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ANALYTICAL CHEMISTRY DIVISION

SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING APRIL 20, 1956



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**SEMIANNUAL PROGRESS REPORT**  
**For Period Ending April 20, 1956**

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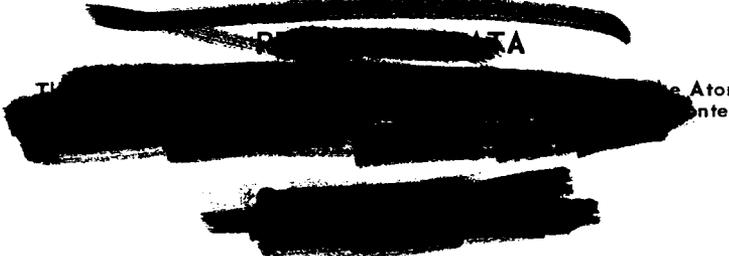
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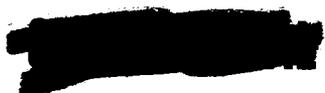
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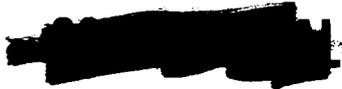


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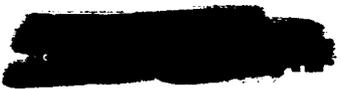
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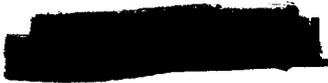
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# ANALYTICAL CHEMISTRY DIVISION SEMIANNUAL PROGRESS REPORT

## SUMMARY - X-10 SITE

### RESEARCH AND DEVELOPMENT

**Ionic Analyses.** - In support of the research of other ORNL divisions, the development of ionic methods for the determination of such elements as aluminum, chromium, tin, zirconium, nitrogen, fluorine, europium, etc., has been the major interest of the Ionic Analyses Laboratory. The work consisted in the development of a spectrophotometric method for the determination of aluminum in the presence of thorium and uranium, especially in the Thorex-process BU stream, and of a method for the simultaneous spectrophotometric determination of chromium(III) and chromium(VI) as ethylenediaminetetraacetate complexes; the determination of nitrogen in magnesium metal by a modified Kjeldahl method, of fluoride adsorbed on an anion resin by a conductometric titration, with lanthanum acetate as the titrant, and of europium in lithium iodide crystals by a polarographic method; the study of a polarographic method for the determination of tin in HR-type fuel, of an amperometric titration of zirconium with cupferron, and of the anodic dissolution of uranium fuel elements and of mercury-titanium amalgams. An apparatus to be used for sampling uranium hexafluoride and fluorine gas has been fabricated and is being tested. The conductance of various thorium oxide slurries was measured for the Chemical Technology Division.

**Analytical Instrumentation.** - The development of analytical instrumentation for the High-Radiation-Level Analytical Facility (HRLAF) has continued. The remotely controlled falling-drop densimeter has been improved, has been tested extensively, and is now ready for use. Procedures and dropping media suitable for the determination of the density of heavy-water solutions for the HRT have been worked out. Drawings of an improved turret for the falling-drop densimeter have been completed, and an additional turret is being fabricated by the ORNL Central Machine Shop. Rapid, internal corrosion, as a result of electrolytic action, of the commercial, thermostatted water bath used with the falling-drop densimeter was corrected by the use of a magnesium rod immersed in the bath. A

Lazy-Susan device has been designed for positioning and holding bottles beneath the pipet of the falling-drop densimeter. All 0.1- and 1-ml remotely servo-controlled pipetters that are to be used in the HRLAF have been fabricated, and one of the 1-ml pipetters has been installed in cell 1 of the HRLAF. The performance of the pipetters has been improved by design changes in the ORNL model Q-1348 control unit. Mechanical drawings of the decapper-stirrer train have been completed, and trains have been fabricated for use with the remotely servo-controlled 1-ml pipetters. Three ORNL model Q-1728 potentiometric titrators of the automatic velocity servo type have been fabricated. The precision of one of the titrators in the ferric and in the ceric titration of uranium is being determined. Design changes have improved the precision of results obtained with the ORNL model Q-1734 filter photometers, and three have been constructed for use in the HRLAF. The dual-D.M.E. (dropping-mercury-electrode) polarograph has been modified for use in the HRLAF. Epoxy casting resin was found to be an undesirable material for use as partitions in a glass, pressurized polarographic cell. A remotely servo-controlled 1-ml pipetter, with a low standard deviation of delivery of aliquots and constructed so that the liquid contents contact only fluorothene and Teflon, has been fabricated for use in the HRLAF. Mounts for the oculars that have modified focal range and that are to be used in the HRLAF have been designed and are being fabricated. An arc stand to be used in the HRLAF by the Spectrographic Analyses Group has been motorized, supplied with a control box having interlocking circuits, and furnished with tantalum inserts for the electrode holders. A remotely operated disposal unit for radioactive samples is being designed for use in the HRLAF. The spectral range of the ORNL model Q-1457 flame spectrophotometer, which is a high-sensitivity, recording instrument, has been extended to the wavelength region of from 7,000 to 12,000 Å; a mount for attaching the Farnsworth 16PM1 photomultiplier tube to the Bausch & Lomb grating monochromator has been designed and



built. The light-measuring circuit of a Leeds & Northrup microphotometer has been modified to obtain greater stability. The simplified apparatus for the pyrohydrolytic determination of fluoride has been improved; revised mechanical drawings are available. A mechanical drawing has been completed of a heater designed for use in the potentiometric titration of uranium by the ferric sulfate method. Participation in the two-year program of ORNL in-line instrumentation assistance to the Savannah River Laboratory (SRL) is continuing. A review has been made of experience gained by ORNL in instrumentation for process control. In-line sampling devices have been designed. Instruments under consideration for SRL application will undergo tests in hot facilities at the ORNL pilot plants. A study is under way of radioactivity buildup on type 304L stainless steel. An a-c polarograph is being designed and will be studied on a laboratory scale with the ultimate objective of developing it into an in-line monitor of the concentration of uranium in waste streams from uranium-production plants.

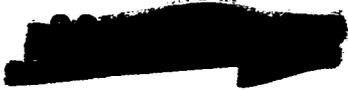
**Radiochemical Analyses.** – The nuclear properties of several nuclides have been investigated, and preliminary values have been determined for pile-neutron activation cross sections of several radioactive species, including  $Y^{89}$ . A brief study of the decay characteristics of the nuclide  $Cr^{55}$  has been made. Alpha disintegration rates have been determined by the use of  $4\pi$  alpha-gamma coincidence counting. A rapid method for the determination of radiozirconium is reported. The application of gamma spectrometry in the determination of neutron flux has continued. The method used for determining  $Pa^{233}$  in Thorex process samples has been modified because of the interference of  $Nb^{95}$  and  $Sb^{125}$ . A brief survey is presented of the work being done for the Electro-nuclear Research Division. Improvements have been made in the solvent-extraction method for radiocerium.

**Activation Analyses.** – Neutron activation analysis has been applied to the determination of microgram or submicrogram quantities of arsenic in silicon and in aluminum oxide; selenium in copper; tantalum in niobium and silicon; cobalt in Inconel, nickel, and Hastelloy; tellurium in indium arsenide; copper in chromium and zirconium; silicon in niobium; uranium in eutectic salts, slag, copper, biological materials, stainless steel, and siliceous

materials; sulfur in chromium, tin, silicon, and indium arsenide; and selenium in indium arsenide. Special studies included the use of activation analysis to determine milligram amounts of silver in milligram amounts of zirconium-silver alloy, uranium in corrosion products from Inconel tubing, and cobalt in alumina. Contaminant elements were identified in selenium, animal tissue, quartz, silicon, and petroleum cracking catalysts. Also, neutron-induced radionuclides in such reactor structural materials as lead, stainless steel, titanium, Inconel, Hastelloy, and aluminum have been identified. The activation analysis method for the determination of particle-size distribution has been studied further and has been applied to a large number of samples. The method of neutron-density analysis has been applied to the determination of boron in aqueous and organic solutions. The use of discriminatory gamma counting has been extended.

**Spectrochemical Analyses.** – Spectrochemical research has resulted in a precise procedure for reproducing the amount of energy per breakdown in the discharge obtained from an air-interrupted spark source, which greatly improved the reproducibility of analytical results. In a further study of the activated cellulose-batch adsorption technique, nonactivated cellulose, when soaked in ethyl ether-nitric acid solution, was shown to be apparently as effective as activated cellulose in separating rare earths from thorium. In determining microgram quantities of rare earths in rare-earth mixtures by the spark method, it was found that the spectrographic line-to-background ratios for the rare earths are greatest when a given amount of power is divided into a large number of consecutive, small discharges and that the shifting encountered in the working curves for the individual rare earths, when the proportions of the rare-earth mixture were changed, is essentially eliminated by placing 30  $\mu g$  of zinc on the electrodes. Microgram quantities of boron were removed quantitatively from methyl alcohol distillates by the use of a small Dowex 1 column, which is inverted before being stripped.

**Inorganic Preparations.** – Large quantities of pure inorganic compounds were prepared for the Chemistry and Physics Divisions and consisted chiefly of anhydrous halides of rare earths, alkaline earths, manganese, cobalt, and bivalent iron. A quantity of  $PdF_3$  was also prepared.



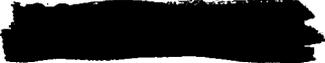
**Optical and Electron Microscopy.** — Particle-size studies were made on a variety of thorium oxide samples. The electron diffraction technique was used to identify the films and corrosion products formed on metals used in reactor engineering. Similar studies were made on two other corrosion products. Electron diffraction data that were taken on sodium tungstate are given. Representative materials studied by optical microscopy and autoradiography are listed. An electron microscopic study was made of metal surfaces on which plutonium was adsorbed. Special uses have been made of evaporated amorphous carbon films, and their use for the replication of metal surfaces is illustrated.

**ORNL Master Analytical Manual.** — Twenty-six new methods, revisions to thirty-eight methods, and tables of contents for the Thorex, Plutonium Isolation, and Purex process subsections have been issued to the *ORNL Master Analytical Manual*. Drafts of a large number of other new methods have been edited. Eight new manuals were issued.

#### SERVICE ANALYSES

Analytical service analyses are summarized in tabular form; special problems are discussed briefly. Ionic analyses related primarily to studies for the HRT. Radiochemical analyses included the determinations of the products of fast-neutron bombardments and of nitrogen-ion bombardments and many neutron-flux measurements. Nondestructive radiochemical measurements were made by gamma spectrometry and by the measurement of total gamma radiation. Many elements in microgram and submicrogram quantities in a variety of materials were determined by activation analysis; particle-size distribution studies were made by this method. Boron was determined by the neutron-density method of analysis. In the General Analyses Laboratory, vanadium and fluoride were determined by spectrophotometric titration. Electrolytic, gravimetric, spectrophotometric, flame-spectrophotometric, polarographic, and volumetric methods were used in the analysis of special samples and alloys. An apparatus for the determi-

nation of water in solids at 500°C was fabricated. Modifications are being made to the bromine-carbon-reduction apparatus. The determination by vacuum fusion of hydrogen, oxygen, and nitrogen in zirconium, titanium, vanadium, lead, nickel, and their alloys was continued. A bath of molten platinum is being used for vacuum-fusion determinations of oxygen in zirconium. Vacuum extraction was used to determine hydrogen in zirconium. A low-pressure, microcombustion carbon apparatus was used for the analysis of iron, steel, and Hastelloy for carbon. The determination of carbon in uranium tetrafluoride of low carbon content is being investigated. Special techniques were developed for determining zirconium in a variety of samples that were received relative to work on the HR chemical processing loops, the fluorination process for recovering uranium, and the dissolution of fuel elements. New fluxes for use in the fluorometric determination of uranium are being studied. Plutonium and uranium determinations were made on blanket solutions from the plutonium producer, on uranyl sulfate samples that had been irradiated in the LITR, and on special sand samples. An alpha-pulse analyzer was put into service in the Radioisotope Production Analyses Laboratory and was used especially for determining  $\text{Np}^{237}$  in the presence of  $\text{Pu}^{239}$ ; the discriminatory gamma scintillation counter was used extensively for  $\text{Pa}^{233}$  determinations by the same laboratory. Personnel are being trained intensively in the special techniques required for work in the HRLAF. Master-slave manipulators have been installed in all work cells in the HRLAF, and the sample-storage cell has been equipped. Several instruments have been set up in one of the work cells. The Reactor Analyses Group is perfecting techniques for the remotely controlled analysis of highly radioactive materials in the HRLAF. The analyses include the automatic titration of sulfate with potentiometric end-point detection, coulometric titration of chloride and chromium, polarographic determinations of various elements, and the measurement of pH. Stainless steel fuel elements were dissolved and analyzed satisfactorily when all operations were made by remote means only.



## SUMMARY - Y-12 SITE

### RESEARCH AND DEVELOPMENT

The staff of the HRP Analytical Chemistry Laboratory has been concerned primarily with the determination of corrosion products both in solutions of uranyl sulfate and in slurries of thorium compounds. Methods developed or investigated for the determination of different elements in solutions of uranyl sulfate included the precipitation of tin on an aluminum carrier and the subsequent polarographic estimation of tin, an internal electrolysis procedure for the deposition of copper, an indirect method for the determination of halides by the flame photometry of silver, estimation of carbon dioxide in gas mixtures by thermal conductivity methods, and a spectrophotometric method for the determination of oxygen as the oxygen-pyrogallol complex in gas-liquid mixtures. The study of the amperometric titration of mercury with tetraphenylarsonium chloride was extended in order to establish the degree of interference of uranyl, cadmium, and stannic ions.

Methods studied for the determination of different constituents in thorium oxide samples included the spectrophotometric determination of gold as the gold-*p*-dimethylaminobenzalrhodanine complex, the removal of fluoride from thorium oxide by pyrohydrolysis, the determination of silicon dioxide as the blue silicomolybdate complex, and the spectrophotometric method for the estimation of titanium as the peroxidized 8-quinolinol complex. It was also established that zirconium can be determined spectrophotometrically by either the quercetin method or the chloranilic acid method after the extraction of zirconium from solutions of thorium oxide into a carbon tetrachloride solution of thenoyltrifluoroacetone. In addition to these methods, studies were made to evaluate the applicability of both the 8-quinolinol and the alizarin red S spectrophotometric method to the determination of aluminum.

The Wagner turbidimetric and the Andreasen pipet methods were applied to the determination of the particle-size distribution of thorium oxide. The effectiveness of both an aqueous and a xylene medium for the dispersion of the oxide was evaluated for samples of thorium oxide that had been ignited at different temperatures and that were subjected to dynamic tests in test loops.

The Methods Development Group has evaluated methods for the following: the determination of small amounts of carbon monoxide in solutions of cuprous chloride, the extraction of uranium with tridecylphosphine oxide, the synthesis of trioctylphosphine oxide, the estimation of the concentration of octanol-2 in solutions of sodium sulfate, and the spectrophotometric determination of molybdenum.

### SERVICE ANALYSES

The Raw Materials Group analyzed a wide variety of samples; the analyses included the determination of the components of the high-molecular-weight organo-phosphorus compounds; the electrodeposition of cobalt; the analysis of two lithium ores, petalite and spodumene; the estimation of boron in organic solutions of boron trifluoride; and the flame photometry of the alkali metals. Additional analyses were made to determine the specific gravity and viscosity of aqueous and organic solutions.

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

A tabulation of the 41,264 analyses which were reported by the service groups is included in which the distribution of the work from different divisions is given. Of these analyses, 97% were made for the Reactor Experimental Engineering and Materials Chemistry Divisions.

## 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
Blosser, H. G., C. D. Goodman, T. H. Handley,* M. L. Randolph	" <sup>14</sup> Mev ( <i>n, α</i> ) Cross-Section Measurements"	<i>Phys. Rev.</i> 100, 429 (1955)
Blosser, H. G., T. H. Handley*	"Survey of ( <i>p, n</i> ) Reactions at 12 Mev"	<i>Phys. Rev.</i> 100, 1340 (1955)
Edgerton, J. H., H. G. Davis, L. C. Henley, M. T. Kelley	"Filter System for Radioactive Exhaust from Flame Spectrophotometer"	<i>Anal. Chem.</i> 28, 557 (1956)
Feldman, C., J. Y. Ellenburg	"Spectrochemical Determination of Boron in Carbon and Graphite"	<i>Anal. Chem.</i> 27, 1714 (1955)
Lyon, W. S., T. H. Handley	"Radioactive Ca <sup>47</sup> "	<i>Phys. Rev.</i> 100, 1280 (1955)
Lyon,* W. S., N. H. Lazar	"Decay of Mg <sup>27</sup> "	<i>Phys. Rev.</i> 101, 1524 (1956)
Lyon, W. S., S. A. Reynolds	"Radioactive Species Induced in Reactor Cooling Water"	<i>Nucleonics</i> 13(10), 60 (1955)
Lyon, W. S., R. R. Rickard	"Gamma-Ray Branching in Sr <sup>89</sup> "	<i>Phys. Rev.</i> 100, 112 (1955)
Menis, O., T. C. Rains	"Colorimetric Determination of Palladium with Alpha-Furildioxime"	<i>Anal. Chem.</i> 27, 1932 (1955)
Shults, W. D., II, P. F. Thomason, M. T. Kelley	"Coulometric Titrations with Electrolytically Generated Uranous Ion"	<i>Anal. Chem.</i> 27, 1750 (1955)
Van Artsdalen, E. R., D. Brown, A. S. Dworkin, F. J. Miller*	"Self-Diffusion in Molten Sodium Nitrate"	<i>J. Am. Chem. Soc.</i> 78, 1772 (1956)
Whitehead, <sup>1</sup> T. H., H. W. Wright*	"Estimation of Acetate in Zinc Plating Baths"	<i>Anal. Chem.</i> 27, 1834 (1955)

### ORAL PRESENTATIONS

Author(s)	Title	Presented at
Blosser, <sup>2</sup> H. G., T. H. Handley*	"( <i>n, p</i> ) Cross-Section Measurements at Medium Energies"	Meeting of Southeastern Sec- tion of the American Physi- cal Society, Nashville, Tenn., March 29-31, 1956
Brooksbank, W. A., Jr., G. W. Leddicotte, W. S. Lyon, <sup>2</sup> S. A. Reynolds	"Slow-Neutron Activation Cross Sections of Sev- eral Elements"	Nuclear Engineering and Science Congress, Clevel- and, Ohio, Dec. 12-16, 1955

<sup>1</sup>Dept. of Chemistry, Univ. of Georgia.

<sup>2</sup>Speaker.



Author(s)	Title	Presented at
Brooksbank, W. A., Jr., G. W. Leddicotte, S. A. Reynolds <sup>2</sup>	"Applications of Ion Exchange in Analytical Chemistry"	Southeastern Regional Meeting, American Chemical Society, Columbia, S.C., Nov. 3-5, 1955
Brooksbank, W. A., Jr., G. W. Leddicotte, <sup>2</sup> J. E. Strain <sup>3</sup>	"Neutrons in Chemical Analysis"	Nuclear Engineering and Science Congress, Cleveland, Ohio, Dec. 12-16, 1955
Ellenburg, J. Y., <sup>2</sup> C. Feldman	"Chemical Separation of Rare Earths from Thorium Prior to Spectrographic Analysis"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Penn., Feb. 27-March 2, 1956
Feldman, C.	"Special Spectrochemical Techniques of Interest to Chemists, Metallurgists, and Biologists"	University of Kentucky, Lexington, Dec. 14, 1955; University of Florida, Gainesville, Jan. 5, 1956
	"The Measurement of Temperatures in Spark Discharges"	University of Florida, Gainesville, Jan. 5, 1956
Feldman, <sup>2</sup> C., W. K. Wittels	"Sample Transport and Temperature Studies in Porous-Cup Discharges"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Penn., Feb. 27-March 2, 1956
Kelley, <sup>4</sup> M. T.	"The Chemical Analysis of Highly Radioactive Materials"	Southeastern Regional Meeting, American Chemical Society, Columbia, S.C., Nov. 3-5, 1956
Leddicotte, G. W.	"Methods of Chemical Analysis for Determining the Rare-Earth Elements"	Conference on Rare Earths in Biochemical and Medical Research, ORINS, Oak Ridge, Tenn., Oct. 27-29, 1955
	"Nuclear Methods in Chemical Analysis"	Seventh Annual Nuclear Sciences Seminar, Oak Ridge, Tenn., Nov. 28-Dec. 10, 1955
Leddicotte, <sup>2</sup> G. W., W. A. Brooksbank, Jr.	"Determination of Trace Elements in Metals and Alloys by Radioactivation Analysis"	108th Meeting, Electrochemical Society, Pittsburgh, Penn., Oct. 9-13, 1955

<sup>3</sup>U. S. Navy.

<sup>4</sup>Presented by P. F. Thomason.





Author(s)	Title	Presented at
Lyon, <sup>2</sup> W. S., W. A. Brooksbank, Jr., S. A. Reynolds, G. W. Leddicotte	"Gamma Spectrometric Analysis in Reactor Technology"	Nuclear Engineering and Science Congress, Cleveland, Ohio, Dec. 12-16, 1955
Lyon, W. S., S. A. Reynolds <sup>2</sup>	"Assay of K-Capture Nuclides with a Proportional Counter Spectrometer"	Southeastern Regional Meeting, American Chemical Society, Columbia, S.C., Nov. 3-5, 1955
Manning, <sup>2</sup> D. L., A. S. Meyer, Jr., J. C. White	"Complexometric Titration of Zirconium Based on Use of Ferric Iron as Titrant and Disodium-1,2-dihydroxybenzene-3,5-disulfonate as Indicator"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Penn., Feb. 27-March 2, 1956
Menis, O., T. C. Rains <sup>2</sup>	"Chloride Determination, Indirect Flame Photometric Method"	Southeastern Regional Meeting, American Chemical Society, Columbia, S.C., Nov. 3-5, 1955
Menis, O., I. B. Rubin <sup>2</sup>	"Determination of Microgram Quantities of Disodium Ethylenediaminetetraacetate"	Southeastern Regional Meeting, American Chemical Society, Columbia, S.C., Nov. 3-5, 1955
Mottern, J. L.	"Chemical Analysis of Highly Radioactive Materials and Design of a High-Radiation-Level Analytical Facility"	3161st Engineer Research and Development Unit, U. S. Army Reserve, Oak Ridge, Tenn., March 14, 1956
Reynolds, S. A.	"Recent Advances in Analytical Radiochemistry"	Virginia Polytechnic Institute, Blacksburg, Nov. 29, 1955
Susano, <sup>5</sup> C. D., O. Menis, C. K. Talbott	"Determination of Uranium by Differential Spectrophotometry"	Southeastern Regional Meeting, American Chemical Society, Columbia, S.C., Nov. 3-5, 1955
White, <sup>2</sup> J. C., A. S. Meyer, Jr., D. L. Manning	"Differential Spectrophotometric Determination of Beryllium"	Southeastern Regional Meeting, American Chemical Society, Columbia, S.C., Nov. 3-5, 1955
Wright, <sup>2</sup> H. W., E. I. Wyatt, S. A. Reynolds, W. S. Lyon	"Half Lives of Several Radionuclides"	Nuclear Engineering and Science Congress, Cleveland, Ohio, Dec. 12-16, 1955

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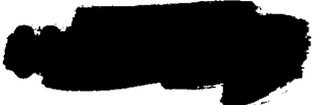
<sup>5</sup>Presented by J. P. Young.



