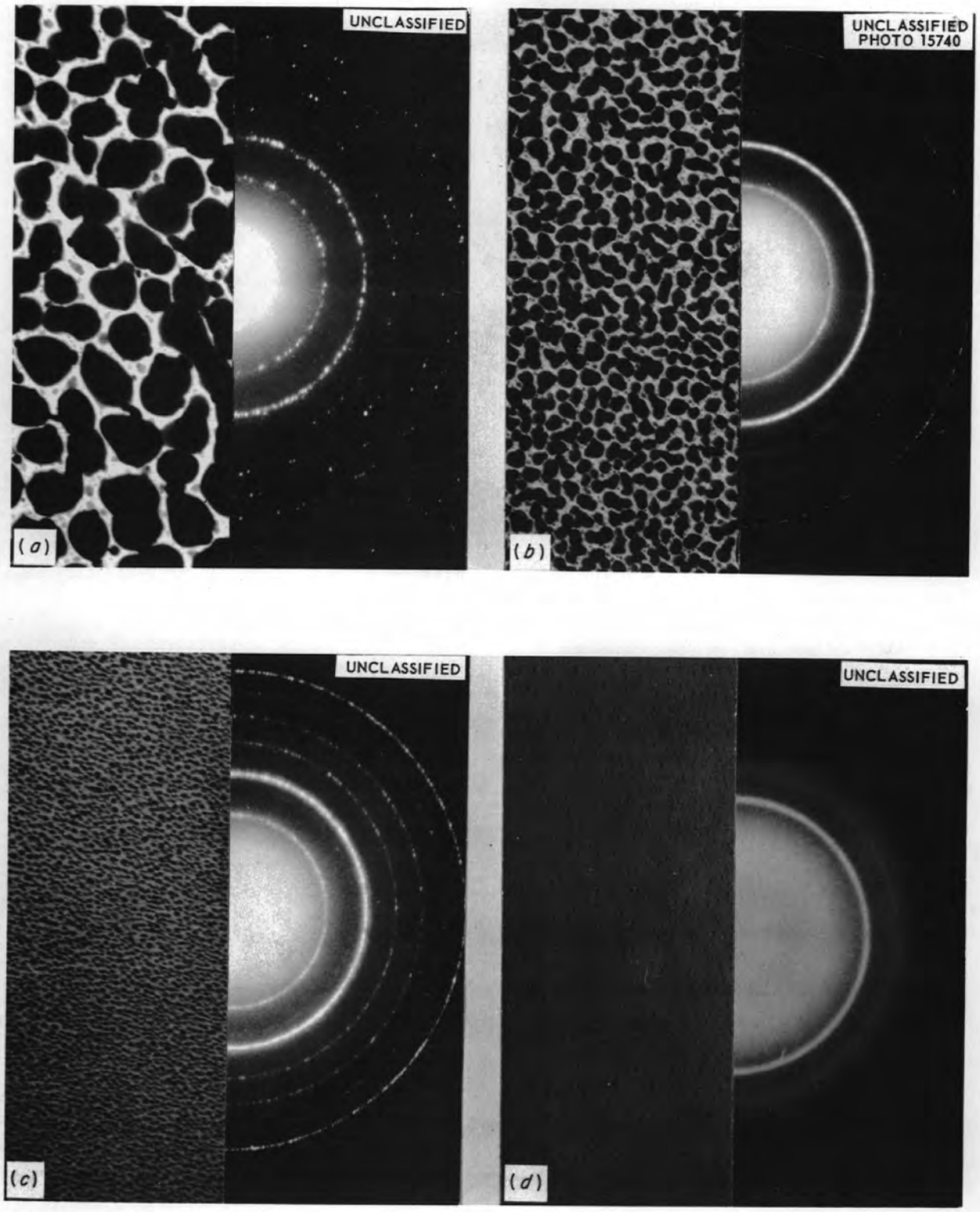

Fig. 5. Changes Produced in Electron-Diffraction Patterns of Thallous Chloride as a Function of Particle Size (46,000 X). (*a*) Apparent crystallite size, 1300 Å. (*b*) Apparent crystallite size, 400 Å. (*c*) Apparent crystallite size, 200 Å. (*d*) Apparent crystallite size, 150 Å.

ORNL MASTER ANALYTICAL MANUAL

Authors of Methods

H. P. Raaen H. P. House

Eight new methods have been issued to the *ORNL Master Analytical Manual* (see "Presentations of Research Results"). Drafts of more than 45 other new methods have been edited. Thirteen new manuals were issued. An inventory of the contents of all copies of the *ORNL Master Analytical Manual* at Oak Ridge plant sites is very nearly completed.

SERVICE ANALYSES

A semiannual summary of the service analyses made at the X-10 laboratories of the Analytical Chemistry Division is given in Table 5.

IONIC ANALYSES

P. F. Thomason

Most of the service work of the Ionic Research and Development Group continued to be for the Chemistry Division relative to their phase and corrosion studies for the HRT. The methods that were used can be found in the *ORNL Master Analytical Manual.*

RADIOCHEMICAL ANALYSES

S. A. Reynolds

Of the service analyses done by the Radiochemical Analyses Group, 67% was for three ORNL divisions. Determinations of cyclotron-produced activities were performed for the Electronuclear Research Division. Nondestructive measurement of plutonium constituted most of the work for the Chemical Technology Division. For the Reactor Experimental Engineering Division, determinations of neutron flux were made. Further details are included in this report (see "Radiochemical Analyses").

ACTIVATION ANALYSES

G. W. Leddicotte

The Activation Analyses Group determined the following elements in a variety of materials: antimony, arsenic, copper, cobalt, zinc, phosphorus, iron, chromium, silver, gold, chlorine, bromine, thorium, silicon, tungsten, sodium, potassium, tin, mercury, uranium, tantalum, nickel, manganese, molybdenum, rare earths, and gallium. In addition, the particle-size distribution in a large number of thorium oxide slurry samples was determined. Also, neutron activation–autoradiographic techniques were applied to the detection of cobalt segregation in gold–cobalt wire.

GENERAL ANALYSES LABORATORY

J. H. Edgerton

General Analyses

J. H. Edgerton P. V. Hoffman
L. C. Henley H. G. Davis
J. E. Lee, Jr. J. F. Emery
G. A. Westerdahl

In the General Analyses Laboratory, a bromination–carbon-reduction apparatus has been installed for the determination of oxygen. It is a modification of that reported by Codell and Norwitz[1] and of the one used by G. Goldberg and J. P. Young of the Analytical Chemistry Division. It is particularly well suited for the analysis of metals and alloys having vapor pressures such that only with great difficulty can they be determined by vacuum fusion. The apparatus has been used for the determination of oxygen in manganese–antimony and lead–calcium alloys and in uranium carbide.

