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ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

FOR PERIOD ENDING DECEMBER 31, 1958

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ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

For Period Ending December 31, 1958

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

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SUMMARY

RESEARCH AND DEVELOPMENT

Activation Analyses (X-10)

The use of neutron activation analysis in the determination of submicrogram and microgram amounts of many elements in a variety of materials is summarized. The analysis of water and of reactor materials and the determination of trace quantities of argon and oxygen are also reviewed briefly. Particle-size-distribution analyses, gamma monitoring, neutron-flux monitoring, radioactivity measurements, and the use of short-half-life radionuclides in analysis are also discussed.

Analytical Instrumentation (X-10)

As a part of the In-Line Instrumentation Program at ORNL, the following instruments are scheduled for construction and plant installation in FY-59: gamma monitors for gross and specific gamma activity, alpha monitor for plutonium loss, a-c polarograph for monitoring uranium loss, radio-frequency monitor for nitric acid concentration in a Darex process stream, gamma absorptiometer for monitoring uranium concentration, and colorimeter for organic process streams. Other radiochemical process control instruments that are scheduled with less priority for construction include an interface-level controller for organic continuous column, a flow-rate meter, and an air-lift metering pump. The principles, descriptive details, current development status, and proposed applications and testing of each of these instruments are presented briefly. A falling-stream cell will be used in one of the gamma monitors, and an electronic scan circuit will be tested for scanning the gamma spectrum of the flowing IAP stream. Two types of transducers for alpha monitors that continuously record the rate of alpha emission from the surface of the stream have been laboratory tested, and both will be evaluated in a plant stream. The design of the a-c polarograph circuit has been improved, and an instrument for monitoring uranium loss will be built. Tests of a radio-frequency instrument for monitoring nitric acid concentration in a prototype test loop are continuing, and a monitor is to be installed on a Darex stream in the Metal Recovery Plant. A gamma absorptiometer in which a chopper technique is used to minimize electrical drift and gamma emission from the stream itself is being constructed for monitoring uranium in the Darex plant.

The development work of the Analytical Instrumentation Group can be summarized as follows. The controlled-potential coulometric titrator has been redesigned, a prototype has been built and tested, and several titrators of the new design are being fabricated by the Instrument Department. The new instrument can automatically perform either reduction or oxidation titrations at limited potential. Circuit improvements include the use of a difference amplifier, a power transistor, silicon-diode-rectified, Zener-diode-regulated potential sources in order to eliminate all batteries, a printed-circuit operational amplifier for electronic integration of cell current, and a new multirange metering circuit having meter-overload protection. The ORNL model Q-1728 velocity-servo potentiometric titrators have been improved by the replacement of the 6BN6 gate by a transistorized gating circuit and by the replacement of batteries by a silicon-diode-rectified, Zener-diode-regulated power supply. A radio-frequency titration instrument, which has been used for the titration of thorium, was designed and fabricated for the HRP Laboratory of the Analytical Chemistry Division. Design improvements have been made to the prototype of the controlled-potential and derivative polarograph; two polarographs, designated ORNL model Q-1988, are being fabricated by the Instrument Department. Significantly improved derivative polarograms are obtained with the redesigned analog type of derivative computer. The variables that determine the useful sensitivity limit of polarography are being investigated. Specialized equipment, including apparatus for controlled-potential coulometric titrations and for surface-area measurements, has been designed and fabricated for the analysis of radioactive samples. Instrumentation for chronopotentiometric analysis at transition times of about 1 sec has been built and tested, and a study of its applications has been initiated. A ratio-readout recording instrument is being designed and fabricated for use in a spectrographic method for the determination of oxygen in metals. The ratio of either the instantaneous or the integrated intensity of an oxygen emission line to that of an agron emission line is to be continuously recorded. A

new high-resolution, high-sensitivity, scanning, recording, single-beam flame spectrophotometer has been designed and will be fabricated and tested. Measurements can be made in the spectral range from the ultraviolet to 8700 Å, and the resolution will be at least 0.2 Å in the first order.

HRP Laboratory (Y-12)

Work has continued by the staff of the HRP Laboratory on the development and improvement of methods for the analysis of solutions of uranyl sulfate, slurries of thorium oxide, and miscellaneous samples. Components to be determined included not only uranium and thorium but also additives and corrosion products of stainless steel and other materials of construction used in test devices. Methods developed or adapted for use in the analysis of uranyl sulfate solutions included flame photometric methods for microgram quantities of silver, neodymium, and iron and polarographic methods for mercury, copper, lead, cadmium, and chloride. For the analysis of slurries of thorium oxide, new or improved methods were devised for the flame photometric determination of aluminum, colorimetric or fluorometric determination of zirconium, removal of certain interferences in the colorimetric determination of titanium, polarographic determination of uranium, and dissolution of high-fired samples without loss of chromium and subsequent determination of the chromium.

Other methods developed or evaluated included a procedure for the separation of molybdenum from many interferences and subsequent determination of this element by flame photometry, a fusion-pyrolysis procedure for removal of ruthenium from steel prior to its estimation colorimetrically, a procedure for the polarographic determination of uranium in tin after volatilization of the major portion of the tin as $SnCl_4$, the high-frequency titration of thorium with disodium ethylenediaminetetraacetate or oxalic acid, and a gamma counting method for establishing the fraction of thorium oxide settled in the determination of size distribution by a sedimentation procedure. Further work is reported on the application of fusion pyrolysis to the separation of fluoride and also chloride from thorium oxide and other materials. Additional fluxes were evaluated for specific applications.

Two extraction studies were made for analytical purposes. The effect of acetic acid concentration and pH on the extraction of thorium with thenoyltrifluoroacetone in organic solvents was investigated over a wide range of acid concentrations and pH values. A similar study was also made of the extraction of aluminum and lanthanum in which the effect of pH, concentration and type of buffer used, type of organic solvent, and period of equilibration on the distribution ratio was evaluated.

Inorganic Preparations (X-10)

The preparations of anhydrous transition-metal halides for the Physics Division and of fused salts as solvent systems needed by the Metallurgy Division were continued. The preparation of high-purity Li^6I was resumed for the Neutron Physics Division. Some high-purity materials for the Solid State Division were prepared successfully. Also, the preparation of a series of solid solutions of $U^{233}F_3$ in alkaline-earth-metal fluorides was undertaken and successfully completed for the Physics Division.

Ionic Analyses (X-10)

The Ionic Analyses Group has studied and developed analytical methods in several areas of analytical chemistry to support the research of several ORNL divisions. In the field of electrochemistry a new method was developed for the coulometric titration of europium. The coulometric determination of uranium in dissolver solutions has been studied. A new technique for the determination of copper, uranium, and nickel in HR fuel has been developed; the three elements are determined in one test portion of the fuel. Polarographic determinations of barium in tetramethyl ammonium iodide, uranium(VI) in various acidic media, and niobium in molten and aqueous ammonium bifluoride have been evaluated. An amperometric titration method for the determination of barium was also evaluated.