TOPICAL REPORTS

Author(s)	Title	Report No.
French, J. R.	"Determination of Alkali Metal and Alkaline-Earth Elements by Flame Photometry: A Bibliography"	ORNL-2001 (Oct. 31, 1955)
Handley, T. H.	"Measurement of Activities in Off-Gas System of the ART"	ORNL CF-56-1-15 (Jan. 5, 1956)
Handley, T. H., W. S. Lyon	"Radiochemical Analytical Requirements for HRT"	ORNL CF-56-1-79 (Jan. 19, 1956)
Handley, T. H., S. A. Reynolds	"Investigation of Chromium-55"	ORNL CF-56-3-65 (March 14, 1956)
House, H. P., <i>et al.</i>	"Methods of Analysis of Anisole-BF <sub>3</sub> Solutions"	ORNL-2014 (Dec. 7, 1955)
Leddicotte, G. W., S. A. Reynolds	"Neutron Activation Analysis"	ORNL CF-55-11-20 (Nov. 2, 1955)
Meyer, A. S., Jr., B. L. McDowell, J. C. White	"Determination of Traces of Uranium Metal by Decomposition of the Hydride"	ORNL-2003 (Dec. 2, 1955)
Miller, F. S., P. F. Thomason	"Automatic Photometric Titration of Sulfate"	ORNL-2040 (Feb. 29, 1956)
Reynolds, S. A.	"Gamma Counting Efficiencies"	ORNL CF-56-1-87 (Jan. 18, 1956)
Reynolds, S. A., W. S. Lyon, E. I. Wyatt	"Radioisotope Assay Methods at Oak Ridge National Laboratory"	ORNL CF-56-1-130 (Jan. 25, 1956)
Stelzner,* R. W., M. J. Kelly, J. W. Landry	"ORNL Inline Instrumentation Program for FY56 and FY57"	ORNL CF-55-12-145 (Dec. 14, 1955)
Susano, C. D., J. S. Decker <sup>6</sup>	"Application of the Beckman Model K Automatic Titrator to the Potentiometric Determination of Uranium"	ORNL-2031 (Jan. 26, 1956)
Toomer, F. M.	"Electron Microscopy of Thorium Oxide Samples"	ORNL CF-56-1-53 (Jan. 11, 1956)
	"Electron Micrographs of Thorium Oxide Irradiated in Cobalt Source for About 500 Hours"	ORNL CF-56-1-112 (Jan. 24, 1956)
	"Electron Microscopy of Thorium Oxide Samples"	ORNL CF-56-1-176 (Jan. 1, 1956)
	"Electron Micrographs of Thorium Oxide Samples"	ORNL CF-56-2-120 (Feb. 27, 1956)
Toomer, F. M., T. E. Willmarth	"Electron Micrographs and Electron Diffraction of Sample 100 H Loop, Run No. 79"	ORNL CF-55-10-40 (Oct. 10, 1955)
	"Electron Micrographs of ThO <sub>2</sub> , Code No. 3434-69-650"	ORNL CF-55-12-73 (Dec. 16, 1955)
White, J. C.	"Chemical Examination of Cold Trap from Intermediate Heat Exchanger Test Stand No. 1"	ORNL CF-55-11-102 (Nov. 17, 1955)

<sup>6</sup>Summer employee from Phoenix College, Phoenix, Arizona.





Author(s)	Title	Report No.
White, J. C., A. S. Meyer, Jr., B. L. McDowell	"Determination of Dissolved Oxygen in Lubricating Fluids"	ORNL-2059 (March 9, 1956)
Willmarth, T. E.	"A Study of the Surface Films on a Stainless Steel Rupture Disc, and an Aperture Plate Formed During Exposure in a Thorium Oxide Slurry Loop"	ORNL CF-56-1-28 (Jan. 9, 1956)
	"Examination of the Scale, and Precipitate from In-pile Loop Run 15-2"	ORNL CF-56-3-46 (March 8, 1956)

METHODS ISSUED TO ORNL MASTER ANALYTICAL MANUAL

Author(s)	Title	Number(s)	Date
<b>New Methods</b>			
Brady, L. J.	"Index of Refraction, Abbe Refractometer Method"	1 10005	2-6-56
	"pH, Measured with a Beckman Model M pH Meter"	1 10006	2-6-56
	"Viscosity, Measurement by Means of the Saybolt Viscosimeter"	1 100082	2-6-56
	"Chromium, Volumetric Perchloric Acid-Ferrous Sulfate Method"	1 212170 9 00712170	2-13-56
	"Chromium, Volumetric Persulfate Oxidation Method"	1 212171 9 00712171	2-24-56
	"Vanadium, Spectrophotometric Hydrogen Peroxide Method"	1 219310 9 00719310	2-24-56
Coombe, D. J., S. A. Reynolds	"Tin-113 in Antimony-125 CF Product Solutions"	9 0733892	9-15-55
Corbin, L. T.	"Table of Contents"	9 01	12-12-55
	"Table of Contents"	9 04	12-12-55
	"Table of Contents"	9 05	12-12-55
French, J. R.	"Ammonia, Spectrophotometric Pyridine-Pyrazolone Method"	1 215610 9 00715610	2-28-56
Goldberg, G.	"Lithium, Volumetric 2-Ethyl-1-Hexanol-Volhard Method"	1 214570 9 00714570	2-13-56
Lynn, E. C.	"Bromide, Gravimetric Silver Nitrate Method"	1 211350 9 00711350	2-29-56
	"Bromide, Volumetric Volhard Method"	1 211370 9 00711370	2-24-56
	"Chloride, Gravimetric Silver Nitrate Method"	1 212050 9 00712050	2-14-56
	"Iron, Volumetric Dichromate Method"	1 214170 9 00714170	2-13-56





Author(s)	Title	Number(s)	Date
Lyon, W. S.	"Single-Channel Gamma Scintillation Spectrometer"	2 00367 5 00367 9 00367	9-26-55
Manning, D. L.	"Beryllium, Differential Spectrophotometric <i>p</i> -Nitrobenzeneazo-Orcinol Method"	1 211011 9 00711011	2-10-56
	"Chromium and Vanadium in Alkali-Metal Hydroxides, Anion-Exchange-Spectrophotometric Method"	1 212111 1 219311 9 00712111 9 00719311	5-10-55
Moore, F. L.	"Total Americium and Curium, Lanthanum Fluoride Method"	2 31031 2 31240 9 003030 9 008240	8-29-55
	"Neptunium-237, Thenoyltrifluoroacetone Method"	2 31530 9 003530	8-29-55
	"Neptunium-239, Lanthanum Fluoride Method"	2 31531 9 008531	8-26-55
	"Plutonium(III,IV) and Plutonium(V,VI), Lanthanum Fluoride Method"	2 31622 9 008622	8-29-55
Ross, W. J.	"Standard Chromous Sulfate Solution"	1 00425 9 00425	8-19-55
Talbott, C. K.	"Thorium, Volumetric Versenate Method"	1 218770 9 00718770	8-12-55
Vaughan, W. F.	"Care and Use of Platinum Ware"	1 001001 9 001001	11-16-55
Williams, C. R.	"Carbon in Inorganic Fluoride Salts, Ammonium Oxalate Separation Method"	9 0922170	11-22-55
Wyatt, E. I.	"Barium-133, Product Analysis Guide"	9 0733084	9-8-55
	"Rubidium-86, Product Analysis Guide"	9 0733721	11-28-55

**Revised Methods**

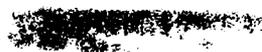
McCutchen, R. L.	"Statistical Treatment of Data"	1 0060 9 0050	R, 11-28-55
Walker, R. L.	"Aluminum, Potassium Fluoride Acid Titration Method"	1 210270 9 00710270	R, 2-16-56
Wilson, G. R.	"Thorium, Spectrophotometric Thoron Method"	1 218710 9 00718710	R, 2-15-56
	"Uranium-233 in Thorex Process Solutions, Hexone Extraction Method"	9 0123920	R, 2-16-56
Wyatt, E. I.	"Antimony-125 CF, Product Analysis Guide"	9 0733042	R, 8-8-55
	"Arsenic-73,74 CF, Product Analysis Guide"	9 0733061	R, 12-8-55
	"Barium-140, Product Analysis Guide"	9 0733081	R, 12-8-55





Author(s)	Title	Number (s)	Date
	"Barium-140, Gamma Ionization Chamber Method"	9 0733082	R. 9-6-55
	"Beryllium-7, Product Analysis Guide"	9 0733101	R. 12-8-55
	"Cadmium-115m HSA, Product Analysis Guide"	9 0733141	R. 12-8-55
	"Calcium-45, Product Analysis Guide"	9 0733151	R. 12-8-55
	"Cerium-141,144, Product Analysis Guide"	9 0733181	R. 12-8-55
	"Cesium-137, Product Analysis Guide"	9 0733191	R. 12-8-55
	"Chlorine-36, Product Analysis Guide"	9 0733201	R. 12-19-55
	"Chromium-51, Product Analysis Guide"	9 0733211	R. 12-8-55
	"Cobalt-60, Product Analysis Guide"	9 0733221	R. 12-19-55
	"Iridium-192, Product Analysis Guide"	9 0733401	R. 12-19-55
	"Iron-55,59, Product Analysis Guide"	9 0733411	R. 12-8-55
	"Mercury-203, Product Analysis Guide"	9 0733491	R. 12-8-55
	"Neodymium-147-Promethium-147, Product Analysis Guide"	9 0733511	R. 12-8-55
	"Nickel-63, Product Analysis Guide"	9 0733541	R. 12-8-55
	"Phosphorus-32, Product Analysis Guide"	9 0733601	R. 12-8-55
	"Potassium-42, Product Analysis Guide"	9 0733641	R. 12-8-55
	"Praseodymium-143, Product Analysis Guide"	9 0733651	R. 12-8-55
	"Promethium-147, Product Analysis Guide"	9 0733661	R. 12-8-55
Wyatt, E. I.	"Ruthenium-103,106, Product Analysis Guide"	9 0733731	R. 12-19-55
	"Scandium-46, Product Analysis Guide"	9 0733751	R. 12-19-55
	"Selenium-75, Product Analysis Guide"	9 0733761	R. 12-19-55
	"Silver-110m, Product Analysis Guide"	9 0733781	R. 12-19-55
	"Sodium-22, Product Analysis Guide"	9 0733791	R. 12-8-55
	"Sodium-24, Product Analysis Guide"	9 0733792	R. 12-8-55
	"Strontium-89,90, Product Analysis Guide"	9 0733801	R. 12-8-55
	"Sulfur-35, Product Analysis Guide"	9 0733811	R. 12-8-55
	"Tantalum-182, Product Analysis Guide"	9 0733821	R. 12-19-55
	"Tungsten-185, Product Analysis Guide"	9 0733911	R. 12-8-55
	"Yttrium-91, Product Analysis Guide"	9 0733961	R. 12-8-55
	"Yttrium-88, Product Analysis Guide"	9 0733962	R. 12-8-55
	"Zinc-65, HSA, Product Analysis Guide"	9 0733971	R. 12-8-55





# ANALYTICAL CHEMISTRY DIVISION - X-10 SITE

## RESEARCH AND DEVELOPMENT

### IONIC ANALYSES

P. F. Thomason

#### Spectrophotometric Determination of Aluminum in the Presence of Thorium and Uranium

R. E. Biggers

A method was requested for the determination of aluminum in the organic BU stream of the Thorex process. The maximum concentrations of thorium, uranium, and aluminum in the BU stream were estimated to be 10, 20 to 500, and 1 ppm, respectively.

A three-stage extraction method has been developed and written for inclusion in the *ORNL Master Analytical Manual*.<sup>1</sup> The aluminum is determined by extraction as aluminum quinolate into chloroform. Quantities of aluminum from 1 to 60  $\mu\text{g}$  can be determined by the use of 10 ml of chloroform. The highest aluminum concentration that can be measured spectrophotometrically is 6  $\mu\text{g}$  of aluminum per milliliter of the chloroform extract. The inclusion of acetate, carbonate, 1,10-phenanthroline, and cyanide complexation renders the method essentially selective for aluminum. The first stage of the extraction utilizes a concentrated acetate buffer (to mask thorium) that contains hydroxylamine hydrochloride, 1,10-phenanthroline, and ammonium carbonate (to mask uranium). The second and third extraction stages are performed by the use of a dilute acetate buffer and an alkaline cyanide solution, respectively.

Since the aluminum is isolated by a series of extractions, the ultimate sensitivity of the method depends upon the size of the test portion of the sample. Aluminum concentrations in the original sample as small as 0.04 ppm can be determined by use of a 25-ml test portion, which is subsequently reduced in volume prior to the aluminum determination.

Statistical evaluation of the method indicated that the relative standard error is  $\pm 3\%$  (95% probability level) at aluminum concentrations of 0.5 and 1.0  $\mu\text{g}$  per milliliter of chloroform extract. A

<sup>1</sup>R. E. Biggers, "Aluminum in the Presence of Thorium and Uranium, Spectrophotometric Oxine (8-Hydroxyquinoline) Method," Method Nos. 1 210211 and 9 00710211 (in press), *ORNL Master Analytical Manual*.

relative standard error of  $\pm 16\%$  (95% probability level) was obtained at an aluminum concentration of 0.1  $\mu\text{g}$  per milliliter of chloroform.

The method is ideally suited for the determination of aluminum in thorium oxide samples, as well as in metallic thorium and in uranium. The repetitive analysis of thorium oxide samples that contained as little as 0.002% aluminum has yielded results of good precision. The method should prove useful for the determination of microgram quantities of aluminum in alloys of uranium and of thorium, the extent of usefulness depending upon the type and amounts of alloying materials. The method has not yet been evaluated for the analysis of alloys. Enough hydrofluoric acid to dissolve solid thorium oxide samples can be used without interference. Detailed information concerning interfering and noninterfering anions and cations is given in the method.<sup>1</sup>

In the analysis of Thorex BU-stream samples it is necessary to remove the aluminum, plus the thorium and uranium, from the organic solvent. A process method was developed<sup>2</sup> for extracting the aluminum from the sample under essentially the same conditions as those used in the pulse-extraction columns in the plant. Directions are also given in the method for the pretreatment of CU-stream samples. After isolation of the aluminum, thorium, and uranium, the aluminum is determined by the method discussed above.<sup>1</sup> Techniques for handling BU- and CU-stream samples that yield pseudo emulsions during the pretreatment of the sample are also given.

#### Simultaneous Spectrophotometric Determination of Chromium(III) and Chromium(VI)

R. E. Biggers

A method was requested for the rapid determination of chromium(III) and chromium(VI) in the presence of iron(III) and nickel, which were expected to be present in 13 M nitric acid used for

<sup>2</sup>R. E. Biggers, "Aluminum in BU and CU Streams of Thorex Process, Spectrophotometric Oxine (8-Hydroxyquinoline) Method," Method No. 9 0122022 (in press), *ORNL Master Analytical Manual*.

corrosion studies on stainless steel. A spectrophotometric method outlined very briefly by Harvey and Hill<sup>3</sup> was investigated further. Horton and Thomason<sup>4</sup> have studied a polarographic-ion-exchange method for the determination of the two chromium species in HR fuel, and Boyd<sup>5</sup> has also investigated a simultaneous spectrophotometric determination of the two chromium species in a solution that contained both aluminum nitrate and nitric acid. Two wavelengths are used for the determination of chromium(III) and (VI) in the same solution. The absorbancy of chromium(III)-Versenate is measured at 600  $m\mu$ , where chromium(VI), iron(III), and nickel(II) cause no interference. The absorbancy of the uncomplexed chromium(VI) is measured at 370  $m\mu$ . Since chromium(III)-Versenate and iron(III) absorb light at this wavelength, it is necessary to correct the absorbancy measurement made at 370  $m\mu$  for their absorbancies.

The complex of chromium(III) with disodium dihydrogen ethylenediaminetetraacetate (Versenate) is formed in an ammoniacal solution of pH 9.5 that contains chromium(III) and (VI), iron(III), and nickel. The absorption spectra of the chromium(III)-Versenate, chromium(VI), iron(III), and nickel were examined under the same conditions. The effect of the concentration of Versenate on the formation of the blue chromium(III)-Versenate complex at pH 9.5 and the effect of heat on the rate of complexation were also studied. The spectral absorbancy curve of the complex shows a broad absorption peak at 600  $m\mu$ . Chromium(VI), iron(III), and nickel absorb only *very* slightly at this wavelength. At very small (ppm) chromium(III) concentrations, there is a very slight interference from iron(III) and chromium(VI). At 600  $m\mu$  the calibration curve for chromium(III)-Versenate at pH 9.5 is linear from 0 to 100 ppm, and the molar absorbancy index is about 120.

<sup>3</sup>A. E. Harvey, Jr., and F. M. Hill, "Simultaneous Spectrophotometric Determination of Chromium(III) and Chromium(VI)," abstracted in *Southern Chemist* XV(3), 108 (1955); a paper presented at Southeastern Regional Meeting of Am. Chem. Soc., Columbia, S. C., Nov. 5, 1955.

<sup>4</sup>A. D. Horton and P. F. Thomason, "Polarographic Determination of Chromium(III) and (VI) and Total Chromium in Homogeneous Reactor Fuels," *Anal. Chem. Semiann. Prog. Rep.* April 20, 1955, ORNL-1880, p 1.

<sup>5</sup>C. M. Boyd, "Simultaneous Spectrophotometric Determination of Trivalent and Hexavalent Chromium," *Anal. Chem. Semiann. Prog. Rep.* Oct. 20, 1955, ORNL-1973, p 34.

A second absorbancy measurement made on the same solution at 370  $m\mu$  allows chromium(VI) to be determined. The measurement at 370  $m\mu$  must be corrected for the absorbancy by the chromium(III)-Versenate complex at this wavelength. A correction for the interference of iron(III) at 370  $m\mu$  can be made if the concentration of iron is known from a separate iron determination. The effect of iron(III) and chromium(III) on the absorbancy of chromium(VI) at 370  $m\mu$  is additive. Calibration curves for chromium(VI) from 0 to 5 ppm at 370  $m\mu$  are linear, and those for iron(III) and chromium(III)-Versenate at 370  $m\mu$  are also linear from 0 to 15 and 0 to 100 ppm, respectively. At 370  $m\mu$  the molar absorbancy index of the uncomplexed chromium(VI) in the Versenate solution at pH 9.5 is about 5000.

Since the demand for this analysis has ceased, work on the method has been discontinued temporarily.

#### Apparatus for Sampling Uranium Hexafluoride and Fluorine Gases

A. D. Horton      P. F. Thomason

A gas-sampling manifold<sup>6</sup> has been fabricated of  $\frac{3}{8}$ -in.-dia copper tubing and of Hoke nickel valves of the diaphragm-needle type. All connections are made by silver soldering. An evacuated U-tube, immersed in a mixture of dry ice and trichloroethylene, will be provided for condensing uranium hexafluoride. The flow of the gas will be measured by a sensitive thermoelectric flowmeter.

Fluorine is to be collected in an evacuated glass bulb of known volume. A mercury manometer, in which the mercury column is protected from the fluorine by a layer of concentrated sulfuric acid, will be used to measure the pressure of the gas sample in the bulb. The manifold has been cleaned with water and acetone and is now being tested under vacuum for leaks.

#### Determination of Europium and Lithium in Lithium Iodide Crystals

A. D. Horton      P. F. Thomason

Europium as  $\text{EuCl}_3$  is of current interest as an activator for lithium iodide crystals used in scintillation counters. The polarographic method

<sup>6</sup>S. H. Smiley, S. C. Schumen, and H. C. Andersen, *Analysis of Gaseous Mixtures of Fluorine, Hydrogen Fluoride, and Nitrogen*, D-31 (April 1, 1946).

of Miller<sup>7</sup> for the determination of europium in lithium iodide has been improved. Europium and lithium ions in 0.5 M hydrochloric acid solution have been separated from iodide ions by ion exchange on hydrogen-form Dowex 50 cation resin of 2% cross linkage. Europium and lithium ions are adsorbed by the resin, and iodide ion, which interferes in the polarographic determination of europium, passes through the resin column. Europium and lithium are eluted from the column with 6 M hydrochloric acid, and the eluate is evaporated to dryness. The residue is dissolved in hydrochloric acid, and the pH of the solution is adjusted to  $5.2 \pm 0.1$  with ammonium hydroxide. Europium is determined polarographically by the standard-addition technique at an  $E_{1/2}$  of  $-0.67$  v vs the S.C.E.

Lithium was determined gravimetrically on a separate aliquot of the sample. Sulfuric acid (1:1) is added to the sample, which is contained in a porcelain crucible, and the iodide is oxidized and is evolved as iodine by evaporating the sample to dryness on a hot plate. The residue is ignited for 30 min at  $600^{\circ}\text{C}$  and weighed as  $\text{Li}_2\text{SO}_4$ .

#### Polarographic Determination of Tin in HR Fuels

P. F. Thomason

It will be necessary to determine tin in HR fuels in order to ascertain the rate of corrosion of the Zircaloy, which contains approximately 2% tin, that is used in the construction of the HRT. Preliminary results have shown that 50  $\mu\text{g}$  of tin can be coprecipitated with 4 mg of iron by use of sodium carbonate as precipitant. The sodium carbonate complexes the uranium and thus prevents its precipitation with the ferric hydroxide. The precipitate of ferric hydroxide and stannic hydroxide is dissolved in a small amount of hydrochloric acid, and the ferric chloride is reduced to ferrous chloride with hydroxylamine hydrochloride. The solution is made 4 M in ammonium chloride and is then polarographed. In this medium, tin gives a well-defined wave at an  $E_{1/2}$  of  $-0.52$  v vs the S.C.E.<sup>8</sup> By this method a recovery of 90 to 95% of the tin has been obtained from a synthetic

<sup>7</sup>H. H. Miller, "Polarographic Determination of Europium in Lithium Iodide," *Anal. Chem. Semiann. Prog. Rep.* Oct. 20, 1953, ORNL-1639, p 1.

<sup>8</sup>J. J. Lingane, "Polarographic Behavior of Chloro and Bromo Complexes of Stannic Tin," *J. Am. Chem. Soc.* **67**, 919 (1945).

HR fuel sample that contained 50  $\mu\text{g}$  of tin and 10 mg of uranium.

#### Amperometric Titration of Zirconium

H. Kubota

Relative to their study of certain volatility processes, the Chemical Technology Division requested a method for the determination of macro amounts of zirconium in radioactive materials that would contain macro amounts of uranium and fluoride and micro amounts of iron. The amperometric determination of zirconium with standard cupferron solution, described by Olson and Elving,<sup>9</sup> was investigated and was found to be adaptable to the prescribed conditions. The titration of an aliquot of a standard zirconium solution with standard cupferron solutions that were prepared by dissolving known weights of cupferron in a known volume gave results that were slightly higher than the known. The relative standard deviation obtained with solutions prepared from cupferron taken directly from reagent bottles without further purification was 1%. The standard deviation was improved to 0.5% by standardizing the titrant against the standard zirconium solution. Small amounts of iron were effectively removed from a 6 M HCl solution of the test portion by one extraction with ethyl ether. It was found advantageous to heat zirconium samples to fumes of  $\text{SO}_3$  in order to break up any polymeric aggregates of zirconium that may have been present prior to the titration. The acid content of the solution was never allowed to become smaller than 2 M after the fuming.

#### Determination of Nitrogen in Magnesium

H. Kubota

The Electronuclear Research Division requested the determination of nitride nitrogen in a specimen of magnesium metal that had been vaporized and coated upon a silver backing. The magnesium was stripped from the silver backing, and the nitride nitrogen content of it was determined by a modified Kjeldahl method; Conway diffusion cells were used. The dissolution of magnesium metal in hydrochloric or sulfuric acid converts all nitrides present to ammonia, which can be determined subsequently by evolution from an alkaline medium into a known amount of standard acid present in

<sup>9</sup>E. C. Olson and P. J. Elving, "Amperometric Titration of Zirconium. Application to Fluoride Solution," *Anal. Chem.* **26**, 1747 (1954).

excess. Because of the very small amount of the magnesium metal sample and its small nitrogen content, the diffusion procedure<sup>10</sup> was adopted. An approximately 0.025 M standard solution of NaOH was found to be best suited for the titration of the excess acid.

The nitrogen content of magnesium powder taken from the laboratory supply shelf (B & A code 1900) was found to be 0.003%. The sample of magnesium metal was found to contain 0.031% nitrogen. Amounts of nitrogen as small as 10  $\mu\text{g}$  were determined with a relative standard deviation of 10%. The method is claimed to be applicable to the determination of microgram amounts of nitrogen with "precision of the order of 1%."

### Conductometric Determination of Fluoride

H. Kubota

The determination of milligram quantities of fluoride fixed on a Dowex 2 resin was desired with a "precision of about 0.5%" by the Chemistry Division. Milligram quantities of fluoride are too small to be determined with good precision and accuracy by the gravimetric lead chlorofluoride method.<sup>11</sup> The volumetric titration<sup>12</sup> with thorium nitrate solution was considered, but a method that was applicable in the presence of the resin was desired.

Most chemical determinations of fluoride depend upon the formation of a complex between the fluoride ion and some metal ion, in which complex a minimum of three or four ligands are bound to the central metal ion. Unless the final complex has an unusually great stability, difficulties due to dissociation can be expected near the equivalence point if a volumetric method is used. It is often possible to compensate for this phenomenon by using a method in which the end point is obtained by graphical extrapolation, such as amperometric or conductometric titration. Standard solutions of fluoride were titrated conductometrically with standard solutions of lanthanum acetate; a relative standard deviation of approximately 0.5% was ob-

<sup>10</sup>P. L. Kirk, *Quantitative Ultramicroanalysis*, p 171-173, Wiley, New York, 1950.

<sup>11</sup>J. C. White, "Fluoride, Lead Chlorofluoride Method," Method Nos. 1 212850 and 9 00712850 (8-12-53), *ORNL Master Analytical Manual*.

