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ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

FOR PERIOD ENDING DECEMBER 31, 1956

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ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT*

For Period Ending December 31, 1956

M. T. Kelley, Director
C. D. Susano, Associate Director

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ANALYTICAL CHEMISTRY DIVISION SEMIANNUAL PROGRESS REPORT

SUMMARY – X-10 SITE

RESEARCH AND DEVELOPMENT

Ionic Analyses. – The major work of the Ionic Research and Development Group has been the development of ionic methods for the determination of ruthenium, rhodium, boron, selenium, fluorine, chromium, tellurium, uranium, and technetium. These methods were needed in support of the research of other ORNL divisions. The work also included the spectrophotometric determination of plutonium in its various valence states in uranyl sulfate solutions and the study of the effect of temperature on the distribution of plutonium among its valence states. The methods included a derivative polarographic method for technetium, a polarographic method for tellurium, a volumetric method for chromium in stainless steel–uranium dioxide fuel elements, a volumetric method for rhodium, a conductometric method for fluorine, a volumetric and a spectrophotometric method for boron in boron carbide, an iodometric method for selenium in stainless steel, a polarographic method for zinc and nickel, and a spectrophotometric method for iron and manganese in titanium metal. Two new organic chelating agents were synthesized and studied as possible selective or specific analytical reagents for uranium. The wavelength scale of the Warren Spectracord was precisely calibrated by means of the hydrogen lines in the 400- to 425-mμ wavelength region.

Analytical Instrumentation. – The development of the remotely operated falling-drop densimeter has been completed and the circuit diagrams for it have been revised. The densimeter was installed and is operating satisfactorily in the High-Radiation-Level Analytical Facility (HRLAF). The input impedance on the 12-v, d-c scale of an RCA Jr. VoltOhmyst has been converted from 11 to 110 megohms. The converted meter is being used successfully as a control monitor for the falling-drop densimeter. Revisions have been made to the mechanical drawings of the titrant delivery unit of the ORNL model Q-1728 automatic potentiometric titrator and to the drawings of the ORNL model Q-1734 filter photometer. These revisions provide maintenance information regarding the existing instruments and also incorporate several design improvements. Safety movement-limit switches, adjustable legs, and frames for quartz windows have been added to the motorized arc stand that is used for remote spectrographic analyses in the HRLAF. The remotely operated "slurper" has been completed and is now in use in the HRLAF for disposing of radioactive samples and for emptying the vacuum traps of the pipetter.

The development of the ORNL model Q-1673, high-sensitivity, recording, derivative polarograph has been completed. The circuit diagram was revised, and two additional polarographs are being fabricated. The performance of this polarograph is very satisfactory; a method that describes the instrument and its use has been written. The instrument can be used for both regular and derivative polarography in the diffusion-current range from 0.005 to 20 μa. It has unique and versatile damping options. Certain performance characteristics of this polarograph are reported. Its resolving power is much better when used for derivative polarography than when used for regular polarography. A high-sensitivity, recording, single-beam, flame spectrophotometer has been designed for operation with a type 16PMI, 6217, 1P21, 1P22, or 1P28 multiplier phototube, the Beckman flame source and gas control panel, and a Bausch & Lomb grating monochromator. Mechanical and electrical drawings of the flame spectrophotometer have been prepared. A prototype has been fabricated and an additional instrument is being built. A light source has been fabricated for the Leeds & Northrup microphotometer. Lucite centering-aid devices were built to simplify placement by the manipulators of volumetric flasks and cones on the stirrer of the HRLAF dilution pipetter.

An attachment has been designed and built for an Argonne model 8, master-slave manipulator which permits the manipulator to be used for opening drawers in the HRLAF storage cell. A mechanical drawing of the attachment has been prepared. Brackets and attachments have been designed and fabricated to permit the remote operation of the Gilmont microburet by the Argonne model 8, master-

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slave manipulator. A basket and blocks were fabricated to facilitate transfer of glassware to and from the working surface of the cells of the HRLAF via the transfer drawers. An apparatus has been designed, fabricated, and installed in the HRLAF for remotely operated coulometric titrations. An improved automatic coulometric titrator for the remotely controlled determination, at constant current, of microgram quantities of chromium and chloride ions in HRT fuels has been designed, constructed, and installed in the HRLAF. The reagent-generating current can be varied from 0 to 1 ma at a stability of ±0.02% over 1-hr periods. The titrator has the features of end-point anticipation, incremental addition rate near the end point, and a preset end point over the ranges 0 to 1400 mv or 1400 to 0 mv. The stability of the preset end point is ±2 mv, and the cell resistance may vary from 0 to 10,000 ohms while the current remains constant to 1 part per 50,000.

A controlled-potential coulometric titrator has been built. The current that passes through the coulometric cell is integrated by means of analog-computer circuitry. The titrator works very satisfactorily for the determination, for example, of 10 mg of uranium(VI) in the presence of nitrate ion. A simplified version of this instrument will be designed and constructed in the near future. A titrant delivery unit has been designed and built that utilizes a synchro-driven Gilmont microburet. It is used in the HRLAF with the automatic, velocity-servo, potentiometric titrator for remotely operated acid titrations of HRP samples. It is planned to build a gamma absorptometer for the bench-top determination of the concentration of plutonium in aqueous solutions. A Brown recorder will be used, and the use of an Am^{241} source is planned.

The ORNL In-Line Instrumentation Group is continuing its program of the development and evaluation of instrumentation for the Savannah River Laboratory (SRL) and Plant (SRP). An all-glass hydraulic mockup of the SRP sampler will be built; the study of the buildup of radioactivity on various materials has been completed; a cell having negligible background has been designed and is being fabricated for the continuous gamma monitoring of the decontamination factor across a solvent-extraction column; a Taylor, high-resolution, differential-pressure, density transmitter is under test; an instrument is being tested for measuring conductivity, density, and temperature while it is immersed in a process stream of liquid; an SRL flow colorimeter is being tested as a monitor of uranium concentration; a plant prototype of an interface controller is being constructed; a non-immersed instrument for radio-frequency measurement of the nitric acid concentrations of plant streams is being developed; and a high-sensitivity, a-c polarograph is being developed.

Radiochemical Analyses. – Progress has been made in the program of determining pile-neutron activation cross sections, as well as capture cross sections for 25-kev neutrons. The intensities of high-energy gamma radiations in UX_2 have been determined. The efficiencies of a number of counters for measuring Np^{239} have been determined. An end-window proportional beta counter and a 20-channel scintillation spectrometer are in use. Methods of assay and purity testing have been developed for several new radioisotope products. A method of analysis is reported for Ru^{103} and Ru^{106} in a mixture. Several radiochemical methods have been developed for use in analyses required by the HRT. Studies, made in cooperation with the Electronuclear Research Division, of the products of proton and nitrogen-ion bombardments have continued. Solvent-extraction methods for iron and strontium have been studied.

Activation Analyses. – Neutron activation analysis was applied to the determination of microgram and submicrogram amounts of many elements in a variety of samples; a tabular summary of these applications is given. New activation analysis methods were developed for the determination of dysprosium in yttrium oxide and of arsenic in naphtha; the 20-channel gamma scintillation spectrometer is used in both these methods. The activation analysis–sedimentation analysis method of determining the particle-size distribution of thorium oxide was applied to thorium oxide suspensions in high-viscosity mediums.

Spectrochemical Analyses. – Chemical procedures were developed for quantitatively separating microgram amounts of niobium and the rare earths from HRT fuel and of niobium from thorium. A procedure was devised for determining concentrations as small as 0.1 ppm of chromium, 0.25 ppm of nickel, and 0.5 ppm of iron in NaK with 4 to 5% average deviation and at a minimum risk of contamination. A quartz, two-piece centrifuge crucible was developed to minimize losses and contamination

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connected with the isolation and ignition of small precipitates. A change to the use of sintered aluminum mounts instead of plastic mounts for polished metallurgical sections greatly facilitated the interpretation of composition changes near the surface of the specimen.

Inorganic Preparations. – Inorganic chemical work continued on the preparation of anhydrous transition-metal halides for the Physics Division and of anhydrous rare-earth and alkaline-earth halides for the Chemistry Division. The preparation of purified UCl_3 was undertaken in connection with the solid solution (UCl_3 in $LaCl_3$) program of the Nuclear Physics and Low-Temperature Group of the Physics Division. The preparations relative to the phosphor program of the Physics Division were continued.

Optical and Electron Microscopy. – Optical and electron microscopy were used in the extensive study of a so-called "standard slurry" of thorium oxide. Many other types of thorium oxide samples were studied. A method of replicating insoluble aggregates or crystallites of thorium oxide for electron microscopy was developed. The nature of zirconium alloys, corrosion products, and surface structures was investigated by means of electron diffraction and microscopy. A number of crystallite samples and metal powders were studied by electron microscopy. Pertinent illustrations are given. A General Electric Diffractograph was recently installed for use in electron diffraction work.

ORNL Master Analytical Manual. – Eighty-nine new and twenty-five revised methods were issued to the *ORNL Master Analytical Manual;* seventeen new manuals were issued. The majority of the classified methods contained in the *Manual* were declassified. Arrangements were made for the AEC Technical Information Service Extension in Oak Ridge to offer the unclassified sections of the *Manual* for public sale; plans are progressing accordingly.

SERVICE ANALYSES

Analytical service analyses are summarized in tabular form; special problems are discussed briefly. Ionic analyses were made primarily in support of the Chemistry Division's corrosion studies for the HRT and fundamental studies of ion-exchange resins. Radiochemical determinations were made of the products of proton and nitrogen-ion bombardments, many neutron-flux measurements were made, and a number of radionuclides were determined on a nonroutine basis. The method of neutron activation analysis was used to determine microgram and submicrogram amounts of elements in a variety of materials; a tabulation of the applications of the method and the nuclear reactions used is given. Two methods were developed by the Laboratory Control Group for the dissolution of samples of uranium-zirconium alloy. The Pilot-Plant Control Laboratory has equipped and used certain cells in the HRLAF for the analysis of Thorex Process solutions of irradiated thorium slugs and of the related radioactive solutions. Techniques and methods for the remotely controlled analysis of samples from the Volatility Process were developed and evaluated. The Isolation Analyses Laboratory made analyses relative to the Thorex Process and to the plutonium-producer blanket studies and assisted the Physics Division in the preparation of Pu^{240} samples needed for studies of the cross section of Pu^{240}. Fused salts and reactor construction materials were tested by the Special Analyses Laboratory for a number of impurities; also, gas-analysis, vacuum-fusion, and surface-area determinations were used on various samples. The half lives of 13 gamma-emitting radionuclides were determined by the Radioisotope Production Analyses Laboratory, and the pertinent data are tabulated. Methods were perfected for radioactive iodine in mixed fission products and for reducing agents in highly radioactive iodine product solutions. Five work cells in the HRLAF have been completely equipped for the remotely controlled performance of a variety of analyses and for the training of personnel. Highly radioactive samples from the Thorex Process, some as active as 100 r/hr, were analyzed; the condition of the facility was evaluated afterward, and certain additional preventive measures were taken to ensure the isolation of the radioactivity within the cells. The Reactor Analyses Group has used the HRLAF to a limited extent for the analysis of samples from HRP in-pile loop and bomb experiments.

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SUMMARY – Y-12 SITE

RESEARCH AND DEVELOPMENT

The staff of the HRP Analytical Chemistry Laboratory has continued work on 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 constituents in solutions of uranyl sulfate included the titrations of free acid by means of the Sargent-Malmstadt automatic titrator, the electrodeposition of copper by internal electrolysis, the spectrophotometric estimation of tin, and the automatic titration of microgram quantities of uranium, sulfate, and fluoride.

Methods studied for the determination of different elements in samples of thorium oxide included the estimation of thorium by the quercetin method, the spectrophotometric determination of titanium, the determination of aluminum, and the removal of fluoride from thorium oxide. In addition, the conversion of pyrophosphate to orthophosphate in suspensions of thorium oxide and a centrifugal sedimentation method for the determination of the particle-size distribution of thorium oxide were studied. The zeta potential of thorium oxide was calculated by means of a microelectrophoretic method. Other studies included the flame photometric determination of lanthanum and the estimation of calcium and barium by means of flame photometry.

The Methods Development Group evaluated methods for the following: determination of boron in fluoride salts, sampling alkali-metal systems with the modified MSA sampler, extraction of uranium with tri-*n*-octylphosphine oxide, determination of oxygen in sodium and NaK by distillation, applicability of tri-*n*-alkylphosphine oxides as extractants for the analytical separation of elements, extraction of chromium with tri-*n*-octylphosphine oxide, spectrophotometric determination of cerium, simultaneous determination of carbide and nitride in metallic lithium, spectrophotometric determination of uranium in a solution of cyclohexane and tri-*n*-octylphosphine oxide, and separation of zirconium and uranium from thorium by extraction into tri-*n*-octylamine.

The Raw Materials Development Group studied the following problems: separating impurities from solutions of uranyl sulfate, removing iron from organic solutions, determining carbon in samples of stainless steel that were contaminated with paper fibers, spectrophotometrically determining vanadium with benzohydroxamic acid, and comparing the intensity of the fluorescence of uranium phosphors as measured by the ORNL model Q and the modified ORNL model R flurophotometers.

A brief summary of the Quality Control Program of the division is given. In addition, experimental data that are pertinent to, but not a part of, the program were evaluated, such as the possibility of using single rather than duplicate determinations in the analysis of samples for uranium and amine, the analysis of a sample of $NaZrF_5$ and a sample of UO_3 to be used as standards, a comparison of the precision of two methods for determining copper in solutions of uranyl sulfate, the reproducibility of calibration data for the estimation of molybdenum by the ethyl acetate–thiocyanate method, studies that pertain to the fluorometric determination of uranium, investigation of the stannous chloride–thiocyanate method for the spectrophotometric estimation of uranium, and volumetric methods for the determination of uranium and of vanadium.

SERVICE ANALYSES

The staff of the HRP Analytical Chemistry Service Laboratory continued to analyze samples of uranyl sulfate and thorium oxide for iron, nickel, chromium, and other impurities. Some condensate samples were analyzed; boron, barium, calcium, lithium, sodium, and potassium were determined in other samples by flame photometric methods. Spectrophotometric titration techniques were applied to the estimation of fluoride and uranium(IV).

The Raw Materials and Miscellaneous Analyses Group analyzed a wide variety of samples; the work included the separation of thorium and rare-earth elements from uranium, phosphate, and other impurities; the analysis of calcined, solid samples for uranium; the analysis of uraniferous ore; and the determination of cerium, zirconium, hafnium, molybdenum, vanadium, sulfate, phosphate, chloride, and fluoride in relation to work which is being done to determine the extraction coefficient of different cations into a variety of amines and organophosphorus compounds. Other analyses included flame photometric and spectrophotometric determinations of miscellaneous elements; the application of

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a variety of methods of separation to remove interferences; the determination of total acid, sulfur dioxide, and the oxides of nitrogen in sulfuric acid solutions that were derived from the process for the enrichment of N^{15}; the chemical composition of plastic materials used in the construction of cages for small animals; the estimation of hydrogen and carbon in zirconium hydride and carbide; the determination of low concentrations of water; and the determination of oxygen in compressed hydrogen gas. Solutions that are being used in the Quality Control Program were also prepared.

A tabulation of the 89,434 analyses which were reported by the service groups is included, and the distribution of the work from different divisions is given.

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PRESENTATIONS OF RESEARCH RESULTS

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

OPEN-LITERATURE PUBLICATIONS

Author(s)	Title	Publication
Brooksbank, W. A., Jr., G. W. Leddicotte, S. A. Reynolds	"Determination of Trace Elements in Titanium by Neutron Activation Analysis"	*Anal. Chem.* **28**, 1033 (1956)
Brucer, M., T. H. Oddie, J. S. Eldridge*[1]	"Thyroid Uptake Calibration. I. Mock-Iodine, a Radioactive Iodine Gamma-Ray Standard"	ORINS-14 (July 25, 1956)
Feldman, C., J. Y. Ellenburg	"Contrast Changes of Eastman Kodak Spectrum Analysis No. 1 Emulsion During Cold Storage and Their Effect on Observed Intensity Ratios"	*Spectrochim. Acta* **7**(6), 349 (1956)
Fisher, D. J., P. F. Thomason	"Rapid Polarographic Determination of Uranium in Nonaqueous Solvents"	*Anal. Chem.* **28**, 1285 (1956)
Halbert, M. L., T. H. Handley,* A. Zucker	"Excitation Functions for Two Nitrogen-Sodium Nuclear Reactions"	*Phys. Rev.* **104**, 115 (1956)
Horton, A. D., P. F. Thomason	"Ion-Exchange–Spectrophotometric Determination of Aluminum"	*Anal. Chem.* **28**, 1326 (1956)
Kelley, M. T., D. J. Fisher	"Unique Polarographic Damping Circuit for Selective Elimination of Current Fluctuations Due to Dropping-Mercury Electrode"	*Anal. Chem.* **28**, 1130 (1956)
Leddicotte, G. W.	"Some Methods of Determination for the Rare Earth Elements"	*Rare Earths in Biochemical and Medical Research, A Conference Sponsored by the Medical Division, Oak Ridge Institute of Nuclear Studies, Oct. 1955*, edited by G. C. Kyker and E. B. Anderson, ORINS-12 (Sept. 1956), p 63
Leddicotte, G. W.	"Activation Analysis – What Can It Do for You?"	*Nucleonics* **14**(5), 46 (1956)
Leddicotte, G. W.	"Activotion Shows Trace-Metal Segregation"	*Nucleonics* **14**(5), 47 (1956)
Lee, J. H., Jr., J. H. Edgerton, M. T. Kelley	"Pyrohydrolytic Separation and Spectrophotometric Titration of Fluoride in Radioactive Samples"	*Anal. Chem.* **28**, 1439 (1956)
Lyon, W. S., S. A. Reynolds	"Alpha-Gamma Coincidence Counting for Flow-Counter Calibration	*Nucleonics* **14**(12), 44 (1956)
Menis, O., H. P. House, I. B. Rubin	"Spectrophotometric Determination of Microgram Quantities of Disodium Dihydrogen Ethylenediamine Tetraacetate"	*Anal. Chem.* **28**, 1439 (1956)

[1]Work done at the Oak Ridge Institute of Nuclear Studies.

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Author(s)	Title	Publication
Moore, F. L.	"Separation of Zirconium from Other Elements by Liquid-Liquid Extraction"	*Anal. Chem.* **28**, 997 (1956)
Susano, C. D., O. Menis, C. K. Talbott	"Differential Spectrophotometric Method for Determination of Uranium"	*Anal. Chem.* **28**, 1072 (1956)
Thomason, P. F.	"Spectrophotometric Determination of Lithium"	*Anal. Chem.* **28**, 1527 (1956)
Tyor, M. P., J. S. Eldridge*[1]	"A Comparison of the Metabolism of Rubidium 86 and Potassium 42 Following Simultaneous Injection into Man"	*Am. J. Med. Sci.* **232**, 186 (1956)
White, J. C., A. S. Meyer, Jr., D. L. Manning	"Differential Spectrophotometric Determination of Beryllium"	*Anal. Chem.* **28**, 956 (1956)

ORAL PRESENTATIONS

Author(s)	Title	Presented at
Horton, C. A.	"The Choice of an Analytical Method for Analysis of Binary Gas Mixtures"	Southwide Chemical Conference, Memphis, Tenn., Dec. 6–8, 1956
Kelley, M. T.,[2] D. J. Fisher	"Studies in Derivative Polarography. I. High-Sensitivity, Recording, Derivative Polarograph"	Southwide Chemical Conference, Memphis, Tenn., Dec. 6–8, 1956
Leddicotte, G. W.	"Activation Analysis"	Industrial Nuclear Technology Conference, Chicago, Ill., May 15–16, 1956
Leddicotte, G. W.,[2] W. A. Brooksbank, Jr., J. E. Strain	"Determination of Trace Elements in Petroleums and Catalysts by Neutron Activation Analysis"	Symposium on Applications of Radioactivity in Petroleum Research and Refinery Operations, Boston, Mass., Oct. 24–26, 1956
Leddicotte, G. W.,[2] W. A. Brooksbank, Jr.	"Qualitative Analysis of Neutron Activation"	2nd Annual Meeting, American Nuclear Society, Chicago, Ill., June 6–8, 1956
Menis, O., H. P. House,[2] C. M. Boyd	"Thorium Oxide as a Catalyst far the Conversion of Pyrophosphate to Orthophosphate"	Southwide Chemical Conference, Memphis, Tenn., Dec. 6–8, 1956
Menis, O., H. P. House,[2] I. B. Rubin	"Spectrophotometric Determination of Titanium"	Southwide Chemical Conference, Memphis, Tenn., Dec. 6–8, 1956
Menis, O., R. G. Ball,[2] D. L. Manning	"Amperometric Titration of Mercury(II) with Tetraphenylarsonium Chloride"	130th National Meeting, American Chemical Society, Atlantic City, N.J., Sept. 17–21, 1956
Menis, O., D. L. Manning,[2] R. G. Ball	"Automatic Spectrophotometric Titrations"	Southwide Chemical Conference, Memphis, Tenn., Dec. 6–8, 1956
Meyer, A. S., Jr.,[2] C. M. Boyd	"The Determination of Water by the Coulometric Titration"	129th Meeting, American Chemical Society, Dallas, Texas, April 8–13, 1956

[2]Speaker.

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Author(s)	Title	Presented at
Moore, F. L., S. A. Reynolds[3]	"Determinotion of Protactinium-233 by Solvent Extroction"	2nd Annual Meeting, American Nucleor Society, Chicogo, Ill., June 6–8, 1956
Ross, W. J., A. S. Meyer, Jr., J. C. White[4]	"Determination of Boron in Fluoride Salts"	Southwide Chemical Conference, Memphis, Tenn., Dec. 6–8, 1956
Wagner, E. B., D. J. Fisher,*[2] M. T. Kelley*	"A Versatile, Automatic, Recording Potentiometric Titrator"	Southwide Chemical Conference, Memphis, Tenn., Dec. 6–8, 1956
Wyatt, E. I., R. R. Rickard[2]	"Determination of Protactinium-233 by Gamma Spectrometry"	2nd Annual Meeting, American Nuclear Society, Chicago, Ill., June 6–8, 1956
Zittel, H. E.,[2] M. T. Kelley	"Studies in Derivative Polarography. II. Applications and Limitations"	Southwide Chemical Conference, Memphis, Tenn., Dec. 6–8, 1956

TOPICAL REPORTS

Author(s)	Title	Report No.
Brooksbank, W. A., Jr.	"Study in Activation Analysis"	ORNL-2226 (Dec. 7, 1956)
Goldberg, G., J. C. White	"Procedure for the Determination of Oxygen in Sodium and NaK by the Distillation Method"	ORNL CF-56-4-31 (April 5, 1956)
Goldberg, G., A. S. Meyer, Jr., J. C. White	"The Sampling of Alkali Metal Systems with the Modified MSA Sampler"	ORNL-2147 (Aug. 21, 1956)
Handley, T. H., S. A. Reynolds	"Development of Radiochemical Methods for HRT"	ORNL CF-56-7-118 (July 23, 1956)
Mann, C. K.,[5] J. C. White	"Extraction of Chromium with Trioctylphasphine Oxide from Acidic Solutions of Alkali Metal Salts and Its Determination *in Situ* as the Chromium-Diphenylcarbazide Complex"	ORNL CF-56-10-86 (Oct. 23, 1956)
Menis, O., D. L. Manning, R. G. Ball	"Determination of Copper in Solutions of Uranyl Sulfate by Internal Electrolysis"	ORNL-2153 (Sept. 5, 1956)
Menis, O., D. L. Manning, R. G. Ball	"Determination of Tin in Solutions of Uranyl Sulfate"	ORNL-2111 (July 25, 1956)
Menis, O., D. L. Manning, G. Goldstein	"Determination of Free Acid in Solutions of Uranyl Sulfate"	ORNL-2178 (Oct. 25, 1956)
Moore, F. L.	"Radiozirconium Determination for the Angular Correlation Experiment"	ORNL CF-56-4-8 (April 4, 1956)
Mullins, W. T., G. W. Leddicotte	"Determination of Chlorine in Fuel Element Dissolver Solutions"	ORNL CF-56-10-95 (Oct. 24, 1956)
Ross, W. J., J. C. White	"Extraction of the Elements with Trioctylphosphine Oxide from Acidic Solutions"	ORNL CF-56-9-18 (Sept. 6, 1956)

[3]Presented by R. R. Rickard.

[4]Presented by C. A. Horton.

[5]Research participant from the University of Texas, Austin.