Additional fluoride pyrohydrolysis units and an apparatus for the determination of water of crystallization in fluoride salts have been built.

An unusually large number of potentiometric determinations of boron, chloride, and uranium constituted the major portion of the analytical work. In addition, alloys and special samples were analyzed by absorption and flame spectrophotometry and by gravimetric, polarographic, and volumetric methods. A total of 35 elements or anions was determined by these methods.

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[1] M. Codell and G. Norwitz, *Determination of Oxygen in Titanium and Titanium Alloys*, NP-5450 (Aug. 20, 1954).

TABLE 5. SUMMARY OF ANALYTICAL SERVICE WORK AT X-10 FOR THE PERIOD ENDING OCTOBER 20, 1955

	Number of Personnel		ORNL Divisions Requesting Analyses																			Others Requesting Analyses						
	Technical	Nontechnical	Analytical Chemistry	Applied Nuclear Physics	ARE	Biology	Chemical Technology	Chemistry	Electronuclear Research	Engineering and Mechanical	General Office	Health Physics	HRP	Laboratory Protection	Materials Chemistry	Metallurgy	Operations	Physics	REED	Stable Isotopes	Solid State	General Electric	K-25	Others	ORINS	Research Director's	Y-12	Total Determinations
Group Making Analyses			Number of Determinations																									
Activation Analyses*	4	5	676	7			403	37				24			13	307	657	25	105		135		4					2,393
General Analyses	7	6			285		337	233		34		394				3803	376	58			416							5,936
Ionic Analyses*	6	1	8				236	465			45					4		62	5	25	21							871
Laboratory and Semi-Works Control	2	8					16,190	72				1				286	28	2										16,579
Optical and Electron Microscopy*	3	1	172			20	623	179					203			30	12				39						59	1,337
Pilot Plant Control	7	13					19,272	8																				19,280
Plutonium Isolation Laboratory	1	2					3,276	1	104							4	3	4						12			3	3,407
Radiochemical Analyses*	6	1	1				338	53	366			1				62	38	44	138		89	101			17			1,248
Radioisotope Production Control	3	16		270			5,267	446				522	8			304	7430	153	141		181	135						14,857
Reactor Analyses	5	4					334	74					1049						43							15		1,515
Special Analyses	5	7					11,238					1396				154												12,788
Spectrochemical Analyses*	6	0	26	7		5	474	172		2		13		2		270	77	6	30		48						12	1,144
Totals	55	64	883	284	285	25	57,988	1740	470	36	45	2351	1260	2	13	5224	8621	354	462	25	929	236	4	12	17	15	74	81,355

*These groups also do research and development.

Quality-control monitoring of five major analyses has been continued. Synthetic compositions that contained stainless steels and boron were prepared for the Spectrographic Laboratory to be used in a check on the methyl borate separation of boron from stainless steels.

Vacuum-Fusion Analyses

H. G. Davis J. H. Edgerton

The analysis of zirconium, titanium, thorium, and other metals and of alloys for hydrogen, nitrogen, and oxygen by vacuum fusion has been continued. In connection with the problem of growth and warpage of fuel plates for the Geneva Conference reactor, the amount of hydrogen evolved from the plates at 25 to 600°C and at 800°C was determined. Samples from the fuel plates were held in a quartz tube that was heated by a thermocouple-controlled split-type furnace and was attached to the vacuum-fusion apparatus. This whole assembly was then out-gassed, and the hydrogen was evolved from the fuel-plate sample and was measured by means of the vacuum-fusion apparatus. The low-oxygen, standard molybdenum samples submitted by the Naval Research Advisory Committee have been analyzed by vacuum fusion, and the results were reported. A new vacuum-fusion apparatus of the most recent design has been constructed and is expected to be in use soon.

The low-pressure carbon microcombustion apparatus has been constructed and will be in operation as soon as it is calibrated.

LABORATORY AND SEMI-WORKS CONTROL GROUP

L. T. Corbin G. R. Wilson C. A. Pritchard

The Chemical Technology Division requested 98% of the analyses done by the Laboratory and Semi-Works Control Group; the Chemistry, Metallurgy, and Operations Divisions requested the other 2%. A special request was received from the Chemical Technology Division for the determination of zinc, zirconium, and uranium in a mixture of the oxides of these metals. The sample was fused in a mixture of 60% potassium pyrosulfate and 40% potassium bisulfate. The melt was dissolved in nitric acid solution, and the solution was analyzed for zinc polarographically in ammonium chloride–ammonium hydroxide supporting electrolyte, as suggested by P. F. Thomason (see "Polarographic Determination of Zinc"). The zirconium was determined colorimetrically by use of Thoron reagent, and the uranium was determined fluorometrically.

PILOT PLANT CONTROL LABORATORY

L. T. Corbin C. E. Lamb

The limit of detection of free fluoride ion by titrating the distillate from pyrohydrolysis[2] is approximately 200 ppm. A change in the method for determining fluoride in thorium oxide and in thorium nitrate has been made in order to decrease the limit of detection to 10 ppm. The distillate collected from pyrohydrolysis is analyzed colorimetrically[3] by the indirect Thoron method rather than by titration. The distillate can also be analyzed fluorometrically,[4] the results being comparable with those obtained by the colorimetric analysis.

A comparison of the dielectric-constant method[5] with the acid-equilibration method[6] for the determination of tributyl phosphate in 125-82 Amsco was made for the Thorex Pilot Plant of the Chemical Technology Division. The methods were compared by use of a series of synthetic tributyl phosphate–Amsco standards. The standards were prepared by diluting known volumes of tributyl phosphate with 125-82 Amsco to a known volume. From the data[7] obtained, it was concluded that the dielectric-constant results were consistently nearer the known values than were the acid-equilibration results.

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[2] J. G. Surak, "Fluoride in the Presence of Nitrate, Pyrohydrolysis Method," Method No. 9 012207 (3-30-55), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols I and III.

[3] A. D. Horton, "Inorganic Fluoride, Thoron Indirect Spectrophotometric Method," Method Nos. 1 212810 and 9 00712810 (3-23-53), *ORNL Master Analytical Manual.*

[4] J. G. Surak, Secret Notebook No. 4661 (1955), ORNL Laboratory Records.

[5] R. L. Walker, "Tributyl Phosphate in Tributyl Phosphate–Amsco Solutions for Purex Process, Dielectric Constant Method," Method No. 9 052101 (5-20-53), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols I and III.

[6] G. R. Wilson, "Tributyl Phosphate in Organic Diluents, Acid Equilibration," Method No. 9 012206 (2-19-53), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols I and III.