In the field of titrimetry, a study was made of chemical changes in UO_2-Al reactor fuel elements during heat treatment. A method for the determination of the oxygen-to-uranium ratio in UO_2 has been developed. Automatic chelometric titrations of several metals, such as yttrium, magnesium, calcium, nickel, and bismuth, have been carried out by use of a mercury indicator electrode. The study of the thermometric titration of acids has been continued this period; the systems studied were

zirconium in hydrofluoric acid, uranyl ion in sulfuric acid and in nitric acid, and thorium in nitric acid. Thermometric redox and precipitation titrations were also studied.

In the field of spectrophotometry, a spectrophotometric determination of small amounts of zirconium in thorium oxide has been evaluated. Studies of the spectral properties of Eu^{2+} and Eu^{3+}, and of $Li^6I(Eu)$ scintillation crystals were conducted. Studies have been made of a simultaneous spectrophotometric determination of cerium and plutonium in fused salts, and of UO_2^{2+}, U^{4+}, and Cu^{2+} in 1 *M* sulfuric acid. Small amounts of H_2O in D_2O were determined spectrophotometrically in the near-infrared region of the spectrum with a Cary model 14PM spectrophotometer. The spectrophotometric studies of the autoreduction of PuO_2^{2+} by products of the alpha-particle radiolysis of water have continued.

The gas-chromatography work has continued, and a method for the quantitative determination of Amsco has been developed.

Miscellaneous wet-chemical methods have been used in the work of the group and include the determination of halides of magnesium and bismuth, sulfates, hydrogen sulfide, beryllium, and lithium in anhydrous hydrofluoric acid.

Mass Spectrometric Analyses (Y-12)

In the Referee Analysis Laboratory two 6-in.-radius mass spectrometers are operating; a 6-in.-radius, 180°, inhomogeneous-field spectrometer has been built and tested; and two 12-in.-radius double-magnet spectrometers are being built.

By means of thermal diffusion, Kr^{86} for use as a primary wavelength standard has been enriched to 99.97%.

ORNL Master Analytical Manual (X-10 and Y-12)

The *ORNL Master Analytical Manual* was displayed at the International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland. With the exception of Section 9 (*Process Methods*), the reprinted *Manual* (TID-7015) is now available from the Office of Technical Services, Department of Commerce, Washington. Thirty-six new methods were issued to it, and the Tables of Contents for three sections were revised. Eight copies of the *Manual* were issued to new custodians.

Optical and Electron Microscopy (X-10)

Descriptions are given of a method for replicating crystals of thorium oxide for electron microscopy, a modification to and uses of an electrolytic stripping method for bulk oxides of steel, and details of the Faxfilm replica technique and its uses for electron microscopy. Use is made of a TV-monitoring-screen method for observing the action of charged submicro and micro particles in liquid media. The nature of the studies made in connection with the Gas Cooled Reactor Project and a representative result of one study are given. Mention is made of work done for the Sherwood Project, the Physics Division, and the Biology Division. The conversion of the Philips electron microscope from 50-Å to 20-Å resolving power and the purchase of a new 35-Å instrument are reported.

Quality Control (X-10 and Y-12)

A brief summary of the quality control program is given. A number of changes and innovations were evaluated and initiated in the control program at Y-12 to improve its effectiveness. In addition to these activities, evaluations of about 30 sets of experimental data, derived from toroid tests in the HRP, were made at Y-12 during the year, and a simply designed experiment was devised and recommended for future toroid tests. A statistical model was also designed for the evaluation of data, secured in the Spectrographic Laboratory, by means of the IBM-704 computer.

Radiochemical Analyses (X-10)

For 26 nuclides, measurements have been made of activation cross sections characteristic of neutrons of 195-kev energy. A liquid scintillation counter was obtained and is being used to measure alpha and beta activities. Instrumental techniques have been used in the identification and measurement of fission gases and fall-out activity, in the measurement of U^{232}, and in other problems. Radiochemical methods have been devised for the determination of Y^{91}, Nd^{147}, radiocesium, and U^{237}. Research on cyclotron-produced radionuclides and on solvent-extraction techniques has continued.

Raw Materials Laboratory (Y-12)

The Raw Materials Laboratory studied the determination of the hydrogen content of paraffin, the use of gold plates in preparing 3 *M* sulfuric acid solutions of plutonium for gross-alpha counting, and the application of the dibenzoylmethane method for the determination of uranium.

Reactor Projects Laboratory (Y-12)

The Reactor Projects Laboratory extended the investigation of the applicability of tri-*n*-octylphosphine oxide (TOPO) as an analytical reagent to a study of the extraction of cerium and tin with TOPO. The effects of temperature on the solubility of TOPO in cyclohexane and on the extraction of nitric acid were determined. The ultraviolet spectra of the uranium-TOPO adduct, $UO_2Cl_2 \cdot 2(TOPO)$, were found to be useful in the direct determination of uranium in the organic phase in the presence of thorium, which is also extracted by TOPO. Further data were obtained on the effect of concentration of hydrochloric acid on the extraction of niobium and tantalum. Additional infrared spectra were obtained on films of metal-TOPO adducts. An ultraviolet spectrophotometric method for the direct determination of nitrate in TOPO-cyclohexane solutions was developed. The iron-TOPO adduct was found to react with *o*-phenanthroline in cyclohexane solution to give the familar ferrous–*o*-phenanthroline complex, thereby providing another example of a direct colorimetric determination in a nonaqueous medium. With respect to fluoride salt analysis, methods were evaluated for the determination of oxides in mixtures of salts, and for yttrium and magnesium. Progress is reported on the development of a cell in which the spectra of molten fluoride salts can be measured. Other methods investigated were microdetermination of fluoride ion in yttrium metal, ultraviolet spectrophotometric determination of cerium, and determination of boron in nitrate solutions.

Spectrochemical and X-Ray Analyses (X-10 and Y-12)

Ammonium bisulfate is superior to potassium pyrosulfate for use in processing samples for spectrochemical analysis because it can be volatilized completely after use, it does not solidify during fusion, and it does not attack platinum or glass. The identity of an acid matrix does not affect the intensity ratio obtained in a porous-cup exposure at the ~1% acid level but does so in many cases at the 10% acid level. The introduction of helium into the analytical gap through a hollow counter-electrode effects a marked increase in the line-background ratio of porous-cup exposures. In the use of triisooctylamine for the extraction of zirconium from 9 *N* hydrochloric acid, it is necessary to prepare the reagent immediately before use. X-ray fluorescence techniques have been developed for determining uranium, niobium, and zirconium in the presence of each other. The conversion of an x-ray instrument for x-ray absorption analysis of solutions is under way.

SERVICE ANALYSES

A summary of the service analyses is given in tabular form, and special problems are discussed briefly.

Activation analysis was used to determine microgram and submicrogram amounts of many elements in many substances and to measure particle-size distributions.

In the Counting Laboratory (Y-12), plutonium was determined by gross-alpha counting. The gamma activity of various fluoride-salt mixtures to which radioisotopes had been added was measured, as well as the residual gamma activity in metallic fuel containers.