<sup>12</sup>J. H. Edgerton, "Fluoride, Modified Willard-Winter Volumetric Method," Method Nos. 1 212870 and 9 00712870 (2-23-53), *ORNL Master Analytical Manual*.

tained. The optimum fluoride concentration was found to be 5 to 10 mg per 100 ml of solution titrated. The fluoride held on Dowex 2 resin was determined by suspending the resin in a volume of water sufficient to make the estimated fluoride concentration come into the optimum range, liberating the fluoride from the resin by the addition of at least an equivalent amount of sodium perchlorate, and then titrating the liberated fluoride conductometrically with standard lanthanum acetate solution. The results of the analysis of triplicate test portions of the resin were 3.25, 3.23, and 3.27 mg of fluoride per gram of air-dried resin.

### Anodic Dissolution Technique

F. J. Miller

Use has been made of anodic dissolution techniques to dissolve stainless steel sandwiches of uranium dioxide into a 5% sulfuric acid solution. Subsequent electrolysis of the solution in a Melaven mercury cathode cell effectively separated the interfering metallic constituents from the uranium.<sup>13-15</sup> The procedure was developed for the Reactor Analyses Group and is peculiarly adaptable to remote handling techniques, which were worked out by the Reactor Analyses Group.

A similar anodic dissolution technique was employed to dissolve Hg-Ti amalgams, which were reported to give difficulty in dissolution.

### Organic Coprecipitants

F. J. Miller

A study was made of the use of methyl violet and tannin as organic coprecipitants in the determination of tin.<sup>16</sup> The results were not promising; therefore the study has been discontinued.

<sup>13</sup>J. Gurney *et al.*, *The Use of the High Current Mercury Cathode in Uranium Determination*, K-1106 (Feb. 26, 1954).

<sup>14</sup>G. E. F. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis*, p 94, Wiley, New York, 1938.

<sup>15</sup>J. A. McLaren *et al.*, *The Electrolytic Dissolution of Metallic Uranium*, K-587 (April 17, 1950).

<sup>16</sup>V. I. Kuznetsov, "Organic Coprecipitants (Collectors). I. The Theoretical Bases of Organic Coprecipitant Action," *J. Anal. Chem. (U.S.S.R.)* 9(4) 221 (1954).

**Conductometric Studies of Thorium Oxide Slurries**

F. J. Miller

A number of measurements of conductance have been made on slurries of various thorium oxide powders in equilibrium water. The results of the measurements were used by the Chemical Technology Division as an indication of the mode of preparation and the temperature of calcination of the thorium oxide.

**ANALYTICAL INSTRUMENTATION**

D. J. Fisher

**Instrumentation for the High-Radiation-Level Analytical Facility (HRLAF)**

**Testing of the Remotely Controlled Falling-Drop Densimeter** (R. B. Quincy, Jr., R. W. Stelzner, D. J. Fisher). – The program to test the remotely controlled falling-drop densimeter<sup>17</sup> is nearing completion. This densimeter will be used in cell 5 of the HRLAF to determine the density or specific gravity of aqueous, radioactive fuel solutions from the Thorex and Metal-Recovery processes and to determine the percentage of deuterium oxide in Homogeneous Reactor type solutions. Synthetic, nonradioactive standards, with a density range and a chemical composition approximating those anticipated for Thorex and Metal-Recovery process type of samples, were prepared. Solutions of aluminum nitrate of appropriate density were used as HR-type standards. The organic dropping medium is a stable, ternary system of Nujol, phenylcyclohexane, and 1,1,2,2-tetrabromoethane. The density and viscosity of this medium are altered by changing the ratio of its constituents in order to obtain conditions for which Stokes' law is valid. For the analysis of Thorex and Metal-Recovery feed solutions the dropping medium has a density that is about 0.03 g/ml less than that of the sample of lowest density and has a relatively high viscosity of about 175 millipoises. A wide density range (i.e., 0.15-g/ml range) is covered by a single oil. For the analysis of HR-type solutions that are 98 to 100% deuterium oxide, only a 0.05-g/ml range is covered by a single oil. Such oils have a viscosity of 50 to 75 millipoises and a density that is 0.01

to 0.02 g/ml less than that of the lightest deuterium oxide sample to be analyzed.

The following experimental parameters were found to give the best results. The size of the drop is 5  $\mu$ l. A stainless steel needle tip having a bore diameter of 0.020 in. is used on the remotely servo-controlled 0.1-ml pipet; this makes possible pierce-sampling through the Buna N diaphragm of the sample bottle. The use of a Teflon tip of 0.013-in. bore diameter gives the same precision of drop formation. A temperature of 30°C was selected for the dropping medium after it was found that an appreciable difference (approximately 10°C) between the temperature of the medium and that of the drop did not affect the precision of the results.

It was found that successive drops formed by the pipetter were not of equal size; this irregularity resulted from the nonlinearity of the Duodial (Helipot Corp. Cat. No. W-10) that was used on the Q-1348 control unit. The standard deviation for a ten-drop series was about 0.5 to 1%. The Duodial has been replaced by an Ackerman dial, which improves the precision by a factor of 3.

It was found that variation in the bias voltages of the 2D21 tubes in the Q-1551 control unit within the range -3 to -5 v does not affect the observed value of fall times provided that the voltages applied to the two tubes are the same.

A study is being conducted of the extent of variation in calibration curves obtained over a period of months. The greatest density range observed among a set of AF-stream Thorex synthetic standards over a two-month period was 0.003 g/ml.

It is planned to develop improved dropping media for use in the measurement of the density of deuterium oxide samples so that a density change corresponding to 0.1 wt % changes in D<sub>2</sub>O content can be accurately detected without the necessity of frequently checking calibration curves.

**Remotely Controlled Turret Assembly for the Falling-Drop Densimeter** (R. W. Stelzner). – Assembly drawings (ORNL-LR-Dwgs. Nos. 12571, 12572, and 12574) and detail drawings (ORNL-LR-Dwgs. Nos. 12573, 12575, and 12576) for a remotely controlled turret assembly for the falling-drop densimeter have been completed. The turret will be fabricated in the ORNL Central Machine Shop for installation in cell 5 of the HRLAF.

<sup>17</sup>R. W. Stelzner *et al.*, "Remotely Controlled Falling-Drop Densimeter," *Anal. Chem. Semiann. Prog. Rep.* April 20, 1955, ORNL-1880, p 6.

The turret assembly of the HRLAF is patterned closely after that of the Thorex model.<sup>18</sup> Six glass "fall tubes" are located symmetrically about a tapered roller-bearing-supported shaft that is driven by a 1-rpm Bodine motor. The fall tubes are indexed in the light beams by a microswitch-detent arrangement. Water, at a temperature of  $30.00 \pm 0.03^\circ\text{C}$ , is circulated at a flow rate of 1 gpm through the annulus of the turret assembly.

A new, enlarged drain ( $\frac{3}{4}$ -in. OD), located on the return line of the water bath at an angle of 45 deg to the vertical, eliminates flooding dangers that would occur in restoring electrical service after failure. [A power-failure lockout circuit (ORNL-Q-1652) has been installed in the falling-drop densimeter that is already located in Building 3019, in order to prevent flooding that might be caused by unattended startup of that equipment after an electrical failure.] The standpipe of the HRLAF turret assembly will be shorter and will be fabricated completely of stainless steel. A grease seal that consists of a felt washer and metallic disk has been placed on the roller bearing. Silver soldering in place of Heliarc welding has been specified throughout the turret assembly in order to minimize heat distortion of machined parts.

**Cathodic Reduction in the Water Bath of the Falling-Drop Densimeter** (L. C. Bate). – It was found that the commercial-model water bath of the falling-drop densimeter had become extensively corroded by electrolytic action and that the small particles of corrosion products had circulated through the water system. A magnesium rod<sup>19</sup> was fastened in the water bath in order to control the corrosion by cathodic protection. During the first six weeks after the magnesium rod was placed in the water bath, the corrosion particles became detached from the corroded parts and were circulated in the water system but caused no trouble to the optical system. The water was replaced, and since then all the metal parts have retained their luster, the water has remained clear, and the magnesium rod has shown little loss.

**Lazy-Susan Type of Bottle Holder for Falling-Drop Densimeter** (L. C. Bate). – Two types of Lazy Susans for positioning and holding bottles

used in conjunction with the falling-drop densimeter were considered. A fork type was designed, built, and tested; it was unsatisfactory because it permitted too much movement of the bottles. A double-jaw type that has one movable jaw proved satisfactory and will be used. The Lazy Susan is attached to the standpipe of the turret of the falling-drop densimeter. It positions a bottle under the pipet; by the rotation of it through a 90-deg arc, the bottle is located where it can be removed from the densimeter.

**Remotely Servo-Controlled 0.1- and 1-ml Pipetters** (M. T. Kelley, D. J. Fisher, R. B. Quincy, H. C. Jones). – All remotely servo-controlled 0.1- and 1-ml pipetters that are required for use in the HRLAF<sup>20</sup> have been fabricated. The pipets have been tested under vacuum and found to be leak-free. The ORNL model Q-1348 control units of the pipetters have been revised to include a variable end-resistor for adjusting the volumes delivered from the 0.1- and 1.0-ml pipets to exactly 0.1 and 1  $\mu\text{l}$  per dial division, respectively. The mechanism of one complete 1-ml pipetter has been inspected and adjusted, and the accuracy and precision of the pipetter have been checked by the titration of aliquots of standard reagent delivered by it. This pipetter is now installed in cell 1 of the HRLAF.

**Decapper-Stirrer Train** (C. L. Burros). – The decapper-stirrer train<sup>21</sup> was built and tested and was found to operate satisfactorily. Mechanical drawings (ORNL-LR-Dwgs. Nos. 10313–10316) of the decapper-stirrer train have been made, and the Central Machine Shop has fabricated four of these units. The decapper-stirrer train is mounted on the same base that holds the remotely servo-controlled 1-ml sampling pipet.<sup>20</sup>

**ORNL Model Q-1728 Potentiometric Titrator of the Automatic, Velocity-Servo Type** (M. T. Kelley, D. J. Fisher). – Circuit diagrams and mechanical drawings were prepared for the ORNL model Q-1728 potentiometric titrator, which is an automatic, velocity-servo type. The Instrument Department of the Instrumentation and Controls Division has

<sup>18</sup>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.

<sup>19</sup>N. Carlisle, "Rust – How You Can Stop It," *Better Homes and Gardens*, p 176 (Sept. 1955).

<sup>20</sup>M. T. Kelley and D. J. Fisher, "Remotely Servo-Controlled Sampling Pipetters," *Anal. Chem. Semiann. Prog. Rep.* Oct. 20, 1955, ORNL-1973, p 4–5.

<sup>21</sup>C. L. Burros and L. C. Bate, "Sample-Bottle Decapper for the High-Radiation-Level Analytical Facility," *Anal. Chem. Semiann. Prog. Rep.* Oct. 20, 1955, ORNL-1973, p 5.

fabricated three of these titrators.<sup>22</sup> The Special Analyses Group is delineating the performance of one of these instruments by the titration of uranium with standard ferric and standard ceric solutions. One of the three titrators will be installed in the HRLAF.

**ORNL Model Q-1734 Filter Photometer** (W. L. Maddox). – Three ORNL model Q-1734 filter photometers have been fabricated and tested. Modifications were made in both the original design and the finished instruments. A new filter holder was designed to facilitate changing the filters. Four of the new filter holders have been fabricated. The original mechanical drawings are being revised to include the modifications.

**Conversion of Dual-D.M.E. (Dropping-Mercury Electrode) Polarograph** (W. L. Maddox). – In addition to the ORNL model Q-1160 polarograph already in use, another polarograph is needed for intermittent use by the Reactor Analyses Group. Until the development and testing of the ORNL model Q-1673 polarograph are completed, a polarograph that was designed originally for use with dual dropping-mercury electrodes<sup>23</sup> will be used. The circuit of this instrument has been modified for adaptation of the instrument for routine work.

**Pressurized Polarographic Cell** (W. L. Maddox, L. C. Bate). – The design features mentioned in the previous report<sup>24</sup> were incorporated into a second model of the pressurized polarographic cell. The S.C.E. and the mercury reservoir are enclosed in the same shell; thus the length of the salt bridge is reduced to a minimum. The two compartments of the cell are separated by a partition cast from Houghton Laboratories' Hysol epoxy resin. It was found that the resin shrinks slightly after a few days, thus allowing sufficient leakage of liquid from the S.C.E. compartment to contaminate the mercury in the reservoir below. In addition, the leakage of gas from the pressure chamber causes bubbling in the S.C.E. Because of this undesirable feature, the resin was rejected, and another cell (described by W. L. Maddox in the section "Reactor Analyses") was used.

<sup>22</sup>M. T. Kelley and E. B. Wagner, "Automatic Velocity-Servo Potentiometric Titrator," *Anal. Chem. Semiann. Prog. Rep.* April 20, 1955, ORNL-1880, p 7.

<sup>23</sup>D. J. Fisher, L. C. Bate, and W. L. Maddox, "Dual Dropping-Mercury-Electrode Polarograph," *Anal. Chem. Semiann. Prog. Rep.* Oct. 20, 1953, ORNL-1639, p 6.

<sup>24</sup>R. W. Stelzner, D. J. Fisher, and L. C. Bate, "Pressurized Polarographic Cell," *Anal. Chem. Semiann. Prog. Rep.* Oct. 20, 1955, ORNL-1973, p 4.

**Plastic Pipet for Remotely Servo-Controlled Dilution Pipetter** (L. C. Bate). – The pipet of the 3-ml remotely servo-controlled dilution pipetter<sup>25</sup> was modified into a 1-ml fluorothene-lined pipet that is provided with Teflon sealing units at each end.<sup>20</sup> The plunger was also constructed of fluorothene so that the sample would contact the plastics only. The Spectrographic Analyses Group will use this pipet in the HRLAF to pipet solutions that are corrosive to stainless steel. The inside diameter of the pipet tip was reduced from 0.040 to 0.020 in. in order to prevent the sample from leaking out. This pipet is operated by means of the ORNL model Q-1348 control unit. The relative standard deviations for the delivery of 10-, 25-, and 100- $\mu$ l increments were found to be 1.67, 1.26, and 0.64%, respectively.

**Mounts for Binocular and Monoculars** (L. C. Bate). – Prototypes of the mounts for the 8  $\times$  30 binocular and monocular and the 20  $\times$  60 monocular of modified focal range have been built and tested. The mechanical drawing of the mounts (ORNL-LR-Dwg. No. 12513) has been supplied to the Central Machine Shop, where eight mounts will be fabricated for use in the HRLAF.

**Motorized Arc Stand** (L. C. Bate). – The arc stand<sup>26</sup> that was designed and built at Iowa State College was motorized to permit remotely controlled operation; it is to be used by the Spectrographic Analyses Group in the HRLAF. For the purpose of positioning the arc and replacing electrodes, a control unit having interlocked circuits (ORNL-LR-Dwg. No. 12380) was designed. Tantalum inserts were fabricated for the electrode holders.

**Remotely Operated Unit for Disposal of Radioactive Samples** (H. C. Jones). – A remotely operated disposal unit for radioactive samples is being designed for use in the HRLAF. The design of the unit is such that the self-sealing diaphragm of the sample-bottle cap (Engineering Dept. Dwg. No. A-15808) will be pierced by two needles. One needle will be connected to a water aspirator, which will permit discharge of the waste sample directly into the hot drain. The other needle will

<sup>25</sup>L. C. Bate, "The 3-ml Remote Control Dilution Pipetter," *Anal. Chem. Semiann. Prog. Rep.* Oct. 20, 1955, ORNL-1973, p 5-6.

<sup>26</sup>J. Weber, Jr., et al., "Excitation Stand for Spectrographic Analysis. A New Design," *Spectrochem. Acta* 5, 345 (1953).

first be vented to the atmosphere to allow for removal of the waste sample, and then it will be connected to a water bottle for rinsing of the sample bottle. The empty sample bottle will then be placed in the disposal container by the master-slave manipulator.

#### Application of the 16PM1 Multiplier Phototube to the High-Sensitivity Recording Flame Spectrophotometer

H. C. Jones            D. J. Fisher  
L. C. Bate             M. T. Kelley

Two research model 16PM1 multiplier phototubes<sup>27</sup> were received from the Farnsworth Electronics Co. These tubes were designed primarily for use in the wavelength region from 7,000 to 12,000 Å. A light-tight casing for the tubes was designed and was constructed from 24ST aluminum. The design of the casing is such that any part of the tube is easily accessible and the tube can be removed from its socket. The casing was constructed with a flange at one end in order to facilitate mounting of the tube on a Bausch & Lomb grating monochromator (Cat. No. 33-86-40-01). The construction of the casing, disassembled and assembled, is illustrated in ORNL photographs Nos. 16289 and 16290, respectively.

The ORNL model Q-1457 flame spectrophotometer was modified by the addition of nine type 5651 voltage reference tubes to the existing sixteen such tubes. This modification increased the maximum output voltage of the flame spectrophotometer from 1300 to approximately 2000 v. The flame spectrophotometer was then used as a power supply for the type 16PM1 multiplier phototube and as a means of controlling and recording the output of the tube.

One of the tubes is now being used in the determination of cesium at a wavelength of 8521 Å. It has proved to be extremely sensitive but shows considerable instability. According to the Farnsworth Electronics Co., the amount of instability observed is an inherent characteristic of this type of tube.

<sup>27</sup>M. T. Kelley and D. J. Fisher, "High-Sensitivity Recording Flame Photometer," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 5.

<sup>28</sup>M. T. Kelley, "Rectifier-Filter for Brown Recorder," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1953*, ORNL-1639, p 6.

#### Modification of the Light-Measuring Unit of the Leeds & Northrup Microphotometer

H. C. Jones            M. T. Kelley  
D. J. Fisher

The electronic light-measuring circuit of the Leeds & Northrup microphotometer (Cat. No. 6700P-1) was found to be unsatisfactory and was replaced by a Welch Densichron, the probe of which was attached to the front of the microphotometer by means of an adapter plate. A rectifier-filter<sup>28</sup> was used to modify the output of the Densichron for the Leeds & Northrup recorder. This arrangement proved to be very satisfactory.

#### Simplified Apparatus for the Pyrohydrolytic Determination of Fluorides

C. L. Burros            D. J. Fisher  
J. G. Surak<sup>29</sup>         L. C. Bate

The pyrohydrolysis apparatus described earlier<sup>30</sup> has been redesigned (ORNL-LR-Dwg. No. 11179), and the Central Machine Shop has fabricated one unit, which is being used by the General Analyses Group. The new design included the following modifications to the apparatus: the wall thickness of the nickel reactor tube was increased; the open end of the reactor tube was tapered inside so that it would form a better seal with the tapered Teflon stopper; the nickel seal plug was redesigned so as to direct the flow of gases to the all-metal condenser; and the cooling capacity of the condenser was increased. A Teflon handle was attached to the open end of the reactor tube to facilitate insertion of the Teflon stopper into the tube.

#### Heater for Automatic Potentiometric Titration of Uranium by the Ferric Sulfate Method

H. C. Jones

A heater (ORNL-LR-Dwg. No. 11823) was designed and constructed for use in the potentiometric titration of uranium by the ferric sulfate method.<sup>31</sup> The heater is of the jacket type and consists of a spool-shaped piece of 24ST aluminum

<sup>29</sup>Summer employee from Marquette University, Milwaukee, Wisc.

<sup>30</sup>M. T. Kelley, J. G. Surak, and D. J. Fisher, "Simplified Apparatus for the Pyrohydrolytic Determination of Fluorides," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 8.

<sup>31</sup>J. H. Cooper, "Uranium, Potentiometric Ferric Sulfate Method," Method Nos. 1 219222 and 9 00719222 (8-3-53), *ORNL Master Analytical Manual*.

that is open at one end and is encased along its full length in a tightly fitting sleeve. The heater is being used to maintain the solution at a constant temperature of  $90 \pm 5^\circ\text{C}$  during the titration; a Variac is used to regulate the output of the heater.

#### ORNL In-Line Instrumentation Assistance to the Savannah River Laboratory (SRL) and Plant (SRP)

R. W. Stelzner

The ORNL In-Line Instrumentation Group (J. W. Landry of the Chemical Technology Division, M. J. Kelly of the Instrumentation and Controls Division, and R. W. Stelzner) has been requested by the AEC under contract 2724 to assist the SRL in a program of in-line instrumentation testing and development. The two-year program, FY-56 and FY-57, is outlined in detail in an ORNL memorandum.<sup>32</sup>

A five-point program for ORNL assistance has been developed through meetings between SRL and ORNL representatives and is quoted<sup>33</sup> below:

1. *Review of Process Control.* – "Make a brief overall study of process control so as to integrate into the SRL program the experience ORNL has gained in continuous operation of their pilot plants."

2. *Development of Sampling Facilities.* – "Study sampling facilities so as to provide means for introducing a continuous sample into any analyzer. Include provisions for handling the contamination and dirt problems in sample cells with and without optical windows."

3. *Development of a Specific Gravity-Conductivity Instrument.* – "Develop plant-type methods and/or instruments for the practical application of the ACD's (SRL Analytical Chemistry Division's) findings on the dual use of specific gravity and conductivity to measure uranium and acid in high concentrations."

4. *Testing of In-Line Instruments in ORNL Hot Pilot Plants.* – "Test SRL instrument candidates in 'hot' facilities at the ORNL pilot plants. The first items which will be ready to go are the ACD's close-coupled alpha and gamma monitor prototypes."

<sup>32</sup>R. W. Stelzner, M. J. Kelly, and J. W. Landry, *ORNL In-Line Instrumentation Program for FY 56 and FY 57*, ORNL CF-55-12-145 (Dec. 14, 1955).

<sup>33</sup>DuPont memorandum from J. N. Wilson to G. Dessauer, *ORNL Program on In-Line Analyzers*, INS-D5 (Sept. 30, 1955).

5. *Laboratory Study of Basic Parameters.* – "Select one basic analytical parameter for laboratory study from among viscosity, refractive index, electropotentiometric methods, or others to be defined. This study will be chosen so as not to conflict with the ACD's program."

The study of process control has been completed. Brief descriptions of process control instrumentation, with the emphasis being on continuous evaporation control, for the ORNL Purex, Metal Recovery, and Thorex pilot plants have been assembled, and a report is being prepared.<sup>34</sup>

Specifications for an all-glass mockup of the SRP sampler have been drawn up from SRP blueprints. This sampler will be used in the development of a continuous in-line sampling system and will be used also for testing any instrument in which the hydraulics of the SRP sampler must be duplicated exactly.

At the request of SRL a study of radioactivity buildup on type 304L stainless steel in specific process streams has been initiated; specimens of type 304L stainless steel (measuring  $0.500 \times 1.000 \times 0.0625$  in.) have been electropolished to a high surface finish, examined metallographically, weighed, and then inserted in the Metal-Recovery ICW stream. The specimens are removed at definite intervals of time for radiochemical analyses for gross beta and gross gamma activities and for ruthenium and zirconium-niobium. A similar program for activity buildup on type 304L stainless steel in the Thorex CW stream is being carried out simultaneously.

Specifications for a Thorex type demister to de-entrain air from the air-lifted samples have been forwarded to SRL.<sup>35</sup>

New testing facilities for in-line instrumentation in the Metal-Recovery Expansion have been arranged with the Design Section of the Chemical Technology Division. Tentative plans call for  $36 \times 72 \times 18$  in. recesses in each of the hot cells and for approximately 30 in-line sampling lines embedded in the concrete. Steel shielding will be added, if required, to make up the loss of concrete. Where shielding is required, lead barriers will form

<sup>34</sup>J. W. Landry, M. J. Kelly, and R. W. Stelzner, "A Review of Process Control at the Oak Ridge National Laboratory Radiochemical Pilot Plants" (in preparation).

<sup>35</sup>Letter from J. W. Landry to R. C. Axtman of the Savannah River Laboratory (March 14, 1956).

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individual cubicles in the recesses for the separate instruments.

It is planned to use a K-25 type of Taylor pneumatic transmitter that has a sensitivity of 0 to 2 in. of water for the measurement of specific gravity. A transmitter of this type has been installed on the A column in the Metal-Recovery Plant. A cell fabricated from fluorothene and stainless steel has been designed for the conductivity measurement. The development of this instrumentation is being undertaken by the Instrumentation and Controls Division.

The first SRL instrument to be tested at ORNL under hot conditions will be a beta-gamma monitor of the swirl type. After a period of bench testing, the instrument will be installed on the Metal-Recovery Plant AW evaporator-overhead that goes to the fractionator. Approximately 5% of the flow will be recycled through the swirl cell. Plans for this installation have been completed.