[7] Memo from L. T. Corbin to M. T. Kelley (9-26-55), on file in the Analytical Chemistry Division office.

An investigation of the neptunium-237, thenoyltrifluoroacetone method[8] was started preparatory to training personnel for the analytical service work relative to the Neptunium Recovery program.

ISOLATION ANALYSES

L. T. Corbin J. H. Cooper

Most of the work done by the Isolation Laboratory was for the Chemical Technology Division relative to HR blanket studies. The principal determination was total plutonium by the thenoyltrifluoroacetone extraction method.[9]

The Isolation Laboratory separated uranium from highly radioactive thorium-dissolver solutions in preparation for mass spectrographic analysis of the uranium. The principal radioactive element, protactinium, was removed from the dissolver solutions by extraction into diisobutylcarbinol. The uranium was adsorbed on an anion-exchange resin, and the remaining radioactive elements were washed through the resin column. The uranium was eluted from the resin, and the solution was concentrated for mass spectrographic analysis.

Relative to their study of the decomposition of oxalic acid with hydrogen peroxide, the Chemical Technology Division requested an analysis for hydrogen peroxide in the presence of oxalic acid. The oxalic acid concentration was determined first by titration with standard sodium hydroxide solution to a pH of 7.5. The same test portion of the sample was then titrated with standard potassium permanganate solution,[10] and the hydrogen peroxide concentration was calculated after correction was made for the oxalate present.

For the Physics Division, samples of plutonium isotopes, as the dioxides, were dissolved by adding hydrofluoric acid to suspensions of the dioxides in boiling nitric acid, and the plutonium concentrations of the solutions were determined by potentiometric titration.[11]

[8] F. L. Moore, "Neptunium-237, Thenoyltrifluoroacetone Method," Method Nos. 2 31530 and 9 008530 (8-29-55), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols I, II, and III.

[9] R. L. Walker, "Total Plutonium, Thenoyltrifluoroacetone Extraction Method," Method Nos. 2 31621 and 9 008621 (5-18-53), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols I and III.

[10] N. H. Furman (ed.-in-chief), *Standard Methods of Chemical Analysis*, 5th ed., vol II, p 2181, Van Nostrand, New York, 1939.

SPECIAL ANALYSES LABORATORY

L. T. Corbin W. R. Laing

Most of the work of the Special Analyses Laboratory came from the Metallex Process Group and from the Thorex Pilot Plant Group of the Chemical Technology Division. The analyses were primarily for sodium, thorium, and chloride in amalgams and for contaminants in thorium oxide. Other work consisted in the analysis of bean roots, stems, leaves, pods, and seeds for potassium, magnesium, calcium, and strontium. Also, plutonium was determined in the presence of milligram quantities of uranium by separation of the plutonium onto a Dowex A-1 column, reduction of the plutonium to the trivalent state and elution of it with hydroxylamine, and spectrophotometric determination of the blue color of plutonium(III) at a wavelength of 602 mμ.[12] Steel samples were analyzed for phosphorus, manganese, silicon, sulfur, and carbon. Spectrophotometric determinations of zinc, vanadium, molybdenum, palladium, and titanium were made.

HIGH-RADIATION-LEVEL ANALYTICAL FACILITY

E. J. Frederick[13]

Equipment and Methods for High-Radiation-Level Analytical Facility

R. H. Powell

Equipment suitable for use in the High-Radiation-Level Analytical Facility[14–17] has been

[11] J. H. Cooper, "Plutonium, Potentiometric Ceric Sulfate Method," Method No. 9 0432620 (9-7-53), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols I and III.

[12] A. J. Frey, "Spectrophotometric Determination of Plutonium in Dissolver Solution," *Manual of Methods, Section 4-P*, NP-5246 (March 31, 1953), p 11161–11164.

[13] Chemical Technology Division.

[14] J. B. Ruch and E. J. Frederick, *Preliminary Survey – Remote Analytical Facilities*, ORNL CF-53-6-64 (June 8, 1953).

[15] E. J. Frederick, *High Radiation Level Analytical Facility – Shielded Space Requirements*, ORNL CF-54-9-172 (Sept. 9, 1954).

[16] R. H. Powell, "Equipment and Methods for Proposed Hot Cell," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 36.

[17] R. H. Powell, "Equipment and Methods for High-Radiation-Level Analytical Facility," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 27–29.

established. Either such equipment has been acquired commercially and altered or orders for the building of the special apparatus have been placed by the Analytical Instrumentation Group, which has designed much of the equipment. Work on the refinement of methods is still in progress. The allocation of work-cell space, according to the requirements[15] of the ANP, Thorex, and HRT projects, has been suggested.[18]

The work-cell mockup of the High-Radiation-Level Analytical Facility has been used to train personnel and to exhibit remote manipulations typical of those used in analytical chemical operations. The cell was a part of the Industrial Exhibit for the Fuel Processing Symposium held at ORNL on July 13, 1955.

[18]R. H. Powell, *High Radiation Level Analytical Facility. Suggested Allocation of Work-Cell Space, Types of Analysis, and Equipment Within Cells*, ORNL CF-55-6-54 (June 8, 1955).

REACTOR ANALYSES

U. Koskela

A program to train both long-time and new employees in the use of the master-slave manipulators is continuing. The manipulators are installed in a hot analytical cell mockup in Building 3019.

The various HR programs supplied the bulk of samples for the analysis made by the Reactor Analyses Group.

ANALYTICAL CHEMISTRY DIVISION - Y-12 SITE

RESEARCH AND DEVELOPMENT

HRP ANALYTICAL CHEMISTRY

O. Menis

Derivative Polarography of the Stannite Ion in the Presence of Uranium

R. G. Ball

The use of the ORNL model Q-1338 derivative polarograph to determine stannite ion in the presence of uranium was investigated. Polarograms were recorded for mixtures of stannite ion and uranium(VI) in a supporting electrolyte that was 0.1 *M* in sodium hydroxide, 1.0 *M* in sodium carbonate, and 0.5 *M* in hydrazine dihydrochloride.[1,2] Sufficient resolution of the derivative peaks was obtained by means of the derivative polarograph to distinguish between the half-wave potentials of the anodic wave for the oxidation $SnO_2^{--} \rightarrow SnO_4^{--}$ and of the cathodic wave for the reduction uranium(VI) → uranium(V); thus it is possible to measure the diffusion current of the stannite ion in the presence of uranium(VI).

As the concentration of stannite ion is increased, the half-wave potential vs the S.C.E. for the oxidation $SnO_2^{--} \rightarrow SnO_4^{--}$ shifts from −0.69 to −0.59 v. A linear relationship was found to exist between the diffusion current and the concentration of stannite ion in the range 60 to 100 μg/ml.