The Raw Materials Laboratory and the Miscellaneous Analyses Laboratory continued to make analyses of a wide variety of materials. Among these were organic solvents, acid leach solutions, samples from the isotopic enrichment program, and samples from reactor waste disposal studies. The analyses included the determinations of uranium, vanadium, iron, and molybdenum; the separation and determination of thorium; the determinations of nitrate, boron, water, sulfur, and fluoride in various samples; and a number of physical measurements.

In the High-Radiation-Level Analytical Facility (HRLAF) modifications were made in order to lessen radiation hazards and to reduce manipulator downtime.

The HRP Laboratory analyzed 14,900 samples, principally solutions of uranyl sulfate and slurries of thorium oxide. In addition to uranium and thorium, additives and other minor components, corrosion products of stainless steel, and dissolved gases were determined. The physical measurements made included pH, conductance, specific gravity,

zeta potential, and particle-size distribution. Thermogravimetric analyses were carried out in ThO_2–metallic oxide mixtures and other materials. The constituents determined and the methods used in their determination are tabulated.

Ionic service analyses were related primarily to the Chemistry Division's research in high-temperature solubilities, HR fuels, and fundamental ion exchange studies. Analyses relative to studies of reactor-fuel reprocessing and to the development of alloy-type fuel elements were made for the Chemical Technology and Metallurgy Divisions, respectively.

An interim Low-Level-Radiation Analytical Laboratory is being put into operation pending construction of the permanent laboratory. The interim laboratory is being equipped with instruments, and standard radiochemical procedures were adapted for the analysis of samples of low activity.

The service facilities of the Analytical Mass Spectrometry Group have been consolidated. A total of 270 cylinders of pure gas was analyzed for the Metallurgy Division, 130 cylinders were certified for the Y-12 Z-area, and over 900 analyses were done for GCR experiments.

A total of 100,918 analyses was performed by the Process Analyses Laboratories for ten divisions, the Chemical Technology Division being the largest contributor. These included analyses of reactor construction materials, fuel plates, fused salts, soils, plants, ion exchange resins, and process solutions. Assistance was given to other divisions on special problems; for example, the Health Physics Division was assisted in the preparation of neptunium oxide pellets for use in radiation dosimetry studies, and Thorex solutions were decontaminated for subsequent mass analyses by the Argonne National Laboratory.

The Radiochemical Analyses Group made gamma spectrometric determinations of fission-product and other activities in many materials for the Health Physics Division. They also made radiochemical analyses on samples from the HRT, the results of which were useful in deducing the behavior of radioelements in HRT fuel.

The Radioisotopes-Radiochemistry Laboratory made a number of radiochemical separations relative to pilot-plant work. They adapted existing methods to the determination of trace quantities of fission products in river water and prepared formal issues of the adapted methods for inclusion in the *ORNL Master Analytical Manual.* The half lives of Ga^{72}, Ru^{106}, and Hg^{203} were measured. Also, a method was developed for leaching iodine from beds of charcoal in which it was entrapped.

During the past year the Reactor Analyses Laboratory participated in seven HRT runs. A coulometric determination for copper and uranium was introduced, modifications were made in the method for determining dissolved oxygen in water, and the evaluation of a commercial pH microelectrode was continued.

The Reactor Projects Laboratory continued to analyze fluoride-salt mixtures of various compositions for the major salts, as well as for the corrosion products, such as nickel, iron, chromium, molybdenum, and niobium. In addition, samples of Inconel and related materials were analyzed. Special samples of graphite were analyzed for uranium and beryllium.

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RESEARCH AND DEVELOPMENT

ACTIVATION ANALYSES (X-10)

G. W. Leddicotte

Quantitative Applications of Activation Analysis

G. W. Leddicotte, L. C. Bate, W. T. Mullins, J. F. Emery, J. E. Strain

Recent applications of neutron-activation analysis in the determination of submicrogram and microgram amounts of various elements in a variety of materials are summarized in Table 1. The induced-radionuclide data are given elsewhere.[1] The neutron irradiations were made in either the ORNL Graphite Reactor, the Low-Intensity Test Reactor (LITR), or the Oak Ridge Research Reactor (ORR). Both radiochemical-separation and nondestructive techniques were used. All analyses were completed by the comparator-sample technique. Specific determinations believed to be of particular interest are discussed separately in this report; descriptions of the radiochemical separations, if any, and of the radioactivity measurements used are included in these discussions.

Nondestructive Analysis by Means of Neutron Activation

G. W. Leddicotte, W. T. Mullins, L. C. Bate, J. F. Emery, J. E. Strain, C. E. Miller[2]

The feasibility of using neutron-activation analysis in the nondestructive determination of trace amounts of elements in various materials has been discussed previously.[3] This technique has now been used in both semiquantitative and quantitative determinations of trace amounts of chromium, antimony, scandium, cobalt, iron, sodium, and manganese in asbestos; chromium, manganese, iron, sodium, and nickel in graphite; titanium and tin in Zircaloy; rubidium, cesium, and sodium in potassium bromide and in potassium chloride; arsenic and antimony in silicon; manganese, copper, and titanium in magnesium oxide; and chlorine in hydrazine. Gamma scintillation spectrometry and decay measurements were used to complete these analyses.

Determination of Oxygen by Activation Analysis

L. C. Bate, G. W. Leddicotte

The activation-analysis method for the determination of oxygen[4] has been used to analyze samples of yttrium, yttrium chloride, and yttrium fluoride for oxygen. When a radiochemical separation is required, the sample is processed in such a way that the radioactive F^{18} (112 m) is precipitated as lead chlorofluoride, PbClF. This compound is weighed in order to determine the chemical yield and is transferred to a suitable mount for the measurement of the radioactivity. Concentrations of oxygen in the sample in the range from 10 to 10^4 μg/g have been determined by this method.

Determination of Submicrogram and Microgram Quantities of Argon by Activation Analysis

J. F. Emery, G. W. Leddicotte

Activation analysis has been used to determine submicrogram and microgram quantities of argon by means of the neutron reaction $A^{40}(n,\gamma)A^{41}$ (110 m). All analyses were made by a nondestructive method in which a gamma scintillation spectrometer is used. The method and some of the results obtained in the analysis of various gases and gaseous mixtures have been described.[5] Quantities of from 0.2 to 16.3 μg were determined in these materials. Also, concentrations of argon as small as 10 μg/g have been determined in ammonium nitrate.

Determination of Rare-Earth Elements in Geological Materials by Neutron Activation

J. W. Winchester[6]

The applicability of neutron-activation analysis in the determination of relative concentrations of

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[1] G. W. Leddicotte, "Types of Neutron Reactions," Method No. 5 10102 (2-2-56), *ORNL Master Analytical Manual;* TID-7015, sec 5.

[2] ORINS participant from Florida State University, Tallahassee.

[3] G. W. Leddicotte *et al.*, "Nondestructive Methods of Assay in Activation Analysis," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 23.

[4] L. C. Bate and G. W. Leddicotte, "Determination of Oxygen by Activation Analysis," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 30.

[5] G. W. Leddicotte *et al.*, *The Use of Neutron Activation Analysis in Analytical Chemistry*, Paper No. 927, Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, September 1–13, 1958.

[6] Summer research participant from Massachusetts Institute of Technology, Cambridge.