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Author(s)	Title	Report No.
Ross, W. J., A. S. Meyer, Jr., J. C. White	"Determination of Boron in Fluoride Salts"	ORNL-2135 (Aug. 7, 1956)
Toomer, F. M.	"Particle Size Determination of Sample of UCl_3 and/or UCl_4"	ORNL CF-56-5-96 (May 15, 1956)
Toomer, F. M.	"Electron Microscopy of Thorium Oxide Samples, L-1 Through L-6"	ORNL CF-56-6-160 (June 26, 1956)
White, J. C.	"The Use of Trialkyl Phosphine Oxides as Extractants in the Fluorometric Determination of Uranium"	ORNL-2161 (Nov. 1, 1956)
Willmarth, T. E.	"A Study of the Yellow Crystalline Layer Formed on Inconel Metal Surfaces Exposed to Fused U Salt Mixtures"	ORNL CF-56-10-93 (Oct. 24, 1956)
Willmarth, T. E., F. M. Toomer	"Examination of Sample CS-22 W by Electron Diffraction and Electron Microscopy"	ORNL CF-56-5-97 (May 14, 1956)

METHODS ISSUED TO *ORNL MASTER ANALYTICAL MANUAL*

Author(s)	Title	Number(s)	Date
	New Methods		
Biggers, R. E.	"Aluminum in the Presence of Thorium and Uranium, Spectrophotometric Oxine (8-Hydroxyquinoline) Method"	1 210211 9 00710211	4-26-56
	"Aluminum in BU and CU Streams of Thorex Process, Spectrophotometric Oxine (8-Hydroxyquinoline) Method"	9 0122022	5-2-56
Brady, L. J.	"Qualitative Identification of Ferrous and Nonferrous Alloys"	1 00901	7-12-56
	"Distillation Range"	1 10001	2-24-56
	"Electrical Conductivity of Industrial Water"	1 10002	5-29-56
	"Dielectric Strength of Insulation Oil of Petroleum Origin"	1 100031	6-22-56
	"Surface Tension of Liquids, Ring Detachment Method"	1 100091	3-13-56
	"Carbon and Hydrogen, Micro Combustion Method"	1 211791 1 213791 9 00711791 9 00713791	11-5-56
	"Carbon and Hydrogen, Macro Combustion Method"	1 211792 1 213792 9 00711792 9 00713792	7-19-56
	"Nitrate (Nitrogen), Gravimetric Nitron Method"	1 215650 9 00715650	5-18-56
Edgerton, J. H., J. E. Lee, Jr.	"Bismuth, Gravimetric Oxychloride Method"	1 211150 9 00711150	6-27-56
Ellenburg, J. Y.	"Rare Earths, Spectrographic Method"	3 130	6-27-56

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Author(s)	Title	Number(s)	Date
Fisher, D. J.	"Automatic Coulometric Titrator (300 ma)"	1 003023 9 003023	10-24-56
	"Flame Spectrophotometer, High-Sensitivity Double-Beam, Recording, ORNL Model Q-1457"	1 003051 9 003051	6-15-56
Fisher, D. J., R. B. Quincy, Jr.	"Pipetter, Remotely Servo-Controlled"	1 003101 9 003101	11-12-56
Horton, A. D.	"Cadmium, Polarographic Method"	1 211420 9 00711420	11-8-56
	"Cobalt, Polarographic Method"	1 212220 9 00712220	10-3-56
	"Nickel and Cobalt, Simultaneous Determination, Polarographic Method"	1 212222 1 215422 9 00712222 9 00715422	11-8-56
	"Iron, Spectrophotometric o-Phenanthroline Method"	1 214110 9 00714110	11-9-56
	"Iron, Polarographic Method"	1 214120 9 00714120	11-9-56
	"Iron, Gravimetric Ammonium Hydroxide Method"	1 214150 9 00714150	11-9-56
	"Lanthanum, Gravimetric Oxalate Method"	1 214351 9 00714351	11-8-56
	"Lead, Polarographic Method"	1 214420 9 00714420	11-8-56
	"Nickel, Spectrophotometric Dimethylglyoxime–Bromine Oxidation Method"	1 215410 9 00715410	11-9-56
	"Tin, Polarographic Method"	1 218920 9 00718920	11-8-56
Laing, W. R.	"Water in Propylenediamine and 2-Ethylhexanol, Coulometric Karl Fischer Titration" (record copy only)	9 03220010	3-28-56
	"Chloride in Propylenediamine Solutions, Volhard Titration Method" (record copy only)	9 032202	3-28-56
Leddicotte, G. W.	"Types of Neutron Reactions"	5 10102	2-2-56
	"Data Record Sheet for Activation Analysis"	5 10124	2-3-56
Lund, J. R.	"Magnesium, Gravimetric Ammonium Phosphate Method"	1 214750 9 00714750	2-22-56
Lynn, E. C.	"Chloride, Volumetric Mohr Method"	1 212072 9 00712072	6-27-56
	"Specification Tests of Lubricating and Electrical Insulating Oil of Petroleum Origin"	1 2300031	7-10-56
Lyon, W. S.	"X-Ray Proportional-Counter Spectrometer"	2 00368	5-17-56
Maddox, W. L.	"pH Indicator, Leeds & Northrup Cat. No. 7664"	1 003121	11-1-56

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Manning, D. L.	"Electrometric Titration Instrument, Sargent 'Ampot'" (record copy only)	1 003027 9 003027	7-12-56
	"Spectrophotometers, Beckman Models B and DU"	1 003030 9 003030	2-6-56
	"Copper in Uranyl Sulfate Solutions, Electrogravimetric Method"	9 082216	11-5-56
	"Hydrogen Fluoride in Inert Gases, Conductometric Method"	1 220003	9-25-56
Marler, M. A.	"Use and Care of Polyethylene"	1 001005	11-2-56
McCown, J. J.	"Iron in Homogeneous Reactor Fuel Solutions, Spectrophotometric 1,10-Phenanthroline Method"	9 082213	5-25-56
McDowell, B. L.	"Magnesium, Volumetric Versene Method"	1 214770 9 00714770	7-11-56
Menis, O.	"Nickel, Spectrophotometric Dimethylglyoxime (Persulfate Oxidation) Method"	1 215410 9 00715410	6-22-56
	"Uranium(IV), Spectrophotometric Ceric Sulfate Titration Method"	1 219280 9 00719280	8-2-56
Pritchard, C. A.	"Uranium(IV), Volumetric Potassium Dichromate Method"	1 219272 9 00719272	5-16-56
Quincy, R. B., Jr.	"Density (Specific Gravity), Falling-Drop Method"	1 100 9 00600	11-2-56
Raaen, H. P.	"Writing Instrumental Methods for the *ORNL Master Analytical Manual*"	05	10-26-56
	"Writing Spectrophotometric Methods for the *ORNL Master Analytical Manual*"	06	10-26-56
Rains, T. C.	"Sulfate (Sulfur), Volumetric Barium Chloride–Tetrahydroxyquinone Method"	1 218172 9 00718172	7-20-56
	"Preparation of Solid Thorium Oxide and Thorium Oxide Slurries for Analysis"	9 082200	7-9-56
Rickard, R. R.	"Antimony in Antimony-124 Product Solutions, Polarographic Method"	9 0732041	3-19-56
	"Chromium in Chromium-51 Product Solution, Spectrophotometric Versenate Method" (record copy only)	9 0732210	3-26-56
Ross, W. J.	"Oxygen in Sodium and in Sodium-Potassium Alloys, Volumetric *n*-Butyl Bromide Method"	1 215871 9 00715871	5-28-56
	"Uranium Dioxide in Uranium Tetrafluoride, Ammonium Oxalate Dissolution Method"	1 220011	9-25-56
Ross, W. J., J. C. White	"Uranium Trifluoride in the Presence of Uranium Tetrafluoride"	9 00720003	3-28-56
Ross, W. J.	"Trivalent Uranium in Fluoride Salt Mixtures, Volumetric Methylene Blue Method"	9 0922920	11-18-55
Rubin, I. B.	"Aluminum, Spectrophotometric Ammonium Aurintricarboxylate (Aluminon) Method"	1 210210 9 00710210	11-9-56

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Author(s)	Title	Number(s)	Date
Rubin, I. B.	"Disodium Dihydrogen Ethylenediaminetetraacetate, Spectrophotometric Cupric Sulfate Method"	1 220006 9 00720006	5-24-56
Stelzner, R. W.	"Automatic Coulometric Titrator (0.5 ma)"	1 003026 9 003026	7-13-56
Talbott, C. K.	"Cobalt, Spectrophotometric Tetraphenylarsonium Chloride–Thiocyanate Method"	1 212210 9 00712210	11-6-56
	"Iron, α,α'-Bipyridyl Spectrophotometric Method"	1 214111 9 00714111	3-23-56
	"Oxygen in Water, Spectrophotometric Modified Winkler Method"	1 215810 9 00715810	5-21-56
	"Sulfate (Sulfur), Volumetric Barium Chloride–Alizarin Red S Method"	1 218173 9 00718173	11-9-56
	"Uranium, Volumetric Zinc Amalgam Potassium Dichromate Method"	1 219270 9 00719270	6-1-56
Wagner, E. B.[6]	"Automatic Potentiometric Titrator, Velocity-Servo, ORNL Model Q-1728"	1 003028 9 003028	6-21-56
	"Filter Photometer, ORNL Model Q-1734"	1 003090 9 003090	4-25-56
Walker, R. L.	"Reducing Normality of Ferrous Sulfate Solutions"	9 00720002	3-29-56
White, J. C.	"Anion-Exchange Separation of Alkali Metals from Other Elements"	1 00706	5-15-56
Williams, C. R.	"Potassium, Gravimetric Sodium Tetraphenylboron Method"	1 216451 9 00716451	3-13-56
	"Sodium, Gravimetric Zinc Uranyl Acetate Method"	1 217950 9 00717950	3-15-56
Wyatt, E. I.	"Antimony-122, Product Analysis Guide"	9 0733040	10-29-56
	"Arsenic-76, Product Analysis Guide"	9 0733063	10-29-56
	"Arsenic-77, Product Analysis Guide"	9 0733064	10-29-56
	"Bromine-82, Product Analysis Guide"	9 0733131	10-29-56
	"Cadmium-115, Product Analysis Guide"	9 0733142	10-29-56
	"Copper-64, Product Analysis Guide"	9 0733231	10-29-56
	"Gallium-72, Product Analysis Guide"	9 0733311	10-29-56
	"Gold-198, Product Analysis Guide"	9 0733331	10-29-56
	"Gold-199, Product Analysis Guide"	9 0733332	10-29-56
	"Hafnium-181, Product Analysis Guide"	9 0733341	10-29-56
	"Iridium-194, Product Analysis Guide"	9 0733402	10-29-56
	"Lanthanum-140, Product Analysis Guide"	9 0733431	10-29-56
	"Molybdenum-99, Product Analysis Guide"	9 0733501	10-29-56
	"Osmium-191, Product Analysis Guide"	9 0733571	10-29-56

[6] Now a member of the Health Physics Division.

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Author(s)	Title	Number(s)	Date
Wyatt, E. I.	"Palladium-109, Product Analysis Guide"	9 0733591	10-29-56
	"Praseodymium-142, Product Analysis Guide"	9 0733650	10-29-56
	"Samarium-153, Product Analysis Guide"	9 0733741	10-29-56
	"Silver-111, Product Analysis Guide"	9 0733783	10-29-56
	"Tungsten-187, Product Analysis Guide"	9 0733912	10-29-56
	"Yttrium-90, Product Analysis Guide"	9 0733960	10-29-56

Revised Methods

Horton, A. D.	"Zirconium in Homogeneous Reactor Fuel, Spectrophotometric Thoron Method"	9 082209	R. 4-4-56
Raaen, H. P.	"Writing Methods for the *ORNL Master Analytical Manual*"	01	R. 10-24-56
	"Authorization and Classification of Methods for the *ORNL Master Analytical Manual*"	02	R. 10-26-56
	"Maintenance of the *ORNL Master Analytical Manual*"	04	R. 10-26-56
Wyatt, E. I.	"Nonvolatile Material"	9 0731001	R. 10-2-56
	"Total Cation Concentration of Aqueous Solutions, Ion Exchange"	9 0732001	R. 10-2-56
	"Nitrates, Brown Ring Test"	9 0732002	R. 9-20-56
	"Total Reducing Agents"	9 0732003	R. 9-20-56
	"Heavy Metals, Spot Test"	9 0732004	R. 9-20-56
	"Adsorption Capacity of Ion-Exchange Resins"	9 0732006	R. 9-20-56
	"Manganese, Spot Test"	9 0732480	R. 9-20-56
	"Gross Beta"	9 002302 9 0733001	R. 9-20-56
	"Antimony-124 HSA, Product Analysis Guide"	9 0733041	R. 9-20-56
	"Antimony-125 CF, Product Analysis Guide"	9 0733042	R. 9-20-56
	"Barium-140, Product Analysis Guide"	9 0733081	R. 9-20-56
	"Barium-133, Praduct Analysis Guide"	9 0733084	R. 9-20-56
	"Cadmium-115*m* HSA, Product Analysis Guide"	9 0733141	R. 9-20-56
	"Calcium-45, Product Analysis Guide"	9 0733151	R. 9-20-56
	"Carbon-14, Product Analysis Guide"	9 0733171	R. 9-20-56
	"Carbon-14, Beta Ionization Chamber Method"	9 0733172	R. 9-20-56
	"Cerium-141, 144, Product Analysis Guide"	9 0733181	R. 9-20-56
	"Cesium-137, Product Analysis Guide"	9 0733191	R. 9-20-56
	"Cobalt-58, Product Analysis Guide"	9 0733225	R. 9-20-56
	"Indium-114*m*, Product Analysis Guide"	9 0733381	R. 9-20-56
	"Iodine-131, Product Analysis Guide"	9 0733391	R. 9-20-56

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ANALYTICAL CHEMISTRY DIVISION - X-10 SITE

RESEARCH AND DEVELOPMENT

IONIC ANALYSES

P. F. Thomason

Quantitative Determination of Plutonium in Its Various Valence States in 1.4 *M* Uranyl Sulfate Solution[1]

R. E. Biggers

The Chemical Technology Division and the Reactor Analyses Group of the Analytical Chemistry Division need a method for determining the concentrations of plutonium(III), (IV), and (VI) in the presence of each other in aqueous solutions. Information regarding the distribution of plutonium among its valence states is also of importance in the plutonium disproportionation studies that are described in the next section. The chemical separation of the valence states of plutonium is slow, extremely difficult, and frequently impossible. In addition, chemical procedures change the relative amounts of the valence states present. It was apparent that a physical method is needed.

The spectra of plutonium(III), (IV), and (VI) in 1.4 *M* uranyl sulfate solution were obtained separately over the wavelength range from about 350 to 1350 mμ. Since each of the spectra shows numerous absorption peaks and considerable fine structure, there are several spectral absorption regions in which plutonium in only one of its valence states absorbs to any appreciable extent. The spectrophotometric method therefore appears to be ideal for the determination of plutonium(III), (IV), and (VI) in the presence of each other.

By analysis of the spectral data, eight wavelengths were chosen for the quantitative determinations. Essentially, plutonium in only one valence state exhibited appreciable absorption at each of the chosen wavelengths. Eight equations, each in three unknowns, were set up for each wavelength. From these, 18 sets of simultaneous equations (three equations in three unknowns per set) were also set up; they represented all possible combinations of the data for the three valence states at the eight wavelengths. The 18 sets of simultaneous equations were solved by use of the Oracle. The least-squares solution of the eight simultaneous equations was also obtained by use of the Oracle.

The equations obtained by use of the Oracle calculations can be used to determine the concentrations of plutonium(III), (IV), and (VI) in the presence of each other by simply substituting in the appropriate equation the light absorbancies of the solution measured at the several wavelengths. Although the calculated equations apply to 1.4 *M* uranyl sulfate solution, the procedure is of general applicability. Since the mediums sometime exert pronounced effects on the absolute absorbancy indices for the various valence states, similar equations should be calculated for other mediums in order to obtain maximum accuracy.

It is likely that a spectrophotometric method used in conjunction with computations by simultaneous equations would also be suitable for the determination of neptunium in its various valence states in various mediums. In addition, it should be possible to determine the concentrations of plutonium(III), (IV), and (VI) and of neptunium(III), (IV), (V), and (VI) in the presence of each other, even in 1.4 *M* uranyl sulfate solution.

A considerable amount of additional work is planned, particularly in order to evaluate this type of method for the quantitative determination of neptunium in its various valence states and of neptunium and plutonium in their valence states in neptunium-plutonium mixtures.

Effect of Temperature on the Distribution of Plutonium Among Its Valence States in Aqueous Solutions of Uranyl Sulfate or Other Sulfates

R. E. Biggers J. M. Chilton[2]

The spectra of plutonium(III), (IV), and (VI) in concentrations from 100 to 430 mg/liter were obtained in several types of sulfate mediums,

[1]This work was done in cooperation with J. M. Chilton of the Chemical Technology Division.

[2]Chemical Technology Division.

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including dilute sulfuric acid, 1.4 *M* lithium sulfate, and 1.4 *M* uranyl sulfate. The general characteristics of the spectra are essentially the same; only minor differences were observed in the wavelengths of the absorption peaks and in the peak heights.

A study was made of the effect of temperature, concentration of sulfate ion, and acidity on the disproportionation of plutonium(IV) into plutonium(III) and (VI); the effect of temperature was studied in particular. The spectra and disproportionation reaction were studied over the temperature range 20 to 90°C by the use of the spectrophotometer of a high-temperature cell compartment of special design. It was found that even in 1.4 *M* lithium sulfate solution, in which plutonium(IV) exists as the sulfate complex, this disproportionation does occur but to a smaller extent than in sulfate solutions more dilute than 1.4 *M*. Considerable disproportionation was observed in 1.4 *M* uranyl sulfate solution.

The conditions under which polycondensed plutonium ions and colloidal plutonium form have been investigated. It was found that when a 1.4 *M* uranyl sulfate solution of plutonium(IV) is heated to 95°C (near the maximum temperature possible in a nonpressurized system) the plutonium(IV) is partially converted into colloidal plutonium. The colloid formed is apparently stable in the hot uranyl sulfate solution; however, when the solution is cooled, a large fraction of the colloidal plutonium is transformed back into plutonium(IV). When the same solution is heated a second time, the plutonium(IV) is again partially converted to colloidal plutonium; cooling the solution after this second heating converts a large fraction of the second colloid back to plutonium(IV). It is therefore possible to build up the concentration of colloidal plutonium from plutonium(IV) in a 1.4 *M* uranyl sulfate solution by a series of such heating-cooling cycles. Partial disproportionation of plutonium(IV) into plutonium(III) and (VI) was also observed to occur during the heating part of the cycle. Reproportionation of plutonium(III) and (VI) into plutonium(IV) occurs during cooling. Evidence has been obtained for the postulate that colloidal plutonium and its precursor, polycondensed plutonium ions, are formed from the sexivalent plutonium.

The results of this study have also shown that in 1.4 *M* uranyl sulfate solution the disproportionation is relatively slow at temperatures below about 80°C. From 80 to 90°C the concentrations of plutonium(III) and (VI) increase almost exponentially.

From the present results it is postulated that complete disproportionation of plutonium(IV) into plutonium(III) and (VI) may occur in a 1.4 *M* uranyl sulfate solution if the temperature of the solution is elevated, by pressurizing the system, to some temperature considerably higher than 95°C.

Development of Organic Chelating Agents for Uranium

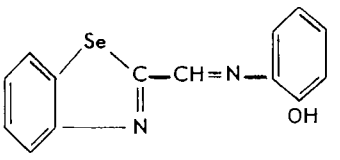
R. E. Biggers

There are many techniques for the determination of uranium after it has been isolated from the sample matrix. However, the separation is usually somewhat lengthy at best. A selective reagent would make possible the determination of uranium in the presence of elements that cause serious interferences.

A general literature survey has been made concerning the reaction of organic reagents with uranium ions. Not one of the reagents known at the present time reacts exclusively with uranium, and, in general, those that show the greatest sensitivity are the least selective. There is a great need for organic reagents that are specific for uranium and for other transuranium elements or that are at least more selective for these elements than are those reagents now known. It would be especially desirable if reagents existed that would differentiate the various valence states of the heavy elements from one another.

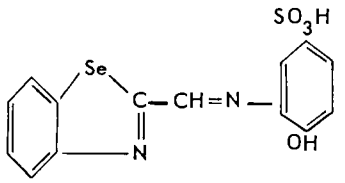
Several types of compounds can be synthesized that would perhaps be specific or selective reagents for uranium. From structural considerations (e.g., ions of the nonoxygenated and oxygenated valence states of uranium have different atomic diameters) it appears that a peculiar type of heterocyclic compound might show some of the properties desired in such a reagent. Two heterocyclic chelating agents, namely, 2-benzoselenazole carboxaldehyde-*o*-hydroxy anil

(1)



and 2-benzoselenazole carboxaldehyde-*o*-hydroxy-*p*-sulfonic acid anil,

(2)



were synthesized and were partially evaluated as possible selective reagents for uranium. Reagent 1 was synthesized by Seyhan[3,4] but was not considered for use as an analytical reagent. To the author's knowledge, reagent 2 has not been synthesized previously.

Under certain conditions, the uranyl chelate of compound 1 is apparently stable and has molar absorbancy indices that range from 4,076 to 14,600. The complexation reaction has been studied as a function of a number of parameters, but the evaluation of compound 1 is not yet complete.

In the visible region of the spectrum the uranyl chelate of compound 2 has molar absorbancy indices that are considerably less than those of the uranyl chelate of compound 1; however, in the ultraviolet region a molar absorbancy index of 66,500 was observed.

Although work on this problem has been temporarily suspended, the preparation of the sulfur analogs of compounds 1 and 2 is contemplated. Other possible new chelating agents are being considered but have not yet been synthesized.

Determination of Technetium

R. E. Biggers

A number of samples of interest to the Chemical Technology Division were analyzed for technetium, which was present both in solutions and in precipitated uranium metal. A derivative polarographic technique was found to give good results on samples which contained technetium in concentrations that ranged from 10 ppm to 10 g/liter. The samples were analyzed after the technetium was converted to the pertechnetate ion and the solution buffered to pH 7. A standard-addition technique was found to be most convenient.

Absorption Spectra of Ruthenium

R. E. Biggers

The visible and ultraviolet absorption spectra of ruthenium in various solutions of interest to the Chemical Technology Division were examined. It was shown that in solutions which contained nitric oxide, nitrogen dioxide, and nitrate ions, definite complexes of ruthenium with these species exist. This was evident from the large number of changes in the absorption spectra which occurred upon treatment of solutions of ruthenium in nitric acid with mixed oxides of nitrogen. These spectra were to be used in the interpretation of anomalies existing in the ion-exchange behavior of ruthenium under certain conditions.

Evaluation of Factors That Affect the Operation of the Warren Spectracord

R. E. Biggers

A general discussion[5] has been given concerning the calibration of the wavelength scale of the Warren Spectracord by the use of lines in the emission spectrum of hydrogen as absolute reference points. After the instrument is zeroed initially on the H_α line (656.273 mμ–656.285 mμ, a close doublet), it is then zeroed more closely on some spectral lines in the 400- to 425-mμ region where the dispersion of quartz is about five times as great as it is in the region of the H_α line.

Power supplies for the discharge lamp and for the Spectracord and the operation of the hydrogen discharge lamp were discussed, as were some critical factors that affect the double- and single-beam operation of the instrument. The temperature of the hydrogen arc was found to be the most critical factor affecting the operation of the Spectracord in the ultraviolet region. At temperatures less than a critical value, a sinusoidal time variation of emission was observed, which resulted in an erratic, sinusoidal operation of the slit servo.

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[3] M. Seyhan, "Notiz über einige Komplexbildner der Azomethin-Reihe," *Chem. Ber.* 85, 436 (1952).

[4] M. Seyhan, "Notiz über die Oxydation von Methylbenzselenazol mit Selendioxyd," *Chem. Ber.* 86, 888 (1953).

[5] J. R. Lund and R. E. Biggers, "Spectrophotometer, Recording, Warren Spectracord," Method Nos. 1 003032 and 9 003032 (in preparation), *ORNL Master Analytical Manual.*

Vapor-Phase Chromatography of Amsco Solvent

A. D. Horton J. G. Surak[6]
P. F. Thomason

A vapor-phase chromatographic apparatus has been constructed for the purpose of determining the composition of Amsco, which is used in the Thorex Process as a solvent for tributyl phosphate. Amsco is formed by the polymerization of low-boiling olefins and has a boiling-point range of 177 to 203°C.

Most of the design and construction of the apparatus were done by Surak.[6] The principal parts of the apparatus, which is illustrated in Fig. 1, are the column and its heating jacket; the thermal-conductivity cell, which is used as a device for sensing the presence of the eluted vapors; and a Brown recorder to record the signal from the thermal-conductivity cell.

The column consists of a ¼-in.-OD by 4-ft-length copper U-tube packed with 75% Celite C-44857–25% dinonylphthalate. The column is heated to 144°C by xylene vapor contained in a pyrex jacket that surrounds the column.

The Gow-Mac thermal-conductivity cell[7] consists of a stainless steel block that contains four sensing units (cells), each of which contains a tungsten filament. The carrier gas (helium) passes through two of the cells, and the eluate (helium plus sample vapor) passes through the other two cells. A variable resistance in the circuit provides a means of balancing the Wheatstone bridge that is formed by the four filaments.

Prior to the admission of a sample to the column the heating jackets on the thermal-conductivity cell and on the sample preheater are heated to a temperature that is 40°C higher than that of the column. The column and the thermal-conductivity cell are flushed with helium at a predetermined flow rate. The optimum flow rate must be established during the actual operation of the apparatus by correlating the flow rate with the quality of resolution obtained on the recorded chromatogram.

When an unvarying horizontal trace is obtained on the recorder chart, the recorder pen is set at zero by adjustment of the balancing resistance in the Wheatstone bridge circuit of the cell. A sample is admitted to the sample preheater by means of a hypodermic syringe. A sample size of 10 to 20 μl is sufficient for use in obtaining a

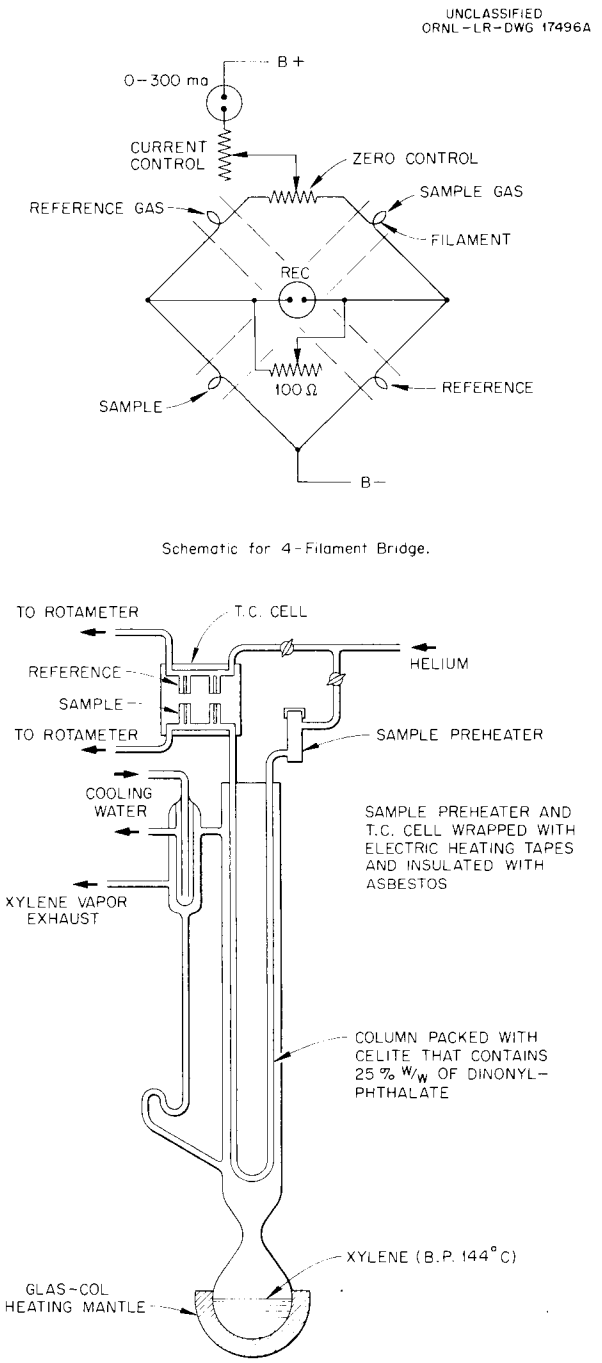

Fig. 1. Schematic Diagram of Vapor-Phase Chromatographic Apparatus.

[6]Summer employee from Marquette University, Milwaukee, Wis.

[7]Thermal-conductivity cell "No. 9225, TE (II) geometry, Tu-4 filaments"; available from Gow-Mac Instrument Corp., 100 Kings Road, Madison, N. J.

chromatogram of a multicomponent mixture at the highest sensitivity of the recorder. When the recording of the chromatogram is complete, the recorder pen should return to the original zero position and record an unvarying horizontal trace.

Elution traces for Amsco 125-82 (American Mineral Spirits Co. odorless paint thinner) that were taken before and after the Amsco was treated in various ways are shown in Fig. 2. Thus far, only semiqualitative results can be reported. The results suggest that Amsco contains branched-chain isomers of *n*-paraffins having from 10 to 12 carbon atoms. Possibly some cyclic compounds and a small amount of unsaturated compounds are also present.

Chromatograms of irradiated Amsco have also been determined. The usual results of the high-level irradiation of Amsco are the degradation of the low- and high-boiling isomers and the formation of additional isomers in the middle-boiling range.

The value of vapor-phase chromatography as an analytical tool is attested to by the large number of literature references available regarding the determination of almost all types of volatile organic compounds (boiling points up to 250°C). More than a half dozen commercial instruments are available.

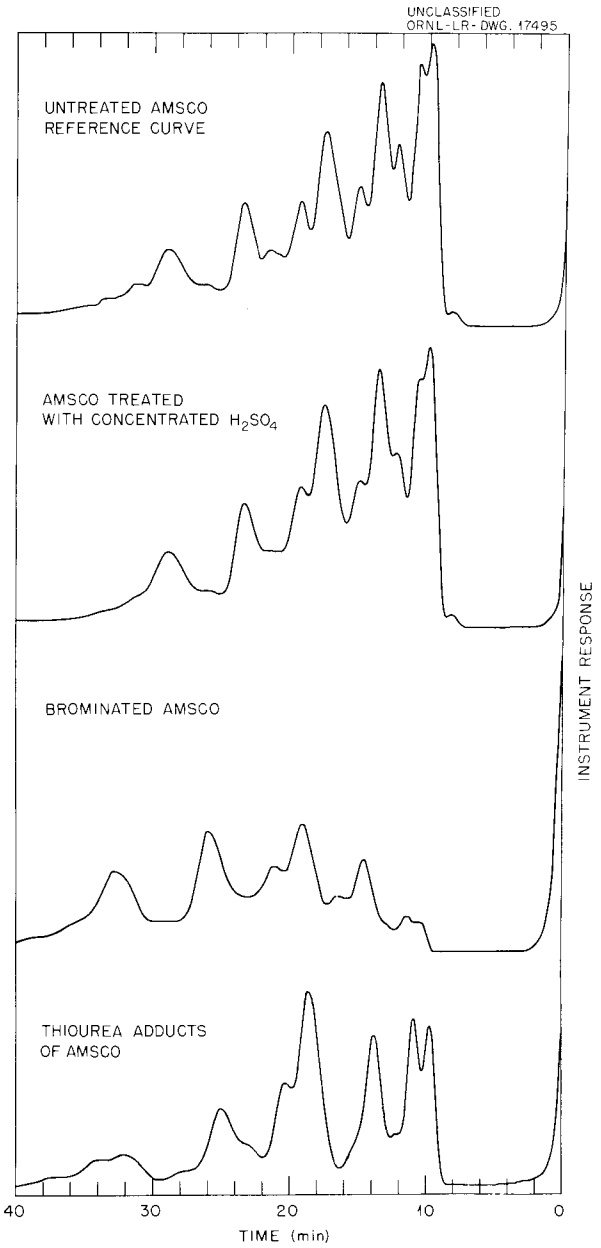

Fig. 2. Elution Traces for Amsco Solvents Eluted from 75% Celite C-44857–25% Dinonylphthalate by Helium.