Amperometric Titration of Mercury with Tetraphenylarsonium Chloride

R. G. Ball

An amperometric method that is based on the reaction of mercury(II) with tetraphenylarsonium chloride[3] was developed for the determination of mercury. Mercury(II) in dilute nitric acid medium is titrated with a standard solution of tetraphenylarsonium chloride at −0.5 v vs the S.C.E. In the range 0.25 to 2.5 mg of mercury in a 50-ml final volume, a linear relationship was found to exist between the volume of titrant and the concentration of mercury. The results indicate that mercury in the concentration range 0.3 to 2.5 mg in a 50-ml final volume can be determined by amperometric titration with a relative standard deviation of 2%. The extent to which other ions interfere is being studied.

Distillation-Polarographic Determination of Tin

C. M. Boyd R. G. Ball

Because it was necessary to determine microgram quantities of tin in solutions of uranyl sulfate that contained both copper and the corrosion products of stainless steels, a method was investigated in which the tin was separated by distillation as the tetrabromide[4] and was then determined polarographically. It was found that as the amount of tin was decreased from 5 to 0.5 mg the efficiency of the distillation increased from 85 to 99%. The recovery of tin appears to be quantitative in the range 500 to 100 μg. When the amount of tin was decreased below 100 μg, however, high results were obtained. It was established that the high values for tin were caused by high reagent blanks. Tests of various brands of hydrogen peroxide showed that the magnitude of the reagent blank is dependent upon the brand of hydrogen peroxide used in the procedure. Of the hydrogen peroxide tested, that from Merck & Co., Inc., gave the lowest reagent blank.

A polarographic method for the estimation of tin was studied in which the diffusion current of the doublet wave for the reductions $SnCl_6^{--} \rightarrow SnCl_4^{--}$ and $SnCl_4^{--} \rightarrow Sn^{\circ}$ was determined in a supporting electrolyte of ethanol–hydrochloric acid that contained 6×10^{-4} *M* tetraphenylarsonium

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[1] I. M. Kolthoff and J. J. Lingane, *Polarography*, vol 2, p 523, Interscience, New York, 1952.

[2] C. J. Rodden (ed.-in-chief), *Analytical Chemistry of the Manhattan Project*, p 603, McGraw-Hill, New York, 1950.

[3] H. H. Willard and G. M. Smith, "Tetraphenylarsonium Chloride as an Analytical Reagent," *Ind. Eng. Chem., Anal. Ed.* **11**, 186 (1939).

[4] M. Farnsworth and J. Pekola, "Determination of Small Amounts of Tin with Dithiol," *Anal. Chem.* **26**, 735 (1954).

chloride.[5] When only 1 to 10 μg/ml of tin was present, the first wave that resulted from the reduction $SnCl_6^{--} \rightarrow SnCl_4^{--}$ was difficult to measure. Best results were obtained when the second wave, that is, the wave for the reduction $SnCl_4^{--} \rightarrow Sn^{\circ}$, was used to determine tin. For a series of samples in which the concentration of tin in the final volume varied from 1 to 10 μg/ml, the relative standard deviation was better than 10%.

Simultaneous Spectrophotometric Determination of Trivalent and Hexavalent Chromium

C. M. Boyd

The spectrophotometric method for the simultaneous determination of trivalent and hexavalent chromium in solutions of aluminum nitrate plus nitric acid and in solutions of nitric acid, which was reported previously,[6] was investigated further. The effects of salts, diverse ions, and concentrations of acid and of salt were established.

The molar absorbancy index of hexavalent chromium was found to be a linear function of nitric acid concentration in the range 1 to 7 *M* nitric acid. A linear reduction in the absorbancy of hexavalent chromium was noted when the concentrations of sodium nitrate, calcium nitrate, and aluminum nitrate were increased; of these salts, aluminum nitrate caused the greatest reduction in absorbancy. Apparently, the hydrolysis of aluminum nitrate contributes to the observed decrease in absorbancy of the hexavalent chromium. The presence of nitric acid increased the effects of salts.

The relative interferences of the diverse ions nickel(II), iron(III), and permanganate were computed for a 1:1 molar ratio of the trivalent or the hexavalent chromium to the diverse ion. Of the ions tested, only permanganate was found to cause serious interference; the interference of the nickel(II) was negligible. Although iron(II) caused a 5% increase in absorbancy of the hexavalent chromium, a correction can be made for this error if the concentration of iron(III) is known, because the effect of iron(III) on the absorbancy of hexavalent chromium is additive.

[5] I. M. Kolthoff and R. A. Johnson, "Polarography of Tin(IV) in Presence of Traces of Tetraphenylorsonium Chloride," *Anal. Chem.* **23**, 574 (1951).

[6] C. M. Boyd, "Spectrophotometric Determination of Mixtures of Chromium(III) and (VI) in Aluminum Nitrate and Nitric Acid Solutions," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 32.

Conductivity and pH Measurements of Aqueous Slurries of Thorium Compounds

C. M. Boyd R. E. Corcoran

Conductivity measurements were used to estimate the concentration of impurities in slurries of thorium oxide and to determine the characteristic behavior of thorium oxide from various sources.[7,8] In these studies experiments were carried out to determine the effect of small amounts of thorium sulfate on the conductivity of aqueous slurries of thorium oxide and to determine the conductivity and pH values, under equilibrium conditions, for slurries of thorium oxide, of thorium sulfate, and of thorium oxide to which thorium sulfate had been added. It was found that the products of the hydrolysis of thorium sulfate are adsorbed on the oxide. Under equilibrium conditions all the anions produced by the hydrolysis of 25 mg of $Th(SO_4)_2$ were adsorbed by 1 g of ThO_2. The concentration of hydronium and of other ions in the aqueous phase can be estimated from conductivity measurements only after adsorption equilibrium is established.

Determination of Carbonate by a Carbon Dioxide Evolution Method

C. M. Boyd R. E. Corcoran

A procedure was developed for the determination of micro quantities of carbonate in thorium oxide. The sample is dissolved in nitric acid that contains a few drops of concentrated hydrofluoric acid, and the carbon dioxide evolved is absorbed in a known amount of a standard solution of barium hydroxide, following which the excess base is titrated potentiometrically with standard acid. This process is carried out in an apparatus similar to that used in a wet-combustion method for the determination of carbon.[9]

The carbonate values that were obtained for standard solutions of sodium carbonate, test portions of which contained carbonate equivalent to

[7] C. M. Boyd, "Determination of Water-Soluble Impurities in Thorium Oxide by Conductance," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 41.