Table 1. Summary of Recent Quantitative Applications of Neutron-Activation Analysis

Element Determined	Induced Radionuclide	Technique[a]	Sample	Observed Concentration of Element Determined (μg/g or μg/ml)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
Al	Al^{28} (2.3 m)	ND	Titanium	1 to 10	0.1
Sb	Sb^{122} (2.8 d) or Sb^{124} (60.9 d)	RC	Germanium	10 to 10^3	0.005
			Fly ash	1 to 10	
A	A^{41} (110 m)	ND	Gases	0.3 to 0.5	0.01
			Ammonium nitrate	0.3 to 2.0	
As	As^{76} (26.4 h)	RC	Platinum aluminate	0.08 to 3.0	0.001
			Naphtha	0.002 to 1.0	
			Germanium	100	
			Animal tissue	0.03 to 10	
		ND	Naphtha	0.002 to 1.0	
			Magnesium hydroxide	0.01 to 0.1	
Br	Br^{82} (35.87 h)	ND	Naphtha	3 to 15	0.001
Cd	Cd^{115} (53 h) or Cd^{115m} (43 d)	RC	Water	0.01	0.01
			Aluminum	0.1 to 1.0	
			Indium	10 to 100	
Ce	Ce^{141} (32 d)	RC	Aluminum	0.1 to 1.0	0.05
			Americium recovery process solutions	10 to 25	
Cl	Cl^{38} (38.5 m)	RC	Santocel	1 to 10	0.05
			Oil	10 to 100	
			Water	0.1 to 10^3	
			Asbestos	10^2 to 10^3	
			Alkyl sulfonates	0.2 to 100	
			Potassium phosphate	10 to 40	
			Polyamides	1 to 10	
			Aluminum-base paints	10 to 100	
Cr	Cr^{51} (27.8 d)	RC	Aluminum	1 to 10	0.10
			Zirconium	1 to 10	

Table 1 (continued)

Element Determined	Induced Radionuclide	Technique[a]	Sample	Observed Concentration of Element Determined (μg/g or μg/ml)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
Co	Co^{60} (5.24 y) or Co^{60m} (10.47 m)	ND	Glass	1 to 10	0.05
			Stainless steel	10 to 100	
			Nickel	0.1	
Cu	Cu^{64} (12.8 h)	RC	Bismuth	10 to 30	0.001
			Titanium	50 to 100	
			Gallium	1 to 3	
			Animal tissue	0.5 to 500	
Au	Au^{198} (2.69 d)	ND	Thorium oxide	0.2 to 1.0	0.001
Hf	Hf^{181} (45 d)	RC	Potassium fluoride–zirconium fluoride	10^2 to 10^3	0.05
In	In^{116m} (53.99 m) or In^{114m} (50 d)	RC	Germanium	10 to 100	0.0001
			Gallium	10 to 100	
Fe	Fe^{59} (45.1 d)	RC	Titanium	10 to 100	2.0
			Zirconium	10 to 100	
La	La^{140} (40.22 h)	RC	Americium recovery process solutions	0.1 to 250	0.01
Mn	Mn^{56} (2.6 h)	RC	Animal tissue	0.1 to 1.0	0.0001
			Titanium	1 to 10	
		ND	Aluminum	0.1 to 1.0	
Hg	Hg^{197m} (23 h)	RC	Gallium	0.1 to 1.0	0.1
Mo	Mo^{99} (66 h)	RC	Aluminum	0.5 to 1.5	0.2
Ni	Ni^{65} (2.56 h)	RC	Glass	100	0.1
			Titanium	1 to 10	
O	F^{18} (112 m)[d]	RC	Lithium	10^1 to 10^3	1.0
			Yttrium chloride	10^1 to 10^3	
			Yttrium fluoride	10^1 to 10^3	
Pt	Pt^{197} (18 h)	RC	Gallium	3 to 30	1.0

Table 1 (continued)

Element Determined	Induced Radionuclide	Technique[a]	Sample	Observed Concentration of Element Determined (μg/g or μg/ml)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
P	P^{32} (14.3 d)	RC	Aluminum	10 to 40	0.04
			Lithium	0.4 to 1.0	
K	K^{42} (12.4 h)	RC	Animal tissue	2 to 20	0.1
Se	Se^{75} (121 d)	RC	Animal feeds	0.02 to 200	0.02
Si	Si^{31} (2.6 h)	RC	Zirconium	1 to 4	1.0
			Zirconium alloys	3 to 10	
			Titanium	3 to 10	
Na	Na^{24} (15.0 h)	RC	Gallium	13 to 270	0.007
		ND	Water	10 to 100	
Sr	Sr^{87m} (2.8 h)	RC	Animal tissue	3 to 5	0.5
			Animal feeds	0.1 to 1.0	
S	S^{35} (87.1 d) or P^{32} (14.3 d)[e]	RC	Sodium fluoride–zirconium fluoride	10 to 200	1.0
			Chromium	10 to 400	
			Hydrofluoric acid solution	8 to 230	
			Gallium arsenide	1 to 10	
			Stainless steel	1 to 10^3	
Ta	Ta^{182} (111 d)	RC or ND	Zirconium	10 to 100	0.002
			Zirconium alloys	0.3 to 100	
Th	Pa^{233} (27.4 d)[f]	RC	Zirconium	1 to 40	0.01
			Zirconium oxide	1 to 40	
			Amalgams	0.02 to 0.3	
Sn	Sn^{125} (9.5 m) or Sn^{125} (9.4 d)	RC	Gallium	0.1	0.1
		ND	Zircaloy	1.0	
Ti	Ti^{51} (5.79 m)	ND	Zircaloy	1.0	

Table 1 (continued)

Element Determined	Induced Radionuclide	Technique[a]	Sample	Observed Concentration of Element Determined (μg/g or μg/ml)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
W	W^{187} (24.0 h) or W^{185} (75.8 d)	RC	Zirconium	0.001 to 0.01	0.001
			Titanium	0.5 to 2.0	
			Zirconium alloys	2 to 240	
			Gallium	0.06 to 0.7	
U	Np^{239} (2.33 d)[g] or Ba^{140} (12.8 d)[h]	RC	Fuel elements	0.01 to 50.0	0.0001
			Thorium oxide	2 to 3	
			Zirconium oxide	0.2 to 100	
			Zirconium	1.0 to 10	
			Water	0.1 to 1.0	
Zn	Zn^{69m} (13.8 h) or Zn^{65} (245 d)	RC	Aluminum	2 to 5	0.02
			Indium	10 to 200	
			Gallium	1 to 10	
Zr	Zr^{97} (17.0 h) or Zr^{95} (65 d)	RC	Aluminum	10 to 20	0.2
			Titanium	10 to 100	

[a]ND = nondestructive assay; RC = radiochemical separations.

[b]The number of determinations varied; therefore a range is given for the element concentration. Also, observed concentrations for naphthas, water, and similar liquid samples are expressed as micrograms per milliliter.

[c]Based on the conditions of irradiation and method of analysis used. This value will vary with the duration of the irradiation, neutron flux, the method of processing the sample after irradiation, and the efficiency of the counter used in the measurement of radioactivity.