An electropotentiometric method (polarography) has been chosen for laboratory study. The final objective will be to develop a production-plant type of instrument that will indicate uranium concentrations in waste streams. Circuit diagrams for an a-c polarograph that will use a phase discriminator method to minimize the condenser current have been drawn up, but final design is not yet set.

### RADIOCHEMICAL ANALYSES

S. A. Reynolds

#### Nuclear Properties

**Neutron Activation Cross-Section Program** (W. S. Lyon). — A program is under way to remeasure pile-neutron activation cross sections for the production of 118 radioactive species. The general method used is to irradiate target materials of very high purity, together with either a cobalt or a manganese monitor, in the ORNL Graphite Reactor. The induced activity in both sample and monitor is measured; from the induced activity in the monitor, the pile-neutron flux can be calculated; from the flux and the activity produced in the target material, the activation cross section can be calculated. When possible, the radioactive species produced are assayed by  $4\pi$  beta-gamma coincidence counting. If this method is impossible or impractical, other methods of assay, such as  $4\pi$  beta counting, absolute beta counting, absolute gamma-scintillation spectrometry, and ion-chamber

measurements, are used. The remeasured values obtained to date are listed below:

Nuclide Produced	Cross Section (barns)
K <sup>42</sup>	1.21
Cr <sup>51</sup>	13.8
Ni <sup>65</sup>	1.38
Cu <sup>64</sup>	3.89
Zn <sup>65</sup>	0.38
Zn <sup>69</sup>	0.095
Ga <sup>72</sup>	5.87
Rb <sup>86</sup>	0.83
Zr <sup>95</sup>	0.063
Mo <sup>99</sup>	0.55
Pd <sup>109</sup>	12.8
Ag <sup>110</sup>	4.83
Cs <sup>134</sup>	39.3
Ta <sup>182</sup>	35.3
W <sup>185</sup>	1.90

**Neutron Cross Section for the  $Y^{89}(n,\gamma)Y^{90}$  Reaction** (W. S. Lyon). — By the use of four different samples of  $Y_2O_3$  of very high purity, the pile-neutron cross section for the production of  $Y^{90}$  by the reaction  $Y^{89}(n,\gamma)Y^{90}$  has been measured. In addition, by the use of one of these samples only, the cadmium ratio through 20-mil cadmium has been obtained for the production of  $Y^{90}$ . This ratio was compared with the cadmium ratio for the production of  $Mn^{56}$  (a  $1/\nu$  absorber), which was produced by the irradiation of manganese in the same position in the reactor as was used for the yttrium (i.e., in a pneumatic tube of the ORNL Graphite Reactor). The results are as follows:

Pile-neutron activation cross section	1.20 ± 0.06 barns
Activity of unshielded $Mn^{56}$	
Activity of Cd-shielded $Mn^{56}$	17.8 ± 1
Activity of unshielded $Y^{90}$	
Activity of Cd-shielded $Y^{90}$	24.1 ± 3

**Chromium-55** (T. H. Handley, S. A. Reynolds). — An investigation<sup>36</sup> of the decay characteristics of  $Cr^{55}$  has shown that the radiation emitted from it contains less than 0.01% gamma radiation. The values of mass number and half life were also confirmed.<sup>36</sup>

<sup>36</sup>T. H. Handley and S. A. Reynolds, *Investigation of Chromium-55*, ORNL CF-56-3-65 (March 14, 1956).

### Measurement of Radioactivity

**4 $\pi$  Alpha-Gamma Coincidence Counting** (W. S. Lyon). – A 4 $\pi$  flow-type counter has been obtained and is now in use for 4 $\pi$  counting. A study has been made of the alpha-counting efficiency of an alpha proportional counter; Am<sup>241</sup> was used as the source of alpha radiation. The disintegration rate of the Am<sup>241</sup> was obtained by 4 $\pi$  alpha-0.060-gamma coincidence counting. The alpha-counting efficiency obtained indicates that the "polished-platinum" efficiency (i.e., the efficiency of a source mounted on polished platinum) is 51.2  $\pm$  0.2%.

### Radioisotope Analysis

**New Radioisotope Products and Methods** (W. S. Lyon). – Methods of assay have been developed for the following new radioisotope products: Mo<sup>99</sup>, W<sup>187</sup>, Au<sup>199</sup>, and Ag<sup>111</sup>.

### Fission-Product Methods

**Determination of Radiozirconium for the Angular-Correlation Experiment** (F. L. Moore). – A method was developed and tested for the determination of radiozirconium in aluminum foils used as collectors of fission fragments in the fission-fragment angular-correlation experiment, which is being conducted by the Electronuclear Research Division. The method, which involves thenoyltrifluoroacetone extraction of radiozirconium, was found to give an average carrier recovery of about 80% and excellent decontamination of radiozirconium from other radioelements. Details of the procedure are reported elsewhere.<sup>37</sup>

### Reactor Analyses

**Neutron-Flux Determinations** (H. W. Wright). – Since the last report<sup>38</sup> there has been an increase in the number of neutron-flux measurements made by the gamma spectrometric determination of Cr<sup>51</sup> and Zr<sup>95</sup>. The technique employed is to expose samples of known composition in a known neutron flux and then to compare their Cr<sup>51</sup> and Zr<sup>95</sup> gamma photopeaks with those of the same photopeaks in similar samples exposed to a neutron flux of unknown value.

<sup>37</sup>F. L. Moore, *Radiozirconium Determination for the Angular Correlation Experiment*, ORNL CF-56-4-8 (April 4, 1956).

<sup>38</sup>H. W. Wright, "Neutron-Flux Determinations," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 10.

### Process Analysis

**Determination of Pa<sup>233</sup> in Thorex Process Solutions** (F. L. Moore). – The analytical method for the determination of Pa<sup>233</sup> in Thorex process solutions<sup>39</sup> has been revised slightly in order to eliminate Sb<sup>125</sup> interference and to increase Nb<sup>95</sup> decontamination. The revision provides for extracting the Pa<sup>233</sup> from the diisobutyl carbinol into 6 M sulfuric acid-6 M hydrofluoric acid. The revised method will be included in a paper to be submitted for publication in *Analytical Chemistry*.

### Electronuclear Research Program

T. H. Handley

The measurement of the cross sections of ( $n, \alpha$ ) reactions is being continued in cooperation with members of the Electronuclear Research Division. In addition, the experimental measurement of ( $n, p$ ) cross sections at medium neutron energies (i.e., 12 to 16 Mev) is in progress. Also, excitation functions for nitrogen-induced nuclear reactions in several light elements are being determined. In general, adaptation of well-known radiochemical procedures was sufficient for determining the excitation functions. A procedure for the radiochemical determination of N<sup>13</sup> was developed and will be reported in detail in the open literature (presumably in *Analytical Chemistry* or *Nucleonics*). In cooperation with members of the Electronuclear Research Division an experimental search for a long-lived radionuclide of nitrogen was made but was unsuccessful. A number of analyses of special targets, such as Al<sup>26</sup>, Y<sup>88</sup>, and Ni<sup>63</sup>, were also made for that division.

### Solvent-Extraction Methods

**Liquid-Liquid Extraction Method for Cerium** (F. L. Moore, G. W. Smith<sup>40</sup>). – A procedure has been developed for the liquid-liquid extraction of cerium in either tracer (i.e., with no added carrier) or macro amounts. The method involves oxidation of the cerium with sodium bromate, followed by extraction of the cerium into 0.5 M thenoyltrifluoroacetone (TTA) from 0.5 M sulfuric acid. The method will be published in the open literature (presumably in *Analytical Chemistry*).

<sup>39</sup>F. L. Moore, "Protactinium-233 in Thorex Process Solutions, Diisobutylcarbinol Extraction Method," Method No. 9 0123670 (9-30-54) *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and III.

<sup>40</sup>Present address, Curtiss-Wright Corp., Clifton, N. J.

### Electrolytic Methods

#### Preparation of Plutonium Sources (F. L. Moore).—

Two plutonium sources were prepared for the Biology Division by the electrodeposition of plutonium on platinum foils. The area of each deposit was 1 cm<sup>2</sup>, and the deposits contained approximately 126 and 292 μg of Pu<sup>239</sup>.

### ACTIVATION ANALYSES

G. W. Leddicotte

#### Quantitative Applications of Activation Analysis

**Cobalt in Nickel, Inconel, and Hastelloy** (G. W. Leddicotte, W. A. Brooksbank).— Microgram and submicrogram quantities of cobalt in nickel, Inconel, and Hastelloy have been determined by means of the neutron reaction  $\text{Co}^{59}(n,\gamma)\text{Co}^{60}$  (5.3 y). In each analysis the irradiation period was at least 87.5 hr in one of the ORNL reactors. After being irradiated, the samples were processed by a radiochemical procedure involving either an ion-exchange separation of the cobalt as the hexachlorocobaltic anion on a Dowex 1 resin column or the precipitation of the cobalt as potassium cobaltinitrite. The comparator technique was used in each case; additional details concerning these analyses follow.

As indicated in a previous report,<sup>41</sup> some interference in the cobalt determination could be expected from the products of the reactions of fast neutrons upon nickel, that is,  $\text{Ni}^{60}(n,p)\text{Co}^{60}$  (5.3 y) and  $\text{Ni}^{58}(n,p)\text{Co}^{58}$  (72 d). Interference from these sources was avoided by irradiating the samples in periphery positions of the reactor, in which positions there are no fast neutrons. Concentrations of cobalt as small as 10<sup>-6</sup> g per gram of nickel have been determined in this manner.

Of particular interest in the Inconel samples was the determination of the distribution of the cobalt. The cobalt concentration was found to be  $1.60 (\pm 0.08) \times 10^{-3}$  g per gram of Inconel and was uniform throughout the samples. Interference from  $\text{Co}^{58}$  (72 d), produced by the reaction  $\text{Ni}^{58}(n,p)\text{Co}^{58}$ , was eliminated by use of the gamma discriminatory counter<sup>42</sup> to measure the separated cobalt radioactivity.

Concentrations of cobalt as small as 10<sup>-6</sup> g per gram of Hastelloy were determined in several specimens of Hastelloy.

**Cobalt in Alumina Pellets Used as Neutron-Flux Monitors** (W. A. Brooksbank).— Activation analysis has been applied to determining an element (in this instance, cobalt) in a previously activated material without encountering interference from the initial activity. Alumina pellets that contained cobalt and that were used by the Solid State Division to monitor the neutron flux obtained in in-pile experiments were analyzed. The quantity of cobalt in the pellets varied; therefore it was necessary to know the quantity of cobalt in each pellet in order to calculate the neutron flux. Cobalt in the radioactive alumina pellets was determined by reirradiating the pellets; in the reirradiation, the neutron flux and the irradiation time were equal to or greater than those of the in-pile experiments. In each analysis the initial  $\text{Co}^{60}$  radioactivity of each pellet was measured in a gamma ionization chamber, after which the pellet was reirradiated in the LITR for a period of 30 hr. Following a decay period of at least 10 days, the  $\text{Co}^{60}$  radioactivity was again measured by means of the gamma ionization chamber. A cobalt (0.38%)–aluminum alloy was used for the cobalt standards, which were irradiated; then the standards and the alumina pellets were measured simultaneously. The difference in  $\text{Co}^{60}$  radioactivity in each pellet was then compared with the  $\text{Co}^{60}$  from the cobalt comparator in order to determine the total inactive cobalt in the pellets. The quantity of cobalt in the pellets was found to range from 0.049 to 0.071 mg per pellet.

**Tantalum in Niobium and Silicon** (R. E. Druschel, G. W. Leddicotte).— Microgram and submicrogram amounts of tantalum have been determined in niobium and in silicon by the neutron reaction  $\text{Ta}^{181}(n,\gamma)\text{Ta}^{182}$  (111 d). In each instance the  $\text{Ta}^{182}$  radioactivity was determined without the sample having to be destroyed. The photopeak areas displayed in a spectral analysis that was made by means of a single-channel gamma-scintillation spectrometer were used in calculating the results. Concentrations of tantalum as small as

<sup>41</sup>H. A. Mahlman, "Determination of Microgram Amounts of Cobalt in Nickel," *Anal. Chem. Semiann. Prog. Rep.* April 20, 1954, ORNL-1717, p 16.

<sup>42</sup>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.

$2.00 \times 10^{-6}$  and  $0.45 \times 10^{-6}$  g per gram of niobium and of silicon, respectively, were observed.

**Tellurium in Indium Arsenide** (W. A. Brooksbank). – The series of  $(n, \gamma)$  reactions on  $\text{Te}^{122}$ ,  $\text{Te}^{124, 126, 128, 130}$  to produce  $\text{Te}^{123, 125, 127, 129}$ ,  $\text{Te}^{131}$  were used to determine microgram amounts of tellurium in indium arsenide. An isotopic-carrier technique was used for the separation of the tellurium. The beta activity of the separated tellurium radioisotopes was measured by means of a Geiger-Mueller counter. The comparator technique was used in measuring the tellurium present. The results obtained in the analysis of several samples that were irradiated for 5.0 days in the ORNL Graphite Reactor showed tellurium concentrations of the order of  $43.2 \pm 0.2 \mu\text{g}$  per gram of indium arsenide.

**Selenium in Copper and in Indium Arsenide** (G. W. Leddicotte, J. E. Strain,<sup>43</sup> W. A. Brooksbank). – The neutron reaction  $\text{Se}^{74}(n, \gamma)\text{Se}^{75}$  (127 d) has been used to determine microgram and submicrogram quantities of selenium in copper and in indium arsenide. A radiochemical procedure involving the separation of the selenium carrier, which was added to the solution of the irradiated sample, by distillation and a final precipitation of elemental selenium was used. The separated radioactivity was measured by gamma counting; the comparator technique was used. Concentrations of selenium of  $104.0 \pm 7.0 \mu\text{g}$  per gram of indium arsenide and as small as  $0.20 \mu\text{g}$  per gram of copper were determined.

**Arsenic in Silicon and in Aluminum Oxide** (W. A. Brooksbank, G. W. Leddicotte). – The neutron reaction  $\text{As}^{75}(n, \gamma)\text{As}^{76}$  (26.8 h) has now been used to determine microgram and submicrogram amounts of arsenic in silicon and in aluminum oxide. Isotopic-carrier and comparator techniques of analysis were used. The separated  $\text{As}^{76}$  was measured by beta counting. Concentrations of arsenic as small as 1.0 and  $0.22 \mu\text{g}$  per gram of silicon and of aluminum oxide, respectively, were determined.

**Silicon in Niobium** (W. T. Mullins). – Niobium has been analyzed for microgram amounts of silicon by the neutron reaction  $\text{Si}^{30}(n, \gamma)\text{Si}^{31}$  (2.7 h). The method of analysis described previously<sup>44</sup> was used. Concentrations of silicon as small as  $5.0 \mu\text{g}$  per gram of niobium were determined.

**Copper in Chromium and in Zirconium** (W. T. Mullins, G. W. Leddicotte). – The determination of microgram and submicrogram amounts of copper by the neutron reaction  $\text{Cu}^{63}(n, \gamma)\text{Cu}^{64}$  (12.8 h) has been extended to include the analysis of chromium and of zirconium for copper. A radiochemical separation of the  $\text{Cu}^{64}$  by isotopic carrying was made, and the radioactivity of the  $\text{Cu}^{64}$  was measured by gamma counting. The comparator technique was used. Concentrations of copper as small as 4.0 and  $0.30 \mu\text{g}$  per gram of chromium and of zirconium, respectively, were determined.

**Uranium in Various Materials** (W. A. Brooksbank, G. W. Leddicotte). – The determination of microgram and submicrogram amounts of natural and enriched uranium by activation analysis has been extended. Concentrations of  $\text{U}^{235}$  as small as  $1.0 \mu\text{g}$  per gram of corrosion products from an Inconel test loop were determined by the reaction  $\text{U}^{235}(n, \text{fission})\text{Ba}^{140}$ . The  $\text{Ba}^{140}$  was separated by an adaptation of the radiochemical procedure used in determining fission products.<sup>45</sup>

The neutron reaction  $\text{U}^{238}(n, \gamma)\text{U}^{239} \xrightarrow[23.5 \text{ m}]{\beta^-} \text{Np}^{239}$  (2.3 d) was used to determine the concentration of uranium in samples of eutectic salts, slag, copper, biological materials, stainless steel, and siliceous materials. The method described elsewhere<sup>46</sup> was used in these analyses. Typical results are shown below:

Sample	Uranium Concentration Range ( $\mu\text{g/g}$ )
Eutectic salts	<1.0
Slag	10 to $10^3$
Copper	10 to $10^3$
Biological materials	<1.0
Stainless steel	1 to 10
Siliceous materials	10 to $10^3$

**Sulfur in Various Materials** (W. A. Brooksbank). – Microgram quantities of sulfur were determined in chromium, tin, silicon, and indium arsenide by the

<sup>44</sup>W. T. Mullins and G. W. Leddicotte, "Determination of Microgram Amounts of Silicon," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 16.

<sup>45</sup>D. N. Hume, N. E. Ballou, and L. E. Glendenin, "Barium (Hydrochloric Acid-Ether Method)," *A Manual of the Radiochemical Determination of Fission Product Activities*, CN-2815 (June 30, 1945), p 19-22.

<sup>46</sup>H. A. Mahlman and G. W. Leddicotte, "Determination of Microgram and Submicrogram Amounts of Uranium," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 15.

<sup>43</sup>U. S. Navy.

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fast-neutron reaction  $S^{32}(n,p)P^{32}$  (14.3 d). Isotopic-carrier and comparator techniques of analysis were used. Typical results obtained in these analyses follow:

Sample	Sulfur Concentration ( $\mu\text{g/g}$ )
Chromium	<10.0
Tin	<10.0
Silicon	1 to 5
Indium arsenide	98, 31

**Silver in Zirconium-Silver Alloys** (W. T. Mullins). - Activation analysis has been used to assay small amounts (milligrams or, at most, fractions of a gram) of zirconium-silver alloys for silver content. The neutron reaction  $Ag^{109}(n,\gamma)Ag^{110m}$  (270 d) was used in the analyses. After an approximate five-week irradiation in the LITR, the test samples were dissolved and the  $Ag^{110m}$  was separated from contaminant radioelements by an isotopic-carrier technique. The  $Ag^{110m}$  was then measured by gamma counting; the comparator technique was used. Typical results showed that the silver content of the samples was of the order of 1.25 wt %.

<sup>47</sup>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 16-17.

### Activation Analysis as a Qualitative or Semiquantitative Method

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

The applications of activation analysis as a qualitative method have been reported previously.<sup>47-49</sup> The method has now been applied to the qualitative analysis of petroleum cracking catalysts, selenium, quartz, silicon, and animal tissue. In these applications, most of the analyses were completed either by a radiochemical separation method or by the use of a direct measurement of gamma activity by means of a single-channel gamma scintillation spectrometer. Table 1 shows the results of these investigations.

### Identification of Radionuclides Induced in Structural Materials

J. H. Oliver      W. A. Brooksbank  
G. W. Leddicotte      S. A. Reynolds<sup>50</sup>

The induced radionuclides that have been identified or determined in certain metals and alloys

<sup>48</sup>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.

<sup>49</sup>J. H. Oliver *et al.*, "Activation Analysis as a Qualitative or Semiquantitative Method," *Anal. Chem. Semiann. Prog. Rep.* Oct. 20, 1955, ORNL-1973, p 14.

<sup>50</sup>Radiochemical Analyses Group.

TABLE 1. RESULTS OF QUALITATIVE ANALYSIS OF CERTAIN MATERIALS BY ACTIVATION ANALYSIS

Sample	Radioelements <sup>a</sup>	
	Positively Identified	Probably Present
Petroleum cracking catalysts	Au <sup>198</sup> , Mo <sup>99</sup> , Na <sup>24</sup> , Cu <sup>64</sup> , As <sup>76</sup> , Fe <sup>59</sup> , Co <sup>60</sup> , Mn <sup>56</sup> , P <sup>32</sup> , S <sup>35</sup> , Ni <sup>65</sup> , Al <sup>28</sup> , Si <sup>31</sup>	W <sup>187</sup> , Zr <sup>95,97</sup> , Nb <sup>95</sup> , Hg <sup>197,203</sup>
Selenium	As <sup>76</sup> , Mo <sup>99</sup> , Cu <sup>64</sup> , Cd <sup>115m,115</sup> , Ni <sup>65</sup> , Zn <sup>65,69</sup> , Fe <sup>59</sup> , Co <sup>60</sup> , Sb <sup>122,124</sup> , Ge <sup>71,75</sup> , Cr <sup>51</sup> , Ca <sup>45</sup> , Se <sup>75</sup> , Te <sup>129m,131m</sup>	Sn <sup>125</sup>
Quartz	Au <sup>198</sup> , Si <sup>31</sup>	As <sup>75</sup> , Sb <sup>122,124</sup>
Silicon	Si <sup>31</sup> , Na <sup>24</sup> , P <sup>32</sup> , Al <sup>28</sup> , <sup>b</sup> Ta <sup>182</sup>	Au <sup>198</sup>
Animal tissue	Cr <sup>51</sup> , Mn <sup>56</sup> , Na <sup>24</sup>	As <sup>76</sup> , Cu <sup>64</sup>

<sup>a</sup>Products of (n,γ) reactions, unless indicated otherwise.

<sup>b</sup>Formed by the reaction  $Si^{28}(n,p)Al^{28}$ .

used as structural materials for reactors are listed in Table 2. The analyses were made on either the radioactive sample coupons that were used in loop studies or the nonradioactive structural material itself after it was activated. The techniques of analysis involved either a direct measurement of the radioactive sample or a radiochemical separation.

### Use of Discriminatory Gamma Counting

W. A. Brooksbank      R. E. Druschel

The method of discriminatory gamma counting<sup>51</sup> has been extended to the determination of the radioisotopes listed in Table 3; the instrumental conditions are indicated.

<sup>51</sup>W. A. Brooksbank, S. A. Reynolds, and G. W. Leddicotte, "Use of Discriminatory Gamma Counting," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 12.

Of particular interest is the determination of microgram amounts of iron in zirconium.<sup>52</sup> The need for complete decontamination of Fe<sup>59</sup> from the Zr<sup>95</sup>-Nb<sup>95</sup> is eliminated by use of the discriminatory counter. Sodium-22 is used as a secondary standard to establish the pulse-height setting (PHS) for counting the Fe<sup>59</sup>. The nuclides Zr<sup>95</sup> and Nb<sup>95</sup> have gamma activities whose spectra overlap; therefore a photopeak appears at 720 kev but has no effect on the region of the spectrum where Fe<sup>59</sup> is counted. However, at high counting rates, two photons of Zr<sup>95</sup> and/or Nb<sup>95</sup> may strike the crystal simultaneously and be recorded as a unit photon of approximately 1.4-Mev energy. This "pile up" would then cause interference in the Fe<sup>59</sup> determination. The results of a study of these effects are shown in Table 4.

<sup>52</sup>W. T. Mullins, "Determination of Iron in Hafnium and in Zirconium," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 16.

TABLE 2. INDUCED RADIONUCLIDES IN STRUCTURAL MATERIALS FOR REACTORS

Sample	Radionuclides	
	Positively Identified	Probably Present
High-purity lead	Sb <sup>122,124</sup> , Ag <sup>110m</sup> , As <sup>76</sup> , Cu <sup>64</sup> , Na <sup>24</sup>	
Stainless steel (type unspecified)	Mn <sup>56</sup> , Sb <sup>122,124</sup> , Zn <sup>65</sup> , Co <sup>58,60</sup> , <sup>a</sup> Fe <sup>59</sup> , Ni <sup>65</sup> , Cr <sup>51</sup> , Mn <sup>54</sup>	Cr <sup>55</sup> <sup>b</sup>
Type 304 stainless steel	W <sup>187</sup> , Cr <sup>51</sup> , Fe <sup>59</sup> , Co <sup>58,60</sup> , <sup>a</sup> Cu <sup>64</sup> , Mn <sup>56</sup>	Cr <sup>55</sup> <sup>b</sup>
Type 347 stainless steel	W <sup>187</sup> , Cr <sup>51</sup> , Ta <sup>182</sup> , Fe <sup>59</sup> , Mn <sup>56</sup>	Cr <sup>55</sup> <sup>b</sup>
Titanium	W <sup>187</sup> , Cl <sup>38</sup> , V <sup>52</sup> , Mn <sup>56</sup> , Si <sup>31</sup> , Cu <sup>64</sup> , Ni <sup>65</sup> , Ta <sup>182</sup> , Na <sup>24</sup> , Th <sup>232</sup> (Pa <sup>233</sup> ), Sc <sup>47,48</sup> <sup>c</sup>	Rare earths, Sc <sup>46</sup> <sup>c</sup>
Inconel	Cr <sup>51</sup> , Ni <sup>65</sup> , Fe <sup>59</sup> , Co <sup>58,60</sup> , <sup>a</sup> Mo <sup>99</sup>	Cr <sup>55</sup> <sup>b</sup>
Hastelloy	Mo <sup>99</sup> , Cr <sup>51</sup> , Co <sup>58,60</sup> , <sup>a</sup> Fe <sup>59</sup>	
Aluminum	Na <sup>24</sup> , Ca <sup>45</sup> , Ga <sup>72</sup> , Cu <sup>64</sup> , Ni <sup>65</sup> , Fe <sup>59</sup> , Mg <sup>27</sup> , Mn <sup>56</sup> , Si <sup>31</sup> , Co <sup>60</sup> , Zn <sup>65</sup> , Zr <sup>95</sup>	As <sup>76</sup> , Sb <sup>122,124</sup>
Nichrome	Cr <sup>55</sup> , Ni <sup>65</sup> , Cr <sup>51</sup> , Co <sup>60</sup> <sup>a</sup>	Co <sup>58</sup> <sup>a</sup>

<sup>a</sup>Co<sup>59</sup>(n,γ)Co<sup>60</sup>; Ni<sup>60</sup>(n,p)Co<sup>60</sup>; Ni<sup>58</sup>(n,p)Co<sup>58</sup>.