Determination of Tellurium in HRT Fuel

F. J. Miller

A preliminary study was made of means for the separation and chemical determination of fission tellurium that will be present in HRT fuel. The polarographic method of Lingane and Niedrach[8] was deemed the most suitable. For analyses made on standard solutions of tellurium, a linear plot of diffusion current vs concentration over the range 1 to 50 μg of tellurium per 10 ml of solution was obtained in an ammonium hydroxide–ammonium chloride buffer solution of pH 8.4.

Determination of Ruthenium in Aqueous and Organic Solutions

F. J. Miller

Two sets of samples that contained ruthenium were submitted by the Chemical Technology Division for analysis. The first set was a series of aqueous solutions that were heavily salted with aluminum nitrate; the second set was a series of organic solutions that consisted of Amsco solvent, tributyl phosphate, and ruthenium. The aqueous solutions were made strongly basic with sodium hydroxide, the ruthenium was oxidized to the tetraoxide by passage of a stream of chlorine gas

[8] J. J. Lingane and L. W. Niedrach, "Polarography of Selenium and Tellurium. II. The +4 States," *J. Am. Chem. Soc.* 71, 196 (1949).

through the solution,[9] and the solution was distilled. The ruthenium tetraoxide was then trapped in 6 *M* HCl that was saturated with sulfur dioxide, and the ruthenium in the distillate was determined spectrophotometrically with thiourea.[10] The organic samples were first distilled from a mixture of water, nitric acid, and perchloric acid. The distillate was then made alkaline and was redistilled during passage of chlorine gas at a temperature of less than 110°C. The ruthenium content of the distillate was determined spectrophotometrically with thiourea.[10]

Determination of Chromium in Stainless Steel–Uranium Dioxide Fuel Elements

F. J. Miller

A method was desired by the Laboratory Control Unit for the determination of chromium in samples that resulted from the dissolution of stainless steel–uranium dioxide sandwich-type fuel elements in aqua regia. The chromium was oxidized to dichromate by heating the sample with perchloric acid. The cooled, diluted sample was then titrated potentiometrically with a standard solution of ferrous sulfate by use of the Beckman model K titrator.[11–13]

Determination of Submilligram and Milligram Amounts of Rhodium

F. J. Miller

A request was received for the determination of rhodium in an aqueous solution. The amount of rhodium estimated to be present was too small to permit accurate gravimetric assay to be made without tedious effort; therefore a volumetric procedure was adapted for use.[14] The sample was heated to fumes with sulfuric acid, cooled, and diluted; then sodium bismuthate was added. The resulting slurry was allowed to stand for 2 hr and was then filtered; the filtrate was titrated potentiometrically with a standard solution of ferrous sulfate by means of a platinum-calomel electrode system.

Analysis of Titanium Metal

R. M. Rush

Two samples of "pure" titanium metal were submitted by the Metallurgy Division for the quantitative determination of certain impurities. The iron content was determined by the spectrophotometric, *o*-phenanthroline procedure.[15] The manganese content was determined spectrophotometrically after periodate oxidation of the manganese to permanganate.[16]

The zinc and nickel contents were determined polarographically and spectrophotometrically, respectively, after an ion-exchange separation. The sample was dissolved in hydrofluoric acid, and the solution was made about 0.1 *M* in HCl. The solution was then passed through a column of Dowex 50 cation-exchange resin, and the titanium was eluted as the nonadsorbable TiF_6^{--} complex. The nickel and zinc were then eluted from the column with 6 *M* HCl, and the eluate was passed through a Dowex 1 anion-exchange column. The nickel was not adsorbed, whereas the zinc was retained and was later eluted by 0.005 *M* HCl.[17] The nickel was determined polarographically in a 1 *M* ammonium hydroxide–1 *M* ammonium chloride supporting electrolyte. The zinc was determined spectrophotometrically by the Zincon procedure.[18]

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[9] N. H. Furman, *Scott's Standard Methods of Chemical Analysis*, 5th ed., Vol. 1, p 737–741, Van Nostrand, New York, 1939.

[10] M. Kilpatrick *et al.*, *The Chemistry of Ruthenium, Annual Report Covering the Period June 1, 1948, to August 31, 1949*, AECU-652 (M-4444), Illinois Institute of Technology, Chicago.

[11] G. F. Smith and G. P. Smith, "The Determination of Chromium in Stainless Steel, Using Perchloric, Phosphoric, and Sulfuric Acids," *J. Soc. Chem. Ind. (London)* **54**, 185T (1935).

[12] H. H. Willard and R. C. Gibson, "Determination of Chromium and Vanadium in Ores and Alloys After Oxidation with Perchloric Acid," *Ind. Eng. Chem., Anal. Ed.* **3**, 88 (1931).

[13] H. H. Willard and P. Young, "Direct Determination of Chromium and of Vanadium in Steel," *Ind. Eng. Chem., Anal. Ed.* **6**, 48 (1934).

[14] V. S. Syrokomsky and N. N. Proshenkova, "Volumetric Determination of Rhodium," *J. Anal. Chem. Russ.* **2**, 247 (1947), as abstracted in *Analyst* **73**, 361 (1948).

[15] G. Norwitz and M. Codell, "Colorimetric Determination of Iron in Titanium Alloys," *Anal. Chim. Acta* **11**, 350 (1954).

[16] J. M. Thompson, "Determination of Impurities in Titanium Metal," *Anal. Chem.* **25**, 1231 (1953).

[17] K. A. Kraus and G. E. Moore, "Anion Exchange Studies. VI. The Divalent Transition Elements Manganese to Zinc in Hydrochloric Acid," *J. Am. Chem. Soc.* **75**, 1460 (1953).

[18] R. M. Rush and J. H. Yoe, "Colorimetric Determination of Zinc and Copper with 2-Carboxy-2′-hydroxy-5′-sulfoformazylbenzene," *Anal. Chem.* **26**, 1345 (1954).

Determination of Boron

H. Kubota

In Amounts Greater Than 1 mg. – The determination of boron in reactor fuels is important because of the high neutron cross section of boron. A general method for solubilizing borides by successive fusions with sodium carbonate and sodium nitrate[19] was utilized for the determination of boron in boron carbide and boron nitride. The melt was dissolved in acid, and any hydrolyzable metal ions were removed by precipitation with base and subsequent filtration. The filtrate was made acidic, boiled for 1 min, cooled to about 70°C, and titrated with standard base to the free-acid end point, as indicated by bromcresol green–methyl red mixed indicator. A few grams of mannitol was added, and the borate-mannitol complex was titrated to the phenolphthalein end point. Titrations were also performed with a Beckman model K automatic titrator; pH 5.0 and 9.0 were taken as the respective end points for the free acid and the borate. For the titration of aliquots of a standard solution of boric acid, the relative standard deviation was 0.4% when the titrations were made manually and was 0.2% for titrations made by means of the automatic titrator. The relative standard deviation was less than 1% for replicate determinations of boron in samples.

In Amounts of 0.02 to 1 mg. – A procedure similar to the one described above was used for determining the residual boron in a mixture that consisted of uranium tetrafluoride, zirconium tetrafluoride, sodium fluoride, and potassium fluoride and that originally contained 1% boron before heat treatment. The sample was fused with a sodium carbonate–calcium carbonate flux. The melt was suspended in warm water, a few drops of a solution of thorium nitrate were added, and the suspension was filtered. The filtrate was acidified with HCl, made basic, and filtered. The filtrate was acidified, and the borate was determined titrimetrically by means of a Dow automatic titrator. The end points were indicated by the points of inflection on the free-acid and the borate-mannitol titration curves. A nitrogen blanket was used over the solution to minimize carbonate interference.

In Amounts Less Than 0.02 mg. – Traces of boron in stainless steels and in uranium tetrafluoride were solubilized by sodium carbonate fusion. Calcium carbonate was added to the flux whenever the sample contained fluoride. The melt was covered with water and carefully acidified in order to break up the cake. The resulting suspension was made slightly alkaline and filtered. From this solution an appropriate aliquot was taken that contained 2 μg or less of boron and was acidified and reacted with an ethanolic curcumin solution. The boron-curcumin complex was developed by evaporating this mixture at 55°C and baking the dry cake for 15 min longer at the same temperature.[20] The complex was dissolved in 25 ml of ethanol and the solution was filtered. The transmittancy of the filtrate relative to a curcumin solution that contained no boron was read on the Beckman model B spectrophotometer at a wavelength of 540 mμ. The boron content was obtained by reference to a calibration curve. A relative standard deviation of 15% was attained.

Determination of Selenium in Stainless Steel

H. Kubota

Traces (ppm) of selenium in stainless steel were determined iodometrically according to a modification of the 1950 ASTM method.[21] Standard-addition procedures gave good results in the ppm range when microgram amounts of selenium were present.

Conductometric Determination of Fluoride

H. Kubota

The conductometric determination of fluoride, which was described in a previous report,[22] was extended to the analysis of condensates obtained by the Willard-Winters distillation. Ideal titration curves were obtained when the distillation temperature was controlled at 135°C in order to prevent any perchloric or sulfuric acid from passing over from the sample solution to the distillate. The use of a constant-temperature jacket for the still was

[19] H. Blumenthal, "Determination of Boron in Metal Borides," *Anal. Chem.* 23, 992 (1951).

[20] W. T. Dible, E. Truog, and K. C. Berger, "Boron Determination in Soils and Plants," *Anal. Chem.* 26, 418 (1954).

[21] "Selenium by the Sulfurous Acid–Iodometric Method," *1950 Book of A.S.T.M. Methods for Chemical Analysis of Metals*, p 94–95, American Society for Testing Materials, Philadelphia, 1950.

[22] H. Kubota, "Conductometric Determination of Fluoride," *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 4.

studied. Possible ways of reducing the volume of distillate are being considered so that the method can be used for the determination of microgram quantities of fluoride.

ANALYTICAL INSTRUMENTATION

D. J. Fisher

Remotely Operated Falling-Drop Densimeter for the High-Radiation-Level Analytical Facility (HRLAF)

R. W. Stelzner, H. C. Jones, R. B. Quincy, Jr., M. T. Kelley, L. C. Bate, D. J. Fisher

The development of the remotely operated, falling-drop densimeter has been completed. Several improvements were made to the instrument during the last phases of the testing period.[23] It was found that sanding the type 925 phototubes to frost them sometimes caused the glass envelopes to fracture after the tubes were installed, probably because of the release of strains that were introduced during sanding. The tubes are now sprayed with acrylate-methacrylate resin (Plexiglas), and then a single sheet of cleansing tissue is pressed into the wet plastic coating and left there. This method of frosting has been satisfactory. The circuit diagrams of the Q-1551 and Q-1348 control units have been revised to show all changes that have been made to the circuits. The precision of three Standard Timer model S-1 timing clocks was checked against a standard frequency by means of a scaling circuit. After the repair of one of the clocks, the precision of each of the three clocks met the manufacturer's specification of ±0.01 sec. The new, remotely controlled turret assembly[24] operates very satisfactorily. The 1-rpm Bodine motor was replaced by a ¼-rpm New England gear motor. As a result of the improvements made to the circulating water system, the water can be shut off and turned on without the occurrence of flooding. The remotely operated falling-drop densimeter was installed in the HRLAF and is operating satisfactorily.

[23] R. B. Quincy, Jr., R. W. Stelzner, and D. J. Fisher, "Testing of the Remotely Controlled Falling-Drop Densimeter," *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 5.

[24] R. W. Stelzner, "Remotely Controlled Turret Assembly for the Falling-Drop Densimeter," *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 5–6.

Conversion of Vacuum Tube Voltmeter to 12-v, d-c, 110-Megohm Input Impedance

H. C. Jones

An RCA WV-77A Jr. VoltOhmyst vacuum tube voltmeter was converted from 11- to 110-megohm input impedance. The full-scale deflection of the voltmeter is 12 v. The wiring diagram for this conversion will be issued as one in the Q-1551 series of drawings. The converted voltmeter is now being used with the falling-drop densimeter in the HRLAF; it was very easily modified and has been very stable in use.

Revisions of Mechanical Drawings of the ORNL Model Q-1728 Titrant Delivery Unit and Q-1734 Filter Photometer

H. C. Jones, W. L. Maddox

The mechanical drawings of the ORNL model Q-1728 titrant delivery unit (ORNL-LR-Dwgs. Nos. 15319 and 15319, Part 1) and of the Q-1734 filter photometer (ORNL-LR-Dwgs. Nos. 13584 and 13584, Parts 1, 2, and 3) have been revised in order to provide accurate maintenance information regarding the existing instruments and to incorporate into the drawings several design changes.

Modifications to the Motorized Arc Stand

H. C. Jones

The motorized arc stand[25] for remote use in the HRLAF has been modified to include microswitches in all its circuits in order to limit the movement of the electrode holders and of the platform. The circuit diagram of the stand (ORNL-LR-Dwg. No. 12380-R1) has been corrected to show this modification. Adjustable legs were added to the arc stand to increase its height by about 5 in.; and window frames, hinged at the bottom and having spring locks on top, were installed on each side of the electrode holders. The frames were designed to accommodate $2\frac{1}{4} \times 2\frac{1}{4}$ in. quartz windows.

[25] L. C. Bate, "Motorized Arc Stand," *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 7.

Remotely Operated Unit for Disposal of Radioactive Samples

H. C. Jones

A remotely operated unit for the disposal of radioactive samples[26] has been constructed and is now in use in cell 1 of the HRLAF. The disposal unit is also used to empty the vacuum traps of the dilution pipetter and of the falling-drop densimeter.

ORNL Model Q-1673 High-Sensitivity, Recording, Derivative Polarograph

M. T. Kelley D. J. Fisher

The development of the ORNL model Q-1673 high-sensitivity, recording, derivative polarograph has been completed.[27] The circuit diagram has been revised, and two more polarographs are being built under the direction of G. A. Holt by the Instrument Department of the Instrumentation and Controls Division. The performance of the first of these polarographs has been checked and is described by Zittel and Kelley in the next section of this report. The performance, particularly in derivative polarography, is very satisfactory and exceeds that of the older polarograph, model Q-1338. Also, it has been shown that the instrument will analyze solutions at concentrations of the order of 10^{-6} *M* by derivative polarography without the use of the curve follower. The instrument has been used at a full-scale current of 0.005 μa. A method[28] that describes the instrument and its use has been written for inclusion in the *ORNL Master Analytical Manual.*

Studies on the Capabilities and Limitations of the ORNL Model Q-1673 Polarograph

H. E. Zittel[29] M. T. Kelley

The new, ORNL model Q-1673, high-sensitivity, recording, derivative polarograph has been evaluated for both regular and derivative polarography in the diffusion-current range from 0.1 to 20 μa. It has unique and versatile damping options, which include the use of a parallel-T–RC (resistance capacitance) section and of a diode section. Certain performance characteristics of this polarograph have been evaluated. Derivative polarograms of thallium(I), lead(II), and indium(III) in 0.1 *N* KCl that were obtained by means of this polarograph were definitely much more symmetrical than those obtained by means of the ORNL model Q-1338 polarograph. For these ions, and also for the uranyl ion in 0.1 *N* HNO_3, the derivative peak height was found to be directly proportional to the concentration of the ion in the range studied (i.e., 0.5 to 10 μg/ml). This relationship was also found to hold for the iodate ion over the range studied, 1 to 25 μg/ml. Derivative polarograms of solutions that contained various amounts of thallium(I), lead(II), and indium(III) were taken in order to evaluate the ability of the instrument to resolve waves having close values of $E_{1/2}$. The resolving power of this polarograph is much better for derivative polarography than for regular polarography. The derivative polarograms of lead(II) ($E_{1/2} = -0.40$ v) and indium(III) ($E_{1/2} = -0.56$ v) were clearly resolved, there being very little mutual enhancement. The derivative waves of indium(III) and thallium(I) ($E_{1/2} = -0.46$ v) were also clearly resolved with even less enhancement. The derivative waves of lead(II) and thallium(I) ($\Delta E_{1/2} = 0.06$ v) were not completely resolved. The width of the derivative peak at the half height should be $90.7/n$ mv, where n is the electron change. For thallium(I), lead(II), indium(III), and uranyl ions, the value of n could be easily determined by this simple measurement, but for iodate ion, which undergoes an irreversible reaction, the observed value of half-wave width was far from the value corresponding to that for a reversible reaction.

High-Sensitivity, Recording, Single-Beam Flame Spectrophotometer

H. C. Jones

The circuit diagram (ORNL-LR-Dwg. No. 13150) of a single-beam flame spectrophotometer has been completed. The spectrophotometer was designed for operation with a 16PMI, 6217, 1P21, 1P22, or 1P28 multiplier phototube. It is intended that this flame spectrophotometer operate in the same

[26] H. C. Jones, "Remotely Operated Unit for Disposal of Radioactive Samples," *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 7–8.

[27] M. T. Kelley and D. J. Fisher, "Model Q-1673 Polarograph with Diode Filter," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 4.

[28] D. J. Fisher, "Polarograph, ORNL Model Q-1673, High-Sensitivity, Diode Filter, Derivative, Recording," Method Nos. 1 003042 and 9 003042 (in press), *ORNL Master Analytical Manual.*

[29] Summer research participant from Fisk University, Nashville, Tenn.

manner as the ORNL model Q-1457 flame photometer when the latter is operated as a single-beam instrument. The range of the voltage supply has been extended to include all values of voltage from 600 to 2000 v. Provision is made to scan wavelengths by a motor that drives in synchronism with the chart drive of the recorder. Mechanical drawings of the housing and dark slide for the 6217 photomultiplier tube and of adapters necessary for attaching the Beckman Cat. No. 9125 flame housing to the Bausch & Lomb Cat. No. 33-86-40-01 grating monochromator have also been completed; they are as follows: 6217 Photomultiplier Tube Housing, ORNL-LR-Dwg. No. 15914; Monochromator Adapter Ring, ORNL-LR-Dwg. No. 15911; Flame Housing Adapter, ORNL-LR-Dwg. No. 15912; Base Plate and Adapter Plate for the Flame Housing and Monochromator, ORNL-LR-Dwg. No. 15913. These accessories are to be used in conjunction with the flame spectrophotometer. A prototype flame spectrophotometer has been fabricated, and a second spectrophotometer is being built by the Instrument Department of the Instrumentation and Controls Division.

Microphotometer Light Source

L. C. Bate W. L. Maddox
H. C. Jones

A constant-intensity light source for slit illumination was constructed for the Leeds & Northrup microphotometer that is used by the Spectrochemical Group. A 10-v, 7.5-amp bulb having a vertical filament is used as a source of light. The bulb is mounted in an upright position on an aluminum base; openings in the base allow for cooling by convection. The light is passed through a lens and then through a slit located 18 cm from the lens. The light then passes through a half-silvered mirror into the microscope of the Leeds & Northrup microphotometer. The half-silvered surface of the mirror is used to reflect the field-illumination light into the microphotometer. A blower for cooling the lamp was tried but was not used, because the motor of the blower caused the filament in the light source to vibrate.

Flask-Centering Aids for Use with Dilution Pipetter of the High-Radiation-Level Analytical Facility (HRLAF)

L. C. Bate

Volumetric flasks, as well as cones, of various capacities from 1 to 200 ml must be placed by the manipulators on the stirrers that are positioned below the tips of the 1-ml, remotely servo-controlled pipetter in the HRLAF. The flasks must be on center with the pipet tip so that the tip will not be damaged. In order to facilitate this operation with the manipulators, Lucite blocks were made that are provided with handles and that fit over the stirrers. Holes of a size appropriate for the various flasks are bored in the top surfaces of the blocks. Storage racks are provided for those blocks that are not in use. The blocks are convenient to use, and when they are in place, the flasks are easily and rapidly centered for pipetting. The cost of fabricating the blocks is reasonable. Construction details are given in ORNL-LR-Dwg. No. 13142.

Drawer-Opening Attachment for Argonne Model 8 Master-Slave Manipulator

L. C. Bate C. L. Burros

Use of the Argonne model 8 master-slave manipulator to open the drawers in the storage cell of the HRLAF is desired, but the hand of the manipulator cannot be used because of the excessive strain that would be imposed upon the hand. Several types of hooks were designed, built, and attached to the wrist of the manipulator, but they did not permit free use of the manipulator hand and did not allow the hand to reach to the cell floor in order to pick up sample bottles. Therefore a bracelet with a bar attached at a 45-deg angle and with a pin attached to the bar at a 70-deg angle was constructed to fit the wrist of the slave. This device performs satisfactorily. A mechanical drawing of it (ORNL-LR-Dwg. No. 14931) has been prepared.

Adaptation of Gilmont Microburet for Use in the High-Radiation-Level Analytical Facility (HRLAF)

W. L. Maddox

The Gilmont microburet possesses several advantages that make it suitable for use in the

HRLAF. Notable among these are its small size and the ease of reading the volume delivered. The buret is designed for semipermanent mounting on a ring stand or other support. In order to make the device more flexible, a bracket for it was designed that makes possible its placement by means of master-slave manipulators. A clothespin-like fitting is fastened to the buret in such a way that the buret can be set into a slot in another fitting, which is mounted at a convenient place inside the hot cell. A large knob is fitted onto the operating screw of the buret so that the manipulator hands can deliver the solution conveniently.

The adapted buret could be used, for example, to deliver the standard-addition volume in remote polarographic analyses.

Basket and Blocks for the Transfer of Glassware for Use in the High-Radiation-Level Analytical Facility (HRLAF)

L. C. Bate

A basket and holding blocks were needed for the transfer of glassware to and from the working surfaces of the HRLAF cells via the access drawer. The basket was fabricated from cadmium-plated iron grating, is $6\frac{1}{4} \times 9\frac{1}{4} \times 1\frac{1}{2}$ in., and contains six Lucite blocks, each 3 in.^{2} in area. Each block contains the maximum number of holes into which glassware usually transferred into and out of the cell may be placed so that it does not tip over in transit. Mechanical drawings were prepared for the fabrication of these devices.

Cell Assembly for Coulometric Titration by Remote Control

W. L. Maddox

An apparatus has been designed and fabricated for remotely operated coulometric titrations in the HRLAF. The basic component of this apparatus is the ORNL model Q-1712 motorized Lab-Jack.

A framework is erected over the Lab-Jack to support the electrode system, which is mounted on a Lucite plate. A handle is provided to permit removal and replacement of the plate by master-slave manipulators. This arrangement facilitates the changing of the electrode system.

Electrical connections are made through banana plugs that are inserted into fittings secured to the base plate of the Lab-Jack.

Provision is made for cooling the test solution and for centering the titration vessel over a magnetic stirring apparatus by having a vessel of coolant mounted permanently on the stirrer. The stirrer, in turn, is mounted on the platform of the Lab-Jack.

ORNL Photograph No. 18314 shows the assembly that is now in use in the HRLAF.

Automatic, Constant-Current, Coulometric Titrator

R. W. Stelzner W. L. Maddox

An improved automatic, constant-current, coulometric titrator for the remotely controlled determination of microgram quantities of chromium and chloride ions in HRT fuels has been designed, constructed, and installed in the HRLAF. This newer model retains many of the design features of an instrument described previously.[30] New features of the titrator are automatic switching of a multivibrator gate to perform incremental titration as the end point is approached; a cascode, type 5751 vacuum tube as a constant-current source; electronically regulated power supplies for the automatic cutoff circuit and for the constant-current generating circuit; a d-c operated, type 2D21 thyratron latching relay circuit, which initiates incremental generation of the reagent and locks out the anticipation trigger; and an isolated, a-c operated, type 2D21 thyratron relay circuit for the cutoff of reagent-generating current and of the timing clock.

The instrument has been used by the Reactor Analyses Group for the analysis of radioactive samples. The over-all relative standard deviation of the remotely performed chromium determinations at the 10-μg level is about 2%.[31]

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[30] R. W. Stelzner, "Automatic Coulometric Titrator for Homogeneous Reactor Fuels," *Anal. Chem. Semiann. Prog. Rep. April 20, 1955*, ORNL-1880, p 9.

[31] W. R. Warren, private communication to R. W. Stelzner, Nov. 14, 1956.

The instrument has the following characteristics:

Reagent-generating current	Variable, 0 to 1 ma
Reagent-generating current stability	±0.02% in 1 hr
End-point anticipation	On-off, variable, 0 to 100 mv
Incremental rate of titrant generation	On 0.5 sec Off 5.0 sec
(As end-point potential is closely approached, on time of reagent-generating current narrows.)	
End-point potential	Variable, 0 to 1400 mv, or 1400 to 0 mv
End-point stability	±2 mv
RC time delay	20 sec
(Value may be changed by selection of a different RC time constant.)	
Cell resistance	May vary from 0 to 10,000 ohms with current constant to 1 part per 50,000

Controlled-Potential Coulometric Titrator

H. C. Jones M. T. Kelley

A titrator for the coulometric determination of uranium(VI) at controlled potential has been constructed and is now being tested. The titrator was constructed according to the specifications given by Booman[32] with the exception of the power supply. The highest current range was not needed; therefore the power supply was modified accordingly. The current passing through the electrolysis cell is integrated by means of analog-computer circuitry. The instrument appears, at the present time, to be operating very satisfactorily for the determination of 10 mg of uranium(VI) in the presence of nitrate ion; but conclusive evidence as to its accuracy, interference tolerances, and dependability are dependent upon subsequent tests. A simplified version of this instrument will be designed and constructed in the near future.

Automatic Potentiometric Titrator for Free Acid in HRP Samples

W. L. Maddox

A titrant delivery unit that utilizes a synchro-driven Gilmont microburet having a digital counter has been devised for use with the automatic velocity-servo potentiometric titrator for remotely operated acid titrations in HRP samples.

The unit is being tested to determine the best procedure for the titration of free acid in samples that contain uranium and corrosion products and whether the unit offers any advantage for this application over the ORNL model Q-1728 titrant delivery unit.

Gamma Absorptometer

M. T. Kelley W. L. Maddox

It is planned to build a gamma absorptometer for the bench-top determination of the concentration of plutonium in aqueous solutions. The detector will be a scintillation crystal backed by a photomultiplier tube, the current output of which will be recorded on a Brown recorder modified to have high-input impedance. The source will probably be Am^{241} and will be provided with lead shields and collimators.

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

R. W. Stelzner J. W. Landry[33]
M. J. Kelly[34]

Development and evaluation of instrumentation by the ORNL In-Line Instrumentation Group have continued under the program described in a previous report.[35] Glass piping for the all-glass, hydraulic mockup of an SRP sampler has been received at ORNL, and drawings for installation of the mockup have been completed. Construction of the mockup has not been started.

The study of the buildup of radioactivity on type 304L stainless steel has been completed. It is concluded that the sorption of radioactivity (in this case, Ru^{106} and Zr^{95}-Nb^{95} from Purex aqueous solutions) by type 304L stainless steel is too great to permit its use as a material of construction for in-line sample cells. The sorbed

[32] G. L. Booman, *An Instrument for Controlled Potential Electrolysis and Precision Coulometric Integration*, IDO-14370 (May 3, 1956).

[33] Chemical Technology Division.

[34] Instrumentation and Controls Division.

[35] R. W. Stelzner, "ORNL In-Line Assistance to the Savannah River Laboratory (SRL) and Plant (SRP)," *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 9–10.

activity could not be effectively removed by washes with strong nitric acid. Other materials investigated along with type 304L stainless steel were Lucite, polystyrene, tantalum, Inconel, fluorothene, titanium, polythene, gold, Teflon, type 347 stainless steel, and Boltaron (polyvinyl chloride). In general, smooth-finished plastics sorb less radioactivity than do metals; for example, after 90 hr of exposure to Purex IAW solution, Lucite had sorbed gross gamma activity equal to approximately 600 counts/min/in.^{2}, as compared with 10,000 for type 347 stainless steel. The various materials sorbed the radioactivity within the first 6 hr of exposure. Highly polished fluorothene is a satisfactory material of construction for in-line cells for use in Purex aqueous streams, but not for organic streams because in radioactive organic solutions fluorothene sorbs too much radioactivity.

The ORNL In-Line Instrumentation Group is fabricating a cell that will sorb a negligible amount of radioactivity. An air-lifted sample is allowed to fall in streamline fashion in an air envelope. Shielded gamma heads will be mounted to monitor continuously the gamma activity of the stream. Two new, type Q-1840 gamma scintillation heads have been fabricated at ORNL. The signal from a gamma scintillation head will be fed into a built-in preamplifier, a type A1D linear amplifier, a Q-1511 linear count-rate meter, and a recorder. It is planned to use the two heads to monitor both the feed and the product streams of a pulsed-solvent extraction column in order to establish the decontamination factor (DF) across the column at any instant of time.

A Taylor, high-resolution, differential-pressure transmitter (K-25 type) has been operating in the ORNL Metal Recovery pilot plant for the continuous determination of the densities of process solutions. Two cascaded transmitters of this type have been sent to SRL for installation in the SRP.