[d]Produced by the reactions (1) $Li^6(n,\alpha)H^3$ and (2) $O^{16}(H^3,n)F^{18}$.

[e]Produced by the reaction $S^{32}(n,p)P^{32}$.

[f]Produced by the reaction $Th^{232}(n,\gamma)Th^{233} \xrightarrow[(23.5\ m)]{\beta^-,\gamma} Pa^{233}$.

[g]Produced by the reaction $U^{238}(n,\gamma)U^{239} \xrightarrow[(23.4\ m)]{\beta^-,\gamma} Np^{239}$.

[h]Produced by the reaction $U^{235}(n,f)$ fission products, i.e., Ba^{140}, etc.

rare-earth elements in geological materials has been investigated. Chemical separations and radioactivity measurements in which gamma spectrometry and radioactive decay are used have been studied. The preliminary results of this investigation have been reported.[7]

Determination of Trace Quantities of Elements in Water

R. L. Blanchard[8] G. W. Leddicotte

Neutron-activation-analysis techniques, similar to those used in most trace-element analyses, have been applied to the determination of trace quantities of elements in water from various natural sources. Elements such as calcium, chlorine, copper, magnesium, phosphorus, potassium, silicon, sodium, strontium, and zinc, all of which are usually determined in a conventional water analysis, were determined. Those elements that have not been determined previously by conventional water-analysis methods are listed in Table 2.

Use of Activation Analysis in Reactor Technology

G. W. Leddicotte J. F. Emery
W. T. Mullins

Neutron-activation analysis was used in studies of fuel elements, structural materials, and cooling water for reactors. Both nondestructive and radiochemical techniques were used, and the radioactivity measurements were made by means of gamma scintillation spectrometry. Information pertinent to these studies is given below.

U^{235} and U^{238} in High-Temperature Reactor Materials. – The neutron-activation determination of the isotopic concentration ratio, U^{235}/U^{238}, which was described earlier,[9] is now being used in an investigation of the contamination of aluminum-clad fuel plates with uranium. The contamination may be caused either by diffusion of the uranium through the plates or by contact of the plates with uranium during the fabrication process. Uranium present in aluminum in concentrations as small as 0.1 $\mu g/g$ is being determined by activation analysis; the determination is based on the reaction

$$U^{238}(n,\gamma)U^{239} \xrightarrow[2.34\ m]{\beta^-,\ \gamma} Np^{239}$$

or $U^{235}(n,f)Ba^{140}$.

Analysis of Materials for the Construction of Reactors. – Typical results are given in Table 3 that were obtained in the analysis of materials to be used either in the construction of a reactor or near a reactor. Qualitative analyses, as well as quantitative determinations of submicrogram and microgram amounts of many elements, have been

[7] J. W. Winchester, *A Preliminary Investigation of a Chromatographic Column Separation of Rare Earths Using Di(2-ethylhexyl) Phosphoric Acid*, ORNL CF-58-12-43 (to be published).

[8] U.S. Public Health Service trainee, assigned to ORNL Analytical Chemistry Division.

[9] G. W. Leddicotte, "Use of Activation Analysis in the Isotopic Analysis of Uranium," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 29.

Table 2. Elements Determined in Water by Activation Analysis

Source of Sample	Element Determined* (ppm)							
	Sb	As	Ba	Br	I	Mn	Rb	Th
Chicago, Ill.	0.030	<0.00002	0.010	0.32	0.027	0.0004	0.20	<0.001
Oak Ridge, Tenn.	0.030	0.00002	0.021	0.18	0.002	0.0014	<0.20	0.021
Cincinnati, Ohio	0.016	<0.00002	<0.005	0.12	0.027	0.0026	<0.20	<0.001
Denver, Colo.	0.023	<0.00002	<0.005	0.18	0.007	0.0098	<0.20	<0.001
New York, N.Y.	0.040	<0.00002	0.006	0.07	0.004	0.0049	<0.20	<0.001
Atlanta, Ga.	0.057	<0.00002	0.005	0.17	0.027	0.0028	<0.20	<0.001
Charlottesville, Va.	0.044	<0.00002	<0.005	0.05	0.018	0.040	<0.20	<0.001

*The presence of argon in each of the samples was indicated by qualitative analysis.

Table 3. Results of Analysis of Certain Materials for the Construction of Reactors

Material	Induced Radioactivities Observed	Elements Determined by Neutron-Activation Analysis	
		Element	Concentration (ppm)
Asbestos	Sc^{46} (83.9 d)	Sc	1 to 25
	Co^{60} (5.24 y)	Co	10 to 20
	Cr^{51} (27.8 d)	Cr	Present
	Fe^{59} (45.1 d)	Fe	Present
	Sb^{124} (60 d)	Sb	Present
	Mn^{56} (2.576 h)	Mn	Present
	Na^{24} (15.06 h)	Na	Present
Graphite	Fe^{59} (45.1 d)	Fe	<10
	V^{52} (3.76 m)	V	<5
	Sb^{124} (60 d)	Sb	Present
	Na^{24} (15.06 h)	Na	Present
Santocel	Cl^{38} (38.5 m)	Cl	1 to 10
Aluminum paint	Cl^{38} (38.5 m)	Cl	10 to 100
Alkyl sulfonates	Cl^{38} (38.5 m)	Cl	0.2 to 100

made either by nondestructive or destructive activation analysis methods. Some of these results have been reported.[10]

Analysis of Water from Cooling-Water Supply of the ORR. – The results of a typical analysis of the water from the cooling-water system of the ORR are summarized in Table 4. Both the radioactivity originally present in the water and the radioactivity induced during activation analysis were used to obtain the results. The radionuclides present were identified by means of gamma spectrometry and radioactive decay measurements, whereas the concentrations of the elements of interest were determined by the usual activation-analysis, comparator-sample techniques.

Nuclear Methods of Chemical Analyses

G. W. Leddicotte

A general program to investigate the possible use of any nuclear phenomenon in a chemical analysis was recently begun in the Analytical Chemistry Division. Preliminary investigations are now being made of the use of short-half-life (10 s to 30 m) radionuclides (see "Use of Short-Half-Life Radionuclides in Activation Analysis," this report) in activation analysis. In addition, neutron-absorption and neutron-resonance methods are being studied. Other nuclear phenomena will be considered as this program is continued.

Use of Short-Half-Life Radionuclides in Activation Analysis

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J. E. Strain
W. T. Mullins
C. E. Miller

A preliminary investigation has been made of the feasibility of the use of short-halt-life (10 s to 30 m) radionuclides in activation analysis. The isotopes investigated thus far are listed in Table 5.

[10] G. W. Leddicotte and W. S. Lyon, *Special Radiochemical Analysis in the Operation of ORNL Reactors*, a paper presented at the Second Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tennessee, Sept. 29–Oct. 1, 1958.