[8] R. E. Corcoran, "Conductivity and pH Measurements of Aqueous Slurries of Thorium Compounds," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 32.

[9] O. Menis, "Analysis of Uranyl Sulfate Solutions – Carbon," *Anal. Chem. Quar. Prog. Rep. June 26, 1952*, ORNL-1361, pp 48, 49.

250 to 750 μg of CO_2, and for a Bureau of Standards sample of fluorspar were 10 to 25% less than the known values.

Determination of Carbon Dioxide in Oxygen

C. M. Boyd R. E. Corcoran

A semiquantitative method was devised for the determination of carbon dioxide in the oxygen off-gases from dynamic tests in the HR loops. The amount of carbon dioxide in the oxygen is used as a measure of the decomposition of carbon bearings in the loop. The carbon dioxide is absorbed from a rapid stream of oxygen by a barium hydroxide solution that is contained in a gas-scrubbing tower of special design. Samples of the barium hydroxide solution are periodically removed from the tower and are titrated with standard acid. The change in hydroxyl concentration is a measure of the carbon dioxide absorbed by the barium hydroxide solution.

In order to test the efficiency of the gas-scrubbing tower for removing carbon dioxide, oxygen that contained known amounts of carbon dioxide was passed through the tower at a flow rate of 1 ft^3/hr. The recovery of carbon dioxide varied from 80 to 165% for 0.02 to 0.17 g of carbon dioxide in 5 ft^3 of oxygen. Because approximate values for the carbon dioxide content were sufficient, the recovery was considered to be acceptable.

Particle-Size Distribution of Thorium Oxide

H. P. House N. M. Ferguson

Sedimentation methods are being investigated for use in establishing the particle-size distribution of thorium oxide. In one method that is being studied, the Andreasen pipet is used to determine the particle-size distribution after the thorium oxide has been dispersed in a suitable medium. Because it is essential that the solid aggregates be completely dispersed, several factors relative to the maximum dispersion of thorium oxide were investigated. The degrees of effectiveness of sodium pyrophosphate (0.002 *M*), sodium oxalate (0.01 *M*), and hydrochloric acid (0.001 to 1.0 *M*) as dispersing or wetting agents were determined. Tests were also made in which the method of agitation, as well as the agitation time (5 min to 24 hr), was evaluated. It was noted that maximum dispersion was attained when the thorium oxide was mechanically shaken with 0.1 *M* hydrochloric acid for 15 hr or more.

Sedimentation studies made with the Andreasen pipet showed the particle-size distribution of a sample of thorium oxide (designated as Lindsay No. 8) in 0.1 *M* hydrochloric acid to be as follows:

Particle Diameter (μ)	Per Cent of the Slurry
>3.0	2
1 to 3.0	20
0.4 to 1.0	6
<0.4	72

Because the Andreasen pipet method does not distinguish between particles of diameter less than 0.4 μ, that fraction of the suspension that contained particles of diameters less than 0.4 μ was submitted to T. E. Willmarth for electron microscopy. Willmarth reported that the diameters of the primary particles in that fraction were 0.01 μ or less but that those of the secondary particles ranged from about 0.04 to 0.1 μ.

Other dispersing agents are being tested to determine their relative effectiveness in the dispersion of thorium oxide that has been fired at different temperatures.

Spectrophotometric Determination of Silicon Dioxide in Thorium Oxide

D. L. Manning M. L. Hubbard

A spectrophotometric method was investigated for the determination of silicon dioxide in thorium oxide as the silicomolybdate complex. The elimination of thorium interference and the dissolution of thorium oxide without loss of silicon dioxide were studied particularly. The reaction whereby the silicomolybdate complex is developed was carried out under the conditions recommended in the literature.[10-12] It was found that thorium molybdate precipitates under those conditions.

[10] M. A. DeSesa and L. B. Rogers, "Spectrophotometric and Polarographic Determinations of Soluble Silicate," *Anal. Chem.* **26**, 1278 (1954).

[11] A. B. Carlson and C. V. Banks, "Spectrophotometric Determination of Silicon in the Presence of Zirconium, Beryllium, Aluminum, and Calcium," *Anal. Chem.* **24**, 472 (1952).

[12] J. D. H. Strickland, "The Preparation and Properties of Silicomolybdic Acid. I. The Properties of Alpha Silicomolybdic Acid," *J. Am. Chem. Soc.* **74**, 862 (1952).

The silicomolybdate complex was reduced to the heteropoly acid, and then the thorium molybdate precipitate was dissolved by adding tartrate and raising the pH from 1.4 to 3.0.

Because it was necessary to convert the insoluble silicon dioxide to a soluble silicate without the loss of silicon as the volatile tetrafluoride, the procedure for dissolving thorium oxide was modified. The sample is heated in a mixture of nitric acid and perchloric acid until fumes of perchloric acid are observed; then the solution is diluted with water, two drops of hydrofluoric acid are added, and the solution is warmed for 30 min. Under these conditions, 0.3 to 4.0 g of thorium oxide was dissolved without apparent loss of silicon. Studies are being continued to determine the optimum concentration of acid, the heating time that results in maximum precision and sensitivity, and the minimum time required to ensure complete dissolution of any insoluble silicon dioxide.

Indirect Flame Photometric Determination of Chloride

O. Menis, T. C. Rains

An indirect flame photometric method was developed for the determination of chloride in the concentration range 0.5 to 10 ppm. The chloride ions are reacted with a dilute solution of silver nitrate, the silver chloride that is formed is removed by centrifugation, and the luminescence of the solution that is caused by the residual silver is measured at a wavelength of 328 mμ. The chloride equivalent to the silver removed by precipitation is determined from the decrease in luminescence of the solution.

The method has been used to determine chloride in solutions that were highly colored and in organic compounds that were dissolved in 0.01 to 1.0 *M* nitric acid. This simple method is rapid and is applicable to the determination of chloride in concentration ranges for which ordinary potentiometric or turbidimetric methods are unsatisfactory. The relative standard deviation is about 5% for data taken by this method in the chloride concentration range 0.5 to 10 ppm.

Spectrophotometric Determination of Ethylenediaminetetraacetic Acid as the Copper Complex

I. B. Rubin

Studies of the determination of ethylenediaminetetraacetic acid, which were discussed previously,[13] were continued. Optimum conditions for the experimental variables were established as follows: formation of the cupric ethylenediaminetetraacetate complex in a 0.1 *M* disodium hydrogen phosphate buffer solution of pH 11 and measurement of the absorbancy at a wavelength of 250 mμ against a reference solution that consists of copper sulfate and the buffer solution.