<sup>b</sup>3.6-min β<sup>-</sup>; γ, <0.01%.

<sup>c</sup>Ti<sup>46</sup>(n,p)Sc<sup>46</sup>; Ti<sup>47</sup>(n,p)Sc<sup>47</sup>; Ti<sup>48</sup>(n,p)Sc<sup>48</sup>.

TABLE 3. INSTRUMENTAL CONDITIONS FOR DISCRIMINATORY GAMMA COUNTING

Radioisotope	Degree of Amplification (gain)	PHS, PHS Units (v)	Slit Width (v)	Photopeak Energy (MeV)
Cr <sup>51</sup>	16	312	2	0.320
V <sup>52</sup>	8	735	5	1.45
Fe <sup>59</sup>	~8	620	5	1.29
Co <sup>60</sup>	8	625	5	1.33
Pa <sup>233</sup>	16	99	1	1.02

TABLE 4. INTERFERENCE OF Zr<sup>95</sup> AND Zr<sup>95</sup>-Nb<sup>95</sup> IN THE REGION OF THE 1.29-MeV GAMMA PHOTOPEAK OF Fe<sup>59</sup>

Zr <sup>95</sup> Activity (counts/min)		Zr <sup>95</sup> -Nb <sup>95</sup> Activity (counts/min)	
Taken*	Detected in Region of 1.29-MeV Gamma Photopeak of Fe <sup>59</sup>	Taken**	Detected in Region of 1.29-MeV Gamma Photopeak of Fe <sup>59</sup>
9.10 × 10 <sup>3</sup>	0	8.40 × 10 <sup>3</sup>	0
2.30 × 10 <sup>4</sup>	0	4.20 × 10 <sup>4</sup>	0
4.60 × 10 <sup>4</sup>	0	8.40 × 10 <sup>4</sup>	0
9.10 × 10 <sup>4</sup>	0	4.20 × 10 <sup>5</sup>	92
2.30 × 10 <sup>5</sup>	0	8.40 × 10 <sup>5</sup>	336
4.60 × 10 <sup>5</sup>	0	2.10 × 10 <sup>6</sup>	2,674
1.10 × 10 <sup>6</sup>	536	5.25 × 10 <sup>6</sup>	16,758
2.90 × 10 <sup>6</sup>	4,374		
5.70 × 10 <sup>6</sup>	17,224		

\*Taken as a 2-ml aliquot of a 2 N HNO<sub>3</sub> solution of Zr<sup>95</sup>.

\*\*Taken as a 2-ml aliquot of a 2 N HNO<sub>3</sub> solution of Zr<sup>95</sup>-Nb<sup>95</sup>.

These data indicate that iron can be determined in zirconium metal by gamma discriminatory counting without interference from the Zr<sup>95</sup> and Zr<sup>95</sup>-Nb<sup>95</sup> if the Zr<sup>95</sup> and/or Zr<sup>95</sup>-Nb<sup>95</sup> contamination is below 1 × 10<sup>5</sup> counts/min.

#### Particle-Size Distribution

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

The activation analysis-sedimentation method for the determination of particle-size distribution<sup>53</sup> is used constantly for the analysis of thorium

oxide samples. Some special studies of the effects of pH and of the concentration of pyrophosphate, HCl, and other dispersing agents were made during this period. Results of the experiments will be presented in a topical report.

The activation analysis-sedimentation method has also been used to determine particle-size distribution in zirconium oxide slurries.

<sup>53</sup>G. W. Leddicotte and H. H. Miller, "Particle-Size Distribution," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 21.

## Boron in Aqueous and Organic Solutions

W. A. Brooksbank

The neutron-density method described previously<sup>54</sup> was used to determine boron in water, in 1,4-dioxane, and in pyridine solutions. Concentrations of boron as small as 0.05 mg per milliliter of solution were determined with a relative standard deviation of 0.5%.

## New Applications of Activation Analysis

G. W. Leddicotte

Inquiries were received regarding the suitability of activation analysis for the determination of contaminant elements in ores, beryllium, animal tissues, and zirconium. Samples have been accepted for the determination of contaminant amounts of aluminum and of vanadium in silicon, of phosphorus in aluminum, of arsenic in human tissue, and of boron in steels.

## SPECTROCHEMICAL ANALYSES

C. Feldman

### Improving the Precision of Energies of Individual Breakdowns Furnished by Air-Interrupted Spectrographic Spark Sources

C. Feldman

For a given set of electrical circuit parameters, the sum of the quantities of energy (in watts) dissipated in the auxiliary and analytical spark gaps is equal to  $\frac{1}{2}C(V_0^2 - V_r^2)$ , where  $C$  is the capacitance of the power condenser in microfarads,  $V_0$  is the voltage to which this condenser is charged, and  $V_r$  is the voltage remaining on the condenser after the discharge ceases.

In air-interrupted spectrographic spark sources,<sup>55</sup>  $V_0$  is equal to the breakdown potential of an adjustable auxiliary gap that is in parallel with the condenser. Manufacturers recommend setting  $V_0$  by adjusting the separation of the auxiliary gap to an accurately reproduced value. It was found, however, that a given intensity ratio might vary considerably from one exposure to another if the

auxiliary gap had been reset between exposures and that excellent reproducibility was obtained only as long as the gap was not reset between exposures. This effect was particularly noticeable for small (i.e., approximately 2-mm) auxiliary gaps.

It was assumed that these changes in intensity ratio corresponded to changes in the energy ( $\frac{1}{2}CV_0^2$ ) stored in the power condenser and thus were caused by failure to accurately reproduce the breakdown voltage  $V_0$  from exposure to exposure. However, it was felt that an attempt to reproduce  $V_0$  merely by reproducing the gap separation would be futile, because the breakdown voltage for any gap depends not only on the gap separation but also on the electrode surface condition and dielectric strength of the gap. Since inevitable slight changes in the geometry of the auxiliary electrode and in atmospheric conditions make it necessary to set the  $V_0$  before each run, the following procedure was adopted:

1. With the power off, the auxiliary gap was widened until no discharge was possible at or near the breakdown voltage to be used.
2. With the power still off, the indicator of the autotransformer (Powerstat) in the primary of the high-voltage transformer was turned to zero.
3. The power was turned on.
4. The indicator of the Powerstat was turned up until the voltmeter that was placed across its variable arm reached some predetermined setting (e.g., 55 v). This setting corresponded to some definite secondary voltage, which was to be  $V_0$ .
5. The auxiliary gap was then narrowed until one discharge occurred reliably on each half-cycle, as shown by an oscilloscope.
6. The Powerstat indicator was then increased until the desired number of discharges per half-cycle was attained. If there were too many to count on an oscilloscope screen, the indicator was turned up to give a predetermined reading on the r-f ammeter (see below).

Steps 1 through 5 ensure the reproduction of the amount of energy ( $\frac{1}{2}CV_0^2$ ) available for each individual discharge despite possible changes in electrode surface, atmospheric humidity, dust conditions, etc. Step 6 regulates the number of such discharges per half-cycle. The reproducibility of several intensity ratios between exposures when  $V_0$  was determined by visually resetting the

<sup>54</sup>W. A. Brooksbank, J. E. Strain, and G. W. Leddicotte, "Neutron-Density Method for Rapid Determination of Certain Elements," *Anal. Chem. Semiann. Prog. Rep.* April 20, 1954, ORNL-1717, p 18.

<sup>55</sup>J. H. Enns and R. A. Wolfe, "An Air Interrupter Type Spectrographic Light Source," *J. Opt. Soc. Amer.* 39, 298 (1949).

auxiliary gap to a given separation before each exposure is compared in Table 5 with the reproducibility obtained when  $V_0$  was set for each exposure by the above procedure.

After the new procedure was adopted, it was found that unaccountable changes in intensity ratios still occurred occasionally. By use of an oscilloscope having a driven (self-triggered) sweep, it was found that these changes were due to changes in  $V_r$  and were probably caused by variations in the shape of the current vs time curve of a given discharge, the variations resulting from alteration of the geometry of the auxiliary gap.

#### Separation of Small Amounts of Rare Earths from Thorium

J. Y. Ellenburg      C. Feldman

Further study of the activated cellulose-batch adsorption method<sup>56</sup> has shown that

1. 1 g of activated cellulose can adsorb 5 to 7 mg of rare earths under the conditions described;<sup>56</sup>
2. activated cellulose, although prepared by prolonged treatment with  $\text{HNO}_3$ , appears to contain little if any combined nitrogen, as indicated by nitrogen determinations that were made by P. F. Thomason;<sup>57</sup>

<sup>56</sup>C. Feldman, "Separation of Rare Earths from Thorium by Adsorption on Activated Cellulose, Batch Method," Method Nos. 1 00705 and 9 00650 (3-23-55), ORNL Master Analytical Manual.

3. nonactivated cellulose, if soaked for 3 hr in an ethyl ether-nitric acid mixture, will retain 99% of added europium tracer and therefore that activation of the cellulose is apparently not necessary;
4. various cellulose and other fiber products, both raw and purified, retain approximately 90% of added europium tracer activity when treated according to the regular procedure.<sup>56</sup>

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

J. Y. Ellenburg      C. Feldman

**Determination of Optimum Parameters of Jaco Varisource.** — Since samples were prepared for spectrographic exposure by evaporating a solution atop a waterproof, graphite electrode,<sup>58</sup> power-source parameters were investigated by determining whether a given quantity of energy gave a higher line-to-background ratio when delivered in a single discharge or when broken up into several small discharges. It was found that both line-to-background ratios and net line intensities were greater when a given quantity of energy was broken

<sup>57</sup>Ionic Analyses Group.

<sup>58</sup>J. Y. Ellenburg and C. Feldman, "Determination of Microgram Quantities of Rare Earths in Rare-Earth Mixtures: Spark Method," *Anal. Chem. Semiann. Prog. Rep.* Oct. 20, 1955, ORNL-1973, p 20.

TABLE 5. EFFECT OF AUXILIARY-GAP-SETTING TECHNIQUE ON PRECISION OF LINE-INTENSITY RATIOS

Line Pair	Relative Mean Deviation of Observed Intensity Ratio Between Exposures (%) with $V_0$ Regulated Before Each Exposure	
	By Visually Resetting Auxiliary Gap Separation	By Narrowing Auxiliary Gap to Give Breakdown at Fixed Secondary Voltage
Dy 3531.71		
Y 3600.73	7.3	0.95
Gd 3422.47		
Y 3600.73	6.3	2.7
Sm 3568.26		
Y 3600.73	8.3	1.4
Dy 3531.71		
Y 3710.29	5.2	1.2

up into small, successive bursts. Optimum conditions for the determination of individual rare earths were found to be  $C = 0.0025 \mu\text{f}$ ;  $L = 61 \mu\text{h}$  (including residual inductance); separation of auxiliary gap, approximately 2 mm; approximately 23 breaks per half-cycle; and 5.5 r-f amperes.

**Swamping Out of Interelement Effects.** — Previous work<sup>58</sup> had shown that the working curves of individual rare earths in a rare-earth mixture were shifted when the proportion of rare earths in the mixture changed. Several elements were added to the electrodes to swamp out this effect; of those tried, zinc appeared to be the most promising and was selected for further study. It was found that the presence of 30  $\mu\text{g}$  of zinc on the electrodes (i.e., distributed between them) eliminated all afore-mentioned shifts in the working curves and even overcame the severe general suppression of rare-earth lines caused by lanthanum. This was accomplished at a relatively small cost in absolute sensitivity (0 to 30%). The recoveries of sub-microgram quantities of rare earths when present in mixtures of different proportions are shown in

Table 6; in each case, 30  $\mu\text{g}$  of zinc was also present on the electrodes. Working curves were prepared separately for each rare earth; known amounts of the element and 30  $\mu\text{g}$  of zinc (plus an internal standard) were used on the electrodes.

**Absolute Detection Limits.** — For the above technique the smallest quantities (in  $\mu\text{g}$ ) of the individual rare earths which can be measured in rare-earth mixtures with an average deviation of 5% or less are: Ce, 0.2; Dy, 0.03; Gd, 0.03; La, 0.1; Nd, 0.2; Sm, 0.2; Y, 0.01.

#### Concentration of Microgram Quantities of Boron from Methyl Alcohol Distillates

C. Feldman      W. R. Musick

Quantities of boron ranging from 0 to 100  $\mu\text{g}$  are often determined by distillation of the boron away from gross quantities of metal. The high degree of dilution of boron in the distillate makes determination more difficult by any method. Methods of concentrating the distillate that involve heat greatly increase the risk of loss of boron, even in

TABLE 6. RECOVERY OF SUBMICROGRAM QUANTITIES OF RARE EARTHS IN RARE-EARTH MIXTURES OF DIFFERENT PROPORTIONS

(30  $\mu\text{g}$  of zinc present on spectrographic electrodes)

Mixture	Amount of Rare Earths on Electrodes ( $\mu\text{g}$ )	Rare Earth	Amount Added ( $\mu\text{g}$ )	Amount* Found ( $\mu\text{g}$ )
Aluminum	4.34	Gd	0.20	$0.19_2 \pm 0.00_8$
		Dy	0.20	$0.19_0 \pm 0.01$
		Sm	0.40	$0.40 \pm 0.01_3$
		Ce	0.50	$0.49_5 \pm 0.00_5$
		Nd	1.00	$1.05 \pm 0.05$
		Y	0.020	$0.020 \pm 0.0013$
Boron	4.74	Gd	0.080	$0.075 \pm 0.004$
		Dy	0.080	$0.083 \pm 0.003$
		Sm	0.24	$0.24_5 \pm 0.00_5$
		Ce	1.50	$1.43 \pm 0.07$
		Nd	2.00	$2.08 \pm 0.08$
		Y	0.020	$0.019 \pm 0.001$

\*Average deviations given for triplicate exposures.

the presence of alkali. A search was therefore begun for other methods.

With suitable changes the method of Silverman *et al.*<sup>59</sup> was found to be applicable to methyl alcohol distillates that contain 10 to 15 vol % of aqueous 0.15 N Cu(OH)<sub>2</sub>. A 6 × 50 mm column of Dowex 1 was converted to the hydroxide form, and the sample solution (acidified to a pH of approximately 2.5 with HCl) was passed through the column. The column was then inverted and stripped with 1:1 HCl or 20 vol % H<sub>2</sub>SO<sub>4</sub>. Inversion of the column before stripping was found necessary in order to obtain complete recovery of 50 μg of boron with 5 ml of stripping acid. Without the inversion, recoveries averaged approximately 80%, even when 20 ml of stripping acid was used.

### INORGANIC PREPARATIONS

D. E. LaValle

#### Special Preparations

D. E. LaValle

The special inorganic preparations consisted chiefly of the production of large quantities of anhydrous halides. For the Fused Salts Group of the Chemistry Division, 400- to 500-g quantities of the rare-earth chlorides and bromides and of the alkaline-earth chlorides were prepared. The general method of preparing the rare-earth halides was simply to dehydrate them by very slow heating in vacuum to 400°C and then to purify them by sublimation. The alkaline-earth halides were dehydrated by being heated up to 400°C in a muffle furnace in air and then heated to 800°C in a quartz flask while the respective hydrogen halide gas was passed through the material by means of a tube extending nearly to the bottom of the flask.

The anhydrous halides prepared for the Nuclear Physics and Neutron Diffraction Group of the Physics Division were the chlorides and bromides of manganese and of bivalent iron and the chloride of cobalt in various physical modifications. These halides were all sublimed finally in order to attain the desired crystal structures.

About 50 g of PdF<sub>3</sub> was also prepared for the same group. Attempts to prepare it by the action of fluorine gas on PdCl<sub>2</sub> at 250°C gave a product

that consisted of 80% PdF<sub>3</sub> and 20% PdF<sub>2</sub>. The PdF<sub>3</sub> was finally prepared pure by the action of BrF<sub>3</sub> on the mixture of PdF<sub>3</sub> and PdF<sub>2</sub> (ref 60).

### Miscellaneous Preparations and Purifications

R. H. Sampley

The materials listed below were either prepared or purified, in the quantities listed, for the Physics Division.

Prepared	Purified
EuCl <sub>3</sub> , 4.55 g	EuCl <sub>3</sub> , g amounts
HI, liter amounts	HI, liter amounts
LaBr <sub>3</sub> , 400 g	Li <sup>6</sup> Cl solution, liter amounts
LaCl <sub>3</sub> , 400 g	LiI·3H <sub>2</sub> O, kg amounts
LaF <sub>3</sub> , 30 g	Xylene, 25 gal
Li <sub>2</sub> CO <sub>3</sub> , kg amounts	
Li <sup>6</sup> CO <sub>3</sub> , 57 g	
LiCl solution, 8 liters	
LiI, kg amounts	
Li <sup>6</sup> I, 200 g	
PbF <sub>2</sub> , 28 g	
MnBr <sub>2</sub> , 57 g	

Other inorganic chemical work done for the Physics Division included cleaning and pickling of metals, electroplating small parts, identifying various alloys, analyzing LiCl solution, and preparing electroplating baths and target materials.

### OPTICAL AND ELECTRON MICROSCOPY

T. E. Willmarth

F. M. Toomer      T. G. Harmon

#### Electron Microscopy of Thorium Oxide

The physical characteristics of thorium oxide preparations, particularly with respect to the changes produced in the size and shape of particles by various methods of preparation and after-treatment, have continued to be of interest in microscopy studies. Typical samples included, among many others, thorium oxide peptized by thorium nitrate solution, raw Fernald thorium oxide, thorium oxide collected from an HR loop condensate system, thorium oxide precipitated at 10°C and circulated in an HR loop for 100 hr, and thorium oxide that was pyrohydrolyzed at 300°C,

<sup>59</sup>L. Silverman, W. Bradshaw, and W. Taylor, *Removal of Deuterated Boric Acid from Deuterium Oxide Solution by Ion Exchange Resin*, NAA-SR-863 (June 15, 1954).

<sup>60</sup>A. G. Sharpe, "Simple and Complex Fluorides of Some Noble Metals," *J. Chem. Soc. Part IV*, 3444, esp. 3449 (1950).

precipitated at 10°C, and then ignited at 900°C. The results of particle-size determinations made by electron microscopy were in good agreement with the results of measurements made by other methods.

#### Studies of Thin Films and Corrosion Products

The examination of oxide films and corrosion products formed from metals used in reactor engineering was continued. Electron microscopy and diffraction were utilized to determine the nature and the physical appearance of products that resulted from the exposure of metals in the in-pile MTR autoclave and in the HR-type thorium oxide slurry loops. The results of two such examinations are discussed below.

Samples of the precipitate and scale that had formed during the exposure of Zircaloy-2 to uranyl sulfate solutions in the in-pile MTR autoclave were studied in order to identify the chief constituent of each. Electron diffraction results indicated<sup>61</sup> that in both precipitate and scale the chief component was cubic-phase  $ZrO_2$ . These results suggest that the monoclinic-phase  $ZrO_2$ , which is the phase usually found on Zircaloy-2 in out-of-pile tests under similar but nonradioactive conditions, is changed to cubic-phase  $ZrO_2$  by radiation.

After extended operation of an HR-type thorium oxide slurry loop, a type 347 stainless steel rupture disk was taken from the vapor phase and a type 347 stainless steel aperture plate was taken from the aqueous phase; the disk and plate were examined for extent and type of corrosion. Chemical analysis of the solution had already indicated the presence of chloride in the system. Microscopic examination of the film stripped from the rupture disk disclosed that marked, intergranular corrosion had taken place and that a nonuniform crystalline layer completely covered the grain faces. Electron diffraction of this film gave a ring pattern which identified the crystals as haematite ( $Fe_2O_3$ ) deposited over a thin substrate of magnetite ( $Fe_3O_4$ ), which existed at the metal-oxide interface. Similar examination of the film that was removed from the aperture plate disclosed no perceptible corrosion and indicated that the principal film constituent was not a corrosion

product but was, rather, thorium oxide, which apparently had plated out from the slurry. Again, a thin layer of magnetite was found at the metal-oxide interface.<sup>62</sup> These results indicated that the presence of chloride ion, under the operating conditions of a particular HR thorium oxide slurry loop, is much more corrosive to metals located in the vapor phase of the system than it is to those positioned in contact with the aqueous slurry.

In addition to these problems, which dealt directly with work associated with reactor technology, other films and corrosion products that were produced during certain experiments of the Chemistry and Physics Divisions were investigated. Several of interest include the following. A thin black film was examined that had formed on a type 347 stainless steel plate, which had been maintained below the  $H^+ \rightarrow H_2$  potential (reversible) in 0.1N  $H_2SO_4$  at 85°C for 1 hr and then allowed to passivate spontaneously after release of the polarizing current. Electron microscopy and diffraction of this film, after it was removed from the steel, indicated that it was composed of colloidal and submicro platelets of copper, which had plated out under the conditions of the experiment; the distilled water used in the experiment was thought to be the source of the copper. A hard, glasslike material that was plugging a small-bore aluminum aperture, used in a Physics Division's hydrogen ion generator, was identified by electron diffraction as aluminum silicate. It had apparently formed by a reaction between the aluminum of the aperture and the quartz glass used in the system.

#### Electron Diffraction Crystallography

During the photographing of the pattern of a dispersion of sodium tungstate ( $Na_2WO_4$ ) crystals, it was observed that an increase in the intensity of the electron beam at the sample position, the increase in intensity being induced by bringing the electron beam into sharp focus at the plane of the sample holder, had caused a significant change in the nature of the diffraction pattern. Numerous rings appeared that were not observed with the beam at low intensity (i.e., unfocused). Photographic records were made of both patterns

<sup>61</sup>T. E. Willmarth, *Examination of the Scale, and Precipitate from In-pile Loop Run 15-2*, ORNL CF-56-3-46 (March 8, 1956).

<sup>62</sup>T. E. Willmarth, *A Study of the Surface Films on a Stainless Steel Rupture Disc, and an Aperture Plate Formed During Exposure in a Thorium Oxide Slurry Loop*, ORNL CF-56-1-28 (Jan. 9, 1956).

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in order to permit measurements and comparisons of lattice spacings. These data, together with the spacings shown on the ASTM x-ray index card for  $\text{Na}_2\text{WO}_4$ , are given in Table 7. With the exception of several weak lines, the experimental values for the lines of pattern 1 (unfocused electron beam) are in good agreement with the indexed values taken from the ASTM x-ray card and based on an examination of the compound by Lindqvist.<sup>63</sup> In each case the strong lines are those of the face-centered, cubic structure. However, pat-

tern 2 (focused electron beam) has the spacings of a material having a simple cubic structure.

Other diffraction patterns from single crystals of material and produced by a sharply focused electron beam gave reflections from the 211 plane, a plane that is forbidden in the face-centered, cubic structure. It appears that the structure resulting from bombarding the sample with electrons in the

<sup>63</sup>J. Lindqvist, "Crystal Structure Studies on Anhydrous Sodium Molybdates and Tungstates," *Acta Chem. Scand.* 4, 1066 (1950).