Table 4. Results of Analysis of Water from Cooling-Water System of ORR

Radionuclides Identified by Analysis of Radioactivity		Elements Determined Quantitatively by Neutron-Activation Analysis	
Radionuclide	Source Nuclide	Element	Concentration (μg/ml)
Na^{24} (15.06 h)	Na^{23}	Cd	0.03
Cu^{64} (12.80 h)	Cu^{63}	U^{238}	0.0017
Mn^{56} (2.576 h)	Mn^{55}	U^{235}	4.1
A^{41} (110 m)	A^{40}	Al	0.03
K^{42} (12.44 h)	K^{41}		
F^{18} (112 m)	O^{18}		
Xe^{133} (5.270 d)	U^{235}		
Xe^{135} (9.2 h)	U^{235}		
Kr^{85m} (4.4 h)	U^{235}		
I^{133} (20.8 h)	U^{235}		
I^{134} (52.5 m)	U^{235}		
Cd^{115} (53 h)	Cd^{114}		
Te^{132} (77 h)	U^{235}		

Table 5. Short-Half-Life Radionuclides Considered for Use in Activation Analysis

Radionuclide	$t_{1/2}$ (m)	Gamma Energy (Mev)	Limit of Measurement (μg)
Co^{60m}	10.47	0.059	2.0
Rh^{104m}	4.4	0.053	0.1
Pd^{109m}	4.75	0.19	10.0
Pt^{199}	31	0.070	100.0
Cu^{66}	5.10	1.04	5.0
Sn^{125}	9.5	0.15, 0.32	10.0
Ti^{51}	5.79	0.32	2.0
Al^{28}	2.27	1.78	1.0

In all cases samples of reagent-grade materials were irradiated in the pneumatic tube of the Graphite Reactor for 1 min. The gamma spectra of the samples were taken immediately by means of a Radiation Counter Laboratories (RCL) 256-channel anolyzer having a 3 × 3 in. crystal of thallium-activated sodium iodide and a 1.333-mg/cm^2 Lucite absorber. The spectra were observed first on a 0- to 2-Mev gain, then on a 0- to 0.5-Mev gain, and finally on a 0- to 0.02-Mev gain; the observations were continued until the first significant photopeaks having sufficient intensity to characterize the sample appeared. The visual display on the RCL instrument was used for these observations. Decay measurements were made on the most intense photopeaks in order to further characterize the spectrum.

The sensitivities tabulated in Table 5 are based on the assumption that with a background of 0.2 count/sec in 10 channels the instrument can

characterize the gamma radiation from an isotope having a photopeak area of 5 counts/sec in 10 channels in the pure spectrum.

In the Rh^{104m} spectrum (Fig. 1), a 0.097-Mev gamma ray was found which seems to belong to Rh^{104m}; measurements at a geometry of 9.3 cm are shown in Fig. 1. Decay measurements were made on the spectrum, and the ratio of the 0.053- to 0.097-Mev peaks remained constant. Measurements were also made at geometries of 14.3 and 5 cm; for these measurements the ratio of the 0.053- to the 0.097-Mev peak also remained constant. Since this gamma ray has not been reported in the literature, further work will be done to characterize this spectrum.

Radioactivity Measurements

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Comparison of Beta with Gamma Counting for the Measurement of 2.56-h Ni^{65}. A comparison was made of the relative errors of gross gamma counting, discriminatory gamma counting, and beta counting for the measurement of 2.56-h Ni^{65}. The data reported[11] indicate that gross gamma and beta counting has some merit and that discriminatory gamma counting is not practical for Ni^{65}.

[11] C. E. Miller, *Comparison of Beta with Gamma Counting for the Measurement of 2.56-h Ni-65*, ORNL CF-58-12-26 (Dec. 10, 1958).

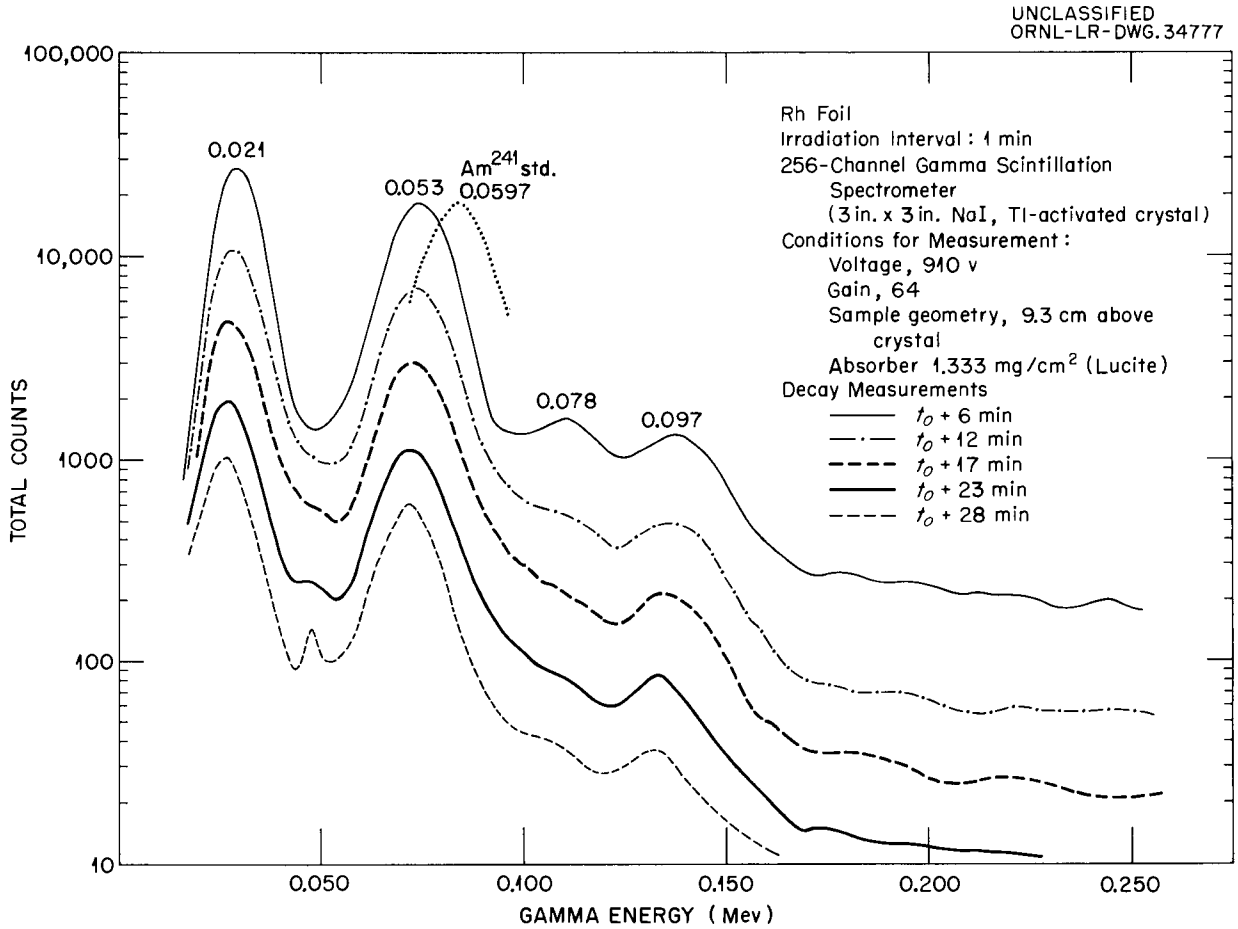

Fig. 1. Gamma Spectrum of Rh^{104m} (4.4 m).