An instrument which measures conductivity, density, and temperature when it is immersed in a process stream of liquid is being tested in the ORNL Metal Recovery pilot plant by the In-Line Instrumentation Group. This unit will present signals to a computer, and the nitric acid and uranium concentrations, expressed in molarity and in grams per liter, respectively, will be indicated on a recorder.

A flow colorimeter that monitors the concentration of uranium in the range 45 to 55 g/liter in a process stream has been received from SRL for testing in a high-level radiochemical pilot plant. The unit is being recalibrated to monitor uranium concentrations in the range 25 to 35 g/liter, which is consistent with present concentration levels in the ORNL Metal-Recovery pilot plant.

The technique of controlling the level of the interface between the aqueous and organic layers in a liquid-liquid extraction column by means of a conductivity probe and controller has been found feasible. A plant prototype instrument is being constructed.

At the request of SRL, a radio-frequency monitor for nitric acid concentration has been set up on an air-lifted circulation loop. The unit has operated satisfactorily for aqueous solutions of nitric acid, and it is planned to start tests on synthetic 25 Process IAF solutions. An instrument more rugged than the laboratory prototype and suitable for plant use is being designed. SRL has also requested that the instrument be tested on the monitoring of the neutralization of waste.

The experimental design of a high-sensitivity, a-c polarograph is being continued. A stable and reliable amplifier for a-c and d-c signals has been found by use of a d-c operational amplifier. With very nearly 100% feedback, inverted d-c signals over the range 0 to −1 v for inputs of 0 to +1 v are obtained linearly. The input and output signals of the amplifier cancel each other so that, even though a measuring resistor of high value is in the circuit, the polarizing potential is applied only to the resistance of the polarographic cell. Similarly, a-c voltages cancel each other over the frequency range 0 to 100,000 cps. The use of the operational amplifier permits a selection of any operating frequency within this range. Experimental work on a demodulator that will discriminate between the phase of the faraday current and the phase of the condenser current is being started.

RADIOCHEMICAL ANALYSES

S. A. Reynolds

Nuclear Properties

Pile-Neutron Activation Cross-Section Program (W. S. Lyon). – The program previously outlined[36] for remeasuring a number of pile-neutron activation cross sections has been continued. Monitors used

[36] W. S. Lyon, "Neutron Activation Cross-Section Program," *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 10.

have been either cobalt or manganese. Correction has been made for the cadmium ratio of the monitor (10 for cobalt, 18 for manganese) according to the method suggested by Harvey.[37] This method consists in multiplying the activity of the monitor by the expression 1 – (1/Cd ratio). Table 1 is a compilation of all data obtained thus far. Activation cross sections larger than about 10 barns probably have large contributions from the capture of fast neutrons; consequently, cadmium-ratio experiments are planned in order to obtain data that will be useful in correcting for this effect.

TABLE 1. PILE-NEUTRON ACTIVATION CROSS SECTIONS

Nuclide Produced	Cross Section (barns)	
	Observed	Reported in the Literature
K^{42}	1.45	1 ± 0.2
Cr^{51}	16.6	11 ± 5
Cu^{64}	4.66	3.9 ± 0.8
Ni^{65}	1.45	2.6 ± 0.4
Zn^{65}	0.46	0.5
Zn^{69}	0.100	0.1 ± 0.3
Ge^{71}	3.47	3 ± 1
Ga^{72}	6.18	3.4 ± 0.7
Ge^{75}	0.55	0.45 ± 0.1
As^{76}	6.7	4.2 ± 0.8
Br^{82}	4.1	3.5 ± 0.5
Rb^{86}	1.00	0.72
Sr^{87}	1.73	1.3 ± 0.4
Zr^{95}	0.075	0.1 ± 0.05
Mo^{99}	0.58	0.13 ± 0.05
Pd^{109}	13.5	12 ± 3
Ag^{110}	5.78	2.8 ± 0.5
Sb^{122}	12.6	6.8 ± 1.5
Ba^{131}	11.4	0.024
Cs^{134}	47.2	26 ± 5
Ba^{139}	0.23	0.5 ± 0.1
La^{140}	8.1	8.4 ± 1.7
Ce^{143}	0.91	1 ± 0.2
Pr^{143}	10.9	10.3
Gd^{159}	3.89	4 ± 2
Ta^{182}	42.4	19 ± 7
W^{185}	2.28	2.1 ± 0.6
W^{187}	51.0	34 ± 7

Cross Section for the $Ge^{76}(n,\gamma)Ge^{77m}$ Reaction (W. S. Lyon, J. S. Eldridge). – In the pile-neutron cross-section program described above, the cross section and the half life of the product nuclide for the reaction $Ge^{76}(n,\gamma)Ge^{77m}$ have been measured by the use of enriched Ge^{76} target material. The half life of Ge^{77m}, which was determined as an average of six measurements, was 53.6 ± 0.9 s. This value was obtained from the beta activity of neutron-irradiated $Ge^{76}O_2$ as measured by means of a proportional counter and an automatic recorder.

For the $Ge^{76}(n,\gamma)Ge^{77m} \xrightarrow[53.6\ s]{\beta^-} As^{77}$ reaction sequence, a cross section of 0.117 ± 0.012 barn was obtained by measuring the beta activity of Ge^{77m} produced by the neutron irradiation of $Ge^{76}O_2$. The weighed samples of $Ge^{76}O_2$ were quantitatively transferred from the irradiation tube to a sample mount, and their beta activities were measured by means of a previously calibrated proportional counter.

A cross section of 0.035 ± 0.005 barn was obtained (a conversion coefficient, α_K, of 0.9 was assumed for the gamma radiation of 0.16-Mev energy) for the $Ge^{76}(n,\gamma)Ge^{77m} \xrightarrow[53.6\ s]{IT} Ge^{77}$ reaction sequence. This determination was made by measuring the intensity of the gamma radiation from the isomeric transition; a 3 × 3 in. sodium iodide scintillation detector and a multichannel analyzer were used.

Both the beta and the gamma measurements were made simultaneously by locating the beta counter above and the gamma counter below the sample of irradiated $Ge^{76}O_2$.

25-kev Neutron-Capture Cross-Section Program (W. S. Lyon, N. H. Lazar,[38] R. L. Macklin[38]). – A program is under way to measure a large number of cross sections for the capture of 25-kev neutrons from an antimony-beryllium source. This work will be reported in a Physics Division report; preliminary results will be discussed in a paper to be

[37] J. A. Harvey, private communication to W. S. Lyon, Feb. 1956.

[38] Physics Division.

given at the winter meeting of the American Physical Society in New York (Jan. 30, 1957).

Gamma-Ray Intensities in UX_2 (W. S. Lyon, J. S. Eldridge, F. L. Moore). – The intensities of three gamma rays associated with the decay of UX_2 have been obtained by scintillation spectrometry; separated UX_1-UX_2 was used as the source material. The UX_1-UX_2 was prepared from a 10 *M* HCl solution of uranyl nitrate by extracting the uranium into a 5% solution of methyldioctylamine in xylene. The thorium was then carried on a lanthanum fluoride precipitate that was formed by the addition of lanthanum carrier and hydrofluoric acid.

The gamma-ray spectrum of the UX_2 was studied by the use of a single-channel analyzer and a 3×3 in. crystal of sodium iodide. The gamma rays studied and their observed intensities are as follows: 0.76 Mev (0.47 ± 0.05%), 1.00 Mev (0.66 ± 0.07%), and 1.82 Mev (0.07 ± 0.01%).

Measurement of Radioactivity

Determination of Efficiencies of Counters for Np^{239} (W. S. Lyon). – The efficiencies of a number of counters for Np^{239} have been determined by preparing U^{239}, obtaining its absolute disintegration rate by 4π beta-gamma coincidence counting, allowing the U^{239} to decay to Np^{239}, and using this Np^{239} to obtain the counting efficiency. Details of the work are given in a paper that has been submitted for publication in *Analytical Chemistry.*

End-Window Proportional Beta Counter (S. A. Reynolds). – A methane-flow type of proportional counter, which has a mica window, is in use for the measurement of high-level beta activity. The detector and the amplifier-scaler unit were designed by J. K. East[39] and by H. N. Wilson,[39] respectively. The amplifier-scaler contains "glow-transfer" tubes, which furnish a reliable, direct-reading decade scale instead of the binary scale that is in common use. The counter has been employed for the measurement of beta-counting rates as high as 5×10^5 counts/min. The rack for samples is of sufficient height to permit counting at about 1% efficiency; therefore a source that contains about 5×10^7 d/min (~0.02 mc) could be measured with the device. It is believed that the counter will show very stable performance and therefore that it can be used to determine half-periods of long-lived beta emitters.

Instrumental Analyses

Twenty-Channel Gamma Scintillation Spectrometer (W. A. Brooksbank,[40] G. W. Leddicotte,[40] S. A. Reynolds). – A new gamma scintillation spectrometer has been put into service. The detector is a 3×3 in., thallium-activated crystal of sodium iodide, and the analyzer is a 20-channel device of the type designed by P. R. Bell of the Physics Division. The instrument is particularly useful for studies of the spectra of rapidly decaying sources and of samples of low activity.

Radioisotope Analysis

Methods of Assay for New Radioisotope Products (W. S. Lyon). – Methods of assay for new, short-lived radioisotope products, as well as methods for the detection of radioactive impurities in these products, have been developed. Among the nuclides for which methods have been developed or are being developed are Ga^{72}, Br^{82}, Cd^{115}, Pr^{143}, $Os^{191,193}$, Ir^{194}, Hg^{197}, and Au^{199}.

Fission-Product Methods

Analysis of Ru^{103}-Ru^{106} Mixtures (W. S. Lyon). – A method has been devised for the quantitative determination of Ru^{103} and Ru^{106} in the presence of each other. Information regarding the ratio of Ru^{103} to Ru^{106} is often useful in the elucidation of the period of irradiation or decay of thorium or uranium slugs. The method involves a radiochemical separation of ruthenium, followed by a gamma spectrometric study of the radioactive ruthenium. Ruthenium-106 is determined by integrating beneath the 640-kev gamma-ray peak and dividing by an efficiency factor that has been determined previously by experiment. Ruthenium-103 is determined by integrating beneath the unresolved 490-kev–525-kev peak and then subtracting from this integrated area the contribution made to it by the 525-kev gamma-ray peak of Ru^{106}. The 525-kev contribution is calculated from the previously determined quantity of Ru^{106}. The area of the 490-kev peak thus determined is divided by the efficiency factor, established experimentally, for Ru^{103}. The method has been applied successfully to a number of process samples.

[39] Instrumentation and Controls Division.

[40] Activation Analyses Group.

Reactor Analyses

Radiochemical Analyses for the HRT (T. H. Handley). – Radiochemical procedures for the determination of cesium, niobium, phosphorus, copper, and sulfur were adapted to meet the particular requirements of the HRT program.[41] The use of sodium tetraphenylboron as a precipitating agent for cesium is worthy of mention. The precipitation of cesium was found to be a good decontamination step. Further details of the procedure for cesium will be reported in the open literature, presumably in *Analytical Chemistry*.

Analyses for Plutonium and Neptunium in HR Solutions (F. L. Moore, H. W. Wright). – Tentative radiochemical methods for the determination of plutonium and Np^{239} in HR fuel, that is, concentrated uranyl sulfate solution, have been developed. The methods appear to be adequate for their intended purposes.

Neutron-Flux Determinations (H. W. Wright). – Approximately 50 satisfactory determinations of neutron flux were made per month by use of the method previously described.[42]

Electronuclear Research Program

T. H. Handley

In cooperation with members of the Electronuclear Research Division, a survey has been made of the radionuclides produced by irradiation of the elements terbium through hafnium with 22-Mev protons in the ORNL 86-in. cyclotron. Ion-exchange separations of the products were performed, and sources of the radionuclides were prepared by electrodeposition for use in a 180-deg, permanent-magnet, photographic-recording electron spectrograph. An oral presentation of the work was given,[43] and a paper has been submitted to *The Physical Review* for publication.

Studies of excitation functions for nitrogen-induced nuclear reactions in several light elements have been completed. A paper that gives the details of this experiment has been submitted to *The Physical Review* for publication.

Solvent Extraction Methods

Liquid-Liquid Extraction of Iron (F. L. Moore). – The extraction of iron(III) from a strong solution of nitric acid or perchloric acid into 2-thenoyltrifluoroacetone (TTA) in xylene has been found to be highly efficient. The data given below show the effect of the concentration of nitric acid in the aqueous phase on the extraction of Fe^{59}(III) tracer into a 0.5 *M* solution of TTA in xylene.

HNO_3 Concentration (*M*)	Fe^{59} Tracer Extracted (%)
1.8	8.2
2.3	11.1
4.5	30.1
6.8	65.3
10.2	95.0

Aqueous solutions of nitric acid that contained Fe^{59} tracer (less than 1×10^5 counts/min/ml) were extracted for 10 min with equal volumes of 0.5 *M* TTA-xylene.

The results of further experiments, in which iron(III) in the concentration of 2 mg/ml was used in addition to tracer Fe^{59}, indicated the same general behavior of the iron(III) as that given above for Fe^{59} tracer.

Previous studies of the extraction behavior of iron(III) in the TTA-xylene system have suggested that the pH range of the aqueous phase of 2 to 4 is optimum for analytical separation work. Although iron(III) extracts readily under these conditions, the selectivity of the extraction is very poor. From the experience of the writer, it is known that the extraction of iron(III) into 0.5 *M* TTA-xylene from strong solutions of nitric acid will prove to be more highly selective than will methods currently employed, such as ether extraction or anion exchange from a hydrochloric acid system. The technique should be useful for separations and may also offer a highly selective spectrophotometric technique for iron(III), since the species extracted is highly colored. Further studies of the method are being made by J. G. Surak.[44]

Liquid-Liquid Extraction of Radiostrontium (F. L. Moore). – A series of exploratory extractions was

[41] T. H. Handley and S. A. Reynolds, *Development of Radiochemical Methods for HRT*, ORNL CF-56-7-118 (July 23, 1956).

[42] H. W. Wright, "Neutron-Flux Determinations," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 10.

[43] J. W. Mihelich *et al.*, *Nuclear Spectroscopy of Neutron Deficient Isotopes in the Rare Earth Region*, a paper presented at the meeting of the American Physical Society in Chicago, Ill., November 22–24, 1956.

[44] Marquette University, Milwaukee, Wis.

made for the purpose of removing radiostrontium from aqueous solution. Thenoyltrifluoroacetone dissolved in a suitable solvent was the only extractant found for the effective removal of radiostrontium from aqueous solution.

Thenoyltrifluoroacetone hydrolyzes in solutions of pH greater than 7. However, it was found that the addition of acetone to the solvent markedly improved the efficiency of the extraction of radiostrontium. The conditions employed in all the experiments were as follows. An aqueous solution that contained radiostrontium tracer (Sr^{85}-Sr^{89}) was extracted for 5 min with an equal volume of solvent. After the phases had disengaged, they were drawn off and centrifuged. Each phase was then analyzed for radiostrontium. The results are given in Table 2.

The data of Table 3 show the results obtained with solvents for TTA other than xylene. Amsco was found to be the poorest solvent of those investigated. However, the addition of alcohols, such as diisobutylcarbinol (DIBC), *n*-hexyl alcohol, or *n*-octyl alcohol, to a TTA-Amsco solution gave excellent extraction of radiostrontium.

Miscellaneous Activities

Nonroutine Analyses (T. H. Handley). – In collaboration with the Activation Analyses Group, filings of structural metals for aircraft were irradiated in the ORNL Graphite Reactor. Relative amounts of induced gamma activities were measured by gamma spectrometry, and their decay was followed.

Analysis for Th^{228} in the presence of other thorium isotopes was made by determining the Ra^{224} content of the samples. Radium-224 is a member of the Th^{228} decay chain; therefore, if the Ra^{224} is in equilibrium with its parent, the determination of Ra^{224} serves as an indirect method of determining Th^{228}.

A number of low-level-activity samples, such as water, air filters, and dust, were analyzed for long-lived fission products.

Electrodeposition of Np^{237} (H. W. Wright). – Deposits of Np^{237} that varied in surface density from 7 to 360 $\mu g/cm^2$ were prepared by electrodeposition on nickel plates. The plates were right circular hemicylinders, and the deposit was restricted to the rectangular face. In the determination of the quantity of Np^{237} deposited on each plate, it was necessary to count the alpha activity of each plate directly; this method did not correct for the self-absorption in the heavy deposits.

Preparation of Standard Solutions of Radioisotopes (W. S. Lyon). – At the request of the office of Commissioner W. F. Libby of the USAEC, a series of standard solutions of radioactive nuclides was prepared, assayed, and sent to Dr. Libby. The nuclides sent were Cl^{36}, Ca^{45}, Cr^{51}, Fe^{55}, Y^{91}, Pm^{147}, and W^{185}. Of these, all but Cr^{51} and Fe^{55} were assayed by 4π beta counting. The Fe^{55} was assayed by use of a calibrated x-ray, proportional-counter spectrometer. The Cr^{51} was assayed by x-ray–gamma coincidence counting.

TABLE 2. EFFICIENCY OF EXTRACTION OF RADIOSTRONTIUM FROM AQUEOUS PHASE INTO TTA-XYLENE

pH of Aqueous Phase		Organic Phase	Radiostrontium Tracer Extracted (%)
Before Extraction	After Extraction		
10.5	7.5	0.5 *M* TTA-xylene (10 ml)	38.0
10.5	7.5	0.5 *M* TTA-xylene (7 ml) + acetone (3 ml)	>99.0
10.5	7.5	0.5 *M* TTA-xylene (7 ml) + acetone (3 ml)	>99.0
9.4	6.5	0.5 *M* TTA-xylene (7 ml) + acetone (3 ml)	96.5
8.9	6.4	0.5 *M* TTA-xylene (7 ml) + acetone (3 ml)	94.4
7.9	5.6	0.5 *M* TTA-xylene (7 ml) + acetone (3 ml)	34.7

TABLE 3. EFFICIENCY OF EXTRACTION OF RADIOSTRONTIUM FROM AQUEOUS PHASE INTO VARIOUS SOLUTIONS OF TTA

pH of Aqueous Phase		Organic Phase	Radiostrontium Tracer Extracted (%)
Before Extraction	After Extraction		
10.3	6.1	0.5 *M* TTA–*n*-octyl alcohol (10 ml)	>99.0
10.4	6.7	0.5 *M* TTA–*n*-octyl alcohol (7 ml) + acetone (3 ml)	>99.0
9.5	6.2	0.5 *M* TTA-Amsco (10 ml)	<1.0*
9.6	6.1	0.5 *M* TTA-Amsco (7 ml) + acetone (3 ml)	12.0
10.5	6.3	0.5 *M* TTA-Amsco (7 ml) + ocetone (3 ml)	12.0
10.5	7.0	0.5 *M* TTA in xylene-Amsco (1:1) (10 ml)	<2.0
10.6	7.2	0.5 *M* TTA in *n*-octyl alcohol–Amsco (1:1) (10 ml)	>99.0
10.5	7.0	0.5 *M* TTA in *n*-octyl alcohol–Amsco (1:1) (10 ml)	>99.0*
10.6	7.2	0.25 *M* TTA in Amsco-DIBC** (1:1) (10 ml)	>99.0
10.5	7.2	0.25 *M* TTA in Amsco–*n*-hexyl alcohol (1:1) (10 ml)	>99.0*
10.5	7.2	0.5 *M* TTA-xylene (7 ml) + DIBC (3 ml)	>99.0
10.5		0.25 *M* TTA-DIBC (10 ml)	>99.0
10.5		0.25 *M* TTA in DIBC-Amsco (1:1) (10 ml)	>99.0*

*Some scum was present at the interface.
**Diisobutylcarbinol.

ACTIVATION ANALYSES

G. W. Leddicotte

Quantitative Applications of Activation Analysis

G. W. Leddicotte, W. T. Mullins, W. A. Brooksbank, Jr., R. E. Druschel, L. C. Bate

The recent applications of activation analysis to the determination of microgram and submicrogram amounts of many elements in a variety of materials are summarized in Table 4. The methods developed in the course of this work will be incorporated in the *ORNL Master Analytical Manual.*

Unless indicated otherwise, the radioisotopes induced during these analyses resulted from (n,γ) reactions upon the stable isotopes of the elements being determined. Information regarding these reactions has been reported elsewhere.[45] The neutron irradiations for the analyses were made in either the ORNL Graphite Reactor or the Low-Intensity Test Reactor.

The comparator-sample technique was used in all the determinations. Depending upon the half life of the induced radioisotope, either a nondestructive radioassay or a radiochemical separation was made. In each instance the radioactivity measurements were made by conventional counting equipment. Specific radiochemical separations and radioactivity measurements believed to be of particular interest are discussed separately in this report.

[45] G. W. Leddicotte, "Types of Neutron Reactions," Method No. 5 10102 (2-2-56), *ORNL Master Analytical Manual.*

TABLE 4. SUMMARY OF RECENT QUANTITATIVE APPLICATIONS OF ACTIVATION ANALYSIS

Element Determined	Sample	Technique[a]	Induced Radioisotope	Observed Concentration of Element Determined ($\mu g/g$)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
Al	Magnesium	ND	Al^{28} (2.3 m)	160	0.1
Sb	$LiI \cdot xH_2O$	RC	Sb^{122} (2.3 d) or Sb^{124} (60 d)	8.0	0.005
	Silicon			0.05 to 3.0	
	Sodium			0.05	
	Stainless steel			50.0	
	Tin			35.0 to 50.0	
	Petroleum catalysts			0.4 to 1.0	
As	$LiI \cdot xH_2O$	RC	As^{76} (26.8 h)	0.014	0.001
	Animal tissue			0.03 to 2.0	
	Naphtha			0.001 to 3.3	
	Oil ash			1.4	
	Petroleum catalysts			0.02 to 1.3	
	Nickel			0.04 to 0.20	
Ba	$LiI \cdot xH_2O$	RC	Ba^{139} (85.0 m)	7.2	0.01
Bi	Hastelloy	RC	Bi^{210} (RaE) (5.0 d)	50.0	1.0
Ca	Niobium	RC	Ca^{45} (152 d)	10.0	4.0
	Nickel oxide			68.0	
Cs	Sodium	RC	Cs^{134m} (3.2 h) Cs^{134} (2.3 y)	15 to 1000	0.05
Cl	Process solutions	RC	Cl^{38} (38.5 m)	5.0 to 200.0	0.05
	Plastics			10^5	
	Organic and aqueous solutions			3.0	
	ZnS phosphors			2.0 to 5.0	
	Thorium oxide (pyrohydrolyzed)			0.50 to 1.50	
	Naphtha			0.40 to 5.3	
Cr	Vanadium	RC	Cr^{51} (26.8 d)	3.4	0.10
	$LiI \cdot xH_2O$			3.0	
	Titanium			40.0	
	Tin			1.0	
Co	Nickel	RC	Co^{60} (5.3 y)	3.0 to 100.0	0.05
	Nickel oxide			110	
	Sugar cane			0.30 to 3.0	
	Hastelloy			3500	
	Aluminum			17.0 to 980.0	
	Petroleum catalysts			3.5 to 53.0	
	Sodium			0.05	
	Silicon			0.07 to 1.50	

TABLE 4 (continued)

Element Determined	Sample	Technique[a]	Induced Radioisotope	Observed Concentration of Element Determined ($\mu g/g$)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
Cu	Oil ash	RC	Cu^{64} (12.8 h)	0.007 to 0.70	0.001
	Zirconium			0.60 to 26.0	
	$LiI \cdot xH_2O$			32.0 to 73.0	
	Titanium			30.0 to 40.0	
	Silicon			0.02 to 1.00	
	Germanium dioxide			0.08	
	Aluminum			25.0 to 225.0	
	Petroleum catalysts			0.008 to 44.0	
	Sugar cane			3.0 to 6.0	
	Niobium			18.0	
	Nickel			1.0	
	Animal tissue			200.0	
Au	Silicon	ND	Au^{198} (2.69 d)	0.30	0.001
	Aluminum phosphate			0.02	
Hf	Zirconium oxide	RC	Hf^{181} (45 d)	2000 to 3000	0.05
	Zirconium			66.0 to 215.0	
Ir	Rhodium chloride	RC	Ir^{194} (19.0 h) Ir^{192} (74.4 d)	10.0 to 15.0	0.0001
Fe	Zirconium alloys	RC	Fe^{59} (45.1 d)	15.0 to 10^4	0.2
	Zirconium oxide			10^4	
	Silicon			1.0 to 120.0	
	Petroleum catalysts			3000	
	Grasses and grains			330 to 4600	
	Nickel oxide			800	
	Copper			10.0 to 35.0	
	Nickel			0.20 to 0.30	
	Sodium			7.0 to 36.0	
La	Silicon	RC	La^{140} (40.0 h)	0.08	0.001
Mn	Magnesium oxide	ND or RC	Mn^{56} (2.6 h)	4.0 to 270.0	0.0001
	Titanium dioxide	RC		1.0 to 3.0	
	Nickel oxide			4.5 to 6.3	
Hg	$LiI \cdot xH_2O$	RC	Hg^{197m2} (23 h)	0.50	0.10
Mo	Zirconium alloys	RC	Mo^{99} (67 h)	0.6 to 34.0	0.20
	Inconel			220	
	Tungsten			27.0 to 56.0	
	Sugar cane			0.20 to 2.0	
Ni	Sodium	RC	Ni^{65} (2.56 h)	0.4 to 1.0	0.10
	Petroleums			0.1 to 300.0	
Os	Electrolytic iron	RC	Os^{191m}(14 h) Os^{191} (16.0 d) Os^{193} (30.6 h)	900.0	0.02

TABLE 4 (continued)

Element Determined	Sample	Technique[a]	Induced Radioisotope	Observed Concentration of Element Determined ($\mu g/g$)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
Pd	Nickel	RC	Pd^{109} (13.6 h)	0.20	0.005
P	Aluminum	RC	P^{32} (14.3 d)	0.08 to 25.0	0.04
	Petroleum catalysts			20.0	
	Silicon			2.0 to 5.0	
K	Aluminum	RC	K^{42} (12.4 h)	1.0 to 16.8	0.02
Ru	$LiI \cdot xH_2O$	RC	Ru^{97} (2.8 d)	3.0	0.2
Sm	Cerium	RC	Sm^{153} (47 h)	0.1 to 2.0	0.0005
Sc	Beryllium	RC	Sc^{46} (85 d)	10.0	0.005
Se	Stainless steel	RC	Se^{81m} (56.5 m) or Se^{75} (127 d)	3.0	0.02
Si	$LiI \cdot xH_2O$	RC	Si^{31} (2.6 h)	400.0	1.0
Ag	Aluminum phosphate	RC	Ag^{110m} (270 d)	10.0	0.1
	Nickel			0.8 to 4.5	
Na	Separated palladium isotopes	RC	Na^{24} (15.0 h)	45	0.007
	Aluminum			10.0 to 80.0	
	Stainless steel			0.5 to 5.0	
Sr	$LiI \cdot xH_2O$	RC	Sr^{87m} (2.8 h)	12.0	0.5
S	Silicon	RC	P^{32} (14.3 d)[d]	97 to 183	1.0
Ta	Titanium	RC	Ta^{182} (111 d)	2.5	0.002
Te	Hastelloy	RC	Te^{131m} (30 h)	16.0 to 30.0	0.2
Tl	$LiI \cdot xH_2O$	RC	Tl^{204} (3.5 y)	5.0	0.2
Th	Water	RC	Pa^{233} (27.4 d)[e]	0.02 to 4.0	0.01
Sn	$LiI \cdot xH_2O$	RC	Sn^{125} (9.4 d)	150.0	0.5
	Zirconium alloys				
W	Thorium	RC	W^{138} (24.0 h)	45.0	0.001
	Zirconium and zirconium alloys			4.0 to 260.0	
	$LiI \cdot xH_2O$			0.03	
	Sand ore			1.30	
	Scheelite ores			10^4	
	Nickel			0.8	
V	Jet fuel oils	ND	V^{52m} (3.74 m)	0.10	0.005
	Oil ash				
Zn	Animal tissue	RC	Zn^{69m} (13.8 h)	350.0	0.02
	$LiI \cdot xH_2O$			5.0 to 18.0	
	Titanium			15.0	
	Silicon			0.04 to 8.0	

TABLE 4 (continued)

Element Determined	Sample	Technique[a]	Induced Radioisotope	Observed Concentration of Element Determined (μg/g)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
Zr	Aluminum	RC	Zr^{97} (17.0 h)	10^2 to 10^3	0.2
	Lead-zinc alloys			230.0	
	Nickel			14.0 to 44.0	
	Palladium-zinc alloys			28.0 to 71.0	

[a]ND = nondestructive radioassay; RC = radiochemical separation.