TABLE 7. DIFFRACTION DATA ON SODIUM TUNGSTATE ( $\text{Na}_2\text{WO}_4$ )

X-Ray Spacings Taken from ASTM Index			Electron Diffraction Spacings Calculated from Patterns					
$d$ (Å)	$I/I_1$	$hkl$	Pattern 1 (Beam Unfocused)			Pattern 2 (Sharply Focused Beam)		
			$d$ (Å)	$I/I_1$	$hkl$	$d$ (Å)	$I/I_1$	$hkl$
			6.357	W	110	6.358	W	110*
5.19	S	111	5.19	S	111	5.19	S	111
			4.495	W	200	4.50	W	200*
						3.67	W	211*
3.18	S	220	3.18	S	220	3.18	S	220
						3.01	M+	221*
2.72	S	311	2.715	S	311	2.723	S	311
						2.598	W	222*
2.25	W	400	2.24	W	400	2.25	W	400
2.06	M	331	2.052	W	331	2.06	W	331
			2.02	W	420	2.02	W	420*
1.833	S	422	1.83	S-	422	1.83	M-	422
						1.79	W	500*
1.726	M+	511, 333	1.718	M+	511, 333	1.73	M-	511, 333
1.614	M+	440	1.614	M+	440	1.61	M-	440
1.517	M	531	1.513	M-	531	1.51	M-	531
1.419	M	620	1.42	W+	620	1.42	W	620
1.37	M-	533	1.365	W-	533			
1.298	W	444	1.30	W-	444			
1.258	M-	711, 551	1.26	W+	711, 551			
1.200	M+	642	1.21	W+	642			
1.169	M+	731, 553	1.17	W+	731, 553			

\*Lines that belong to the simple cubic structure but that are not evident in x-ray examination.

microscope is a new modification of sodium tungstate that has not been recorded in the literature. Such a result suggests that selected-area electron diffraction may offer possibilities for making comparatively rapid studies of structure modifications occurring in certain compounds as a result of internal electron bombardment. It is proposed to examine some of the molybdate compounds that are closely related to the tungstates in structure in order to observe whether similar changes take place, and thus to delineate the usefulness of the method.

#### Optical Microscopy and Autoradiography

A variety of materials were examined with the optical microscope. These included crystalline material from the HR mockup pressurizer, type 347 stainless steel test pins, Zircaloy-2 test pins, titanium test pins, ion-exchange resins, zirconium tetrachloride, caked material from the walls of thorium oxide slurry loops, crystals formed during phase studies, large-particle-size thorium oxide, and crystals of a uranium-rubidium nitrate (?) complex. Autoradiographs were made of Zircaloy disks and of titanium disks on which plutonium had been adsorbed at 25 and 80°C. Electron micrographs of replicas made from these surfaces were also examined to determine whether a correlation existed between the nature of the metal surface and the uniformity (or nonuniformity) of the plutonium deposit as indicated by the autoradiographs.

#### New Methods and Techniques

Development work relative to specific problems arising in microscopy and electron diffraction has continued. Of interest is the use of evaporated carbon films of a calculated thickness of 300 to 400 Å to entrap and to hold radioactive particles in place on the 200-mesh wire grids that support the sample during examination of it in the electron microscope. This method was developed in order to avoid possible instrument contamination and, at the same time, to maintain an optimum film thickness for good resolution of the particles of the sample. Use has also been made of the carbon-film technique to replicate metallographically polished and etched metal surfaces. Figures 1 and 2 show typical electron micrographs of carbon-replicated surfaces.

The feasibility of designing and building an electron diffractograph that will meet the specific needs of ORNL is under investigation.

#### ORNL MASTER ANALYTICAL MANUAL

Authors of Methods

H. P. Raaen                      H. P. House

Twenty-six new methods, revisions to thirty-eight methods (made primarily in order to bring nuclear data up to date), and tables of contents for the Thorex, Plutonium Isolation, and Purex process subsections have been issued to the *ORNL Master Analytical Manual* (see "Presentations of Research Results"). Drafts of a large number of other new methods have been edited. Eight new manuals were issued.

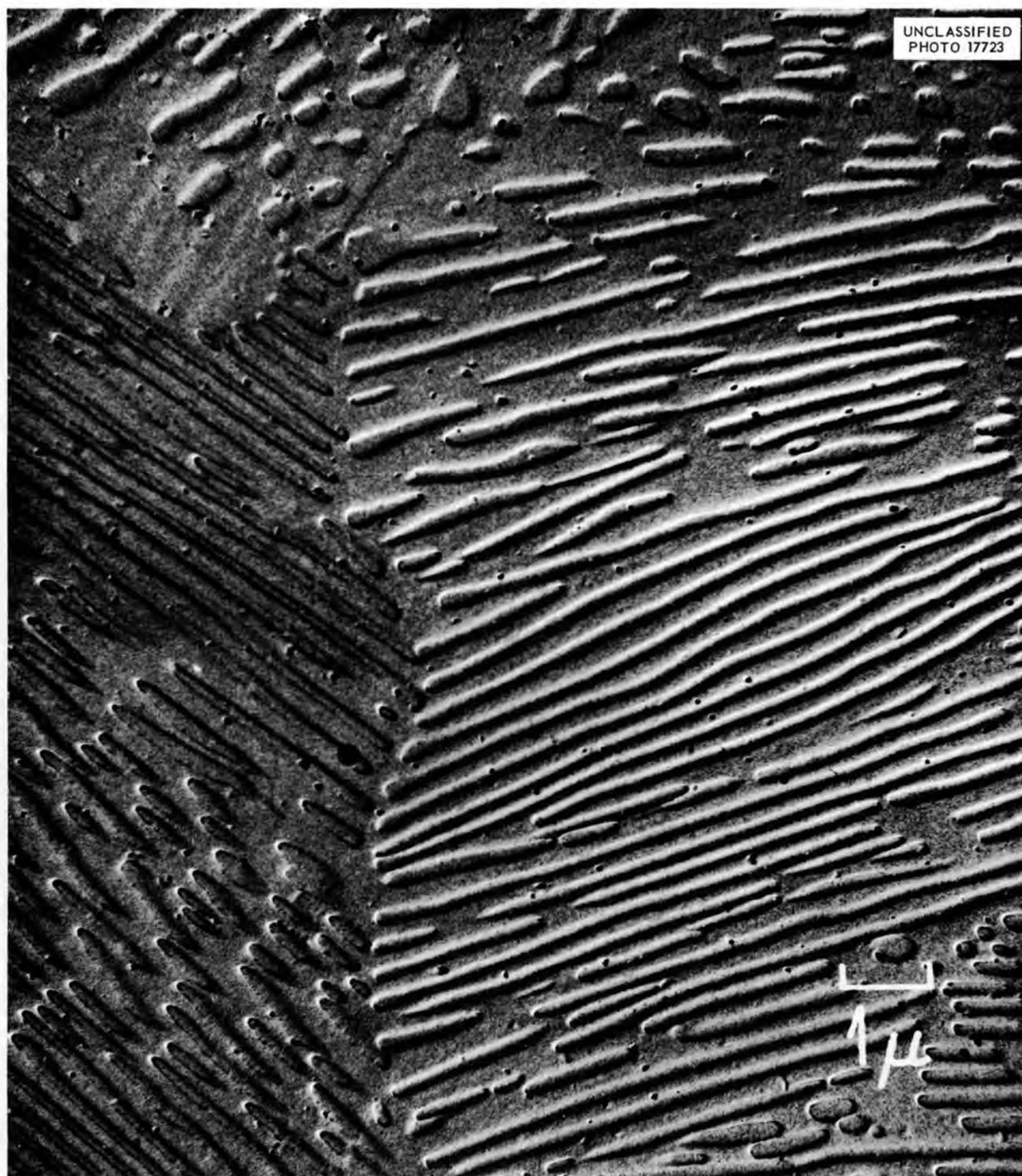


Fig. 1. Carbon-Replicated Surface of Manganese Steel Showing Coarse Pearlite (Shadowcast with Palladium). 15,000X. Reduced 13%.



Fig. 2. Carbon-Replicated Surface of Zircaloy (Shadowcast with Gold).  $\sim 8000X$ . Reduced 14%.

## SERVICE ANALYSES

A semiannual summary of the service analyses made at the X-10 laboratories of the Analytical Chemistry Division is given in Table 8.

## IONIC ANALYSES

P. F. Thomason

The service work of the Ionic Analyses Group increased about 15% during this period. Most of the work 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, 74% was for three ORNL divisions. Radiochemical determinations of the products of fast-neutron bombardments and of nitrogen-ion bombardments constituted most of the work for the Electronuclear Research Division. Many neutron-flux measurements were performed for the Reactor Experimental Engineering Division. For the Solid State Division a number of nondestructive radiochemical measurements were made, principally by gamma spectrometry and by the measurement of total gamma radiation. For further details see "Radiochemical Analyses," Chap. 1.

## ACTIVATION ANALYSES

G. W. Leddicotte

The Activation Analyses Group determined the following elements in a variety of materials: antimony, arsenic, copper, cobalt, chromium, iron, silver, silicon, tungsten, nickel, manganese, molybdenum, selenium, and tellurium. In addition, the particle-size distribution in a large number of thorium oxide samples, both solid and aqueous slurries, was determined. Also, the neutron-density method of analysis was utilized to determine boron in aqueous and in organic solutions.

<sup>1</sup>M. Codell and G. Norwitz, *Determination of Oxygen in Titanium, Zirconium, Chromium, Vanadium, and Steels by the Bromination-Carbon Reduction Method*, a paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Feb. 27-March 2, 1956, Pittsburgh, Penn.

## GENERAL ANALYSES LABORATORY

J. H. Edgerton

## General Analyses

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

Vanadium was determined in stainless steels and alloys by spectrophotometric titration with potassium permanganate solution. After a pyrohydrolytic separation, fluoride was titrated spectrophotometrically with thorium nitrate by the use of alizarin red S as indicator. Electrolytic, gravimetric, spectrophotometric, polarographic, and volumetric methods were used in the analysis of special samples and alloys. A very large number of separations and potentiometric determinations of uranium, boron, chloride, arsenic, manganese, iron, chromium, molybdenum, and cobalt were made on alloys, stainless steels, and eutectic salts. In addition, alloys and special samples were analyzed by flame spectrophotometry for barium, boron, calcium, cesium, indium, lanthanum, lithium, potassium, rubidium, and vanadium.

A high-temperature dehydration apparatus has been fabricated for the determination of water in solid samples by heating the sample to 500°C in a Vycor tube under an atmosphere of purified, inert gas (nitrogen, argon, or helium). The evolved water is absorbed by magnesium perchlorate from the carrier gas stream and is weighed. Water in cement, concrete, and uranium salts has been determined by this method.

The bromination-carbon-reduction apparatus used for the determination of oxygen in alloys and metals has been modified to provide pure bromine at increased saturation of the carrier gas (argon) and is being equipped with a calcium sulfate absorber for scrubbing the product gases. These modifications were suggested from the information reported by Codell and Norwitz.<sup>1</sup>

The quality control program is being continued. The separation of boron from stainless steel by distillation as methyl borate has proved to be very satisfactory.

TABLE 8. SUMMARY OF ANALYTICAL SERVICE WORK AT X-10 SITE

	Number of Personnel		ORNL Divisions Requesting Analyses																	Others Requesting Analyses									
	Technical	Nontechnical	Analytical Chemistry	Applied Nuclear Physics	Biology	Chemical Technology	Chemistry	Electronuclear Research	Engineering and Mechanical	Health	Health Physics	HRP	Instrumentation and Controls	Materials Chemistry	Metallurgy	Operations	Physics	REED	Solid State	AEC	General Electric Co.	K-25	ORSORT	Phillips Petroleum Co.	Pratt & Whitney Aircraft	Research Director's	Y-12	Total Analyses	
Group Making Analyses			Number of Determinations																										
Activation Analyses*	4	5	471	44		184	34			49	587	48	203	187	10	8	141		7	6									1,979
General Analyses	7	6		61		88	249	60		345			4696	360	15														5,874
Ionic Analyses*	5	1				229	623	25					34	4	96		10												1,021
Laboratory Control	3	7				10,649	296								36														10,981
Optical and Electron Microscopy*	3	1				548	223			40			11	11	25	423													1,281
Pilot Plant Control	7	13				24,338	337			16			47			30													24,768
Plutonium Isolation Laboratory	2	2				3,033	9	164							30	4													3,240
Radiochemical Analyses*	5	1		25	2	56	36	205		9					35	199	86		1		2					3	659		
Radioisotope Production Control	3	16		494		5,093	352			1054					8075	253	203	28	20	30									15,602
Reactor Analyses	6	5				30					1850					246	10								10				2,146
Special Analyses	3	8				6,701	100	1170		328			255																8,554
Spectrochemical Analyses*	6	0	1	36		1,258	68		6	1		1	144	87	28	21	26						198		16			1,891	
Totals	54	65	472	660	2	52,207	2327	1564	60	6	1842	2437	1	48	5390	8825	174	1184	476	28	28	36	2	198	10	16	3	77,996	

\*These groups also do research and development.

## Vacuum-Fusion Analyses

H. G. Davis      J. H. Edgerton

The vacuum-fusion analysis of zirconium, titanium, vanadium, lead, nickel, and their alloys for hydrogen, oxygen, and nitrogen has been continued. Special attention has been given to the problem of determining microgram quantities of oxygen in zirconium. The use of a bath of molten platinum and the rigid control of furnace conditions have made possible low and reproducible blanks at high temperatures; as a result, small concentrations (i.e., 10 to 100 ppm) of oxygen are being determined with improved precision.

Vacuum extraction has been used to determine hydrogen in alloys and in zirconium. This technique eliminates the necessity of a molten metallic bath and also greatly increases the precision of hydrogen determinations.

The low-pressure, microcombustion carbon apparatus has been calibrated and placed in operation. Nine determinations of carbon in a National Bureau of Standards iron sample gave an average result of 0.0124% with a relative standard deviation of approximately 7%; the "best value" specified for the sample was 0.011%. The apparatus has been used to analyze iron, steel, and Hastelloy for carbon. The determination of carbon in uranium tetrafluoride of low carbon content by the low-pressure, microcombustion carbon apparatus is being investigated.

## LABORATORY CONTROL GROUP

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

Solid samples that contained zirconium in various forms have been received by the Laboratory Control Group relative to work on the HR chemical processing loops, the fluorination process for recovering uranium, and the dissolution of fuel elements that contain zirconium. The zirconium in the samples was in the form of the finely divided metal, the oxide, or the fluoride. In some samples one or more of the oxides or fluorides of uranium, nickel, chromium, and iron were also present. The zirconium in these mixtures was converted to a soluble form by fusion with a mixture that was 60% potassium pyrosulfate and 40% potassium bisulfate. The melt was readily soluble in a mixture of nitric acid and water. The zirconium was determined by the spectrophotometric Thoron method.<sup>2</sup>

The flux used in the fluorometric determination of uranium has been changed from sodium fluoride to a mixture that is 98% sodium fluoride and 2% lithium fluoride.<sup>3</sup> This permits use of a lower fusion temperature and gives a melt that is easier to remove from the platinum dish.

## PILOT-PLANT CONTROL LABORATORY

L. T. Corbin      C. E. Lamb

The majority of the work of the Pilot-Plant Control Laboratory was relative to the Thorex and Metal-Recovery processes. The personnel of the group are being trained intensively in special techniques required for analyses that are made in the HRLAF.

## ISOLATION ANALYSES

L. T. Corbin      J. H. Cooper

The major portion of the work done by the Isolation Analyses Group was for the Chemical Technology Division relative to the processing of the blanket solution from the plutonium producer. The determinations required were gross alpha, plutonium alpha, uranium, and the plutonium valence states. The gross alpha determination consisted in alpha-counting on small, metallic disks that were exposed to uranyl sulfate-plutonium sulfate solutions under various conditions of temperature and pressure. The gross alpha count was an indication of the amount of plutonium deposited on the disks.

Another major group of samples from the Chemical Technology Division came from the Thorex Pilot Plant. These were U<sup>233</sup> products, which were analyzed for uranium, thorium, iron, pH, specific gravity, gross alpha, gross beta, and gross gamma.

While studying the solubility of the plutonium in a blanket solution, the Chemical Technology Division requested the determination of plutonium in samples of uranyl sulfate that had been irradiated in the LITR. The usual analytical method for determining plutonium is by TTA extraction.<sup>4</sup> However, the presence of Np<sup>239</sup> (small quantities of which may, under certain conditions, extract

<sup>2</sup>A. D. Horton, "Zirconium, Thoron Spectrophotometric Method," Method Nos. 1 219810 and 9 00719810 (2-25-53), ORNL Master Analytical Manual.

<sup>3</sup>F. A. Centanni, A. M. Ross, and M. A. DeSesa, *The Fluorimetric Determination of Uranium*, WIN-34 (Feb. 10, 1956).

<sup>4</sup>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.

into TTA with plutonium) interfered in the counting of the plutonium alpha plates because of the high beta-gamma activity. After the plutonium was reduced to the trivalent state, the highly radioactive  $\text{Np}^{239}$  was extracted according to the extraction procedure<sup>5</sup> for  $\text{Np}^{237}$ . The plutonium was then oxidized to the quadrivalent state and determined according to the TTA extraction method.<sup>4</sup>

Sand samples from the Nevada Testing Site were submitted by the Chemical Technology Division for the determination of plutonium and uranium, which were shown experimentally to adhere to the surface of the sand. A portion of the sand was refluxed with an  $\text{HNO}_3$ -HF mixture for 2 hr, the mixture filtered, and the residue washed. The filtrate and washings were combined and then analyzed for plutonium and uranium.

The Electronuclear Research Division submitted samples for the determination of plutonium and americium. Existing methods<sup>4,6</sup> were used for these analyses.

#### SPECIAL ANALYSES LABORATORY

L. T. Corbin                      W. R. Laing

A variety of analyses were performed by the Special Analyses Laboratory. Amalgams were analyzed for zinc, uranium, titanium, tin, iron, chromium, nickel, and aluminum. Uranium-tin alloys were analyzed for uranium and tin. A testing program to determine the effect of acid concentration and type of container material on the plating and polymerization of protactinium was completed. An apparatus for the measurement of surface area by nitrogen adsorption is being constructed. The fusion of the flux, which is used in the fluorometric determination of uranium, by induction heating is being studied, and several types of flux and of liquid-liquid extractions are being tested.

#### RADIOISOTOPE PRODUCTION ANALYSES

E. I. Wyatt

In the Radioisotope Production Analyses Laboratory, an alpha pulse analyzer has been acquired and put into service. It has been extremely useful

<sup>5</sup>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.

<sup>6</sup>G. W. Smith, "Americium-241," Method No. 2 31030 (5-18-54), ORNL Master Analytical Manual, ORNL CF-53-1-235, Vols I and III.

for the determination of  $\text{Np}^{237}$  in the presence of  $\text{Pu}^{239}$ . A description of the instrument and the procedure for using it will be written for the ORNL Master Analytical Manual.

The discriminatory gamma scintillation counter,<sup>7-9</sup> which is equipped with a well-type sodium iodide crystal, is being used to determine the amount of  $\text{Pa}^{233}$  in Thorex samples by taking a differential count at the 310-keV photopeak; a slit width of 10 keV (1 v) is used. The work is described in a paper to be submitted to *Nuclear Science and Engineering* for publication.

A study was made to determine the fate of  $\text{Pa}^{233}$  in aqueous and organic samples that are stored in glass and in polythene containers. It was found that  $\text{Pa}^{233}$  is lost rapidly to the glass from neutral solutions when stored in glass containers but is not lost from the same type of solution when stored in polythene containers. It was found that  $\text{Pa}^{233}$  was not lost from a TBP-Amsco medium when stored in glass or polythene containers.<sup>10</sup>

#### HIGH-RADIATION-LEVEL ANALYTICAL FACILITY

C. L. Burros

Master-slave manipulators have been installed in all work cells in the HRLAF. The storage cell is complete with a manipulator and sample-storage boxes.

One of the work cells is complete except for the container shield and positioning rack. The shielded container is to be positioned under the disposal chute in order to receive discarded sample bottles, which will be taken to the burial ground. Instruments now set up in the cell include the following: a 1-ml servo pipetter<sup>11</sup> together with a sample-

<sup>7</sup>E. I. Wyatt, "Radioisotope Production Analyses," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 24-25.

<sup>8</sup>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.

<sup>9</sup>W. A. Brooksbank, S. A. Reynolds, and G. W. Leddicotte, "Use of Discriminatory Gamma Counting," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 12-13.

<sup>10</sup>E. I. Wyatt, *A Study of the Behavior of Pa-233 in Glass and in Polythene Containers*, ORNL CF-56-2-86 (Feb. 16, 1956).

<sup>11</sup>M. T. Kelley and D. J. Fisher, "Remotely Controlled Sampling Pipets," *Anal. Chem. Semiann. Prog. April 20, 1955*, ORNL-1880, p 8-9.

bottle decapper and magnetic stirrer;<sup>12</sup> an ORNL model Q-1734 filter photometer;<sup>13</sup> and two Beckman automatic titrators that have modified platforms for beakers.<sup>14</sup>

### REACTOR ANALYSES

U. Koskela

The various HR programs continued to be the source of the majority of the samples submitted to the Reactor Analyses Group. Some work was done for the Solid State Division by the use of the remote facilities in Building 3025.

#### Polarographic Determination of Tin

L. G. Farrar

Tin has been determined polarographically in HRP solutions. A supporting electrolyte of ethanol-hydrochloric acid was used.<sup>15,16</sup> Aluminum hydroxide carrier was used to separate the tin from uranium, but it was found to be unsatisfactory. Following the suggestion of P. F. Thomason<sup>17</sup> (see "Polarographic Determination of Tin in HR Fuels"), ferric hydroxide carrier was tried. An average tin recovery of 90% was obtained. Ammonium chloride was the sole supporting electrolyte.

#### Analyses of Stainless Steel Fuel Elements

J. J. McCown      J. L. Mottern

In order to analyze highly radioactive fuel elements submitted by the Solid State Division, it was necessary to perform all the analytical operations by remote control. A hot cell and master-slave manipulators located in Building 3025 were used. The samples consisted of a stainless steel matrix that contained copper-clad UO<sub>2</sub>. An anodic

<sup>12</sup>C. L. Burros and L. C. Bate, "Sample-Bottle Decapper for the High-Radiation-Level Analytical Facility," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 5.

<sup>13</sup>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.

<sup>14</sup>M. T. Kelley *et al.*, "Instrumentation for the Analytical Cell Exhibit for the Geneva Convention," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 6.

<sup>15</sup>I. M. Kolthoff and R. A. Johnson, "Polarography of Tin(IV) in Presence of Traces of Tetraphenylarsonium Chloride," *Anal. Chem.* **23**, 574 (1951).

<sup>16</sup>C. M. Boyd and R. G. Ball, "Distillation-Polarographic Determination of Tin," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 33.

<sup>17</sup>Ionic Analyses Group.

dissolution technique was used to dissolve the samples (see "Anodic Dissolution Technique"). A platinum cone that contained the sample was connected, as the anode, to a constant-current power supply; the samples were dissolved in 5% sulfuric acid by electrolysis at 4 amp for 8 to 12 hr. An aliquot of the resultant solution was placed in a Melaven type of mercury-cathode cell. The iron, nickel, copper, and chromium were deposited in the mercury by electrolysis for 4 hr at 2 amp.<sup>18</sup> The acid solution that contained the uranium was diluted to such a volume that small aliquots could be removed safely from the hot cell. The uranium was determined colorimetrically and fluorometrically.

#### Determination of pH

U. Koskela      J. Slessinger, Jr.

The ORNL disposable, microelectrode assembly for pH determinations<sup>19</sup> is used in this laboratory in determining the pH of highly radioactive solutions. These electrodes are made and assembled by members of the group. It is anticipated that when the HRT is operating full time the demand for electrodes will be greater than this local supply. In March 1955 the Leeds & Northrup Co. was asked to make the ORNL electrode. However, they sent various microelectrodes of their own design to be tested. All their models failed when exposed to high radiation (i.e., greater than 100 r at contact). In January 1956 the Leeds & Northrup Co. submitted a fused capillary type of electrode in lieu of the ORNL cement-sealed capillary electrode. This electrode tested favorably when compared with an ORNL model. At the present time it is not known whether the Leeds & Northrup electrode can be produced at a reasonable price.

In order to determine the pH of samples in the HRLAF, an electrode-holder assembly was built for remote operation. An ORNL microelectrode is buffered, cleaned, and dried outside the hot cell and transferred inside the hot cell. The master-

<sup>18</sup>J. Gurney *et al.*, *The Use of the High Current Mercury Cathode in Uranium Determination*, K-1106 (Feb. 26, 1954).

<sup>19</sup>H. L. Hemphill, "Disposable Microelectrode Assembly for pH Determinations," Method Nos. 1 001003 and 9 001003 (12-16-54), *ORNL Master Analytical Manual*.

slave manipulators are used to position the electrode into its holder. A motorized Lab-Jack<sup>20</sup> is then used to lift the sample into contact with the electrode (Fig. 3). For easier manipulation, a slight change was made in the shape of the Teflon block of the electrode.