Crystal Discrimination in Gamma Spectrometry. – A study of the use of thallium-activated sodium iodide scintillation crystals of various sizes (4 × 4 in., 1.5 × 1.0 in., and 1.5 × 0.09 in.) is now being made. Preliminary results with the experimental counting apparatus indicate that crystal discrimination will resolve low-energy gamma rays in complex gamma spectra. In effect, low-energy gammas, when observed by means of a thick crystal, are almost completely hidden by the Compton scattering that results from high-energy gammas in the spectrum, whereas the thin crystal has a high efficiency for the detection of low-energy gammas. A formal report of this work will be made when it is completed.

Measurements of Reactor Neutron Spectra

G. W. Leddicotte W. T. Mullins

The Activation Analyses Group is now assisting in the monitoring of the neutron spectra of the irradiation facilities used for experimental purposes. Determinations of both thermal- and fast-neutron flux are made by the use of activation detectors or threshold monitors. Those nuclear reactions that are or can be used in this work are listed below.

Nuclear Reaction	Neutron Energy Measured (kev)
$Mn^{55}(n,\gamma)Mn^{56}$	Thermal
$Co^{59}(n,\gamma)Co^{60}$	Thermal
Np^{237}(fission)	600
U^{238}(fission)	1300
Th^{232}(fission)	2000
$P^{31}(n,p)Si^{31}$	2400
$S^{32}(n,p)P^{32}$	2900
$Al^{27}(n,p)Mg^{27}$	4600
$Si^{28}(n,p)Al^{28}$	5500
$Mg^{24}(n,p)Na^{24}$	6300
$Al^{27}(n,\alpha)Na^{24}$	8100

All the analyses except those involving the fission reactions are completed by nondestructive measurements of the radioactivity. In the instance of the fission reactions, Ba^{140} (12.8 d) is determined by a radiochemical separation. The measurements of the radioactivity are usually completed by gamma counting. Typical results obtained in the determination of the fast-neutron spectrum in hole 10 of the ORNL Graphite Reactor are given in Fig. 2. The results obtained for the $S^{32}(n,p)P^{32}$ reaction are inconsistent with the rest of the data, and additional work is being done to determine possible error sources.

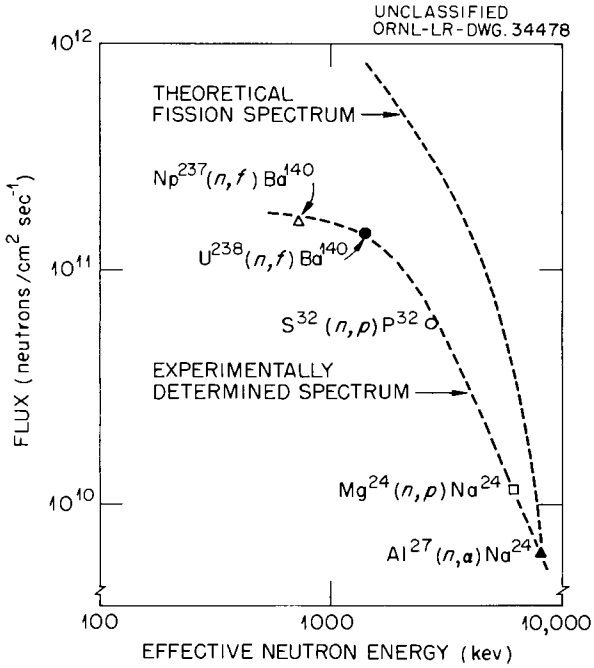

Fig. 2. Fast-Neutron Spectrum of Hole 10 of the ORNL Graphite Reactor.

Neutron Absorption Cross Sections

J. H. Oliver

Assistance was given to the Chemistry Division in its work on the chemistry of the heavier elements. The work on the neutron absorption cross sections of Pu^{240} and U^{233} was of particular interest. The method and the results of the analyses performed in determining the absorption cross section of Pu^{240} will be reported.[12] New information was obtained on the neutron absorption cross sections of Ru^{99} and Ru^{100}.

[12] J. Halperin, J. H. Oliver, and H. S. Pomerance, "The Thermal Neutron Absorption Cross Section of Pu-240," to be published in *J. Inorg. & Nuclear Chem.*

Use of Chemical Dosimeters in Gamma Monitoring

L. C. Bate W. J. Hampton
G. W. Leddicotte

Analytical assistance is now being given in the monitoring and the calibrating of high-level gamma radiation from Co^{60} (5.24 y) sources or nuclear reactors. High-level gamma radiation sources of intensity in the range from 10^3 to 10^7 r/hr have been analyzed by means of chemical dosimeters. The techniques used are described elsewhere.[13]

Particle-Size-Distribution Analysis

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W. J. Hampton G. W. Leddicotte

The previously described methods[14–16] of particle-size-distribution analysis continue to be used in the analysis of thorium oxide, uranium oxide–thorium oxide mixtures, and similar materials. The methods have now been complemented by two additional methods of particle-size-distribution analysis, which were developed for the rapid analysis of pilot-plant-produced thorium oxide but which have also been used for analyzing uranium dioxide–thorium oxide mixtures.

In one method, the "clinker" test,[17] the natural radioactivity of the various oxides is measured and is used to determine the concentration of particles of 10.0-μ diameter or larger. The other method, a modified pipet method, is used for quality control analyses in the pilot-plant laboratories and consists in the pipetting of a known volume of the oxide slurry from a settling tube at various time intervals. The natural radioactivity of the oxides is used to determine the concentrations of the particles of various sizes. A comparison of typical results obtained for thorium oxide by this method with those obtained by the activation analysis–sedimentation method[14] is given in Fig. 3. This method is described elsewhere.[18]

In addition to this work the techniques employed in the determination of particle-size distributions in multicomponent systems by activation analysis[16] have been used to determine the particle-size distribution of hot or irradiated particles originating either as radioactive corrosion products from a reactor or as samples from reactor experiments on blanket media. Some of the results obtained in analyses of this type have been reported.[19]

Other work pertinent to particle-size-distribution analysis of thorium oxide consisted in the evaluation of (1) a physical method of analysis in which electronic sizing[20] is used and (2) dispersant

[13] L. C. Bate, W. J. Hampton, and G. W. Leddicotte, *The Monitoring of Gamma Sources with Ceric Sulphate Dosimeters*, ORNL CF-58-12-47 (to be published).

[14] G. W. Leddicotte and H. H. Miller, *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 21–23 (classified).

[15] L. C. Bate and G. W. Leddicotte, *Determination of Submicron Particle Sizes by an Activation Analysis–Centrifugation Method*, ORNL CF-57-1-116 (Jan. 29, 1957).

[16] L. C. Bate and G. W. Leddicotte, "Determination of Particle-Size Distributions in Multiple-Component Systems by Activation Analysis," *Anal. Chem. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 33–35.

[17] L. C. Bate, W. J. Hampton, and G. W. Leddicotte, *The "Clinker" Test in the Particle Size Distribution Analysis of Thorium Oxide*, ORNL CF-58-12-45 (to be published).