[b]Number of samples analyzed varied; therefore a range of concentration values rather than a single value is given in some cases.

[c]Based on conditions of irradiation and analysis employed. Will vary with the duration of the irradiation and of the separation procedure and with the neutron flux.

[d]By fast-neutron reaction $S^{32}(n,p)P^{32}$.

[e]From the $Th^{232}(n,\gamma)Th^{233} \xrightarrow[23.5\,m]{\beta^-,\gamma} Pa^{233}$ (27.4 d) reaction.

A Critical Study of Activation Analysis

W. A. Brooksbank, Jr. J. A. Dean[46]

The method of activation analysis was evaluated critically by determining the major and minor components of three National Bureau of Standards (NBS) standard aluminum alloys and comparing the results with the results given by NBS, which had been obtained by conventional methods. This evaluation has been reported in detail;[47] the significant results are given in Tables 5 and 6.

This study showed that the method of activation analysis is applicable to the determination of major and minor components of aluminum alloys and could be employed in the analysis of other materials. The difference between the NBS certified results and the activation analysis results was of the order of 10%.

Quantitative Determination of Dysprosium in Yttrium Oxide

L. C. Bate G. W. Leddicotte

A nondestructive method of analysis, employing the 20-channel gamma scintillation spectrometer, was used to determine microgram amounts of dysprosium in yttrium oxide. The following reaction was used:

$$Dy^{164}(n,\gamma)Dy^{165m} \xrightarrow[1.25\,m]{\beta^-} Dy^{165} \; (t_{1/2} = 139.2\ m)$$

The duration of irradiation was 30 min, and the neutron flux was 6.5×10^{11} neutrons/cm^2/sec. Samples of Y_2O_3 that weighed 0.05 to 0.2 g were used in the analysis, and there were four determinations for each sample. In its decay, Dy^{165} emits gamma radiation of 0.046-, 0.091-, 0.27-, and 0.36-Mev energies. One of the gamma spectra obtained for Dy^{165} is shown in Fig. 3; the source of the Dy^{165} was irradiated Dy_2O_3. The higher gamma energies (i.e., 0.27 and 0.36 Mev) were used to assay the irradiated samples. A series of decay curves of these photopeak areas is shown in Fig. 4. A comparator-sample technique was used; the results are given below:

Sample	Dysprosium Concentration (μg/g)
1	336.0 ± 19.0
2	83.0 ± 4.0
3	17.0 ± 1.0

[46]Consultant, University of Tennessee, Knoxville.

[47]W. A. Brooksbank, Jr., *Study in Activation Analysis*, ORNL-2226 (Dec. 7, 1956).

TABLE 5. RESULTS OF THE DETERMINATION OF MAJOR COMPONENTS OF ALUMINUM ALLOYS BY ACTIVATION ANALYSIS AND BY CONVENTIONAL CHEMICAL METHODS

Aluminum Alloy	Method	Concentration of Major Component (wt %)					
		Copper	Iron	Manganese	Nickel	Titanium	Zinc
NBS 85A	NBS*	2.48	0.21	0.66	0.41	0.016	0.019
	AA**	2.65	0.20	0.68	0.45	0.016	0.017
NBS 86C	NBS	7.92	0.90	0.041	0.030	0.035	1.50
	AA	8.37	0.85	0.036	0.037	0.038	1.50
NBS 87	NBS	0.30	0.46	0.30	0.59	0.16	0.077
	AA	0.32	0.50	0.35	0.72	0.17	0.072

*Certified NBS values obtained by conventional chemical methods.

**Activation analysis value; average of results of three to six determinations.

TABLE 6. RESULTS OF THE DETERMINATION OF MINOR COMPONENTS OF ALUMINUM ALLOYS BY ACTIVATION ANALYSIS

Aluminum Alloy	Concentration of Minor Components (μg/g)			
	Antimony	Cobalt	Silver	Zirconium
NBS 85A	0.4	38	2.4	0.8
	0.3	41	2.3	0.8
	0.3	39	2.5	0.9
NBS 86C	0.95	4.1	4.5	0.7
	1.0	3.7	3.9	0.6
	1.1	3.1	4.2	0.7
NBS 87	27.0	53.0	0.7	1.1
	26.0	45.0	0.9	1.3
		53.0	0.9	0.9

The magnitude of the radioactivity induced by this method indicates that the determination of microgram or submicrogram amounts of dysprosium in yttrium oxide or other rare-earth oxides is feasible.

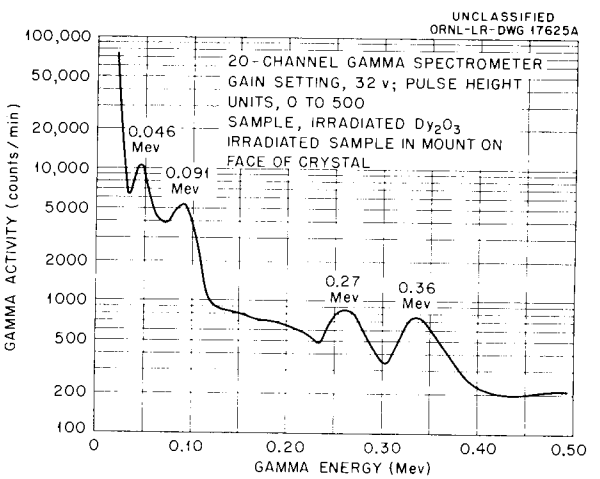

Fig. 3. Gamma Spectrum of Dy^{165} (139.2 m).

Nondestructive Determination of Submicrogram Amounts of Arsenic in Naphtha

G. W. Leddicotte W. A. Brooksbank, Jr.

The 20-channel gamma scintillation spectrometer was used in the nondestructive determination of submicrogram amounts of arsenic in naphtha. The $As^{75}(n,\gamma)As^{76}$ ($t_{1/2}$ = 26.8 h) reaction was used, and the gamma spectral area beneath the 0.549-Mev gamma photopeak of As^{76} was measured (Fig. 5). The 0.541-Mev photopeak of Br^{82} (35.9 h) interfered slightly; however, its contribution to the area measured was determined by a separate radioactivity assay. The comparator-sample technique was used. The results of the analysis of ten different samples of naphtha showed the arsenic content to be in the range of 1.0 to 25.0 ppb. The relative standard deviation of the determinations in this range was approximately 5%. The same method should be applicable to the determination of arsenic in other materials.

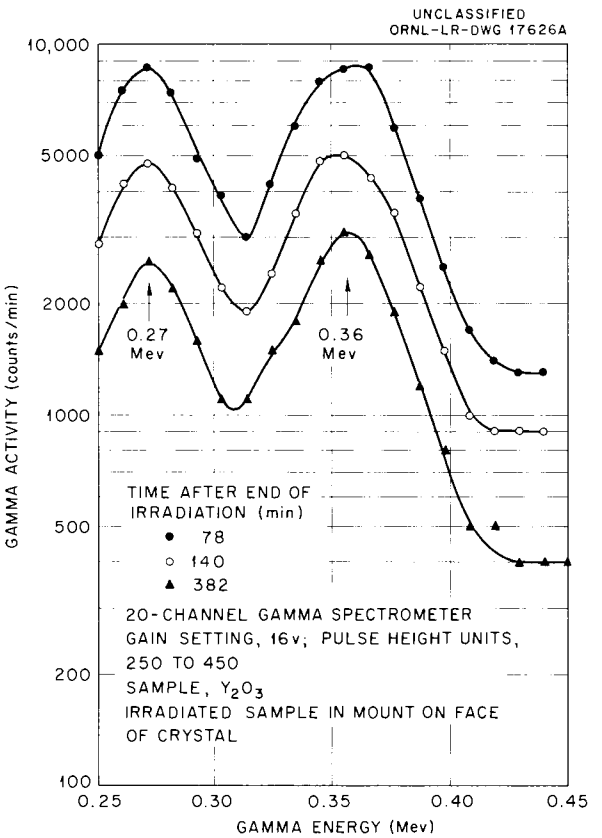

Fig. 4. Decay Curves for the 0.27- and 0.36-Mev Photopeaks of Dy^{165}.

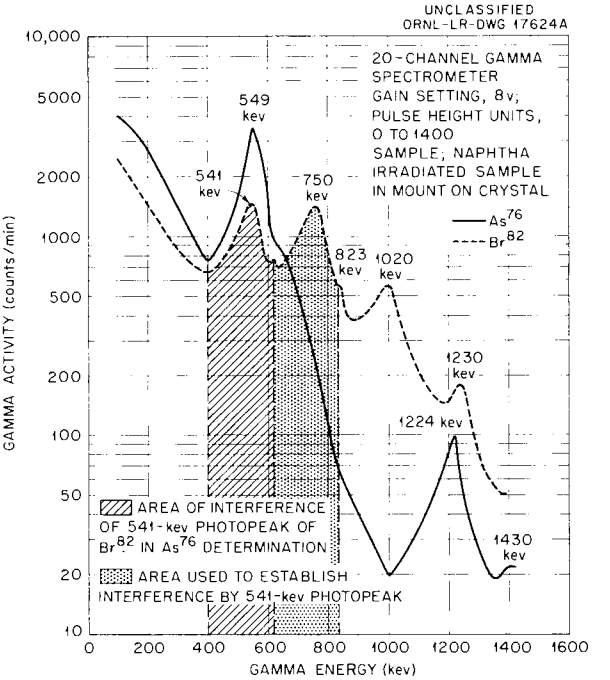

Fig. 5. Gamma Spectrum of As^{76} (26.8 h) in the Presence of Br^{82} (35.9 h).

Determination of Particle-Size Distribution

L. C. Bate G. W. Leddicotte
R. E. Druschel

By Use of High-Viscosity Mediums. – An investigation was made of the use of high-viscosity mediums in the activation-sedimentation method of determining particle-size distribution.[48] A series of solutions composed of glycerine and water, being 0.005 *M* in $Na_4P_2O_7$ and having viscosities of 0.91 (water), 5.04, 10.11, 15.33, and 19.53 centipoises, were used. Typical results obtained in determinations made with the solutions of viscosities 0.91 (water), 5.04, and 19.53 centipoises are plotted in Fig. 6. Similar results were obtained when mediums having viscosities of 10.11

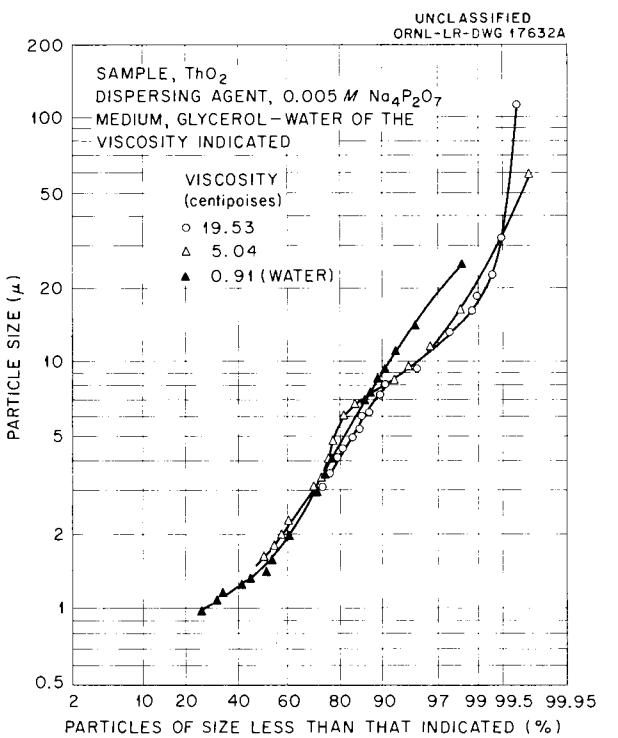

Fig. 6. Particle-Size Distribution Curves for Thorium Oxide in Glycerol-Water Mediums.

[48] G. W. Leddicotte and H. H. Miller, "Particle-Size Distribution," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 21–23.

and 15.33 centipoises were used. The results of this investigation show that it is now possible to determine the distribution of particles in thorium oxide in the particle-size range 0.7 to 118 μ.

By Use of Orthophosphate or Pyrophosphate as Dispersing Agent. – The suitability of sodium orthophosphate as a dispersing agent for thorium oxide was compared with that of sodium pyrophosphate. Some results from this study are given in Fig. 7, plotted for 0.005 *M* $Na_4P_2O_7$ and 0.010 *M* Na_2HPO_4. Similar results were obtained when 0.001 *M* $Na_4P_2O_7$ and 0.002 *M* Na_2HPO_4 were used. This study indicates that each of these compounds can be used as a dispersant in the determination of the particle-size distribution of thorium oxide slurries.

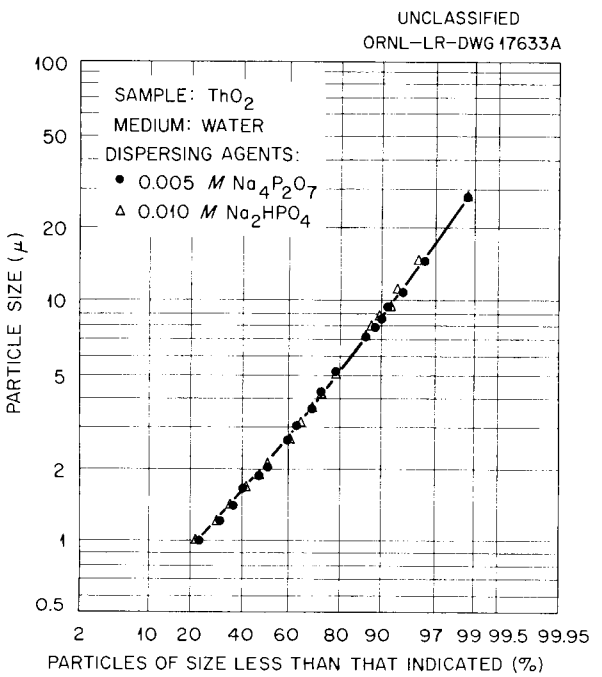

Fig. 7. Particle-Size Distribution Curves for Thorium Oxide in 0.005 *M* $Na_4P_2O_7$ and 0.010 *M* Na_2HPO_4 as Dispersants.

New Applications of Activation Analysis

G. W. Leddicotte

Inquiries were received regarding the suitability of activation analysis for the determination of contaminant elements in diamonds, animal tissue, transistor materials, waters, and soils. Samples of most of these materials have been received and are now being analyzed.

SPECTROCHEMICAL ANALYSES

C. Feldman

Separation of Microgram Amounts of Rare Earths from HRT Fuel

J. Y. Ellenburg

In order to permit achievement of the greatest possible accuracy and sensitivity in the final spectrographic determination of rare earths[49] in HRT fuel (uranyl sulfate solution at pH ~2), the procedure used must effect quantitative recovery of microgram quantities of rare earths from gram quantities of uranium and must furnish the rare-earth fraction in a small volume of liquid (preferably 1 ml) that contains no cations other than those of the rare earths. Attempts to remove uranium from the solution with Dowex 1 resin or TTA gave rare-earth solutions which were unsatisfactory from the standpoint of recovery, purity, and/or final volume. Recovery of rare earths by precipitation with either carbonate, oxalate, or phosphate alone failed to give quantitative or consistent recoveries. The following procedure, however, consistently gave 99.6% recovery of europium tracer in the precipitate.

1. Add ~0.5 g of Na_2CO_3 to 5 ml of HRT fuel and stir the solution until the uranium redissolves as the carbonate complex. (If no turbidity remains, take a fresh sample, add 5 mg of Fe^{+++}, and begin the procedure again.)
2. Add approximately 0.3 g of Na_3PO_4 and allow the solution to stand for 5 min at room temperature.
3. Heat the solution at 80°C for 10 min.
4. Separate, wash, and redissolve the precipitate in a minimum quantity of dilute HCl.
5. Isolate the rare earths from this solution by the TTA procedure for the isolation of rare earths from solutions that contain small amounts of thorium and other metals.[50]

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[49] J. Y. Ellenburg and C. Feldman, "Determination of Microgram Quantities of Rare Earths in Rare-Earth Mixtures; Spark Method," *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 18.

[50] C. Feldman, "Separation of Rare Earths from Thorium by Adsorption on Activated Cellulose: Batch Method," Section VIII D, Methods Nos. 1 00705 and 9 00650, *ORNL Master Analytical Manual.*

Separation of Microgram Amounts of Niobium from HRT Fuel

C. Feldman J. Y. Ellenburg

Extraction with diisopropyl ketone, first applied by Hicks and Gilbert[51] to the extraction of niobium from solutions of niobium and tantalum, was found to give a clean separation of niobium from HRT fuel. The niobium was extracted from a 10 *N* HCl solution and stripped back into a 6 *N* HCl solution. Recoveries of Nb^{95} tracer were in the range 98.6 to 99.8%.

Separation of Microgram Amounts of Niobium from Thorium

C. Feldman

It was feared that the small amounts of HF necessary to dissolve metallic thorium might complex any traces of niobium present and prevent their extraction by the Hicks-Gilbert procedure.[51] Tests with Nb^{95} tracer spiked into thorium salts that were freshly freed of daughter activities showed, however, that recovery of Nb^{95} tracer by this technique was complete.

Determination of Sub-ppm Concentrations of Iron, Nickel, and Chromium in NaK

J. Y. Ellenburg C. Feldman

Concentrations of iron, nickel, and chromium in NaK were expected to be of the order of 10^{-2} ppm. Developmental work on the chemical concentration of the impurities prior to spectrographic exposure showed that contamination by airborne dust made accurate or precise spectrographic analysis for common elements very difficult by any procedure that involved much handling of the sample. In order to avoid handling, the following procedure was used. An aliquot of the sample solution was transferred to a crucible, treated with internal-standard solution, and converted to the anhydrous sulfate. This was mixed in the crucible with pure Ga_2O_3, and the mixture was arced to completion. Sensitivity limits for this procedure are given in Table 7.

[51] H. G. Hicks and R. S. Gilbert, "Extraction of Niobium into Diisopropyl Ketone from Hydrochloric Acid Solutions," *Anal. Chem.* **26**, 1205 (1954).

TABLE 7. SENSITIVITY LIMITS OF SPECTROGRAPHIC DETERMINATION OF IRON, NICKEL, AND CHROMIUM IN NaK WITHOUT PRELIMINARY CHEMICAL CONCENTRATION

Element	Line Pair	Approximate Sensitivity Limit (μg/g of NaK)	Average Deviation (%)
Ni	Ni 3414.8 / Co 3474.0	0.25	4.0
Cr	Cr 4359.6 / Co 3474.0	0.10	5.0
Fe	Fe 3019.0 / Co 3474.0	0.5	4.5

Centrifuge Crucible for Ignition of Small Precipitates Without Loss or Contamination

C. Feldman

When microgram and submicrogram quantities of metals are concentrated by precipitation, there is considerable danger of contamination by dust. If the precipitate is filtered on filter paper and ignited, the ash of the filter paper may contribute quantities of some elements which are greater than the quantities already present in the test sample. The separation of the precipitate from its mother liquor and the transfer of the precipitate to a crucible for ignition usually involve losses. In an effort to avoid these difficulties, the two-piece centrifuge crucible shown in Fig. 8 was developed.

For use, a thin film of silicone stopcock grease is spread on the tapered edges, and the pieces are fitted together. The solution to be centrifuged is added, and the centrifugation is carried out. During centrifugation, centrifugal force tends to tighten the seal at the tapered joint, and no leakage occurs. After the centrifugation and the washing of the crucible the supernatant liquid is withdrawn or decanted until the level of liquid is below the tapered joint; the upper section of the tube is then removed. Some of the remaining supernatant liquid can be drawn off by pipet, if desired; the remainder is evaporated in a drying oven. The crucible is then transferred to a muffle furnace for ignition.

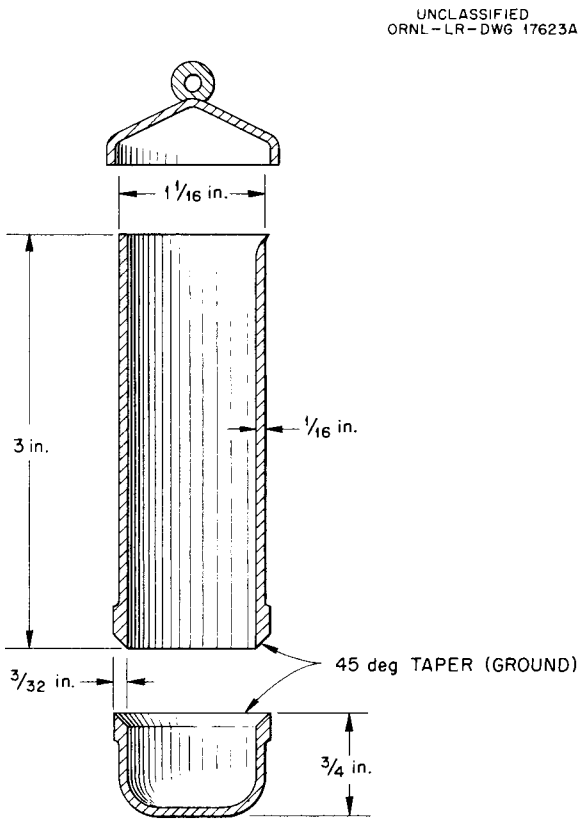


Fig. 8. Two-Piece Centrifuge Crucible (50-ml Size).

Improvements in Microspark Technique

C. Feldman

In order to ensure accurate interpretation of microspark spectra, it is necessary that the spark channel always be normal to the surface of the metal specimen. When the specimen is mounted in plastic, however, the spark tends to cling to the edge of the specimen as the edge passes under the fixed electrode. The spark channel thus is no longer normal to the surface of the specimen, and it becomes difficult to establish a point on the spectrogram which corresponds to the edge of the sample and to correlate spectrum variation with position on the sample.

This difficulty was eliminated by replacing the plastic mount by a sintered aluminum mount. Since aluminum conducts electricity, there is no tendency for the spark to deviate from the vertical as it passes over the edge of the specimen. The abrupt change in composition clearly marks the position of this edge.

Difficulty was experienced at first because polishing tended to tear bits of aluminum from the surface of the mount near the specimen. Polishing the specimen before it is mounted has eliminated the difficulty.

INORGANIC PREPARATIONS

D. E. LaValle

Special Preparations

D. E. LaValle

The special inorganic preparations for the Nuclear Physics and Neutron Diffraction Group of the Physics Division consisted in the preparation of several anhydrous halides of the transition elements (i.e., $MnCl_2$, $MnBr_2$, and $CoCl_2$) in quantities (150 g) large enough to permit the growth of a single crystal. Also, numerous smaller quantities of these halides and of $FeCl_2$ were prepared in attempts to obtain correct crystal structures for the neutron-diffraction studies. The correct structures were obtained when the substances were sublimed under HCl gas; the structures of the substances thus obtained differed from those of the products of sublimation in vacuum.

It was found that when PdF_3 was made by treatment of PdF_2 with BrF_3 it decomposed somewhat when heated to 300°C in order to remove excess BrF_3. Therefore a new preparation was made by treating $PdCl_2$ with BrF_3 and carefully heating the product *in vacuo* to break up $PdF_3 \cdot BrF_3$.

The solid solution (UCl_3 in $LaCl_3$) program for the Nuclear Physics and Low-Temperature Group of the Physics Division was resumed. The initial effort was directed toward obtaining pure UCl_3 and correctly analyzing it for trivalent uranium. A number of preparations of UCl_3 were made by the reaction of UH_3 with HCl gas. Purification was carried out by the iodine sublimation method of Gregory.[52] The analytical aspect of the problem has not yet been resolved.

For the Nuclear Chemistry Group of the Chemistry Division, a new preparation of K_2ReCl_6 was

[52] N. W. Gregory, *Preparation and Properties of the Uranium Halides*, MDDC-1755 (n.d.) (declassified Feb. 18, 1948).

made by the method of reduction with the use of hypophosphorous acid.[53]

For the Fused Salts Group of the Chemistry Division, the anhydrous rare-earth halides $GdBr_3$, YCl_3, and $NdBr_3$ were prepared in 400-g quantities; the anhydrous alkaline-earth halides $CaCl_2$, $SrCl_2$, and $BaCl_2$ were prepared in the same amounts. A quantity of anhydrous CsF (150 g) was also prepared.

The general method of preparing the rare-earth halides in the anhydrous form is to heat them under vacuum to 400°C and then to sublime them in vacuum. When this method fails, as it does for $NdBr_3$, the halide is dehydrated under HCl gas at low pressure and is then sublimed in vacuum. Neither method could be used for YCl_3; the preparation of YCl_3 was successful only when an intimate mixture of Y_2O_3 was heated with excess NH_4Cl and the product then sublimed in vacuum.

The alkaline-earth halides were heated in air to ~300°C and then heated to 1000°C as HCl gas was passed through the powder and through the resulting fused material.

Miscellaneous Preparations and Purifications

R. H. Sampley

The materials listed below were either prepared or treated as indicated, in the quantities designated, for the Physics Division:

Material	Amount
Prepared	
$C_5H_3N_4 \cdot NH_2$ (adenine)	Gram
BeF_2	Gram
$CuSO_4$ solution	8 liters
$EuCl_3$	Gram
HI	10 liters
KI	Gram
$Li_2^6CO_3$	Centigram
Li^6Cl	Centigram
LiF	130 grams
Li^6F	Centigram
Li^6OH	Gram
$LiI \cdot 3H_2O$	Kilogram
$Li^6I \cdot 3H_2O$	Kilogram
$Na_2Si_2O_5$	1800 grams
$Na_2Si_2O_5$, saturated solution	3 liters
$UO_2(NO_3)_2 \cdot H_2O$	Gram
Sn (powdered metal)	Gram
V_2O_3	Gram
Purified	
$C_6H_4(CH_3)_2$ (xylene)	Liter
$EuCl_3$	Gram
HI	Liter
KI	Gram
LiCl	Kilogram
Li^6Cl	Centigram
LiI	Kilogram
Li^6I	Centigram
Dehydrated	
$LaCl_3 \cdot 7H_2O$	Centigram
$LiI \cdot 3H_2O$	Kilogram
$Li^6I \cdot 3H_2O$	Kilogram
Reclaimed	
$EuCl_3$	Gram
LiI	Gram
Li^6Cl	Centigram
Pd	Gram
Ag	Gram
Y_2O_3	Gram

Other inorganic chemical work done for the Physics Division included cleaning of metals; identifying alloys; analyzing qualitatively for carbon, silicon, and silicon carbide; determining the density of "buttons" of AuGe and AuBe alloys; and electropolishing aluminum.

OPTICAL AND ELECTRON MICROSCOPY

T. E. Willmarth

F. M. Toomer T. G. Harmon

Microscopy of Thorium Oxide

The particle size and shape and the surface structure of thorium oxide samples, prepared by

[53] C. L. Rulfs and R. J. Meyer, "Rhenium (IV) Compounds: Synthesis and Properties," *J. Am. Chem. Soc.* 77, 4505 (1955).

various methods and examined after out-of-pile loop runs, were studied extensively by optical and electron microscopy. Among the many samples, the so-called "standard slurry" was of particular interest.

Preliminary optical examination of samples of standard slurries of thorium oxide indicated that they consisted primarily of nearly spherical particles of between 4- and 20-μ size. Examination at high optical magnification suggested that the spheres were actually agglomerates of submicroparticles that were unresolvable by light optics. The spheres also displayed high-order interference colors when observed between crossed Nicols by means of a sensitive tint plate; this phenomenon indicated the presence of a thin surface film. Dispersions of the standard slurries of thorium oxide, when placed in the electron microscope, behaved very differently from other types of thorium oxide preparations. For example, when the slurries were bombarded with a beam of electrons, focused sharply at the sample position with a resultant increase in temperature, considerable shrinkage of the spheres (equivalent to one-half to one-third the sphere diameter) took place; also, some component volatilized and then condensed to form a dense covering over the supporting substrate. Figure 9 is an electron micrograph of a substrate film that is covered with material vaporized from the adjacent sphere. Electron diffraction of this covering layer yielded dim, broad-lined patterns that were partially masked by the strong lines of a fairly broad-lined, but intense, thorium oxide pattern. The volatilized material has not yet been identified. Dispersions of nonspherical thorium oxide preparations, when treated as described, yielded only those diffraction lines that are common to thorium oxide. It is of interest to note that the activation analysis of a sample of standard slurry showed the chlorine concentration to be 217 μg/g in the solid phase and 10 μg/ml in the liquid.[54]

[54] G. W. Leddicotte, private communication to T. E. Willmarth, Nov. 7, 1956.