#### Automatic Titration of Sulfate with Photometric End-Point Detection

J. L. Mottern                      C. P. Baker

Certain modifications were incorporated into the titration assembly described by Miller and Thomason<sup>21</sup> for the automatic titration of sulfate with photometric end-point detection. A 6-v a-c light source was used, a cylindrical absorption

cell was substituted, and the RCA 5652 phototube was replaced by an RCA 929 phototube. These changes were made in order to obtain a smoother titration curve. They permit use of the chart travel of the ORNL model Q-945 automatic titrator<sup>22</sup> for standardizing the titrant against standard sulfuric acid solution, which is an easier method for remote operations than that used by Miller and Thomason.<sup>21</sup> An 80% methanol-20% water solution was used; this medium gave better results for the titration of 0.5 to 0.8 mg of total sulfate than did the approximately 96% methanol-4% water solution.<sup>21</sup>

Thirty-five test portions of a standard solution of sulfate, each of which contained approximately 0.75 mg of sulfate, were analyzed by this method with a relative standard deviation of 0.5%.

#### Coulometric Titrations

W. R. Warren

Chromium and chloride are determined in HR-type solutions by coulometric titrations based on modifications of the methods of Shults and Thomason.<sup>23</sup> The modifications were made in order to use the more rugged equipment that is required for remote operation in the HRLAF. In the coulometric method for chloride the specified agar bridge was replaced by a glass tube that was fitted with a plug of Corning Vycor porous glass and that was filled with a 15% potassium nitrate solution. The anode was changed to an 18-gage silver wire with a  $\frac{1}{4}$ -in.-dia generating loop. The concentration of nitric acid in the electrolyte solution was reduced to 2% in order to decrease the extent of reaction of the acid with the silver electrodes. Aliquots of a standard solution of chloride, each of which contained approximately 20  $\mu$ g of chloride, were titrated with a relative standard deviation of approximately 2%. In the method for chromium a salt bridge, similar to the one used for chloride and filled with 15% ammonium sulfate solution, was substituted for the agar bridge. A 15% ammonium sulfate solution was substituted at the positive side of the generating circuit. The current density at the generating



Fig. 3. pH Electrode Assembly for the High-Radiation-Level Analytical Facility.

<sup>22</sup>W. D. Shults, II, "Automatic Titrator, ORNL Model Q-945," Method Nos. 1 003022 and 9 003022 (7-12-54), ORNL Master Analytical Manual.

<sup>23</sup>W. D. Shults, II, and P. F. Thomason, *Coulometric Titration of Chloride and of Chromium in Homogeneous Reactor Type Solutions*, ORNL-1846 (March 11, 1955).

electrode was increased by reducing the size of the platinum-flag electrode to  $0.64 \text{ cm}^2$ . Homogeneous Reactor type of samples that contained less than  $5 \mu\text{g}$  of chromium were titrated by making a standard addition of  $20 \mu\text{g}$  of chromium to the aliquots that were analyzed. The relative standard deviation of results obtained by this addition method was 0.1%. The titrator units for both the chloride and chromium titrations have been reduced in size and are to be mounted on a motorized Lab-Jack<sup>20</sup> in a cell in the HRLAF.

#### Polarographic Cell Assembly for the High-Radiation-Level Analytical Facility

W. L. Maddox<sup>24</sup>

The dropping-mercury electrode (DME) of the design most frequently used in polarography<sup>25</sup> is not suitable for operations with the master-slave

manipulators. A system has been devised whereby mercury can be raised from a large storage flask into a reservoir and held by air pressure (Figs. 4 and 5). To save space, three cells are assembled in series on a single base. One mercury reservoir serves all three. Each unit is fitted with an S.C.E. and a salt bridge. Electrical connection to the DME is made in the usual manner through a platinum contact in the mercury reservoir. Glass ball-and-socket joints are eliminated by the use of 50-ml centrifuge cones as cells. The connections have been made as flexible as possible in order to minimize the danger of breakage by the manipulator hands. Placement of the cell for analysis

<sup>24</sup>Now in the Analytical Instrumentation Group.

<sup>25</sup>H. H. Miller, "Polarograph, ORNL Model Q-1160, High Sensitivity, Recording," Method Nos. 1 003040 and 9 003040 (12-11-53), *ORNL Master Analytical Manual*.

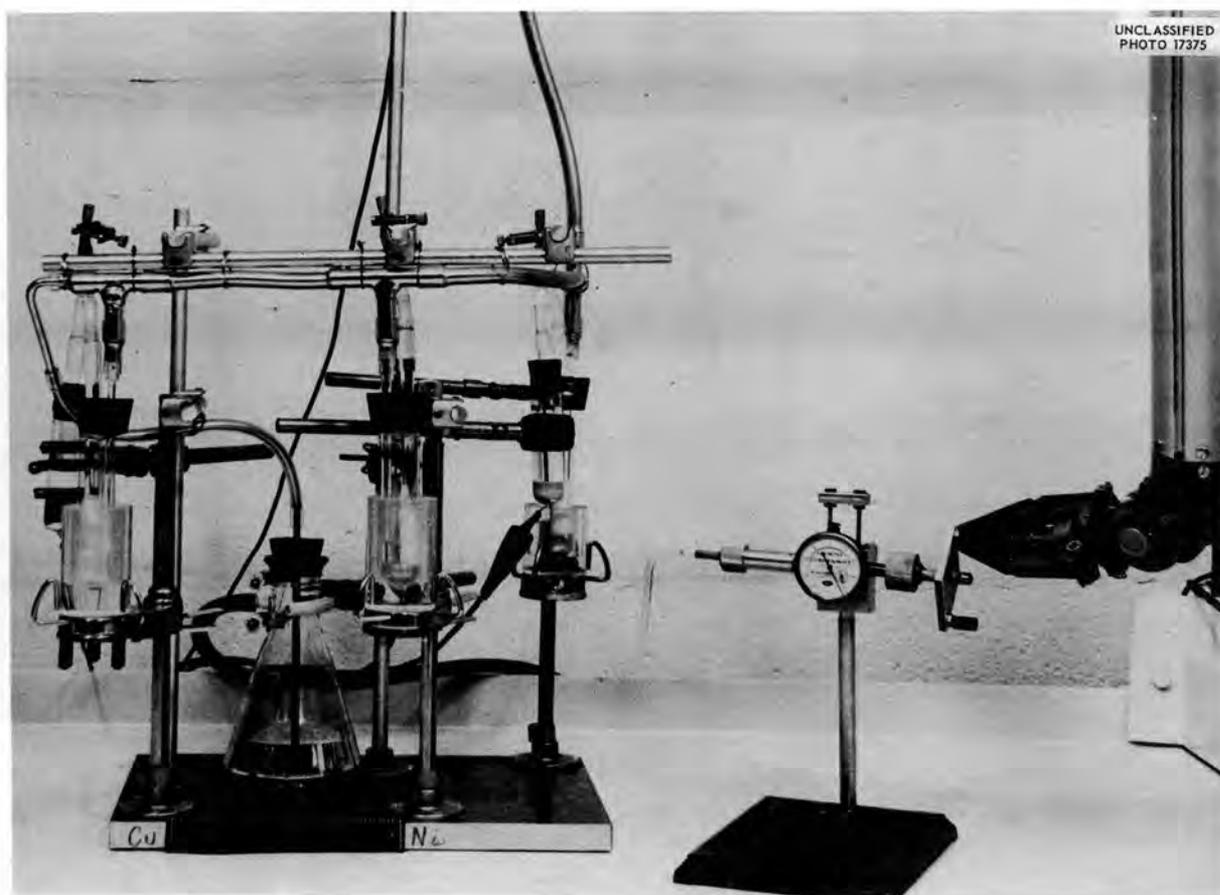


Fig. 4. Polarographic Cell Assembly for the High-Radiation-Level Analytical Facility.

is accomplished by the use of the beaker platform of a modified Beckman model K titrator.<sup>26</sup> Standard

<sup>26</sup>M. T. Kelley *et al.*, "Instrumentation for the Analytical Cell Exhibit for the Geneva Convention," *Anal. Chem. Semiann. Prog. Rep.* Oct. 20, 1955, ORNL-1973, p 7.

additions will be made by means of a Greiner buret that has been altered to permit operations with the master-slave manipulators. Satisfactory polarograms have been taken by means of this apparatus when the operations were made entirely by remote control.

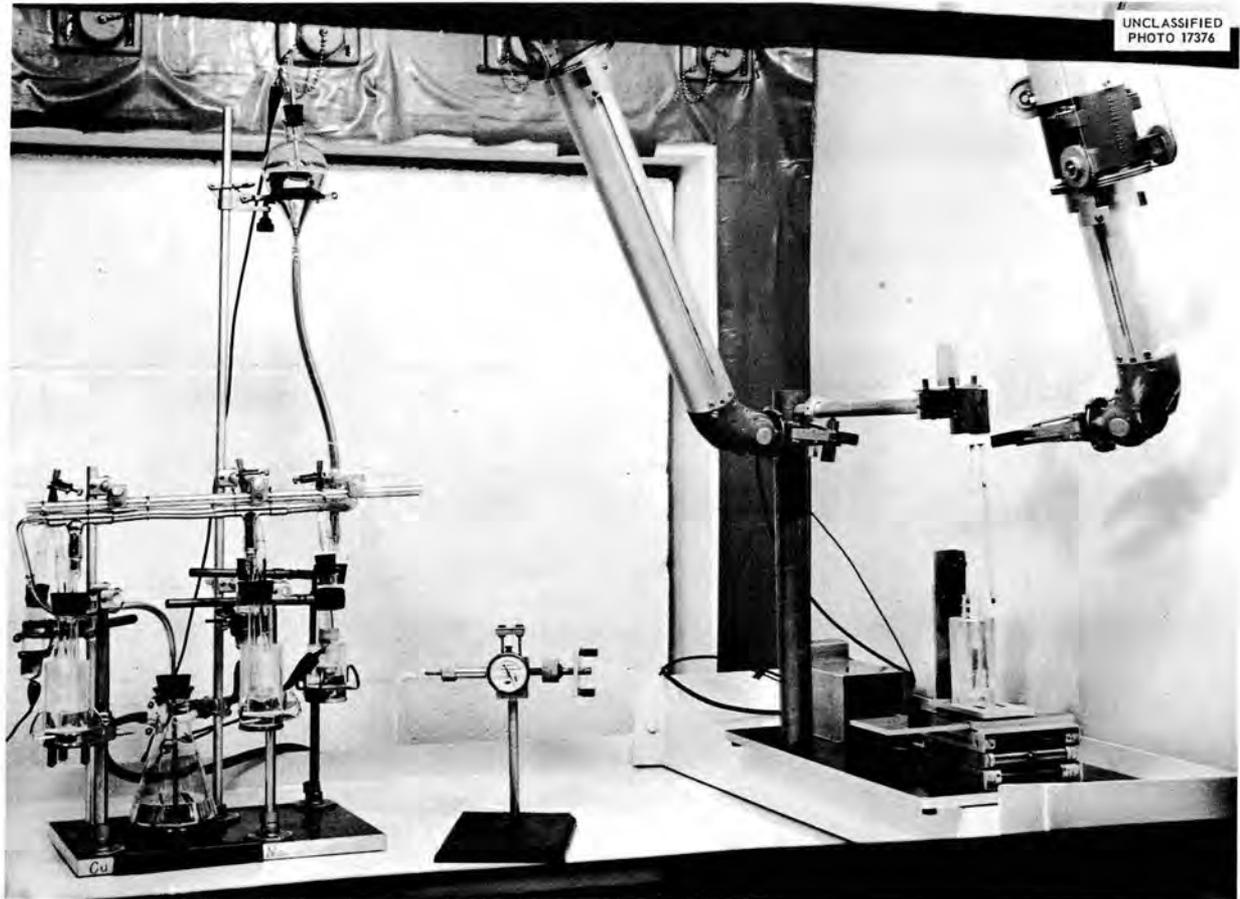
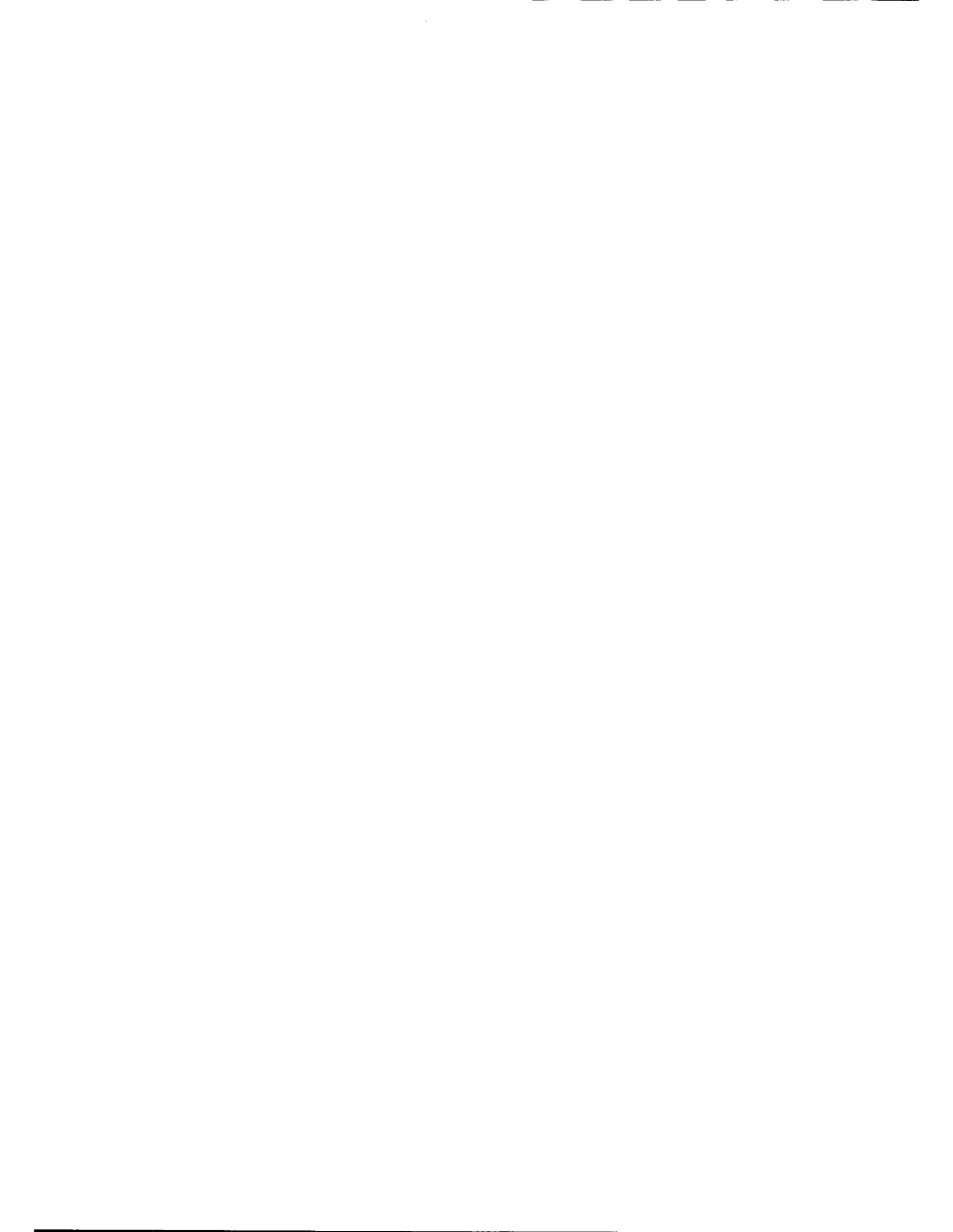


Fig. 5. pH Electrode and Polarographic Cell Assemblies Shown Together in Cell 2 of the High-Radiation-Level Analytical Facility.



# ANALYTICAL CHEMISTRY DIVISION - Y-12 SITE

## RESEARCH AND DEVELOPMENT

### HRP ANALYTICAL CHEMISTRY

O. Menis

#### Precipitation-Polarographic Determination of Tin

D. L. Manning

R. G. Ball

A method was developed for the separation and determination of tin in solutions of uranyl sulfate that contain the corrosion products of stainless steel. It was reported previously<sup>1</sup> that high and erratic results were obtained when quantities of tin less than 100  $\mu\text{g}$  were separated by distillation as the bromide from solutions that contain uranyl sulfate. The erratic results were due, in part, to high and irreproducible reagent blanks. Precipitating tin from an ammonium carbonate solution as the stannic hydroxide in the presence of an aluminum carrier proved to be a more satisfactory method for separating tin from uranium. The precipitate of stannic hydroxide and aluminum hydroxide was dissolved in hydrochloric acid, and then the tin in the solution was determined by the polarographic procedure reported previously.<sup>1</sup>

This precipitation-polarographic method is applicable to the separation and determination of quantities of tin in the range 5 to 50  $\mu\text{g}$  in the presence of as much as 150 mg of uranium(VI) with a relative standard deviation of 10%. However, in those cases in which the presence of large quantities of uranium necessitates more than one precipitation in order to remove the tin, the recovery of tin is low.

#### Amperometric Determination of Mercury with Tetraphenylarsonium Chloride

D. L. Manning

R. G. Ball

The amperometric method for the determination of mercury with tetraphenylarsonium chloride, which was discussed previously,<sup>2</sup> was investigated

<sup>1</sup>C. M. Boyd and R. G. Ball, "Distillation-Polarographic Determination of Tin," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 33.

<sup>2</sup>R. G. Ball, "Amperometric Titration of Mercury with Tetraphenylarsonium Chloride," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 33.

further in order to establish the effects of certain interferences. It was found that the interferences can be divided into the following general types: ions that precipitate with tetraphenylarsonium chloride but do not exhibit a diffusion current at the potential of the titration, for example, cadmium ion; ions that do not precipitate with tetraphenylarsonium chloride but do exhibit a diffusion current at the potential of the titration, for example, uranyl ion; and ions, such as tin(IV), that precipitate with tetraphenylarsonium chloride and also exhibit a diffusion current at the potential of the titration. The maximum mole ratios of cadmium, of uranium, and of tin to mercury that can be tolerated without serious interference are 7, 40, and 6, respectively. The tolerable concentration of excess nitric acid in the titration medium was established to be 4 M. Study of the method is being continued in order to establish the mechanism of the reaction and to identify the products of the reaction.

#### Electrodeposition of Copper by Internal Electrolysis

D. L. Manning

R. G. Ball

In an effort to determine copper gravimetrically and to prevent its interference in other analyses, studies were made of the deposition of copper from solutions of uranyl sulfate by the method of internal electrolysis. It was found that as much as 10 mg of copper can be deposited quantitatively in 1 hr if the initial current is 10 ma. In this electrodeposition method the solution of uranyl sulfate was contained in the cathode compartment of a cell of the type



in which the cadmium metal was immersed in a sulfuric acid solution that was approximately 1 N initially and in which the solution of uranyl sulfate contained about 50 mg of uranium(VI). Since the rate of deposition of copper is dependent on the amount of current, further efforts are being made to increase the current by utilizing a cell having a lower internal resistance.

### Indirect, Flame Photometric Determination of Halides

T. C. Rains

An indirect, flame photometric method for the determination of chloride, which was reported previously,<sup>3</sup> was extended to the determination of microgram quantities of bromide and iodide. This method was applied to the estimation of bromide in the range 2 to 20  $\mu\text{g}$  and of iodide in the range 2 to 30  $\mu\text{g}$ . The relative standard deviation was 5% for the estimation of either bromide or iodide in these ranges. The effectiveness of masking agents, such as ammonia, is being evaluated for the determination of individual halides in the presence of each other.

### Determination of Carbon Dioxide by Thermal Conductivity

R. H. Powell

A differential, thermal conductivity method, the principle of which is outlined by Willard *et al.*,<sup>4</sup> was applied to the determination of carbon dioxide in mixtures of carbon dioxide, oxygen, and water vapor. These gases were in equilibrium with solutions of uranyl sulfate that were withdrawn, under pressure, from HR test loops. A Gow-Mac thermal conductivity unit, model 30-S, and accessory equipment necessary to process, measure, and circulate the gas sample were assembled. After the gas in the sample was separated from the liquid phase and its volume measured, the volume of the gas phase was increased by the addition of a known volume of nitrogen. This mixture of gases was then allowed to flow through two cells, which were connected in series to a carbon dioxide scrubber in the thermal conductivity apparatus. After the carbon dioxide was removed by selective absorption in the scrubber, the residual gas, which was then used as a reference gas, was allowed to flow through a second series of cells in the apparatus. The difference between the carbon dioxide content of the sample and of the reference gas was determined from a potentiometric measurement, which indicated the degree of unbalance of a Wheatstone bridge circuit. The branches of this circuit con-

sisted of hot filaments located in the cells through which the gases flowed. A calibration curve that related the per cent of carbon dioxide to potential was prepared from the results of the analysis of synthetic gas samples. It was found that carbon dioxide in a mixture of gases can be determined by this method over the range 0.7 to 5 vol %; the limit of detection of the method is 0.04 vol %.

### Spectrophotometric Determination of Oxygen in Gas Mixtures

R. H. Powell

The method of Williams *et al.*,<sup>5</sup> which is based on the absorbancy of the oxygen-pyrogallol complex, was adapted to the determination of oxygen in liquid-gas samples that were removed from HR loops in which dynamic tests were being performed. The gas was separated from the liquid phase of the sample and was then reacted with alkaline pyrogallol at 70°C in a closed, glass vessel. The absorbancy of the oxygen-pyrogallol complex was then measured directly in the reaction vessel by means of a Bausch & Lomb filter photometer at a wavelength of 430  $m\mu$ . A calibration curve was prepared for concentrations of 10 to 30 ppm oxygen in gas mixtures; the relative standard deviation of the slope of the curve was 1%.

After the data for the calibration curve had been taken, difficulties resulting from the leakage of air into the apparatus made it impossible to take accurate measurements. Application of several types of stopcock grease did not eliminate the leakage, and therefore the apparatus will have to be modified in order to eliminate the leakage.

### Spectrophotometric Determination of Gold in Thorium Oxide

T. C. Rains

A spectrophotometric method for the determination of gold in thorium oxide that utilizes *p*-dimethylaminobenzalrhodanine as the chromogenic reagent was examined. Since a filter photometer was used in the original work of Polucktov, as discussed by Snell and Snell,<sup>6</sup> the absorption spectrum of the gold-*p*-dimethylaminobenzalrhodanine

<sup>3</sup>O. Menis and T. C. Rains, "Indirect Flame Photometric Determination of Chloride," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 36.

<sup>4</sup>H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, *Instrumental Methods of Analysis*, 2d ed., p 158, Van Nostrand, New York, 1951.

<sup>5</sup>D. D. Williams, C. H. Blachly, and R. R. Miller, "Determination of Trace Oxygen in Gases," *Anal. Chem.* **24**, 1819 (1952).

<sup>6</sup>F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, 3d ed., vol II, p 510, Van Nostrand, New York, 1949.

complex was determined with a Beckman spectrophotometer so that the method could be adapted to this means of measurement. Maximum absorbancy was found to occur in the wavelength region 475 to 510  $m\mu$ . A calibration curve was prepared from which it was found that the absorbancy-concentration relationship is linear at a wavelength of 500  $m\mu$  over the range 3 to 10  $\mu\text{g}$  of gold in a final volume of 10 ml. The relative standard deviation of this method is 4%. Additional tests indicated that thorium oxide does not interfere with the formation and subsequent determination of the gold-*p*-dimethylaminobenzalrhodanine complex.

#### Spectrophotometric Alizarin Red S Determination of Aluminum in Thorium Oxide

T. C. Rains

A spectrophotometric method was evaluated for the determination of aluminum in thorium oxide with alizarin red S<sup>7</sup> after thorium was removed by extraction into a carbon tetrachloride solution of thenoyltrifluoroacetone (TTA). Optimum conditions were determined for the extraction of thorium into the carbon tetrachloride-TTA phase and for the treatment of the aqueous phase prior to the aluminum determination. Since the aluminum-alizarin red S lake is formed at a pH of 4 in a buffered acetate medium, the extraction of thorium from a 6 *M* acetate medium was tested.<sup>8</sup> It was found that three extractions with 10-ml volumes of 0.5 *M* TTA in carbon tetrachloride were required to remove thorium quantitatively from 10 ml of a 1 or 6 *M* acetic acid solution.

Test results for the determination of known amounts of aluminum by this method were low, thus indicating either that aluminum was lost during the extraction step or that the sensitivity of the spectrophotometric method was decreased by some component(s) which entered the aqueous phase during the extraction step. This study will be continued in an effort to resolve and eliminate the difficulty.