Various interferences that were reported previously have been evaluated. In general, only nickel and chromate ions interfere when a large excess of reagent is present; cobalt interferes only when the weight ratio of cobalt to ethylenediaminetetraacetic acid exceeds 1:10. The cupric ethylenediaminetetraacetate complex was found to be stable for over two weeks regardless of whether it was stored in glass or in polyethylene containers. The relative standard deviations for ethylenediaminetetraacetic acid were less than 10% and less than 3%, respectively, in the concentration ranges 5 to 20 and 20 to 60 μg per milliliter of final volume.

Spectrophotometric Determination of Titanium as the 8-Quinolinol Complex

I. B. Rubin

Certain ions cannot be separated from titanium by electrolysis; studies were made to establish the effects of these ions on the determination of titanium by the 8-quinolinol method. As reported previously,[14] titanium is separated from some cations by electrolysis and from thorium by extraction in an acetate medium with a solution of 8-quinolinol in chloroform. Spectrographic tests indicated that ions, such as aluminum, zirconium,

[13] I. B. Rubin, "Spectrophotometric Determination of Ethylenediaminetetraacetic Acid as the Copper Complex," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 34.

[14] I. B. Rubin, "Determination of Titanium in the Presence of Thorium After Separation from Corrosion Products," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 34.

and silicon, that are not removed by electrolysis are extracted along with titanium by the chloroform–8-quinolinol solution.

Although the absorbancies of the 8-quinolinol complexes of these impurities increased the absorbancy of the titanium complex at several wavelengths, the composite absorption spectrum of the complexes of these impurities differs in several respects from the characteristic absorption spectrum of the titanium complex. A comparison of the spectra for the complexes of the impurities with the spectrum for the titanium complex indicates that, at wavelengths from 380 to 440 mμ, the absorbancy of the titanium complex and of the complexes of the impurities is additive; at wavelengths greater than 460 mμ, the absorbancies of the impurities are negligible. Further studies of multicomponent mixtures, the absorbancies of which can be measured at several wavelengths, are being continued.

Determination of Sulfate

C. K. Talbott

Studies were made in order to compare the precision and sulfate recovery obtained by a gravimetric method[15] with those obtained by a volumetric method[16] for the determination of sulfate after removal of cations by an ion-exchange resin. In one series of experiments, uranyl sulfate solutions that were prepared by dissolving UO_3 in standard sulfuric acid solution were eluted through a cation-exchange column of Dowex 50. The sulfate content of the eluate was then determined, by the volumetric and by the gravimetric methods, to be 5.08 and 5.16 mg/ml, respectively. Other gravimetric results of the same order of magnitude were also obtained when uranyl ions were not removed by ion exchange; thus the results indicate that the higher gravimetric values are not caused by coprecipitation of the uranyl ion. The gravimetric results were in all cases 1 to 2% high, whereas the volumetric results were in agreement with the known values. Fischer and Rhinehammer[17] have found that under similar experimental conditions the crystals of barium sulfate are irregular because the crystals are contaminated with other ions. Thus, the higher gravimetric values may be caused by coprecipitation of barium chloride.

RAW MATERIALS

L. J. Brady

Identification of Sources of Kerosene Samples

L. J. Brady C. D. Susano
H. P. House

In an effort to identify the sources of kerosene samples, tests for the following were made by ASTM methods: specific gravity, bromine number, flash point, kauri-butanol value, sulfonation with fuming sulfuric acid, aniline point, acid number, distillation range, and aromatic hydrocarbons by adsorption on silica gel. The test for aromatic hydrocarbons, by which various components of kerosene are selectively eluted with methanol from a column of silica gel, proved to be the best test for characterizing the kerosene. On the basis of tests with silica gel, samples of kerosene obtained from Y-12 Stores were found to have a significantly higher content of the aromatic hydrocarbon fractions than that of a sample of kerosene from the Uinta Refinery in Utah.

MISCELLANEOUS ANALYSES

L. J. Brady H. P. House

Tests of Freon-12 from a Faulty Air-Conditioning Unit

L. J. Brady C. D. Susano

A sample of Freon-12 from a faulty air-conditioning unit was tested and was found to contain appreciable quantities of both fluoride and chloride. The results of control tests for these same constituents in a sample of Freon-12 of high purity were negative; thus it was indicated that the refrigerant from the faulty unit had been decomposed into these highly corrosive acidic products, probably as the result of the motor becoming overheated.

A procedure was recommended for cleaning the line with a mixture of 3 parts trichloroethylene and 1 part methanol (moisture-free) followed by a rinse of trichloroethylene in order to remove the residual, corrosive components before a new air-conditioning unit was installed. The procedure was satisfactory.

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[15] I. M. Kolthoff and E. B. Sandell, *Text Book of Quantitative Analysis*, 3d ed., p 332, Macmillan, New York, 1952.

[16] J. S. Fritz and M. Q. Freeland, "Direct Titrimetric Determination of Sulfate," *Anal. Chem.* **26**, 1593 (1954).

[17] R. B. Fischer and T. B. Rhinehammer, "Rapid Precipitation of Barium Sulfate," *Anal. Chem.* **25**, 1544 (1953).

Spectrophotometric Determination of Iron in Titanium

J. R. Lund

The suitability of the α,α'-bipyridyl method[18] for the determination of iron in titanium was studied. The method was found to be satisfactory if hydrofluoric acid is used to complex the titanium. Tartrate proved to be unsatisfactory as a complexing agent for titanium. The order of addition of the reagents was found to be critical, the best order being as follows: reducing agent (hydroxylamine hydrochloride), chromogenic reagent (α,α'-bipyridyl), complexing agent (hydrofluoric acid), buffer solution (acetic acid–sodium acetate). The pH of the test solution was adjusted to 4 prior to measurement of the absorbancy. For samples that contain 50 to 150 μg of iron and not more than 20 mg of titanium in a final volume of 50 ml, the relative standard deviation is 2%.

The spectrophotometric method in which *o*-phenanthroline is used as the chromogenic reagent was found to be unsatisfactory for this particular type of sample.

Recovery of Uranium from Solids Derived from Monazite Sand

J. R. Lund

The effectiveness of Dowex 1 resin was evaluated for the separation of uranium from other constituents of a chloride solution of the solid residue from a sulfuric acid leach of monazite sand. The residue consisted chiefly of thorium, rare earths, sulfate, phosphate, and a small amount of uranium. The uranium was separated from the other constituents by passing a solution of the residue in 6 *M* hydrochloric acid through a column of Dowex 1 resin in the chloride form and then eluting the uranium from the resin with 0.02 *M* hydrochloric acid. The uranium in the eluate was determined fluorometrically. When solids that were estimated to contain approximately 500 ppm of uranium were tested by this method, the standard-addition procedure being used, the quantity of uranium recovered was within 20% of that estimated to be present.