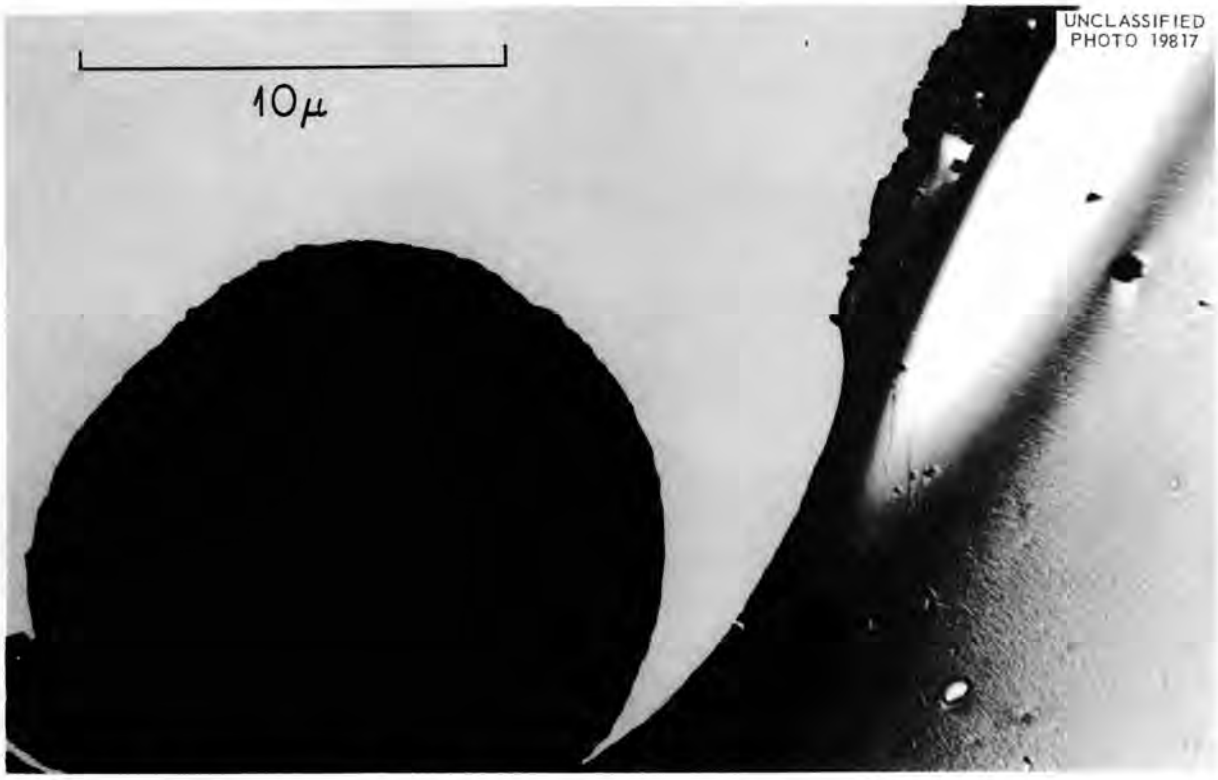


Fig. 9. Electron Micrograph Showing Layer Deposited on Substrate Film by Volatilization of Unknown Constituent in Adjacent Sphere from "Standard" Thorium Oxide Slurry.

In order to study further the surface characteristics of the spheres by electron microscopy, a method of replicating surface detail had to be developed. Numerous difficulties were associated with the curved surfaces, the solubility of thorium oxide, and the manipulation of objects having diameters of the order of 4 to 20 μ; the solubility of thorium oxide was of paramount importance. Most methods of replicating the surfaces of crystallites depend on the solubility of the crystallites in various liquid mediums; it is therefore possible to dissolve them away from the replicating film without distortion or destruction of the film. Inasmuch as thorium oxide is not readily dissolved in this manner, the following satisfactory technique was developed. A suspension of the slurry was dispersed on a glass microscopic slide and dried slowly under an infrared lamp. Heat-softened De Khotinsky cement was then pressed firmly over the spheres and allowed to harden in order for the spheres to be anchored in place so that a replica could be stripped from them. When completely solid, the cement wafer was loosened and removed from the slide. Loosely adhering, small particles were either shaken away or brushed away. Several successive coatings of polyvinyl alcohol were then applied to the cement, dried, and stripped off in order to remove any small, loosely held particles that still clung to the spheres. Finally, a negative replica, made of polyvinyl alcohol, was prepared and then stripped off, and Parlodion was flowed onto this replicating surface. The Parlodion positive was removed by floating the combined films on distilled water and dissolving away the polyvinyl alcohol. Squares of the Parlodion replica were captured on 200-mesh, electron microscopy screens and were examined in the electron microscope. Figure 10 is an electron micrograph taken from such a replica that was shadow-cast with palladium. It shows a 6-μ^2 portion of the surface of a sphere that had a total surface area of approximately 1300 μ^2. Close inspection of numerous such micrographs revealed that the spheres are actually agglomerates of small particles, as was suggested by the optical studies. The order of the size of the particles is approximately 100 Å;

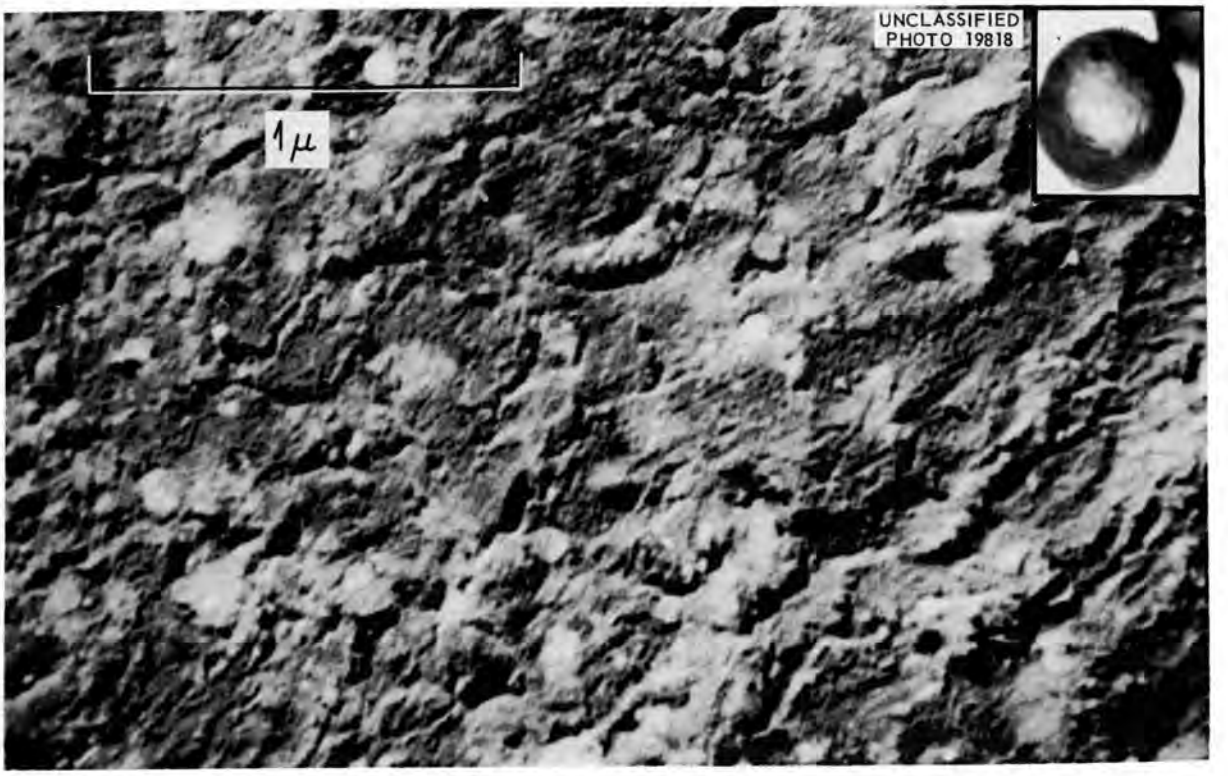


Fig. 10. Replicated Surface of Sphere from "Standard" Thorium Oxide Slurry. Palladium shadow-cast. Inset at upper right shows optical micrograph of sphere at 3000X. Reduced 4%.

apparently the particles are preferentially arranged. An attempt will be made to determine by reflection electron diffraction whether the small particles assume a preferred orientation on the surfaces of the spheres.

In studies of other samples of thorium oxide whose particle size and shape were of importance, the following preparations were investigated: thorium oxide calcined at 650, 800, 900, and 1000°C; British thorium oxide; standard slurry, stirred and unstirred; thorium oxide that had been precipitated from thorium oxalate and then dried and fired for 4 hr at 650°C; thorium oxide calcined at 800°C and pumped as an aqueous slurry for 100 hr at 200°C; thorium oxide prepared by calcination of the oxalate in an atmosphere of hydrogen; thorium oxide and uranium oxide prepared by thermal denitration; pilot-plant thorium oxide autoclaved for 100 hr; and thorium oxide autoclaved for 250 hr.

Examination of Thin Films, Corrosion Products, and Surface Structures

Samples of the bulk coating taken from a zirconium-niobium alloy that had been exposed to an in-pile loop were examined by electron diffraction and microscopy and were found to consist essentially of cubic-phase ZrO_2. There was no evidence of the presence of the stable, monoclinic phase. Additional studies of the corrosion layers on Zircaloy-2 that had been exposed in the in-pile loop[55] indicated that the oxide formed on this alloy is multilayered and that some monoclinic-phase ZrO_2 is present at the metal-to-oxide interface.

A series of samples of crystal-bar zirconium, anodized in 0.1 *N* H_2SO_4 and 0.1 *N* HNO_3 at 20, 70, and 125 v, were investigated in order to determine the nature of the oxide produced and to compare the results with those reported[56] by Charlesby. Electron diffraction of material scraped from the surfaces of the samples gave patterns typical of monoclinic-phase ZrO_2. These results do not agree with those of Charlesby, who reported, especially in the case of films produced on zirconium anodized in sulfuric acid, that an insulating layer of the cubic-phase ZrO_2 was found.

Studies of the oxides, corrosion products, and surface structures of the following were made: Zircaloy-2 on which titanium was possibly deposited; deposits on galvanized sheeting used in the construction of Building 3042; bearing graphite; Inconel tubing exposed to a fused mixture of uranium salts; single crystals of germanium irradiated in the ORNL Graphite Reactor at neutron fluxes that ranged from 10^{14} to 10^{17} neutrons/cm^2/sec; type 347 stainless steel tubing from the leak-detector system of the HRT; and Zircaloy-2 exposed in the Van de Graaff generator.

Electron Microscopy of Crystallites and of Metal Powders

A large number of crystallites and metal powders were studied by electron microscopy. These included the following: UCl_3; UCl_4; U_3O_8 from fall-out studies; $UO_2SO_4 \cdot xH_2O$; UF_4; iron powder; nickel powder; $UO_4 \cdot 2H_2O$ (normal); $UO_4 \cdot 2H_2O$ (fully enriched); the uranium salt of di(2-ethylhexyl) phosphoric acid; colloidal formations in the organic phases of systems used for the extraction of vanadium and uranium; Fe_2O_3-Cr_2O_3 precipitated in quartz tubes from solutions of uranyl sulfate at temperatures of 200, 250, and 300°C; and various types of commercial aluminum oxides. Figures 11 and 12 are electron micrographs of two preparations of uranyl peroxide cake, $UO_4 \cdot 2(?)H_2O$ (normal and depleted); they represent the electron microscopy done in these studies.

Methods and Techniques

A 50-kv General Electric Diffractograph was recently installed in the Optical and Electron Microscopy Laboratory for use in the study of thin films by both reflection and transmission electron diffraction. Techniques to be used in conjunction with this instrument are being dedeveloped so that it may best serve the needs of the laboratory.

ORNL MASTER ANALYTICAL MANUAL

Authors of Methods

H. P. Raaen H. P. House

Eighty-nine new methods and revisions to twenty-five methods were issued to the *ORNL Master Analytical Manual* (see "Presentations of

[55] T. E. Willmarth, *Examination of the Scale and Precipitate from In-Pile Loop Run 15-2*, ORNL CF-56-3-46 (March 8, 1956).

[56] A. Charlesby, "Ionic Currents in Thin Films of Zirconium Oxide," *Acta Metall.* 1, 340 (1953).

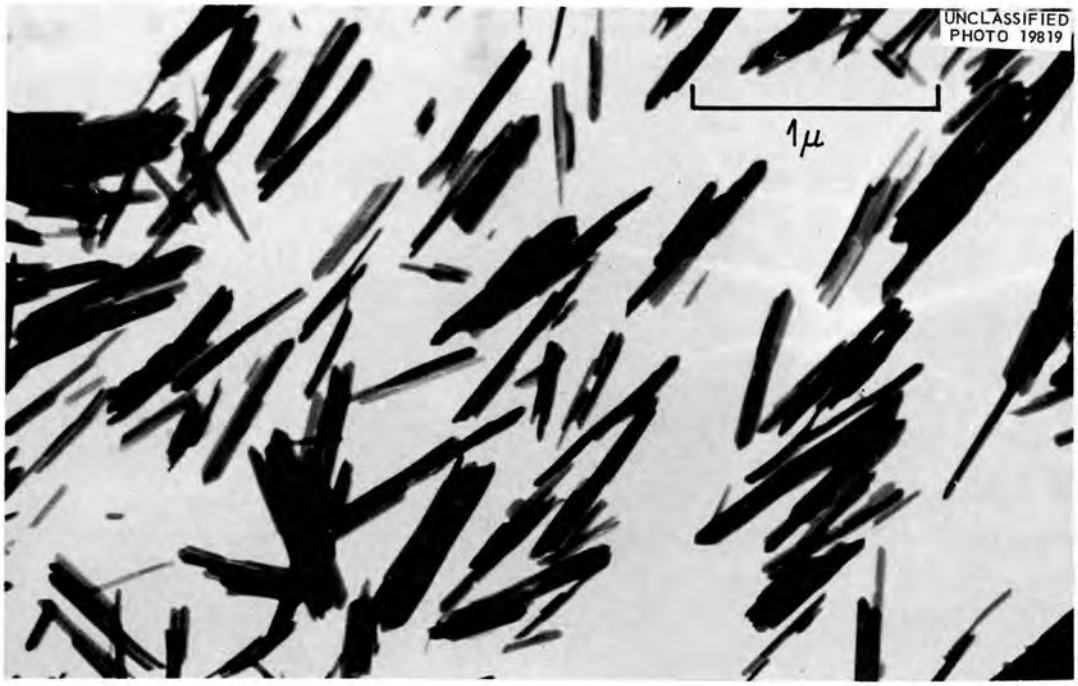


Fig. 11. Electron Micrograph of Crystallites of Normal Uranium Peroxide Cake, $UO_4 \cdot 2(?)H_2O$, Precipitated from Uranyl Nitrate Solution.

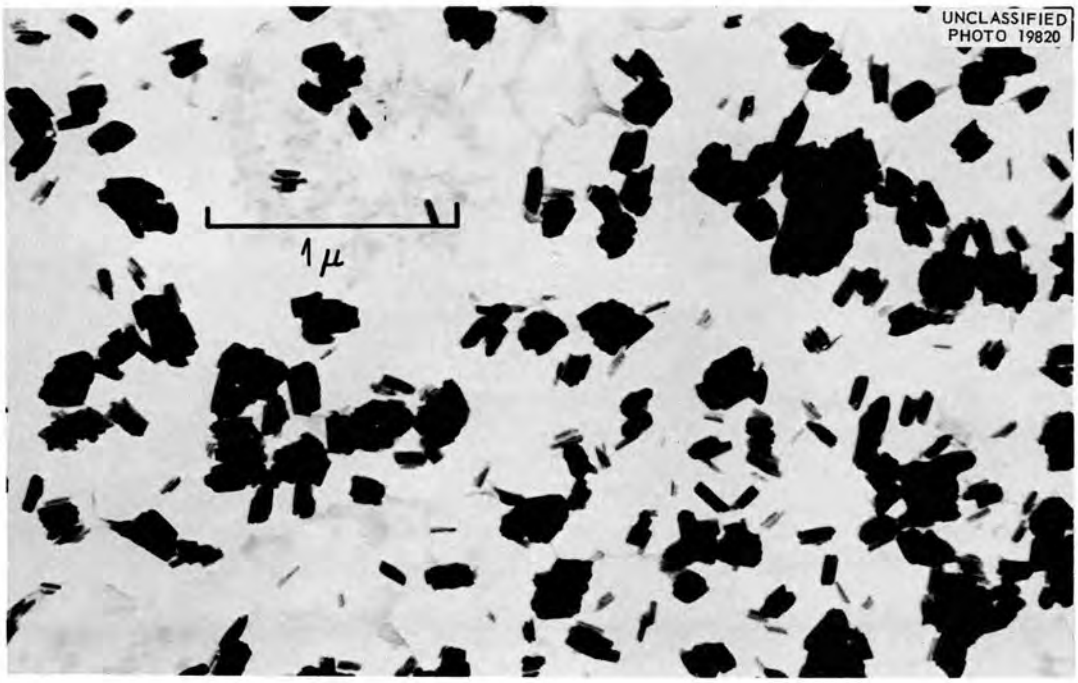


Fig. 12. Electron Micrograph of Crystallites of Depleted Uranium Peroxide Cake, $UO_4 \cdot 2(?)H_2O$, Precipitated from Uranyl Nitrate Solution.

Research Results"). The revisions were made primarily in order to bring nuclear data up to date and to effect the declassification of the maximum number of classified methods. Drafts of a large number of other new methods have been prepared. Seventeen new manuals were issued.

Arrangements have been made for the AEC Technical Information Service Extension in Oak Ridge to announce the availability of the unclassified sections of the *ORNL Master Analytical Manual* and of supplements to it and to offer them for public sale. It is anticipated that sections of the *Manual* will be transmitted to the AEC early in 1957 for this purpose.

The majority of the classified methods contained in the *Manual* were declassified. The physical declassification of single copies of the methods and the rearrangement of methods within the manuals that was necessitated thereby are now being done.

SERVICE ANALYSES

A 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 greater portion of the service work of the Ionic Analyses Group for this period continued to be for the Chemistry Division relative to their phase and corrosion studies for the HRT and their fundamental studies of ion-exchange resins. The methods that were used are contained in the *ORNL Master Analytical Manual.*

RADIOCHEMICAL ANALYSES

S. A. Reynolds

Of the service analyses done by the Radiochemical Analyses Group, 81% was for three ORNL divisions. Radiochemical determinations of the products of proton and 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 Chemical Technology Division, a number of nonroutine analyses for Th^{228}, Pa^{233}, U^{237}, Ru^{103} and Ru^{106}, and other nuclides were done. For further details see "Radiochemical Analyses," p 13.

ACTIVATION ANALYSES

G. W. Leddicotte

Activation analysis has been applied to the determination of microgram and submicrogram amounts of elements in such materials as metals and alloys, petroleum, and biological specimens. The method has also been used to determine the particle-size distribution in thorium oxide.

LABORATORY CONTROL GROUP

L. T. Corbin C. A. Pritchard
G. R. Wilson R. B. Quincy, Jr.

Two methods have been developed for the dissolution of samples of uranium-zirconium alloy (approximately 95% zirconium and 5% uranium). A large sample is dissolved in 8 *M* hydrofluoric acid followed by concentrated nitric acid. If the sample is submitted as turnings so that as little as a few hundred milligrams can be taken for analysis, a test portion is converted to a soluble form by fusion with a mixture that is 60% potassium pyrosulfate and 40% potassium bisulfate. The melt is readily soluble in a 50 vol % solution of nitric acid.

The Volatility Group of the Chemical Technology Division submits for analyses UF_4-NaF-ZrF_4 samples that are dissolved in 0.67 *M* aluminum nitrate–4 *M* nitric acid solution. It has been found experimentally that for a freshly dissolved sample, even though there is enough aluminum present to complex the fluoride, the final aliquot used in the analysis must be fumed nearly to dryness with concentrated nitric and concentrated perchloric acids before the zirconium is determined.[1]

PILOT-PLANT CONTROL LABORATORY

L. T. Corbin C. E. Lamb

Cells 1, 3, and 5 in the HRLAF were equipped and used in July for analyzing the Thorex Process solutions of irradiated thorium slugs and the related radioactive solutions from the process. By remote techniques and existing methods the samples were analyzed for U^{233}, free acid, and thorium; density determinations were also made. Dilutions were made in order to provide solutions for additional analyses that could be performed safely outside the cells.

The equipment in the cells was also used to determine, in solutions of uranium, milligram quantities of uranium by a spectrophotometric method, microgram quantities by a fluorometric method, and free acid. Analyses were made for total plutonium by extraction, precipitation-extraction, and gross counting. Methods that are contained in the *ORNL Master Analytical Manual* were used for these determinations.

Remote techniques that may be suitable for use in pretreating or dissolving Volatility Process (the fluorination process for the recovery of uranium) salts are being evaluated. The residues of high-level radioactive sample solutions were remotely transferred to waste by use of a sample-disposal unit.

[1] A. D. Horton, "Zirconium, Thoron Spectrophotometric Method," Method Nos. 1 219810 and 9 00719810 (2-25-53), *ORNL Master Analytical Manual.*

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

	Number of Personnel		ORNL Requests for Analyses														Others Requesting Analyses							
	Technical	Nontechnical	Analytical Chemistry	Applied Nuclear Physics	Aircraft Reactor Engineering	Biology	Chemistry	Chemical Technology	Electronuclear Research	Health Physics	HRP	Metallurgy	Operations	Physics	Reactor Experimental Engineering	Solid State	AEC	General Electric Co.	K-25	Others	Paducah	Phillips Petroleum Co.	Y-12	
Group Making Analyses			Number of Determinations																					Totals
Activation Analyses*	5	5	501	19	2		81	275	2	29		216	335	16	533	169			10					2,188
Ionic Analyses*	6	1	25				713	297			49	34	4	16	72	18								1,228
Laboratory Control	3	6					130	15,100		4	15		61											15,310
Optical and Electron Microscopy*	2	2	41			11	170	568	4	130		80	8		210	92								1,314
Plutonium Isolation Laboratory	2	2		5			5	4,866	285			2			7									5,170
Pilot Plant Control	6	14					3	27,257			29				26	12								27,327
Radiochemical Analyses*	6	1	2	25			2	127	105	21			43		390	21	7	2	4		3		15	767
Radioisotope Production Control	3	16		800			437	5,903		785		32	10,793		181	329		426				4		19,690
Reactor Analyses	8	8	18				13	215			6772				719	84								7,821
Special Analyses	8	10		90			806	9,504	1375			3822	417	131		1864				89				18,098
Spectrochemical Analyses*	7	0	3	42			163	1,794		4	203	302	46	26	80	46				9				2,718
Totals	56	65	590	981	2	11	2523	65,906	1771	973	7068	4488	11,707	189	2218	2635	7	428	14	98	3	4	15	101,631

*These groups also do research and development.

During the initial work on high-level radioactive solutions many problems were encountered that pertain to the equipment and techniques and to the control of contamination.[2] Corrective measures[3] were taken to improve the operations of the HRLAF.

The majority of the work done by the Pilot-Plant Control Laboratory was relative to the Thorex and Metal-Recovery processes. Analytical requirements for the Volatility Process necessitated provision for making additional types of analyses. The equipment for determining[4] the percentage of fluorine in F_2-N_2 mixtures in the range 0.01 to 100 vol % fluorine was installed, the method was checked, and analyses were made on nonradioactive samples. A known volume of the F_2-N_2 mixture was reacted with a solution of potassium iodide, and the liberated iodine was titrated with a standard solution of sodium thiosulfate.

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 Thorex Process and to the plutonium-producer blanket studies.

The Electronuclear Research Division continued to submit samples for the determination of plutonium and americium. Existing methods were used for these determinations.

The Physics Division, in studying the cross section of Pu^{240}, requested assistance in the preparation of Pu^{240} samples and submitted two batches of Pu^{240} as the oxide. The batches of oxide were dissolved in an HNO_3-HF solution, and the two solutions were mixed thoroughly to give a solution that was evaporated to dryness. The plutonium was calcined in a muffle furnace. The oxide was then weighed and put into special containers for cross-section measurements.

SPECIAL ANALYSES LABORATORY

L. T. Corbin W. R. Laing

A variety of analyses were performed by the Special Analyses Laboratory. Solutions of stainless steel and of Nichrome were analyzed for chromium, nickel, and chloride. The off-gases from the dissolution of stainless steel were analyzed for nitric oxide, nitrogen dioxide, chlorine, oxygen, and hydrogen. Tri-*n*-octylphosphine oxide was found to be satisfactory as an extractant for uranium from sulfate mediums. Uranyl sulfate solutions from test loops were analyzed for total rare earths. Determinations of surface area by nitrogen adsorption were performed on a number of oxides and fluorides. Fused salts and various reactor construction materials were analyzed for impurities. Several alpha sources were prepared for the Health Physics Division by electroplating plutonium onto platinum disks. Vacuum-fusion techniques were used in order to analyze various metals and alloys for oxygen, hydrogen, and nitrogen.

RADIOISOTOPE PRODUCTION ANALYSES

E. I. Wyatt
R. R. Rickard H. A. Parker

The half lives of several gamma-emitting radionuclides were determined; the data are presented in Table 9. The calculations were made by the method of least squares. All the radionuclides listed were either purified by chemical means or were checked for possible impurities by beta-absorption studies, by means of the gamma scintillation spectrometer, or by both. No impurities were observed either before or after the period of decay.

A method for the determination of radioactive iodine in mixed fission products that are contained in organic mediums has been perfected. It will be incorporated into Method No. 2 21391, "Iodine Activity in Aqueous Solutions," of the *ORNL Master Analytical Manual.*

A spot test for the presence of reducing agents in extremely radioactive iodine product solutions has been devised. The method involves destroying the permanganate color with reducing agents on a white spot plate. The lower limit of detection is 0.0005 meq. The method has been incorporated into Method No. 9 0732003, "Total Reducing Agents," of the *ORNL Master Analytical Manual.*

[2] C. E. Lamb, *Initial Operations in HRLAF on Radioactive Samples* (Aug. 6, 1956), a memorandum to L. T. Corbin.

[3] C. L. Burros, *Memoranda of Minutes; Initial Operations in HRLAF, Held in Chemistry Conference Room, August 9, 1956* (Aug. 15, 1956), a memorandum to M. T. Kelley *et al.*

[4] A. D. Horton, "Fluorine in Gas Streams, Volumetric Method" (in preparation), *ORNL Master Analytical Manual.*

TABLE 9. OBSERVED HALF LIVES OF SOME GAMMA-EMITTING RADIONUCLIDES

Radionuclide	Reaction Used to Produce the Radionuclide	Instrument Used	Period of Observation (half lives)	Observed Half Life
Be^7	$Li^7(p,n)Be^7$	GIC[a]	>3	53.5 ± 0.2 d
K^{42}	$K^{41}(n,\gamma)K^{42}$	PC[b]	5	12.46 ± 0.17 h
Sc^{46}	$Sc^{45}(n,\gamma)Sc^{46}$	GIC	3.8	84.2 ± 0.2 d
Co^{56}	$Fe^{56}(p,n)Co^{56}$	GIC	3	77.3 ± 0.3 d
Cu^{64}	$Cu^{63}(n,\gamma)Cu^{64}$	GIC	>5	12.91 ± 0.03 h
Se^{75}	$Se^{74}(n,\gamma)Se^{75}$	GIC	3	119.9 ± 0.6 d
As^{76}	$As^{75}(n,\gamma)As^{76}$	GIC	>5	26.8 ± 0.1 h
Y^{90}	Decay of Sr^{90}	G-MC[c]	2	64.4 ± 0.4 h
Sb^{124}	$Sb^{123}(n,\gamma)Sb^{124}$	GIC	2.5	60.9 ± 0.2 d
Nd^{147}	Fission of U^{235}	GIC	6.3	11.10 ± 0.05 d
W^{187}	$W^{186}(n,\gamma)W^{187}$	GIC	>6	24.04 ± 0.09 h
Au^{198}	$Au^{197}(n,\gamma)Au^{198}$	GIC	4.7	2.73 ± 0.01 d
Au^{199}	$Pt^{198}(n,\gamma)Pt^{199} \rightarrow Au^{199}$	GIC	>5	3.136 ± 0.022 d

[a]Gamma ionization chamber.
[b]Proportional counter.
[c]Geiger-Mueller counter.

It has been determined experimentally that Pm^{147} is lost rapidly from aqueous solutions of pH above 5. For example, when the pH is increased to 6.6, 75% of the activity is lost in the first 3 hr. It is believed that hydrolysis or plating onto the glass occurs or that both processes occur.