#### Removal of Fluoride from Thorium Oxide by Pyrohydrolysis

R. H. Powell

Preliminary tests were made of some factors that affect the rate and efficiency of the removal of

<sup>7</sup>E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2d ed., pp 155, 162, Interscience, New York, 1950.

microgram quantities of fluoride from thorium oxide by the pyrohydrolytic method. The pyrohydrolytic apparatus which was used was constructed in accordance with Y-12 Engineering Dwg. No. E 10f-14163. As originally constructed, the apparatus preheated the steam to only 875°C, but a modification of the apparatus made it possible for the steam to be preheated to 1000°C before it entered the reaction tube, which was also maintained at 1000°C.<sup>9</sup> The fluoride was liberated from the sample as HF by pyrohydrolysis in the reaction tube. The temperatures of the reaction tube and of the steam were measured at the exterior walls of the reaction tube and the steam generator, respectively.

Tests are under way to estimate the precision and accuracy for the determination of microgram quantities of fluoride present as either sodium fluoride or thorium fluoride, which represent fluoride salts that are difficult and simple to pyrohydrolyze, respectively.

#### Spectrophotometric Determination of Silicon Dioxide in Thorium Oxide

D. L. Manning

M. L. Hubbard

The development work, portions of which were previously reported,<sup>10</sup> on a spectrophotometric method for the determination of silicon in thorium oxide was completed. The factors studied included a method for dissolving both thorium oxide and silicon dioxide without loss of silicon as volatile  $\text{SiF}_4$ ; the elimination of interference due to thorium; the control of various factors, such as pH, temperature, and salt concentration, that affect the intensity of the blue color of the silicomolybdate complex; and interference due to phosphate. For silicon in thorium oxide in the concentration range 5 to 150 ppm, the relative standard deviation of the method is less than 10%. The method will be written for inclusion in the *ORNL Master Analytical Manual*.

<sup>8</sup>R. A. Day, Jr., and R. W. Stoughton, *Chemistry of Thorium in Aqueous Solutions. I. Some Organic and Inorganic Complexes*, ORNL-468 (Jan. 5, 1950).

<sup>9</sup>C. D. Susano, J. C. White, and J. E. Lee, Jr., "Apparatus for the Pyrohydrolytic Determination of Fluoride and Other Halides," *Anal. Chem.* **27**, 453 (1955).

<sup>10</sup>D. L. Manning and M. L. Hubbard, "Spectrophotometric Determination of Silicon Dioxide in Thorium Oxide," *Anal. Chem. Semiann. Prog. Rep. Oct.* **20**, 1955, ORNL-1973, p 35.

**Spectrophotometric Determination of Titanium**

I. B. Rubin

H. P. House

A procedure, which the work of Gardner suggested,<sup>11</sup> was developed for the spectrophotometric determination of titanium by which the titanium is extracted into a chloroform solution of 8-quinolinol, and the absorbancy of the titanium-8-quinolinol complex is measured before and after the addition of hydrogen peroxide. After the hydrogen peroxide reaction, the absorbancy of the complex is shifted to a longer wavelength and is also enhanced. On the other hand, the absorbancies of the 8-quinolinol complexes of ions that commonly interfere are not altered by this treatment. Thus the increase of absorbancy of the 8-quinolinol extract of titanium following the peroxide addition was found to be linearly related to the concentration of titanium in the extract. Interferences due to aluminum, iron(II) and (III), chromium(III) and (VI), manganese, nickel, silicon, zinc, and zirconium are thus eliminated. The applicability of the method for samples that contain large amounts of thorium is yet to be ascertained.

**Spectrophotometric Determination of Zirconium**

I. B. Rubin

H. P. House

A spectrophotometric procedure has been developed for the determination of zirconium; it is based on the use of either quercetin<sup>12</sup> or chloranilic acid,<sup>13</sup> after the extraction of zirconium from solutions of thorium nitrate. Microgram quantities of zirconium can be separated from gram quantities of thorium in 2 M nitric acid by a single, 10-min extraction with an equal volume of a 0.5 M solution of thenoyltrifluoroacetone (TTA) in carbon tetrachloride.<sup>14</sup> Microgram quantities of thorium accompany the zirconium, probably because of the emulsification of minute portions of the aqueous phase. This thorium, which is sufficient to interfere seriously with the spectrophotometric determination

<sup>11</sup>K. Gardner, "The Photometric Determination of Small Amounts of Titanium with 8-Hydroxyquinoline," *Analyst* **76**, 485 (1951).

<sup>12</sup>F. S. Grimaldi and C. E. White, "Quercetin as Colorimetric Reagent for Determination of Zirconium," *Anal. Chem.* **25**, 1886 (1953).

<sup>13</sup>O. Menis, *The Determination of Zirconium by the Chloranilic Acid Method*, ORNL-1626 (May 19, 1954).

<sup>14</sup>F. L. Moore, "Radiozirconium Procedure: Simple TTA Separation Without Carrier," *Chem. Quar. Prog. Rep.* Dec. 1948 and Jan. and Feb. 1949, ORNL-336, p 117.

of zirconium, can be removed completely by washing the organic phase twice with volumes of 6 M hydrochloric acid that are equal to the volume of the organic phase. Reducing the iron to the ferrous state prior to the TTA extraction eliminates the interference due to iron, because ferrous iron is not extracted. After the organic phase is washed with hydrochloric acid and evaporated to dryness, the organic matter in the residue is destroyed by reacting it with a mixture of nitric and perchloric acids. The zirconium in an aqueous solution of the treated residue is then determined by either the quercetin or chloranilic acid method. No essential difference in sensitivity or precision was found between the methods when they were applied to solutions that contained 0.4 to 2  $\mu\text{g}$  of zirconium per milliliter of the final solution. The quercetin method is preferred, however, particularly for zirconium in extremely small (approximately 0.1  $\mu\text{g}$ ) amounts, because the reagent blank of the quercetin method is considerably lower than that of the chloranilic acid method.

**Spectrophotometric 8-Quinolinol Determination of Aluminum in Thorium Oxide**

I. B. Rubin

H. P. House

A study was made of the applicability of a colorimetric 8-quinolinol method for the determination of aluminum in thorium oxide, as proposed by Margerum *et al.*<sup>15</sup> By the use of a multiple-extraction technique, microgram quantities of aluminum were separated quantitatively from gram quantities of thorium in a 6 M acetate medium. The interference of iron, even in microgram quantities, with this determination can be circumvented, within limits, by a correction made in accord with the following considerations. The iron complex absorbs at the wavelength of maximum absorbancy of aluminum (i.e., 385  $m\mu$ ) and, to an even greater extent, at 480  $m\mu$ ; the aluminum complex does not absorb at 480  $m\mu$ . The ratio of the absorbancies of iron at the two wavelengths was found to be constant; therefore the absorbancy of the test solution was measured at the two wavelengths; the absorbancy due to iron at 480  $m\mu$ , multiplied by a constant, was subtracted from the absorbancy measured at 385  $m\mu$ . The absorbancy, determined

<sup>15</sup>D. W. Margerum, W. Sprain, and C. V. Banks, "Spectrophotometric Determination of Aluminum in Thorium," *Anal. Chem.* **25**, 249 (1953).

by difference, was used to calculate the aluminum content of the solution.

In connection with this study, some of the samples of thorium oxide were found to contain acid-insoluble aluminum silicate. This material was rendered soluble in hydrochloric acid by fusion with a sodium carbonate-borax flux. The solution thus obtained was satisfactory for the determination of aluminum by the spectrophotometric 8-quinolinol method and of silicon by the molybdenum blue method.

### Particle-Size Distribution of Thorium Oxide

C. M. Boyd

H. P. House

The experimental work on the determination of the particle-size distribution of thorium oxide and of various factors affecting the distribution<sup>16</sup> was continued, with the use and comparison of two sedimentation methods.

The Andreasen pipet method was used to test the relative effectiveness of 0.0005 to 0.2 M solutions of sulfuric acid as dispersing media for thorium oxide (type D-17, ignited at 650°C). Maximum and approximately equal dispersion was attained in 0.05 and 0.005 M acid; however, dispersion was less than that observed previously<sup>16</sup> in 0.1 M HCl for the same sample of thorium oxide (D-17).

The effect of ignition temperature on the particle-size distribution of thorium oxide (D-17) was also determined by the Andreasen pipet method when 0.1 M hydrochloric acid and 0.005 M sulfuric acid were used as the dispersing media. Dispersion was found to be a function of ignition temperature; the order of dispersion, as related to temperature, was as follows: 800 > 1000 > 650 > 1200 > 1400°C. Differences in particle-size distribution as related to ignition temperature were much greater in hydrochloric acid than in sulfuric acid media.

A study of a turbidimetric sedimentation method based on the use of a Wagner turbidimeter showed that the advantages, compared with the Andreasen pipet method, are: less time is required for sedimentation; test portions do not have to be removed during the tests; auxiliary chemical analyses are not required; and smaller samples can be used. Disadvantages of this method are the cumulative errors and the uncertainty incident to the interpretation of turbidimetric readings for very small

particles in the range in which diffraction effects become important. Comparative tests on thorium oxide, the particle size of which ranged from 0.5 to 8  $\mu$ , by the turbidimetric and Andreasen pipet methods, however, yielded results that were in fair agreement over the particle-size range 1.5 to 6  $\mu$ .

Additional studies were made to determine the effectiveness of different reagents as dispersing media for thorium oxide. Xylene and xylene that contained 0.06% oleic acid were tested by both the turbidimetric and the Andreasen pipet methods. Since xylene has a lower viscosity than water, sedimentation is about 30% more rapid in xylene than in aqueous media. It was also found that the dispersion was the same when thorium oxide (type D-17, ignited at 650°C) slurried in xylene containing oleic acid had been agitated for 3 min in a Waring blender as when the same type of thorium oxide slurried in 0.005 M sulfuric acid had been shaken mechanically for 18 hr.

Changes in the particle-size distribution of an aqueous slurry of thorium oxide which occurred while it was circulated in an HR test loop for a period of 20 days were followed by means of the turbidimetric and Andreasen pipet methods. The particle-size distributions were determined after dispersion of the oxide in xylene that contained oleic acid, in 0.005 M sulfuric acid, and in water. In general, the most pronounced increase in dispersion occurred during the first 6 hr of circulation. The dispersion of subsequent samples, taken over the 20-day test period, was, on the whole, fairly constant, although some fluctuations were noted.

### METHODS DEVELOPMENT GROUP

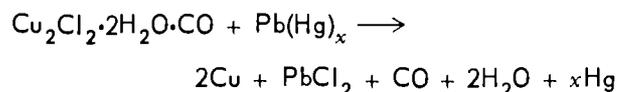
J. C. White

#### Determination of Carbon Monoxide in Solutions of Cuprous Chloride

J. P. Young

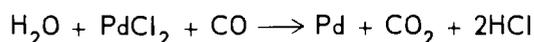
J. R. French

Work is under way to develop a method for the determination of small amounts (micromoles) of carbon monoxide in acidic solutions of cuprous chloride. The proposed method for this determination involves the liberation of carbon monoxide from these solutions by lead-amalgam reduction of the cuprous ion to metallic copper. The equation for the reaction is



<sup>16</sup>H. P. House and N. M. Ferguson, "Particle-Size Distribution of Thorium Oxide," *Anal. Chem. Semiannu. Prog. Rep.* Oct. 20, 1955, ORNL-1973, p 35.

The liberated carbon monoxide is then allowed to react with a solution of palladous chloride according to the equation



The excess palladous ion will then be determined colorimetrically with  $\alpha$ -furildioxime.<sup>17</sup>

An attempt is being made to perform this analysis in a modification of a Conway microdiffusion cell.<sup>18</sup> This cell consists of two concentric glass chambers, the wall of the inner chamber being shorter than that of the outer, and a gastight cover, which is placed over the outer chamber. If a suitable gas absorber is placed in the inner chamber, a gas formed by a reaction that occurs in the outer chamber can diffuse to and be absorbed by the contents of the inner chamber. The cell has been modified in order that cuprous ions, which are present in the samples to be analyzed, may be reduced at a mercury cathode. Any carbon monoxide that is liberated when the cuprous ions are destroyed will ultimately react with the solution of palladous chloride, which is placed in the inner chamber. The study of this proposed method is still in progress.

#### Determination of Octanol-2 in Solutions of Sodium Sulfate

A. S. Meyer, Jr.

W. J. Ross

A study was made of several methods for the determination of small (0.0001 M) concentrations of octanol-2 in kerosene and in 0.5 M solutions of sodium sulfate. Proposed methods that were based on the measurement of physical properties, such as capacitance, boiling point, and surface tension, were too insensitive. Application of macro methods that involve esterification of the octanol-2 with a measured excess of acetyl anhydride<sup>19</sup> or acetyl chloride<sup>20</sup> and subsequent determination of the excess acetylating agent with standard sodium

hydroxide solution was not fully acceptable because consistently low and erratic results were obtained.

Evaluation was made of a modification of the acetyl chloride method,<sup>20</sup> in which octanol-2 was extracted from a solution of sodium sulfate into carbon tetrachloride and was esterified with pyridinium acetyl chloride in toluene. The octanol-2 was then determined by either titrating the excess acetyl chloride with standard sodium hydroxide solution or titrating the acetic acid that is derived from the octyl acetate after the ester has been isolated, hydrolyzed, and steam distilled. The results obtained by these procedures were equivalent to  $75 \pm 4\%$  of the octanol-2 present in the solution of sodium sulfate. Work on this determination has been discontinued.

#### Tridecylphosphine Oxide as an Extractant for Uranium

J. C. White

Studies were made in order to determine the feasibility of using trialkylphosphine oxides as extractants for uranium, because their extraction coefficients are reported<sup>21</sup> to be much larger than those of tributyl phosphate (TBP). Tridecylphosphine oxide (TDPO) was used because the material was available, although trioctylphosphine oxide (TOPO) is also a satisfactory extracting agent.

In these studies a 0.1 M solution of TDPO in Varsol was substituted for TBP-Varsol for the extraction of uranium prior to the determination of uranium by the fluorometric method. In the fluorometric procedure the uranium is extracted from a nitrate medium, after which an aliquot of the organic phase is placed on a gold dish. Following evaporation and fusion with a carbonate-fluoride flux, the fluorescence of the fused mixture is measured with a fluorometer. On the basis of a study of various factors, it was found that the extraction is quantitative even from solutions of sulfuric, phosphoric, oxalic, citric, and tartaric acids that are as concentrated as 1 M. Since higher concentrations of acids were not studied, the upper limit of acid concentration has not yet been ascertained. The extraction of uranium from these media into TBP-Varsol solution is not complete. In the case

<sup>17</sup>O. Menis and T. C. Rains, "Colorimetric Determination of Palladium with Alpha-Furildioxime," *Anal. Chem.* **27**, 1932 (1955).

<sup>18</sup>E. C. Conway, *Microdiffusion Analysis and Volumetric Error*, 3d ed. (rev.), p 7, Lockwood, London, 1950.

<sup>19</sup>C. L. Ogg, W. L. Porter, and C. O. Willits, "Determining the Hydroxyl Content of Certain Organic Compounds. Macro- and Semimicromethods," *Ind. Eng. Chem. Anal. Ed.* **17**, 394 (1945).

<sup>20</sup>D. M. Smith and W. M. D. Bryant, "Rapid Determination of Hydroxyl by Means of Acetyl Chloride and Pyridine," *J. Am. Chem. Soc.* **57**, 61 (1935).

<sup>21</sup>C. A. Blake, K. B. Brown, and C. F. Coleman, *Solvent Extraction of Uranium (and Vanadium) from Acid Liquors with Trialkylphosphine Oxides*, ORNL-1964 (Nov. 4, 1955).

of the extraction into the TDPO-Varsol solution, the nitrate concentration of the aqueous phase is not critical over the range 1 to 12 *M*; solutions of aluminum nitrate that are 0.1, 0.3, and 1.0 *M* can also be used as the source of nitrate ions. It was indicated that the extraction time is not critical; although the samples were extracted for either 5 or 10 min, quantitative results were achieved in 1 min in some cases. Other tests revealed that the ratio of the volume of aqueous to organic phase can be as high as 8 to 1; a higher ratio can possibly be tolerated. In addition, the extraction is quantitative even when the pH of the aqueous phase is as high as 2.3. A study of the effect of other ions on the extraction of uranium with TDPO indicated that no quenching of uranium fluorescence occurs when the following are present in the aqueous phase in the quantities indicated: vanadium(V), 25 mg; arsenic(V), 37 mg; and 10 mg each of nickel(II), iron (III), copper(II), lead(II), tin(II), zinc(II), zirconyl ion(II), molybdenum(VI), and cobalt(II). Only chromium(VI) interferes seriously; tungsten(VI) (10 mg) causes approximately 50% quenching of the fluorescence. As much as 230 mg of thorium(IV) can be present in the aqueous phase without interfering with the extraction of uranium. It was found that chromium(VI), molybdenum(VI), vanadium(V), zirconyl ion(II), and tin(II) are extracted more or less quantitatively, whereas copper(II), nickel(II), cobalt(II), manganese(IV), and zinc(II) were not detected spectrographically in the organic phase.

It is planned to complete the investigation of the feasibility of using TDPO in the fluorometric procedure and also to check its potentialities for the separation of other ions by extraction.

#### Synthesis of Trioctylphosphine Oxide

W. J. Ross

Relative to studies of the potential analytical uses of the trialkylphosphine oxides, a reasonable supply of trioctylphosphine oxide was synthesized by the procedure that was described by Kosolapoff.<sup>22</sup> The resulting trioctylphosphine oxide was thoroughly purified by a series of oxidation, extraction, and recrystallization steps. The final product, representing an over-all yield of 44%, consisted of 99.4% trioctylphosphine oxide having a melting-point range of 51.0 to 51.5°C.

<sup>22</sup>G. M. Kosolapoff, *Organophosphorus Compounds*, p 107, Wiley, New York, 1950.

#### Spectrophotometric Determination of Molybdenum

C. A. Horton

Two spectrophotometric methods were investigated for the determination of less than 50  $\mu\text{g}$  of molybdenum per milliliter of a solution that contained aluminum, uranium, vanadium, iron, sulphate, and phosphate as the chief constituents. After molybdenum as the thiocyanate was extracted from ice-cold solutions into ethyl acetate in one case and into *n*-butyl acetate in the other, the absorbancy of the complex was measured at a wavelength of 470  $m\mu$ . Stannous chloride was added to reduce the effect of interfering ions and to prevent the extraction of their thiocyanates. The method is lengthy and the presence of interferences changed the calibration curves slightly for both procedures; therefore neither method is completely satisfactory. Other methods for the determination of traces of molybdenum in this type of solution will be investigated.

#### QUALITY CONTROL

R. L. McCutchen                      B. J. Ginocchio  
C. D. Susano

The distribution by laboratory of the 6270 determinations, which were evaluated for control purposes, is summarized in Table 9. For purposes

TABLE 9. SUMMARY OF DETERMINATIONS EVALUATED FOR CONTROL PURPOSES

Laboratory	Number of Determinations	
	April Through September 1955	October 1955 Through March 1956
Y-12 Site		
Building 9201-2	685	445
Building 9204-1	303	340
Building 9733-4	165	170
	1153	955
X-10 Site		
Building 3019	3734	3720
Building 3508	375	148
Building 3550	651	471
Building 4500	863	845
General Analyses	260	131
	5883	5315
Grand total	7036	6270

## ANALYTICAL CHEMISTRY PROGRESS REPORT

of comparison, the control data for the previous period are also given.

The control programs in the laboratories of the Analytical Chemistry Division at the X-10 and Y-12 Sites remained essentially the same as those for previous periods. The control work at the Y-12 Site, however, is being reviewed for the purpose of making the control program more effective, and changes that are found to be necessary will be im-

plemented as soon as possible. Review and evaluation of the control program at the X-10 Site are not contemplated at this time.

Biases have been noted from time to time for the control results reported by the various laboratories but, in general, "out-of-control" conditions were not observed. The precision achieved by most of the laboratories is comparable with that attained in earlier periods.

SERVICE ANALYSES

A semiannual summary of the analytical service work at the Y-12 Site is given in Table 10.

HRP ANALYTICAL CHEMISTRY

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

The staff of the HRP Analytical Chemistry Laboratory made 26,500 analyses on 5,485 samples. This represents an increase of 7% in the number of analyses and a decrease of 4% in the number of samples received, compared with the last semi-annual period.

Solutions of uranyl sulfate and of uranyl sulfate that contained either copper sulfate, lithium sulfate, magnesium sulfate, or lithium carbonate were analyzed for uranium, iron, nickel, and chromium and occasionally for aluminum, carbonate, chloride, cobalt, copper, fluoride, lithium, magnesium, manganese, molybdenum, sulfate, titanium, and zirconium. The dissolved oxygen and carbon dioxide in solutions of uranyl sulfate were also determined. Thorium oxide and other compounds of thorium were analyzed in a similar manner; phosphate and silicon in thorium were also determined.

The following solutions were analyzed for iron, nickel, and chromium: 2 M aluminum nitrate in

1 M nitric acid, 2 M magnesium nitrate in 1 M nitric acid, 2 M aluminum sulfate, 7 M nitric acid, and 5% nitric acid. Less frequently, the solutions were analyzed for aluminum, barium, chromium(VI), free acid, magnesium, and nitrate. The density of some of these solutions was also determined.

In addition to this work, lead and tin were determined polarographically, and barium, boron, calcium, lithium, sodium, and potassium were determined by flame photometry.

RAW MATERIALS ANALYTICAL CHEMISTRY

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

The staff of the Raw Materials Analytical Chemistry Laboratory analyzed a total of 7050 samples, 50% of which were submitted by the Raw Materials Process Testing Group of the Materials Chemistry Division. This represents an increase of approximately 18% over the number of samples analyzed during the last semiannual period. Aqueous and organic solutions from solvent-extraction studies of the acid leach solutions from uranium-bearing ores continued to comprise the major portion of the samples. In the continuation of the study of high-molecular-weight organo-phosphorus compounds

TABLE 10. SUMMARY OF ANALYTICAL SERVICE WORK AT Y-12 SITE

	Number of Personnel		ORNL Divisions Requesting Analyses							Others Requesting Analyses		Total Analyses
	Technical	Nontechnical	Materials Chemistry	Chemical Technology	Solid State	Metallurgy	Stable Isotopes	Electronuclear Research	Reactor Experimental Engineering	Y-12	Miscellaneous	
Laboratory Making Analyses			Number of Analyses Reported									
HRP	3	8							26,500			26,500
Raw Materials and Miscellaneous	4	14	13,669	24	96	10	337	17	399	119	93	14,764
Totals	7	22	13,669	24	96	10	337	17	26,899	119	93	41,264



and amines as extractants for uranium, analyses were made for uranium, vanadium, molybdenum, iron, aluminum, sulfate, and chloride. In addition to these analyses, preliminary tests were performed to ascertain the possibility of applying these extractants to the separation of such elements as zirconium and hafnium. A number of samples which were derived from these extractions were analyzed by spectrophotometric methods for zirconium,<sup>1</sup> hafnium, and cerium.<sup>2</sup> This study is also being extended to include the determination of the extraction coefficients of rare-earth elements, such as lanthanum, yttrium, and praseodymium.

The specific gravity and viscosity of a number of aqueous and organic solutions that were submitted by the Process Testing Group were determined; the interfacial tension of designated pairs of these solutions was also measured. In addition, the viscosity of slurries that consisted of a suspension of a finely ground uranium ore in 1 M H<sub>2</sub>SO<sub>4</sub> was determined with a Brookfield viscometer.

Partial analyses were also made of samples of uranium ore both before and after the extraction of the uranium at the pilot plant; the purity of the extracted uranium was determined.

<sup>1</sup>A. D. Horton, "Spectrophotometric Determination of Zirconium," *Anal. Chem.* 25, 1331 (1953).

<sup>2</sup>G. Telep and D. F. Boltz, "Ultraviolet Spectrophotometric Determination of Cerium," *Anal. Chem.* 25, 971 (1953).

#### MISCELLANEOUS ANALYSES

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A total of 807 samples was analyzed by the staff of the Miscellaneous Analyses Laboratory as compared with 573 for the prior semiannual period. The analyses included the determination of boron in both milligram and microgram quantities in organic solutions of boron trifluoride, the estimation of small amounts of carbon in thorium oxide by combustion methods, and the determination by an electrodeposition method of the concentration of cobalt that had either been adsorbed on an ion-exchange resin column or dissolved in an organic solvent, such as pyridine. The alkali metals in solutions of ammonium chloride that were collected as the eluate from ion-exchange resin columns were determined by flame photometry. In addition to these tests two lithium ores (petalite and spodumene) were analyzed for aluminum, silicon, and lithium by volumetric, gravimetric, and flame photometric methods. The services of the Spectrochemical Laboratory were utilized in determining the trace elements present in the ores.

A number of samples of steel and other metals and alloys, comparable with the number of the previous period, were tested for conformance to predetermined specifications.