[18] M. L. Moss and M. G. Mellon, "Colorimetric Determination of Iron with 2,2′-Bipyridyl and with 2,2′,2″-Terpyridyl," *Ind. Eng. Chem., Anal. Ed.* **14**, 862 (1942).

Determination of Nitric Oxide and Nitrogen Dioxide in Gas Mixtures

J. L. Mottern

In the determination of nitric oxide, NO, and of nitrogen dioxide, NO_2, in gas mixtures by a method given in the *ORNL Master Analytical Manual*,[19] the oxides of nitrogen are absorbed in concentrated sulfuric acid that contains some anhydrous nitric acid. The total reducing power of the solution is determined by titration of the resultant nitrosylsulfuric acid with potassium permanganate. Because the reaction involved is slow, the titration is time-consuming and the end point is difficult to detect. An alternate titration procedure, which involves the addition of an excess of ceric sulfate and back-titration of the excess with standard ferrous sulfate solution, was found to be more satisfactory. With ferroin indicator, a sharp end point is obtained, and the uncertainty caused by the slow reaction of nitrosylsulfuric acid with permanganate is eliminated.

Determination of Alkali Metals and Alkaline-Earth Elements by Flame Photometry

J. M. Rogers

Bibliography. – An extensive literature search was made for information concerning the mutual interferences of the alkali metals and of the alkaline-earth elements on the flame photometric determinations of each other. References that appeared in *Chemical Abstracts* and in *Analytical Chemistry* during the period 1935 through 1954 were reviewed. The pertinent references were compiled into a bibliography, which will be issued soon.

Interference Studies. – Further work has been done to ascertain the extent to which the elements listed in column 4 of Table 6, under specific instrumental conditions, interfere with the flame photometric determination of the elements listed in column 1. Optimum instrumental conditions for the determination of these elements were given in a previous report.[20] Selected data from interference studies, which were made under such optimum conditions, are given in Table 6.

[19] W. R. Tyson and D. T. Galm, "Analysis of Gas Mixtures," Method No. 9 051201 (9-17-52), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols I and II.

[20] J. M. Rogers, "Flame Photometry of Alkali Metals and Alkaline-Earth Elements," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 36.

TABLE 6. FLAME PHOTOMETRY OF THE ALKALI METALS AND ALKALINE-EARTH ELEMENTS: MUTUAL INTERFERENCES

Element Determined	Wavelength (mμ)	Concentration (μg/ml)	Interference		Interference Factor (F)**
			Element	Ratio*	
Rb	795	25	K	100	−0.20
				400	
Mg	383	100	K	100	−0.08
				400	−0.13
Ca	622	25	Na	200	+0.50
			Rb	200	+0.62
				400	+1.14
			Cs	200	−0.01
				400	+0.74
			Mg	200	+0.36
				400	+0.45

*Weight ratio, interfering element/element determined.

**Interference factor (F) indicates the amount of enhancement or decrease of the emissivity caused by the interfering element. The observed emissivity × $(1 + F)$ equals the emissivity to be referred to a calibration graph in order to ascertain the concentration of the element being determined.

Nitrous Oxide: A Bibliography

J. M. Rogers

A method for the determination of nitrous oxide, N_2O, was required for the analysis of mixtures of gases that consisted principally of nitric oxide, NO, and nitrogen dioxide, NO_2. Consequently, a survey of the literature from 1914 through 1954 was made with respect to the determination of nitrous oxide in gas mixtures. The results of this review were compiled into a bibliography.[21] With the exception of a few references from *Analytical Chemistry*, most of the material was taken from *Chemical Abstracts*.

Determination of Nitrite in Nitric Acid and in Sulfuric Acid

J. M. Rogers

A number of spectrophotometric methods for the determination of nitrite in nitric acid and in sulfuric acid solutions were tested. Of these, a method which appears in the literature[22] was found to be the most satisfactory after it was modified by the substitution of sulfanilamide for sulfanilic acid.[23] Nitrite is reacted with sulfanilamide and with 1-naphthylethylenediamine dihydrochloride to produce a colored compound. A linear relationship was found to exist between the absorbancy, which was measured at a wavelength of 550 mμ, and the nitrite concentration in the range 5 to 20 μg in 50 ml of final solution. Concentrations of nitric acid as great as 0.8 *M* or of sulfuric acid as great as 1.2 *M* in the final 50-ml volume have little or no effect on the absorbancy. At higher concentrations of sulfuric acid the absorbancy is decreased. The relative standard deviation was 3% for the determination of 5 μg of nitrite in a final volume of 50 ml; as little as 0.1 μg of nitrite can be determined with a corresponding decrease in precision.

Determination of Nitrogen in Sulfuric Acid

J. M. Rogers

A spectrophotometric method, in which brucine is used as the chromogenic reagent,[24] was examined

[21] J. M. Rogers, *Nitrous Oxide: A Bibliography*, ORNL CF-55-9-169 (Sept. 13, 1955).

[22] M. B. Shinn, "Colorimetric Method for Determination of Nitrite," *Ind. Eng. Chem., Anal. Ed.* 13, 33 (1941).

[23] N. F. Kershaw and N. S. Chamberlin, "Determination of Nitrites. Discussion of the Shinn Method as Applied to Examination of Water," *Ind. Eng. Chem., Anal. Ed.* 14, 312 (1942).

[24] F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, 3d ed., vol II, p 798–99, Van Nostrand, New York, 1949.

for the determination of small concentrations of nitrogen (nitrite or nitrate) in sulfuric acid that contains dissolved sulfur dioxide. Brucine reacts with nitrite or with nitrate in a sulfuric acid solution to form an intensely colored complex, which is initially red and then changes to yellow. The yellow complex, which is measured spectrophotometrically, has an absorption maximum at a wavelength of 410 mμ. The absorbancy per unit quantity of nitrogen is the same for both nitrate and nitrite. The relationship of absorbancy to concentration of nitrate or of nitrite is not linear in the range 10 to 100 μg of nitrate in a final volume of 50 ml. Consequently, a calibration curve rather than a calibration factor is used for this analysis. A relative standard deviation of 5 to 10% was established for nitrogen in the concentration range 2 to 10 μg/ml. It was found that sulfur dioxide at a concentration of 30 mg/ml does not interfere.

Determination of Strontium by Flame Photometry

J. M. Rogers

Optimum instrumental conditions for the determination of strontium by flame photometry were established (as shown below); the relative standard deviation of data for a strontium concentration of 1 μg/ml was about 25%.