HIGH-RADIATION-LEVEL ANALYTICAL FACILITY

C. L. Burros

Five work cells in the HRLAF have been completely equipped for the performance of a variety of analyses and for the training of personnel. Approximately 95% of the equipment needed in the other two work cells has been installed.

Modifications made in the HRLAF have included the following: provision of through-the-wall conveyers that run from the HRLAF to the reactor and to the Pilot-Plant Control Laboratory, replacement of the single door to the tunnel with a double door, installation of a partition in the west zone, and enlargement of the north exit door. The through-the-wall conveyers and the double door to the tunnel will facilitate the handling of samples and the preparation of dilutions. The partition in the west zone will help to prevent the spread of radioactive contamination. The enlargement of the north door permits a master-slave manipulator to be removed or installed without passing through the west zone.

The Thorex pilot plant submitted the first radioactive samples for analyses on July 16; they were solutions of irradiated thorium slugs that contained protactinium and fission products. At contact, the activity of most of the samples was ~50 r/hr; the activity of a few was greater than 100 r/hr.

The facility was found to be contaminated after two days of operation. Most of the beta contamination was on the floor in the west zone; the activity of smears taken there ranged from 300 to 400 counts/min. On the dock the contamination was greatest near the tunnel door; the activity of smears taken there ranged as high as 1600 counts/min. Immediate action was taken to decontaminate the facility, and the contamination in most of the contaminated areas was reduced to less than 100 counts/min.

Additional preventive measures that were taken after this initial startup to control the spread of radioactive contamination have included the following: additional training of personnel who use the facility; use of stainless steel plates for receiving reactor samples in the west zone; use of a dolly having a disposable, paper cover for receiving pilot-plant samples at the loading tunnel, and use of plastic covers for the tunnel cart, master station, and monorail control panel.

Throughout the initial operation of the HRLAF two minor mechanical failures occurred in the storage cell. The cart froze at the "in" position, and the tong on the master-slave manipulator lost a spring and pin.

REACTOR ANALYSES

U. Koskela L. G. Farrar

The Reactor Analyses Group started limited operations in the HRLAF on August 23, 1956. All samples from HRP in-pile loop and bomb experiments are now unloaded remotely in the storage cell of the HRLAF. The following analyses have been performed to date: determination of pH; spectrophotometric determinations of iron, zirconium, and manganese; coulometric determination of chromium; and polarographic determinations of copper and nickel. Ion-exchange separations have been performed remotely prior to either analysis of the sample or removal of it to the outside. Thus far no evaluation of analysis time or of the accuracy of the procedures has been made.

ANALYTICAL CHEMISTRY DIVISION - Y-12 SITE

RESEARCH AND DEVELOPMENT

HRP ANALYTICAL CHEMISTRY

O. Menis

Automatic Titration of Free Acid in Solutions of Uranyl Sulfate

D. L. Manning G. Goldstein

A method was developed for the titration of free acid in solutions of uranyl sulfate by means of the Sargent-Malmstadt automatic, differential titrator. This titrator can be used to detect automatically the inflection point of the potentiometric titration curve and to terminate the titration at the point of maximum voltage change. Advantages in the use of this instrument as compared with other automatic titrators are that the end-point potential does not have to be preset and that graphical methods are not necessary for determining the end point. A platinum-rhodium indicator electrode and a saturated calomel reference electrode are used with the Sargent-Malmstadt titrator. The platinum-rhodium electrode is not affected by appreciable quantities of fluoride. Since the hydrolysis of uranyl salts causes interference in the titration, fluoride is added to the samples to complex the uranyl ion. By the use of the Sargent-Malmstadt titrator, from 0.1 to 1.0 meq of acid in a 50-ml volume can be titrated accurately and rapidly in the presence of as much as 200 mg of uranium and 150 mg of fluoride. The relative standard deviation of the method is 2%; however, when the test solutions each contain more than 200 mg of uranium, the relative standard deviation is increased to approximately 5%. This technique is discussed in more detail in ORNL-2178.[1]

Electrodeposition of Copper by Internal Electrolysis

D. L. Manning R. G. Ball

The electrodeposition method for the determination of copper, which was discussed in a previous report,[2] was investigated further with the objective of increasing the current and thereby increasing the deposition rate of copper. In order to attain this objective, the internal resistance of the electrolysis cell was considerably lessened by the use of a porous alundum thimble of low resistance rather than an agar-salt bridge to separate the anode and cathode sections of the cell. By this means the internal resistance was reduced to such an extent that as much as 40 mg of copper can be deposited in 30 min. For samples that contain 5 mg of copper the relative standard deviation is of the order of 2%, whereas for larger amounts of copper the relative standard deviation is correspondingly less because the error is primarily that incident to weighing. The use of the electrodeposition method offers the added advantage that copper can thus be removed from solutions, and at the same time be determined gravimetrically, prior to the determination of other components with which it would interfere. This work is discussed in ORNL-2153.[3] Formal methods[4,5] for this determination were written for issue to the *ORNL Master Analytical Manual.*

Spectrophotometric Determination of Tin(IV)

J. R. Lund

A preliminary study was made of the feasibility of using a spectrophotometric method for the determination of tin in very low concentrations, that is, 1 to 5 μg/ml, in solutions of uranyl sulfate that contain corrosion products of stainless steel. DeSesa and Rogers[6] reported that the chlorostannate ion absorbs light strongly in the ultraviolet region of the spectrum, the maximum absorption occurring at 220 mμ; therefore it appeared possible that the

[1] O. Menis, D. L. Manning, and G. Goldstein, *Determination of Free Acid in Solutions of Uranyl Sulfate*, ORNL-2178 (Oct. 25, 1956).

[2] D. L. Manning and R. G. Ball, "Electrodeposition of Copper by Internal Electrolysis," *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 35.

[3] O. Menis, D. L. Manning, and R. G. Ball, *Determination of Copper in Solutions of Uranyl Sulfate by Internal Electrolysis*, ORNL-2153 (Sept. 5, 1956).

[4] R. G. Ball, "Copper, Electrogravimetric Internal Electrolysis Method," Method Nos. 1 212321 and 9 00712321 (11-1-56), *ORNL Master Analytical Manual.*

[5] D. L. Manning, "Copper in Uranyl Sulfate Solutions, Electrogravimetric Method," Method No. 9 082216 (11-5-56), *ORNL Master Analytical Manual.*

[6] M. A. DeSesa and L. B. Rogers, "Analytical Applications of the Absorption Spectra of the Halide Complexes of Heavy Metals. I. Spectrophotometric Determination of Iron with Hydrochloric Acid," *Anal. Chim. Acta* 6, 534 (1952).

absorbancy of this ion could be made the basis for the tin determination after the separation of tin from uranium by the method of coprecipitation with aluminum hydroxide, which was developed by Manning and Ball.[7] For solutions that contained from 0.3 to 1.5 μg of tin per milliliter either alone or together with aluminum, a satisfactory calibration factor [i.e., 4.5 μg of Sn(IV) per milliliter per unit absorbancy] was obtained. The relative standard deviation of the method is 4%. When the method was applied to solutions of uranyl sulfate from which a separation of tin was made by coprecipitation with aluminum hydroxide, the results were high and erratic, evidently because of the interference of ions that were not eliminated in the separation procedure. The sensitivity of this method, as indicated by a favorable calibration factor, is excellent. Before the method can be used for the desired application, however, a satisfactory means must be found for the separation of the tin from corrosion products that interfere with the determination.

Automatic Spectrophotometric Titration of Microgram Quantities of Uranium(IV), Sulfate, and Fluoride

D. L. Manning R. G. Ball

A Warren Spectracord was modified in order that it could be used for making automatic, spectrophotometric titrations. The modifications consisted in the attachment of a time-drive accessory and a Lingane-type, constant-flow buret. A rectangular titration cell of 2-in. light path was used. By means of this modified instrument, methods were developed for the spectrophotometric titration of microgram quantities of uranium(IV), sulfate, and fluoride.

The titration of uranium(IV) was conducted according to the general procedure of Bricker and Sweetser,[8] who manually titrated milligram quantities of uranium(IV) to a spectrophotometric end point. In the automatic titration, 0.001 *M* ceric sulfate was used as the titrant. The absorbancy measurements were made at a wavelength of 340 mμ and were plotted automatically vs the volume of titrant. The end point of the titration was established by extrapolating the two straight segments of the titration curve to a point of intersection. From 12 to 240 μg of uranium(IV) in 35 ml of 0.25 *N*, deaerated sulfuric acid can be titrated by this method; under these conditions the relative standard deviation is 3%.

Attempts to titrate extremely small amounts (~25 μg) of sulfate in a methanol medium[9,10] with a solution of barium perchlorate as the titrant and Thoron as the indicator were unsuccessful because barium sulfate is appreciably soluble in methanol. The minimum amount of sulfate that could be titrated in methanol was approximately 40 μg. It was found, however, that by using 85% isoamyl alcohol–15% methanol as the titration medium a minimum of 6 μg of sulfate can be titrated spectrophotometrically. The addition of some methanol is necessary in order to produce a medium that is miscible with water. From 6 to 50 μg of sulfate in 35 ml can be titrated automatically, the relative standard deviation being approximately 5%.

Microgram quantities of fluoride were also titrated automatically by means of the Warren Spectracord. The well-established thorium nitrate, spectrophotometric titration[11] method, in which alizarin red S is the indicator, was used as the basis of this automatic titration. As thorium nitrate is added, the absorbancy remains unchanged up to the end point; at this point, the alizarin red S reacts with excess thorium to form a colored, highly absorbing complex, the absorbancy of which is linearly proportional to the excess of thorium that is added. The straight segments of the titration curve are extended until they intersect; the point of intersection represents the end point of the titration. It was found that the optimum conditions for the automatic titration of microgram quantities of fluoride are as follows: a 35-ml volume, a 0.0005 *M* solution of thorium nitrate as the titrant, a pH of 3 ± 0.1, and a wavelength of 520 mμ. From 5 to 50 μg of fluoride in 35 ml can be titrated under these conditions; the relative standard deviation is 5%.

[7] D. L. Manning and R. G. Ball, "Precipitation-Polarographic Determination of Tin," *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 35.

[8] C. E. Bricker and P. B. Sweetser, "Spectrophotometric Titration of Uranium and Iron," *Anal. Chem.* **25**, 764 (1953).

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

[10] F. J. Miller and P. F. Thomason, *Automatic Photometric Titration of Sulfate*, ORNL-2040 (Feb. 29, 1946).

[11] M. P. Matuszak and D. R. Brown, "Thorium Nitrate Titration of Fluoride," *Anal. Chem.* **17**, 100 (1945).

The spectrophotometric titration procedure was also applied to the determination of microgram quantities of thorium; the procedure is described in the following section of this report.

These methods of automatically titrating uranium(IV), thorium, sulfate, and fluoride represent a considerable saving of time and labor because each titration requires less operating time than the corresponding manual procedure. The operation of the Warren Spectracord does not require attention during the titration; therefore, while one sample is being titrated, other samples can be prepared. The data are plotted automatically, a factor which represents a saving of additional time and effort.

Spectrophotometric Determination of Thorium by the Quercetin Method

D. L. Manning G. Goldstein

A method was developed for the determination of microgram quantities of thorium in which quercetin (3,3′,4′,5,7-pentahydroxyflavone) is used as the chromophoric reagent. Within the pH range 2.7 to 3.5, two molecules of quercetin react with one of thorium to yield a yellow-colored complex that exhibits maximum absorbancy at a wavelength of 425 mμ. The instability constant of the thorium-quercetin complex is approximately 1.2×10^{-10}, and the molar absorbancy index is approximately 25,000 as compared with 15,000 for the thorium-Thoron complex. Quercetin is therefore considered to be somewhat more sensitive. Over the thorium concentration range 0.4 to 6 μg/ml the relationship of concentration vs absorbancy adheres to Beer's law; however, the optimum thorium concentration for minimum error, as established by the Ringbom method,[12] is 1 to 4 μg per milliliter of the solution that is used for the absorbancy measurement. Interferences, such as iron(III), zirconium(IV), titanium(IV), aluminum(III), chromium(VI), vanadium(V), nickel(II), and manganese(II), can be eliminated by adsorbing these ions on an anion-exchange resin[13] and then extracting the thorium from the eluate into a 0.5 *M* solution of thenoyltrifluoroacetone (TTA) in carbon tetrachloride from an acetate-buffered solution of pH 2. From 10 to 200 μg of thorium can be determined by this spectrophotometric method; under these conditions the relative standard deviation is 3%. Alternately, the thorium-quercetin complex can be titrated with a solution of ethylenediaminetetraacetic acid (EDTA), which bleaches the yellow color of the complex. The spectrophotometric titration can be made automatically by means of a Warren Spectracord modified as described above. Smaller amounts of thorium (< 10 μg) can be determined with greater precision by the titration technique than by a direct measurement of the absorbancy. In addition, the spectrophotometric titration method is subject to less interference from materials such as aluminum, nickel, and chromium(III) and (VI); consequently small quantities of these materials can be tolerated in the titration procedure without prior separation. A paper that describes the direct spectrophotometric method has been submitted to *Analytical Chemistry* for publication.

[12] A. Ringbom, "Über die Genauigkeit der colorimetrischen Analysenmethoden I," *Z. anal. Chem.* 115, 332 (1939).

[13] K. A. Kraus, F. Nelson, and G. W. Smith, "Anion-Exchange Studies. IX. Adsorbability of a Number of Metals in Hydrochloric Acid Solutions," *J. Phys. Chem.* 58, 11 (1954).

Conversion of Pyrophosphate to Orthophosphate in Suspensions of Thorium Oxide

H. P. House C. M. Boyd

Thorium oxide in aqueous suspensions has been found to catalyze the conversion of pyrophosphate to orthophosphate. The rate of conversion was determined as a function of the ratio of thorium oxide to pyrophosphate, of initial concentration of pyrophosphate, and of temperature. Under the various conditions studied, the reaction half-life periods for the conversion reaction were found to be as shown in Table 10.

Of the three variables studied, the amount of catalyst per unit amount of reactant and the temperature affect the reaction rate to a much greater extent than does the initial concentration of pyrophosphate. The reaction is greatly accelerated by both a rise in temperature and an increase in the ratio of thorium oxide (g/liter) to tetrasodium pyrophosphate (*M*). The fraction of pyrophosphate that is converted to orthophosphate per unit of time decreases somewhat with an increase in the concentration of tetrasodium pyrophosphate. In order to calculate the activation energy of the reaction by the Arrhenius equation, the order of the reaction must be established and the velocity constant must be determined at two or more temperatures. Although the reaction did not conform to any specific order throughout the entire conversion period, it

TABLE 10. REACTION HALF-LIFE PERIODS FOR CONVERSION OF PYROPHOSPHATE TO ORTHOPHOSPHATE

Variable	Composition of the Suspension			Reaction Half Life (hr)
	Temperature (°C)	ThO_2 (g/liter)	$Na_4P_2O_7$ (*M*)	
Ratio of ThO_2 (g/liter) to $Na_4P_2O_7$ (*M*)	25	20	0.05	210
		40		62
		60		42
Initial concentration of $Na_4P_2O_7$ [with ratio of ThO_2 (g/liter) to $Na_4P_2O_7$ (*M*) constant]	25	20	0.025	55
		40	0.050	62
		80	0.100	84
Temperature	25	40	0.050	62
	50			7.4
	70			1.0
	100			0.1

did approximate first order over the range 10 to 50% conversion. It was assumed that the reaction is first order over this range at 25, 50, 70, and 100°C; velocity constants were then computed, and the activation energy was found to be 20 kcal/mole.

Centrifugal Sedimentation Method for Determining the Particle-Size Distribution of Thorium Oxide

H. P. House C. M. Boyd

A centrifugal sedimentation method has been applied to the determination of the particle-size distribution of the fraction of thorium oxide which consists of particles of diameter less than 2 μ. The principal advantages of centrifugal rather than gravity sedimentation for particles of diameter much smaller than 2 μ are that the length of time for sedimentation is not inconveniently long and that large errors caused by convection and diffusion are prevented. Particle-size-distribution measurements were made for particles of diameter in the range 0.1 to 2 μ by means of an International clinical centrifuge. The limiting diameter (D) as a function of time was calculated by the Svedberg, centrifugal sedimentation equation.[14] The cumulative amount of thorium oxide deposited, which was determined spectrophotometrically, was then plotted vs $1/D^2$. From this graph the quantity of particles larger than a given diameter was evaluated by correcting the cumulative amount deposited for the presence of particles of smaller diameter by Oden's method of tangential intercepts.[15]

A determination was made of the particle-size distribution of the solid phase of a thorium oxide slurry that had been circulated through a test loop; for the measurements the solid was dispersed in three mediums: 0.005 *M* H_2SO_4, 0.001 *M* $Na_4P_2O_7$, and xylene containing oleic acid. In each medium, test results were reproducible within 5%; however, results from tests in the three mediums differed appreciably. The dispersion of the thorium oxide into extremely small particles (i.e., of diameter <0.2 μ) was much greater in the xylene medium than in the other two mediums.

Data determined by centrifugal sedimentation on the particle-size distribution for the fraction of particles of diameter smaller than 2 μ correlate well with particle-size-distribution data determined by the Andreasen gravitational method for particulate matter of diameter greater than 2 μ. This is indicated by the single straight line which is formed when the distribution data obtained by the two methods are plotted together on log-probability graph paper.

The centrifugal sedimentation method has been applied to samples of thorium oxide of such fineness that complete particle-size-distribution data

[14] T. Svedberg and J. B. Nichols, "Determination of Size and Distribution of Size of Particles by Centrifugal Methods," *J. Am. Chem. Soc.* 45, 2910 (1923).

[15] R. D. Cadle, *Particle Size Determination*, p 205–206, Interscience, New York, 1955.

could not be obtained by gravitational sedimentation. The centrifugal sedimentation method has been used satisfactorily to determine the relative effectiveness of various mechanical methods for preparing thorium oxide of extreme fineness. Should the need arise, the present equipment can easily be modified to determine the distribution of particles of diameter as small as 30 mμ.

Spectrophotometric Determination of Titanium

H. P. House I. B. Rubin

The previously described[16] procedure for the spectrophotometric determination of titanium, based on the reaction of the titanium–8-quinolinol complex with hydrogen peroxide, was applied to solutions that contained relatively large amounts of thorium. The absorbancy index of the titanium–8-quinolinol peroxide complex in the chloroform extract was found to be constant with change in titanium concentration; however, the presence of 0.2 to 1 g of thorium in the solution from which the titanium was extracted was observed to decrease the absorbancy index of the titanium complex by 15%. The time required for the color to develop fully is in excess of 1 hr; thus, for solutions that contain more than 0.2 g of thorium, it is best to establish the calibration factor by use of standard solutions of titanium that also contain thorium. Under these conditions 20 to 100 μg of titanium can be determined in the presence of as much as 1 g of thorium; the relative standard deviation under these conditions is 6%.

Zeta Potential of Thorium Oxide by a Microelectrophoretic Method

C. M. Boyd H. P. House

Information is desired relative to the magnitude and sign of the zeta potential (the difference of potential between a charged particle and the medium in which it is suspended) of thorium oxide, because the stability of suspensions and the effectiveness of dispersing agents are both closely related to the zeta potential. This information may also be useful in the characterization of particular preparations of thorium oxide. Of a number of methods available for the measurement of zeta potentials,[17] the microelectrophoretic technique appeared to be the most suitable for suspensions of thorium oxide, because no drastic change of medium or physical alteration of the solids is required. In this method a microscope is used to observe and to measure the rate of migration of individual particles in an electric field of known potential gradient. From the observed migration rate the zeta potential is calculated by means of the Helmholtz-Perrin equation.[18]

The zeta potentials of thorium oxide (type D-17, ignited at 650°C) in various aqueous mediums were found to be as follows:

Medium	Zeta Potential (mv)
Water	+42
0.0001 *M* HCl	+85
0.0001 *M* $Na_4P_2O_7$	−63
0.0001 *M* KOH	−63

These values are in substantial agreement with those which O'Connor[19] determined for a sintered thorium oxide by the streaming-potential method. The positive sign of the zeta potential of thorium oxide in water is attributed by O'Connor to the hydration of the surface of the oxide and the subsequent ionization of hydroxyl groups. The change in the magnitude and sign of the charge with additions of different electrolytes is caused by the adsorption and/or exchange of anions or cations to various degrees.

Determination of Aluminum in Thorium Oxide

F. L. Layton

A study is being made of a spectrophotometric method for the determination of aluminum in thorium oxide in which eriochrome cyanine R is used as the chromophoric reagent.[20] For standard solutions of aluminum that contain from 3 to 30 μg of aluminum, the relative standard deviation is 3%. Thorium interferes in the procedure; however, an attempt is being made to separate the thorium from aluminum by extracting the thorium into 0.5 *M* solution of

[16] I. B. Rubin and H. P. House, "Spectrophotometric Determination of Titanium," *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 38.

[17] H. R. Kruyt (ed.), *Colloid Science*, Vol. I, p 197–234, Elsevier, New York, 1952.

[18] J. Perrin, "Mecanisme de l'electrisation de contact et solutions colloidales," *J. chim. phys.* 2, 601 (1904).

[19] D. J. O'Connor, *The Ion Exchange and Ion Adsorption Properties of Neutron Irradiated Thoria*, AERE, C/R 1767 (March 2, 1956).

[20] U. T. Hill, "Direct Photometric Determination of Aluminum in Iron Ores," *Anal. Chem.* 28, 1419 (1956).

thenoyltrifluoroacetone (TTA) in carbon tetrachloride or chloroform. No definite conclusions have yet been reached regarding the feasibility of this extraction procedure for the elimination of thorium interference.

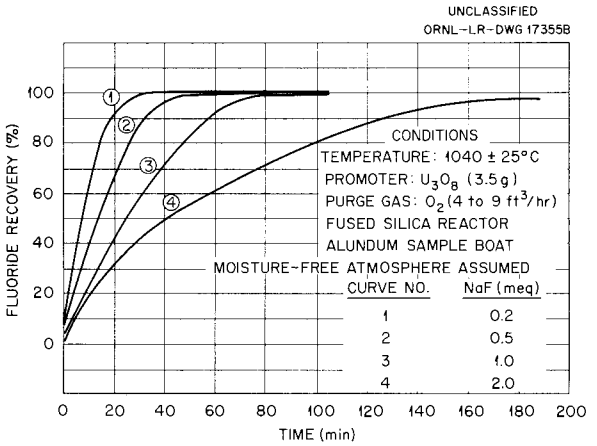
Removal of Fluoride from Thorium Oxide

R. H. Powell

In the evaluation of the precision and accuracy attainable in the determination of fluoride in thorium oxide by the pyrohydrolysis method of Warf *et al.*,[21] tests were made which involved several modifications of the apparatus and the procedure. These modifications included the following: the use of nitrogen, helium, or oxygen instead of steam to purge the reactor; substitution of a fused silica or alundum reactor for a nickel reactor; replacement of the U_3O_8 promoter by a U_3O_8-Al_2O_3 mixture or by MnO_2; the use of an alundum rather than a nickel sample boat.

As a result of these studies, it was established that if an all-nickel apparatus is used, if steam is omitted, and if oxygen, nitrogen, or helium is used to purge the apparatus, then the recovery of fluoride is less than 70% complete. The residual fluoride can be recovered subsequently by purging the apparatus with steam. If, however, a fused silica reactor and an alundum sample boat are substituted for the all-nickel apparatus and if oxygen or an inert gas that is mixed with oxygen is used to purge the apparatus, the recovery of fluoride is essentially 100% complete. By this means and at a reactor temperature of 1040 ± 25°C, quantities of fluoride from 0.2 to 2 meq were recovered quantitatively from sodium fluoride. The rate of reaction as a function of quantity of fluoride recovered is shown graphically in Fig. 13. The recovery of fluoride as hydrofluoric acid was determined by an acidimetric titration and was confirmed by a spectrophotometric titration with a solution of thorium nitrate as the titrant. It was found that U_3O_8-Al_2O_3 mixtures and MnO_2 are equally effective promoters and are as effective as U_3O_8 alone. Further studies are being continued in order to elucidate the mechanism of the reaction between metallic fluorides and U_3O_8 or other promoters in the presence of oxygen. These studies include the examination of intermediate products and an evaluation of the role of water vapor in the reaction.

[21] J. C. Warf, W. D. Cline, and R. D. Tevebaugh, "Pyrohydrolysis in the Determination of Fluoride and Other Halides," *Anal. Chem.* 26, 342 (1954).



Rate 13. Rate of Recovery of Fluoride from Sodium Fluoride by Pyrolysis.

Flame Photometric Determination of Lanthanum

T. C. Rains

The determination of lanthanum[22] by flame photometry is being studied. Calibration curves (radiant intensity vs concentration) were established for 20 to 100 μg of lanthanum per milliliter of aqueous solution at a wavelength of 442 mμ. The emissivity of lanthanum in nonaqueous solutions is being studied in an effort to increase the sensitivity of the method. Organic solvents produce strong carbon bands in the region of 436 mμ; thus these solvents interfere with radiant-intensity measurements of 442 mμ. Consequently, the lanthanum oxide band at a wavelength of 560 mμ is now being used with organic-aqueous mediums. Of four mediums studied other than water, 50% methanol appears to be the most promising. In this medium the radiant intensity is proportional to the lanthanum concentration over the range 4 to 20 μg/ml, and the sensitivity is approximately ten times that attained in an aqueous medium. Optimum operating conditions for the Beckman flame photometer with the spectral-energy recording attachment No. 92300 were found to be as follows:

Photomultiplier tube (RCA-1P28) voltage, v	675
Width of slit, mm	0.05
100% adjustment, units	10.0
Oxygen pressure, psi	10
Hydrogen pressure, psi	6

[22] P. T. Gilbert, Jr., "Flame Photometry – New Precision in Elemental Analysis," *Industrial Laboratories*, p 41 (Aug. 1952).

The effect of thorium(IV), fluoride, and other ions on the determination of lanthanum is being studied.

Flame Photometric Determination of Calcium and Barium

J. R. Lund

During the study of an indirect method for the determination of fluoride, based on the precipitation of the fluoride as calcium fluoride or barium fluoride and the subsequent determination of the excess calcium or barium by flame photometry, it was observed that the radiant intensity could be increased fiftyfold by aspirating the alkaline-earth salts into the flame in isopropyl alcohol solution rather than in aqueous solution. Measurements of radiant intensity were made at a wavelength of 418 mμ for calcium and 556 mμ for barium; flame backgrounds were also measured at these wavelengths, and corrections were made for subsequent measurements.

For 1 to 8 μg of calcium per milliliter of a 99% solution of isopropyl alcohol, a calibration factor of 0.1 μg of calcium per milliliter per unit radiant intensity (measured on the per cent–transmittance scale of a Beckman spectrophotometer) was obtained. The relative standard deviation in the determination of the calibration factor was 4%. For 3 to 30 μg of barium per milliliter of 90% isopropyl alcohol, a calibration factor of 0.35 μg of barium per milliliter per unit radiant intensity was obtained.

In the application of this method to the indirect determination of fluoride, test results for fluoride proved to be very erratic.

METHODS DEVELOPMENT GROUP

J. C. White

Determination of Boron in Fluoride Salts

W. J. Ross A. S. Meyer, Jr.

A method has been developed for the determination of microgram amounts of boron in fluoride salts. Samples of fluoride salts are dissolved at room temperature in a solution that contains aluminum chloride and hydrochloric acid, and the solution is then diluted with an equal volume of ethyl alcohol. A reproducible fraction of the boron is extracted when the aqueous solution is equilibrated with an equal volume of ethyl ether for 5 min. The boron in the ether phase is determined spectrophotometrically with carminic acid. The partition coefficient of boron, C_o/C_a, is 0.59 ± 0.02 when the aqueous phase is 4 *M* in hydrochloric acid and 2 *M* in aluminum chloride. This coefficient is independent of temperature between 13 and 28°C. The method has been applied successfully to the determination of as little as 10 μg of boron. The relative standard deviation for samples that contain 200 μg of boron is 3%.

Sampling of Systems of Alkali Metals with the Modified MSA Sampler

G. Goldberg A. S. Meyer, Jr.

Two significant modifications have been made to the MSA sampler for alkali metals: a vacuum-tight, modified Wilson seal has been substituted for the packing gland and the gate valve has been replaced with a vacuum-tight, Teflon-packed, Jamesbury valve. A complete description of the modified sampler and a stepwise procedure for its application to the sampling of dynamic or static systems of alkali metals are given in ORNL-2147.[23]

Use of Tri-*n*-alkylphosphine Oxides in the Fluorometric Determination of Uranium

J. C. White

Tri-*n*-octylphosphine oxide and tri-*n*-decylphosphine oxide were shown to be excellent extractants for uranium in its fluorometric determination. These phosphine oxides can be used to extract uranium quantitatively from solutions that are as concentrated as 12 *M* with respect to such acids as sulfuric, phosphoric, and hydrochloric. The extraction is also quantitative in the presence of anions, such as citrate, oxalate, and tartrate, that form strong complexes with the uranyl ion in solution. A simple extraction procedure was developed which is applicable under essentially all conditions. In this procedure 5 ml of 6 *M* HNO_3 is added to a 1-ml aliquot of the sample, and the solution is then shaken for 5 min with 5 ml of a 0.1 *M* solution of the phosphine oxide in Varsol. Although these phosphine oxides are not commercially available, their synthesis is not particularly difficult.