Wavelength, mμ	461
Slit width, mm	0.076
Oxygen pressure, psi	20
Hydrogen pressure, psi	6
Photomultiplier tube (RCA 1P28) voltage, v	660

QUALITY CONTROL

R. L. McCutchen C. D. Susano

Although the control work in the laboratories of the Analytical Chemistry Division at the Y-12 and X-10 Sites continued to increase during this period, the control program itself was not expanded. The types of materials which were tested for control purposes, as well as the number of laboratories that participated in the control program, remained essentially the same as for the previous period. In general, the precision that was achieved by the laboratories during earlier periods was maintained during the past six months.

The distribution, by laboratory, of the 6351 determinations, which were evaluated for control purposes, is summarized in Table 7. For purposes of comparison, the control data for the previous period are also given.

TABLE 7. SUMMARY OF DETERMINATIONS EVALUATED FOR CONTROL PURPOSES

Laboratory	Determinations Evaluated for Control Purposes	
	October 1954 Through March 1955	April Through September 1955
Y-12 Site		
HRP	359	303
Raw Materials	200	165
Total	559	468
X-10 Site		
Building 3019	2601	3734
Building 3508	350	375
Building 3550	493	651
Building 4500	972	863
General Analyses	230	260
Total	4646	5883
GRAND TOTAL	5205	6351

SERVICE ANALYSES

A semiannual summary of the analytical service work at the Y-12 Site is given in Table 8.

HRP ANALYTICAL CHEMISTRY

O. Menis C. K. Talbott
T. C. Rains

The staff of the HRP Analytical Chemistry Laboratory made 24,850 determinations on 5,720 samples; this represents an increase of 17% in the number of samples over that for the last semiannual period. Solutions of uranyl sulfate and of uranyl sulfate plus copper sulfate were analyzed for uranium, iron, nickel, and chromium and occasionally for aluminum, cobalt, molybdenum, lithium, magnesium, zirconium, titanium, and chloride. Thorium oxide and other compounds of thorium were analyzed in a similar manner.

Solutions of 2 *M* aluminum nitrate in 1 *M* nitric acid, 2 *M* aluminum sulfate, 7 *M* nitric acid, and 5% nitric acid were tested for iron, nickel, and chromium. Occasionally, these solutions were analyzed for aluminum, nitrate, barium, and acid normality. In addition to this work, lead and zinc were determined polarographically; and barium, calcium, lithium, sodium, and potassium were determined by flame photometry.

TABLE 8. SUMMARY OF ANALYTICAL SERVICE WORK AT Y-12 SITE

	Number of Personnel		ORNL Divisions Requesting Analyses							Others Requesting Analyses		
	Technical	Nontechnical	Materials Chemistry	Chemical Technology	Chemistry	Metallurgy	Stable Isotope Research and Production	Electronuclear Research	REED	Y-12	Miscellaneous	Total Determinations
Laboratory Making Analyses			Number of Determinations									
HRP Analytical	3	8							24,850			24,850
Miscellaneous Analyses	2	10	16,255	45	145	343	497	44	770	4	183	18,286
Raw Materials	2	6	16,071									16,071
Special Samples	2	2	589									589
Totals	9	26	32,915	45	145	343	497	44	25,620	4	183	59,796

[redacted]

RAW MATERIALS ANALYTICAL CHEMISTRY

L. J. Brady A. F. Roemer, Jr.
E. C. Lynn J. J. McCown

The staff of the Raw Materials Analytical Chemistry Laboratory analyzed a total of 5956 samples, 40% of which were submitted by the Raw Materials Process Testing Group of the Materials Chemistry Division. Usually, these samples were analyzed for uranium, vanadium, iron, aluminum, and molybdenum and less frequently for titanium, phosphate, sulfate, nitrate, and chloride. Aqueous and organic solutions that resulted from solvent-extraction studies comprised a major part of the total samples tested. Increased emphasis was placed on studies of high-molecular-weight organo-phosphorus compounds as extractants for uranium; most of the organic solutions tested were kerosene solutions of one or more of these compounds.

Separation techniques that proved to be most effective in the removal of impurities from solutions include the following: ion exchange, solvent extraction, precipitation-filtration, and electrolysis.

MISCELLANEOUS ANALYSES

L. J. Brady E. C. Lynn

A total of 573 samples was analyzed by the staff of the Miscellaneous Analyses Laboratory. Specification testing of steels, other alloys, and nonferrous metals continued. The variety and number of nonferrous metals that were analyzed during this period were greater than in the preceding period. Microgram quantities of boron were determined in aqueous extracts from organic solutions of boron trifluoride. A spectrophotometric method,[1] in which carmine is used as the chromogenic reagent, was found to be satisfactory for this analysis. Ion-exchange resins that had been in contact with solutions of various metal ions were analyzed to determine the amount of metal adsorbed on the resin. The spectrophotometric method of Kruse and Mellon[2] was used to determine small concentrations (ppm) of ammonia in aqueous suspensions of calcium hydroxide. Other widely divergent types of analyses and tests performed by this group included the determination of dissolved sulfur dioxide in solutions of sulfuric acid, the conversion of nitrate to ammonia by digestion with Devarda's alloy, the identification and determination of alkali metals in solutions of their fluoride salts, the determination of the fluoride content of samples of titanium tetrafluoride, the detection and identification of the decomposition products in used Freon-12 gas, and the determination of the carbon and hydrogen contents of a variety of organic compounds.

ANALYSES OF SPECIAL SAMPLES

H. P. House J. L. Mottern
J. R. Lund J. M. Rogers

A total of 677 determinations was made on 196 samples. A wide variety of special samples was analyzed. Mixtures of oxides of nitrogen were analyzed for nitrous oxide, nitric oxide, and nitrogen dioxide; sulfur dioxide, sulfuric acid, and total nitrogen were determined in sulfuric acid solutions; nitric acid was analyzed for nitrite and nitrate; ferrous sulfate solutions were analyzed for iron and nitrite; solutions of boron trifluoride were analyzed for boron; lithium, sodium, potassium, rubidium, and cesium were determined in solutions of alkali metals; the density and viscosity of organic liquids were measured; and the interfacial tension of various pairs of liquids was determined.

In addition to the analysis of special samples, the absorption spectra of 45 solutions of nitric acid that contained the corrosion products of stainless steel were determined.

[1] J. T. Hatcher and L. V. Wilcox, "Colorimetric Determination of Boron Using Carmine," *Anal. Chem.* **22**, 567 (1950).

[2] J. M. Kruse and M. G. Mellon, "Colorimetric Determination of Ammonia and Cyanate," *Anal. Chem.* **25**, 1188 (1953).

[redacted]