Determination of Oxygen in Sodium and in NaK by Distillation

G. Goldberg

A distillation method has been adapted to the determination of oxygen in sodium and in NaK.

[23] G. Goldberg, A. S. Meyer, Jr., and J. C. White, *The Sampling of Alkali Metal Systems with the Modified MSA Sampler*, ORNL-2147 (Aug. 21, 1956).

In addition to the detailed procedure a description of the apparatus that is used, as well as a schematic diagram and a photograph of it, is included in another report.[24] By use of this apparatus the alkali metals have been sampled directly at operating temperatures as high as 1400°F.

Extraction of the Elements into Hydrocarbon Solutions of Tri-*n*-octylphosphine Oxide from Acidic Solutions

W. J. Ross

A preliminary survey was completed of the applicability of the tri-*n*-octylphosphine oxide for the separation of elements by solvent extraction. The experimental work was undertaken to ascertain which elements can be extracted into hydrocarbon solutions of the phosphine oxides from aqueous solutions of various mineral acids. Only qualitative data have been taken to date.

Extraction of Chromium into 0.2 *M* Tri-*n*-octylphosphine Oxide in Benzene from Acidic Solutions

C. K. Mann[25]

A method was developed for the spectrophotometric determination of small quantities of chromium which is based on the extraction of chromium(VI) into a 0.2 *M* solution of tri-*n*-octylphosphine oxide in benzene followed by the formation of the chromium-diphenylcarbazide complex *in situ*. The molar absorbancy index of the chromium-diphenylcarbazide complex in the nonaqueous phase is identical with that in water; however, the extraction makes possible a twentyfold concentration of chromium, with consequent increase in the sensitivity of the method. Chromium in the sexivalent state only is extracted into the benzene solution of tri-*n*-octylphosphine oxide. Of the three oxidizing agents for chromium that were investigated, namely, bromine, sodium bromate, and sodium bismuthate, bromine was found to yield the best results. A procedure has been recommended[26] for the determination of 0.2 to 1 μg of chromium per gram of alkali metal with a relative standard deviation of 9%.

Spectrophotometric Determination of Cerium

A. S. Meyer, Jr. B. L. McDowell

A method was developed for the spectrophotometric determination of cerium in samples of fluoride salts that is based on the reaction of cerium with Tiron (sodium-1,2-dihydroxybenzene-3,5-disulfonate). The method is subject to serious interference from iron, uranium, and zirconium. Iron and uranium form colored complexes with the Tiron, whereas zirconium consumes the reagent to form a colorless complex. All these interferences are eliminated by extracting them into a solution of tri-*n*-octylphosphine oxide in cyclohexane. Approximately 20 mg of zirconium or 25 mg of uranium can be extracted into 20 ml of a 0.1 *M* solution of tri-*n*-octylphosphine oxide in cyclohexane. Zirconium extracts readily from a sulfate solution only, whereas chloride must be present for uranium and iron to be extracted efficiently.

The color of the cerium-Tiron complex is developed in a test portion of the extracted solution which contains 50 to 700 μg of cerium by adjusting the test portion to a pH greater than 8 with sodium hydroxide solution after the addition of 25 mg of Tiron. In order to ensure maximum precision, the ionic strength of the resulting solution is adjusted by the addition of 1.25 g of Na_2SO_4 before the solution is diluted to a volume of 25 ml. After 6 hr the absorbancy of the solution is measured at a wavelength of 500 mμ against a reference solution of the reagents. A concentration of cerium as low as 0.1% in a 1-g sample of fluoride salt can be determined. A relative standard deviation better than 2% has been obtained for the determination of cerium in concentrations from 3 to 12% in samples of fluoride salts.

Determination of Lithium Carbide and Lithium Nitride in Metallic Lithium

T. W. Gilbert, Jr. A. S. Meyer, Jr.

A method was developed for the simultaneous determination of lithium carbide (Li_2C_2) and lithium nitride (Li_3N) in metallic lithium. The lithium sample is dissolved in water in a stainless steel bomb in order to hydrolyze the carbide and the nitride to acetylene and ammonia, respectively. These gases, in addition to the hydrogen which is

[24] G. Goldberg and J. C. White, *Procedure for the Determination of Oxygen in Sodium and NaK by the Distillation Method*, ORNL CF-56-4-31 (April 5, 1956).

[25] Research participant from the University of Texas, Austin.

[26] C. K. Mann and J. C. White, *Extraction of Chromium with Trioctylphosphine Oxide from Acidic Solutions of Alkali Metal Salts and Its Determination* in Situ *as the Chromium-Diphenylcarbazide Complex*, ORNL CF-56-10-86 (Oct. 23, 1956).

also evolved on dissolution of the sample, are passed first into boric acid solution to absorb the ammonia, which is determined with Nessler's reagent, and then into a 1.5 *M* solution of silver perchlorate to absorb the acetylene, which forms a soluble silver complex in this medium. The absorbancy of this second solution is measured at 297 and 313 mμ in order to determine the acetylene present. The use of the two wavelengths allows a wide range of concentrations of acetylene to be determined directly. On the basis of a 2.5-g sample of lithium and 5 ml of acetylene-absorbing solution, the applicable concentration range of acetylene at 297 mμ is 10 to 220 ppm, calculated as carbon, and at 313 mμ it is 55 to 1100 ppm.

Determination of Uranium in an Extractant Solution of Cyclohexane and Tri-*n*-octylphosphine Oxide

C. A. Horton

A sensitive, spectrophotometric method has been developed for the determination of uranium in an extractant that is 0.1 *M* tri-*n*-octylphosphine oxide in cyclohexane. After uranium has been extracted from a nitrate or chloride system into 0.1 *M* tri-*n*-octylphosphine oxide in cyclohexane, a 0.5 vol % ethanolic solution of dibenzoylmethane is mixed directly with the solution of the uranium–tri-*n*-octylphosphine oxide complex in cyclohexane. Sufficient pyridine is added to make the solution 0.05 vol % with respect to pyridine, after which the absorbancy of the solution is measured at 405 mμ. The molar absorbancy index is of the order of 18,000 as compared with 1,330 for the ascorbic acid complex of uranium and with 2,000 for the thiocyanate complex.

Separation of Zirconium and of Uranium from Thorium by Extraction from Sulfuric Acid Solutions into a Benzene Solution of Tri-*n*-octylamine

J. P. Young J. R. French

Methods for determining thorium and zirconium in NaF-ZrF_4-ThF_4-UF_4 have been investigated. The separation of zirconium and uranium from thorium in solutions of sulfuric acid by extraction into a solution of tri-*n*-octylamine in benzene was studied. Crouse *et al.*[27] found that the extraction coefficient for uranium from 0.5 *M* sulfuric acid into 0.1 *M* tri-*n*-octylamine in kerosene is 37 and that for zirconium the coefficient is >60. Brown *et al.*[28] found that thorium is not extracted into a solution of tri-*n*-octylamine in kerosene. Preliminary tests on the extraction of zirconium and uranium from thorium by means of tri-*n*-oxtylamine in benzene indicated that thorium was being extracted or otherwise lost but that zirconium was not completely removed from the aqueous phase in one equilibration. It was also found that thorium cannot be extracted into 0.1 *M* tri-*n*-octylamine in benzene from 0.5 *M* solutions of sulfuric acid if the amines are converted to the salt form prior to extraction.

Extraction isotherms have been obtained for the extraction of zirconium from 0.5 and 1 *M* sulfuric acid solutions into 0.1, 0.25, and 0.5 *M* solutions of tri-*n*-octylamine in benzene. The quantity of zirconium that can be extracted into the organic phase varies directly with the amine concentration of the organic phase and inversely with the sulfuric acid concentration of the aqueous phase. By the use of these extraction isotherms, it is possible to determine the number of extractions required in order for the concentration of zirconium in the aqueous phase to be reduced to any desired value. It is planned to investigate possible separations of other substances by extraction into benzene solutions of tri-*n*-octylamine.

RAW MATERIALS ANALYTICAL CHEMISTRY

L. J. Brady

Separation of Impurities from Solutions of Uranyl Sulfate

E. C. Lynn L. J. Brady

A comparison was made of the effectiveness of a filtration method and a solvent-extraction method for the removal of cupferrates of vanadium and of other metals from solutions of uranyl sulfate prior to the determination of uranium by titration with ceric sulfate solution. It was found that as much as 9% of the uranium present is retained with the precipitate if impurities in excess of 10 mg are removed by filtration after these impurities are precipitated with cupferron. If, however, an equivalent amount of impurities is precipitated with cupferron and the cupferrates are then dissolved by

[27] D. J. Crouse *et al.*, *Progress Report on Uranium Extraction with Organonitrogen Compounds*, ORNL-2099 (May 14, 1956).

[28] K. B. Brown *et al.*, *The Use of Amines as Extractants for Uranium from Acidic Sulfate Liquors: A Preliminary Report*, ORNL-1734 (May 27, 1954).

and extracted into chloroform, an insignificant quantity of uranium is lost. As a result of this comparison, the separation of impurities from solutions of uranyl sulfate is being accomplished by the solvent-extraction method.

Recovery of Iron from Organic Solutions

E. C. Lynn L. J. Brady

A comparison was made of the results of the recovery of iron from samples of organic extractants (organo-phosphorus compounds) by two different methods. These two methods are being used in the Raw Materials Laboratories of the Analytical Chemistry Division to transfer the extracted iron from the organic phase to an aqueous phase prior to the spectrophotometric determination of the iron. The first method consists in decomposing the organic compounds by wet oxidation with nitric and perchloric acids. The second method is based on the removal of iron from the organic phase by alternate extractions into a 10% solution of sodium carbonate, in order to remove the uranium and precipitate the iron, and then into a 5 *M* solution of hydrochloric acid, to dissolve the iron and distribute it in the aqueous phase. The results that were obtained by a subsequent spectrophotometric method after removal of the iron from a series of eight samples by each of the foregoing techniques indicate that the recovery of iron is essentially the same for both methods; therefore any preference for one method over the other for the removal of iron from a particular sample must be based on other factors, such as the time required, the amount of sample available for test, and the necessity of determining more than one element in the sample. For example, both urcnium and iron can be determined in the extracted sample, whereas uranium cannot be determined in the sample prepared by wet oxidation because of the interference of phosphate.

Determination of Carbon in Samples of Stainless Steel Contaminated with Paper Fibers

J. M. Peele L. J. Brady

Since unusually erratic results were being obtained in the analysis of certain samples of stainless steel, the samples were subjected to critical examination and found to be contaminated with paper fibers. These fibers had been introduced into the samples inadvertently, by collection of the sample on soft tissue during the machining process, before the samples were submitted for analysis. Since none of the original metal specimen was available for resampling, it was necessary to determine the carbon content of the contaminated samples. Attempts to remove the fibers by washing the samples with benzene and acetone were unsuccessful because the paper remained entwined among the jagged pieces of metal. In subsequent tests on the determination of carbon in standard samples of steel to which paper fibers had been added, it was found that the paper can be removed by prefiring the samples in an oxygen atmosphere at a temperature from 550 to 575°C without adverse effect upon the results of the determination of carbon in the steel by conventional methods.[29] Since analysis of the standard samples showed that excellent results had been obtained with the prefiring technique, it was used, with excellent reproducibility, for removing paper fibers from stainless steel samples that had been contaminated during a preparatory process, prior to determining the carbon content.

Spectrophotometric Determination of Vanadium with Benzohydroxamic Acid

L. J. Brady

The method of Wise and Brandt[30] for the determination of vanadium by means of benzohydroxamic acid and hexanol has been adapted for analyzing samples that contain small concentrations of vanadium in the presence of large concentrations of iron and uranium. The interference of iron and uranium can be eliminated by adsorbing these elements onto an anion-exchange resin (Dowex 1) from a 4 *M* solution of HCl. In 4 *M* HCl, vanadium is not adsorbed onto the resin. This modified method is being applied in the analysis of samples for which the amount of vanadium in the test portion is below the limit of quantitative measurement of the peroxide method. Only about 0.03 mg of vanadium is required for a determination by the benzohydroxamic acid method. The precision of the results of this method compares favorably with that attained by the peroxide method.

[29] "Total Carbon by the Direct-Combustion Method," Method E 30-47, p 77–79, *1950 Book of A.S.T.M. Methods for Chemical Analysis of Metals*, American Society for Testing Materials, Philadelphia, 1950.

[30] W. M. Wise and W. W. Brandt, "Spectrophotometric Determination of Vanadium(V) with Benzohydroxamic Acid and 1-Hexanol," *Anal. Chem.* 27, 1392 (1955).

Comparison of Fluorescence of Uranium Phosphors

J. R. Lund

A comparison was made of the intensity of fluorescence of uranium phosphors when they were prepared by various methods and when they were measured by the ORNL model Q and the modified ORNL model R fluorophotometers. In the range 0.1 to 1 μg of uranium per phosphor and for a given method of preparation of the phosphors, the precisions of the results obtained with the two instruments were essentially the same.

The observed ratio of the concentration of uranium to intensity of fluorescence (calibration factor) was essentially the same for phosphors prepared from two different flux materials – 2% LiF–98% NaF and 91% $NaKCO_3$–9% NaF. The intensity of the fluorescence of phosphors prepared from an LiF-NaF flux was essentially the same whether the organic extract of uranium was added directly to the flux or whether a portion of the aqueous solution containing the uranium was added to the fusion dish and evaporated to dryness before the addition of the flux. With the carbonate flux, however, the technique of adding the extract directly to the flux resulted in a decrease in intensity of fluorescence of approximately 50%.

It was found experimentally that tri-*n*-decylphosphine oxide in Varsol is a better extractant than a 10% solution of tributyl phosphate (TBP) in Varsol for uranium in its fluorometric determination. For each instrument and for each flux material, greater sensitivity and better precision were obtained by use of the phosphine oxide extractant than by the TBP extractant.

QUALITY CONTROL

R. L. McCutchen B. J. Ginocchio[31]
C. D. Susano

The scope of the control work in the Analytical Chemistry Division laboratories at the Y-12 Site was reviewed and was revised to meet the needs of these laboratories. Such a review of the control program for the laboratories at the X-10 Site was considered to be unnecessary, because the types of materials being analyzed therein remained unchanged.

The frequency with which standards are tested for control purposes in the Y-12 laboratories was decreased as much as possible commensurate with the maintenance of the required precision of test results. In some cases the control work was expanded to include certain analyses that heretofore had not been a part of this program and to provide additional information regarding the analyses of different types of materials.

Trends to both high and low values were observed on occasions in most of these laboratories during this year, but prompt, remedial action eliminated the potential biases in most cases. In general, the precision achieved in most of the laboratories was comparable with that attained in previous periods.

The distribution by laboratory of the 9826 determinations that were evaluated for control purposes in the X-10 and Y-12 laboratories is given in Table 11. For purposes of comparison, similar data for the previous six-month period are included.

TABLE 11. SUMMARY OF DETERMINATIONS EVALUATED FOR CONTROL PURPOSES

Laboratory	Number of Determinations	
	October 1955 Through March 1956	April Through December 1956
X-10 Site		
Building 3019	3720	5678
Building 3508	148	262
Building 3550	471	626
Building 4500	845	1202
General Analyses	131	385
	5315	8173
Y-12 Site		
Building 9201-2	445	391
Building 9204-1	340	551
Building 9733-4	170	711
	955	1653
Grand Total	6270	9826

In connection with the Statistical Quality Control Program, experimental data that were pertinent to, but not a part of, the program were evaluated. The results of some of the evaluations are given below.

[31] Special Analyses Laboratory, X-10.

Analysis of Samples from the Pilot Plant.[32] – Uranium and amine data for samples from the Pilot-Plant Section of the Raw Materials Process Testing Group were evaluated to determine the feasibility of using single rather than duplicate determinations. It was established that the use of a single determination does not have a deleterious effect on the precision of the test results.

Analysis of a Sample of $NaZrF_5$.[33,34] – The composition of a sample of $NaZrF_5$, designated as No. 499, was established in order that this material could be used as a standard sample.

Analysis of UO_3.[35,36] – A sample of UO_3, designated as NBL No. 18, was analyzed in cooperation with the New Brunswick Laboratory to establish the composition of this material so that it can be used as the basis for an AEC standard.

Determination of Copper in Solutions of Uranyl Sulfate.[37] – The results from an electrolytic method and a spectrophotometric, diethyldithiocarbamate method for the determination of copper in solutions of uranyl sulfate were compared and were found to be essentially the same. The relative standard deviation of the results in both cases was about 4%.

Determination of Molybdenum by the Ethyl Acetate–Thiocyanate Method.[38] – The relative standard deviation of the calibration data for the determination of molybdenum by the ethyl acetate–thiocyanate method was found to be about 5%. The effect of iron on the extraction of molybdenum was also evaluated and found to be negligible if the quantity of iron in the test portion of the sample is 20 mg or less.

Fluorometric Determination of Uranium. – A number of investigations were made in an effort to improve the reproducibility and reliability of uranium values that are secured by means of a fluorometric method in which a Photovolt fluorophotometer is used to measure the intensity of fluorescence. The results of studies undertaken in connection with the Quality Control Program are summarized below, whereas the results of other investigations are presented in other sections of this report.

The variables which were investigated were the reproducibility of uranium values as a function of the scale of the fluorophotometer on which the intensity of fluorescence is measured;[39] the effects of changing the batches of flux[39] and of the age of the flux;[40] the relationship of the intensity of fluorescence to the uranium content of the phosphor;[40] the differences in calibration data for the 10- and 100-scales of the fluorophotometer;[40] the reproducibility of measurements within and among days, as well as within and among extracts;[40] the effect of substituting, in the fluorophotometer, a meter having a linear-type scale for one having a nonlinear scale;[40] a comparison of values as related to the use of mechanically vs manually cleaned glassware;[41] the relationship of the fluorescence to the original weight of the flux, as well as to the weight of the phosphor after being fused in a muffle furnace at 800°C;[41] the effect of substituting a new Photovolt fluorophotometer for one that has been in use in the laboratory for some time.[41]

It became apparent during these tests that none of the variables investigated were critical factors in the fluorometric method for the determination of uranium. Small improvements in precision were attainable, of course, by closer control of one or

[32] R. L. McCutchen and C. D. Susano, "Analysis of Samples from the Pilot Plant," *Statistical Quality Control Quar. Rep. Anal. Chem. Div., July–Sept., 1956*, ORNL CF-56-10-12, p 72.

[33] R. L. McCutchen and C. D. Susano, "Preparation of a Standard Sample of $NaZrF_5$ for Control Purposes," *Statistical Quality Control Quar. Rep. Anal. Chem. Div., Jan.–March, 1956*, ORNL CF-56-4-195, p 60–62.

[34] R. L. McCutchen and C. D. Susano, "Analysis of a Sample of $NaZrF_5$ for Use as a Standard," *Statistical Quality Control Quar. Rep. Anal. Chem. Div., April–June, 1956*, ORNL CF-56-7-152, p 64.

[35] R. L. McCutchen and C. D. Susano, "Analysis of UO_3: NBL No. 18," *Statistical Quality Control Quar. Rep. Anal. Chem. Div., July–Sept., 1956*, ORNL CF-56-10-12, p 72.

[36] C. D. Susano, *Cooperative Analysis of a Standard Sample of UO_3, NBL-18*, ORNL CF-56-9-103 (Sept. 25, 1956).

[37] R. L. McCutchen and C. D. Susano, "Copper in Solutions of Uranyl Sulfate," *Statistical Quality Control Quar. Rep. Anal. Chem. Div., April–June, 1956*, ORNL CF-56-7-152, p 62.

[38] R. L. McCutchen and C. D. Susano, "Molybdenum by the Thiocyanate Method," *Statistical Quality Control Quar. Rep. Anal. Chem. Div., Jan.–March, 1956*, ORNL CF-56-4-195, p 58.

[39] "Uranium by the Fluorometric Method," *ibid.*, p 64–66.

[40] R. L. McCutchen and C. D. Susano, "Uranium by the Fluorometric Method," *Statistical Quality Control Quar. Rep. Anal. Chem. Div., April–June, 1956*, ORNL CF-56-7-152, p 66–70.

[41] R. L. McCutchen and C. D. Susano, "Fluorometric Determination of Uranium," *Statistical Quality Control Quar. Rep. Anal. Chem. Div., July–Sept., 1956*, ORNL CF-56-10-12, p 73.

more of the variables; but in order to effect a significant increase in precision, standardization of the fusion process by which the phosphor is prepared will be necessary. The use of a muffle furnace in which the temperature is gradually increased from 100 to 800°C was considered as a possible means of standardizing the fusion process, and the results of one series of experiments confirmed this possibility. However, the practicality of adopting this technique for the preparation of the phosphors has not been established.

Determination of Uranium by the Stannous Chloride–Thiocyanate Method.[42,43] – Several studies were made of the spectrophotometric, stannous chloride–thiocyanate method for determining uranium in an effort to improve the precision of the results. It was established that the preparation of the chromogenic reagent is a critical factor in this method. When this variable was controlled, the relative standard deviation was decreased by a factor of 2 (i.e., from 10 to 5%).

Volumetric Determination of Uranium.[43] – Uranium values, which were determined by two volumetric methods, were compared in order to justify the substitution of the zinc–ceric sulfate method for the automatic titrator–potassium dichromate method. The substitution was found to be justified.

Volumetric Determination of Vanadium.[44] – In the usual volumetric method for the determination of vanadium, 0.1 *N* $FeSO_4$ solution is used to titrate 75 to 100 mg of vanadium; the relative standard deviation for this titration is 0.5%. For the determination of smaller quantities of vanadium (i.e., 15 to 20 mg), 0.02 *N* H_2SO_4 was used as the titrant; the relative standard deviation under these conditions was found to be about 3%.

[42] R. L. McCutchen and C. D. Susano, "Uranium by the $SnCl_2$-Thiocyanate Method," *Statistical Quality Control Quar. Rep. Anal. Chem. Div., April–June, 1956*, ORNL CF-56-7-152, p 72-74.

[43] R. L. McCutchen and C. D. Susano, "Volumetric Determination of Uranium," *Statistical Quality Control Quar. Rep. Anal. Chem. Div., July–Sept., 1956*, ORNL CF-56-10-12, p 74.

[44] R. L. McCutchen and C. D. Susano, "Vanadium by the Volumetric Method," *Statistical Quality Control Quar. Rep. Anal. Chem. Div., Jan.–March, 1956*, ORNL CF-56-4-195, p 68.

SERVICE ANALYSES

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

HRP ANALYTICAL CHEMISTRY

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

The staff of the HRP Analytical Chemistry Laboratory made 53,300 analyses on 9,290 samples. Solutions of uranyl sulfate and of uranyl sulfate that contained copper sulfate, lithium sulfate, or magnesium sulfate were analyzed for uranium, iron, nickel, and chromium. Occasionally these solutions were analyzed for aluminum, chromium(VI), cobalt, copper, lithium, magnesium, manganese, molybdenum, tin, titanium, uranium(IV), zirconium, sulfate, fluoride, chloride, bromide, iodide, and excess acid. The pH of most of the solutions was also measured. In addition, the dissolved oxygen and carbon dioxide in solutions of uranyl sulfate were determined. Thorium oxide and other compounds of thorium were analyzed for thorium and for impurities similar to those determined in solutions of uranyl sulfate; phosphate, silicon, and lead were also determined. The dissolved hydrogen in slurries of thorium oxide was determined occasionally.

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, 7 *M* nitric acid, and 5% nitric acid. Less frequently, these solutions were analyzed for aluminum, chromium(VI), copper, free acid, magnesium, and nitrate. The density of some of these solutions was also determined.

In addition to this work, uranium, chloride, sulfate, conductance, and pH were determined on some condensate samples, palladium and ruthenium were determined on a few samples, and the concentration of hydrogen peroxide was established occasionally. Barium, boron, calcium, lithium, sodium, and potassium were measured by flame photometric methods, and fluoride and uranium(IV) were determined by spectrophotometric titration techniques.

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

	Number of Personnel		ORNL Divisions Requesting Analyses							Others Requesting Analyses		
	Technical	Nontechnical	Aircraft Reactor Engineering	Chemistry	Chemical Technology	Metallurgy	Solid State	Reactor Experimental Engineering	Stable Isotopes Research and Production	Y-12	Miscellaneous	
Laboratory Making Analyses			Number of Analyses Reported									Totals
Raw Materials and Miscellaneous	4	12	24	3,094	17,651	472	43	369	153	97	205	22,108
HRP	4	8						53,300				53,300
9201-2	4	6	5828	7,399		63					736	14,026
Totals	12	26	5852	10,493	17,651	535	43	53,669	153	97	941	89,434

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 9223 samples, 45% of which were submitted by the Raw Materials Process Testing Group of the Chemical Technology Division.

The analysis of acid leach solutions and of organic extractants, derived from solvent-extraction studies, constituted the major portion of the work of this laboratory. In addition, a significant number of samples of finely divided uraniferous ore, suspended in dilute sulfuric acid, were analyzed to determine the degree of retention of the uranium extractant in the suspension after the sample had been processed by methods which are designed to facilitate quantitative removal of the extractant. The weight of the suspended solid in these samples was also determined. Calcined, solid samples that resulted from solvent-extraction and precipitation studies were analyzed to determine the purity of the uranium product and the concentration of the impurities which accompany the uranium.

Thorium and rare-earth elements were precipitated as fluorides in order to separate them from uranium, phosphate, and other impurities that are found in solutions derived from leaching monazite sand with sulfuric acid. The fluoride precipitates were dissolved in 15% solutions of nitric acid that were saturated with aluminum nitrate; the thorium was then separated from the rare-earth elements by extraction with mesityl oxide.[1] The concentration of the thorium in the extract was determined by the spectrophotometric Thoron method of Thomason *et al.*[2] A variety of less common samples have been analyzed for such components as cerium, zirconium, hafnium, molybdenum, vanadium, sulfate, phosphate, chloride, and fluoride. These analyses are related to the determination of the extraction coefficients for different cations extracted into a variety of amines and organophosphorus compounds, dissolved in organic diluents, and to the subsequent elucidation of the mechanism of the extraction processes.

[1] C. V. Banks and C. H. Byrd, "Spectrophotometric Determination of Thorium in Monazite Sands," *Anal. Chem.* 25, 416 (1953).

[2] P. F. Thomason, M. A. Perry, and W. M. Byerly, "Determination of Microgram Amounts of Thorium," *Anal. Chem.* 21, 1239 (1949).

MISCELLANEOUS ANALYSES

L. J. Brady E. C. Lynn
J. R. Lund J. M. Peele

A total of 2883 samples, which represents approximately three times as many samples as were analyzed during the previous semiannual period, were submitted to the Miscellaneous Analyses Laboratory for analysis. The major portion of these samples was derived from studies of methods for the isotopic enrichment of various materials by chemical-exchange reactions. Spectrophotometric and flame photometric methods were applied extensively in the determination of miscellaneous elements in different solutions. A variety of methods of separation, which include solvent extraction, precipitation, electrolysis, and ion-exchange techniques, were used to separate the interferences prior to the preparation of samples for isotopic assay. Solutions of sulfuric acid, derived from the process for the enrichment of N^{15} by the Nitrox system,[3] were analyzed for total acid, sulfur dioxide, and the oxides of nitrogen.

During this period, tests for ascertaining the conformance of ferrous and nonferrous metals and alloys to specification requirements were continued. In addition, a wide variety of miscellaneous samples, not related to the research studies discussed previously, were analyzed for the chemical composition of plastic materials used in the construction of cages for small animals; the estimated amount of hydrogen and carbon in zirconium hydride and zirconium carbide, respectively; the oxygen content of compressed hydrogen gas; and the low concentrations of water in various liquid organic compounds. Numerous standard solutions that contained known concentrations of various elements were also prepared in this laboratory. These standards are being used in the Quality Control Program of the Analytical Chemistry Division.

[3] N. C. Bradley and G. M. Begun, "Nitrogen Enrichment Unit," *Chemical Separation of Isotopes Section, Semiann. Prog. Rep. June 30, 1956*, ORNL-2176, p 16–19.