[18] L. C. Bate and G. W. Leddicotte, *A Production Control Method for Determining the Particle Size Distribution of Thorium Oxide and Thorium Oxalate*, ORNL CF-58-12-44 (to be published).

[19] G. W. Leddicotte and W. S. Lyon, *Special Radiochemical Analysis in the Operation of ORNL Reactors*, a paper presented at the Second Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tennessee, Sept. 29–Oct. 1, 1958.

[20] R. H. Berg, L. C. Bate, and G. W. Leddicotte, *Particle-Size Distribution of ThO_2 by Electronic Sizing*, a paper presented at the Second Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tennessee, Sept. 29–Oct. 1, 1958.

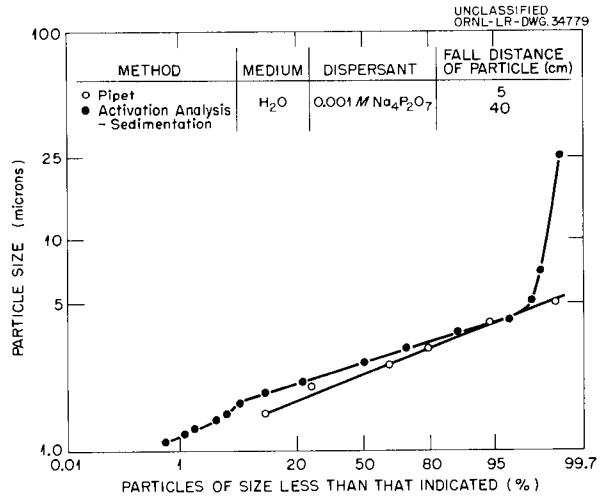

Fig. 3. Comparison of Rapid-Pipet Method with the Activation Analysis–Sedimentation Method for Particle-Size Distribution of Thorium Oxide.

agents that can be used in particle-size analysis. From the results of this latter study it was possible to recommend a method for preparing low-porosity thorium oxide.[21]

ANALYTICAL INSTRUMENTATION (X-10)

D. J. Fisher

In-Line Instrumentation Program at ORNL

M. J. Kelly[22] T. S. Mackey[23]
J. W. Landry[23] R. W. Stelzner

A schedule for the construction and plant installation of the following instruments, based upon their present developmental status, has been set with a top priority for FY-59:

1. gamma monitors for gross and specific gamma activity,
2. alpha monitor for plutonium loss,
3. a-c polarograph for uranium loss,
4. radio-frequency monitor for nitric acid concentration in a Darex process stream,
5. gamma absorptiometer for uranium concentration,
6. colorimeter for organic process streams.

Other radiochemical-process-control equipment that is scheduled for construction with less priority includes:

1. interface-level controller for organic continuous column,
2. flow-rate meter,
3. air-lift metering pump.

Gamma Monitors. – Two plant-type, in-line gamma spectrometers have been constructed for the continuous recording of gross and specific gamma emissions from flowing streams. Fluorothene sampling cells with highly polished interior surfaces are used. One of the instruments, patterned after a Hanford model, is designed so that the flowing stream will fill the cell; it will be installed in the Head-End Aqueous Product (HAP) stream in Building 3019. The other instrument is designed in such a way that the flowing stream will fall through the cell without contacting the cell surface; it will be installed in the IAP stream in the Metal Recovery Plant. These instruments will measure zirconium-niobium, gross, and ruthenium gamma activities in the product streams.

Provision for testing two methods of scanning the gamma spectrum of the flowing stream has been incorporated in the design of the gamma spectrometers. In the first, a 50-kilohm, 10-turn Helipot drives a pulse-height-selection circuit through the required 100-v span; in the second, a computer-type integrating circuit that uses parallel R-C feedback and a constant-current input drives the pulse-height-selection circuit from $+(100 + e)$ v to $+e$ v, where e is the positive pulse-height zero-set voltage. A synchronous motor-driven timer closes a microswitch at the end of the 100-v drop in potential and thereby automatically resets the circuit for another gamma scan.

Electronic equipment for the gamma monitors includes an ORNL model Q-1840A scintillation-detector head that contains a built-in cathode-follower preamplifier, an Atomic Instrument Co. model 312 high-voltage power supply, an ORNL model Q-1593 DD2 linear amplifier, an ORNL model Q-1454 logarithmic count-rate meter, and a standard 10-mv Brown strip-chart recorder.

Alpha Monitor. – An alpha monitor for the continuous recording of the rate of alpha emission from the surface of a quiescent stream by means of a scintillator (a silver-activated zinc sulfide phosphor) mounted on the end of an RCA 6655 multiplier phototube has been laboratory tested. The phosphor is embedded in the first few millimeters of a Lucite disk ($\frac{1}{8}$ in. thick, 2 in. in diameter). The disk is located a few millimeters above the surface of the slowly moving stream and is protected from chemical contamination and chemical attack by a covering of $\frac{1}{4}$-mil-thick Teflon. The plant-type cell, fabricated of stainless steel, ensures a quiescent surface by control of the liquid flow rate at a low value by the use of a weir and a constant-head reservoir. Plant testing for plutonium monitoring is scheduled for the IAW or IIAW streams; these streams contain only a very small amount of americium and neptunium alpha activity.

A second technique for alpha counting of raffinate streams consists in floating a thin layer of a liquid scintillant (5 g of *p*-terphenyl dissolved in 1 liter of phenylcyclohexane) on the slowly moving stream. An RCA 6655 multiplier phototube is mounted with its end window immersed in the organic phase.

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[21] L. C. Bate and G. W. Leddicotte, *Preparation of Low Porosity Thorium Oxide*, ORNL CF-58-12-46 (to be published).

[22] Instrumentation and Controls Division.

[23] Chemical Technology Division.

Transfer of activity from the aqueous phase to the organic phase is not a problem if the aqueous stream carries no entrained or dissolved organic liquid. A stainless steel cell for a plant-type instrument is being fabricated for evaluation in the Metal Recovery Plant.

A-C Polarograph. – Polarographic analysis has been selected for the continuous recording of uranium concentration in the DW raffinate stream of the Metal Recovery Plant. This is an aqueous stream having a usual uranium concentration of the order of parts per million and an alarm point, indicating excessive loss of uranium, of 320 ppm.

The a-c polarographic circuit has been revised to incorporate a controlled-potential three-electrode system. Both automatic cancellation of the voltage drop across a high-valued measuring resistance and electrical phase discrimination have been retained in the circuit design. Membrane polarography of a flowing stream has received no further study.

Radio-Frequency Monitor. – A radio-frequency monitor based upon a 250-Mc parallel-transmission-line oscillator is to be installed in the Metal Recovery Plant on a stream whose nitric acid and uranium concentrations are 2 *M* and 1.35 ± 0.10 *M*, respectively. The temperature of the stream is constant; thus the need for a heat exchanger in the loop is eliminated. The stream is highly radioactive, but a side stream can be pulled from the cell into the accessible area of the sample gallery. Tests on Metal Recovery solutions in a prototype test loop are continuing.

Gamma Absorptiometer. – A gamma absorptiometer, patterned closely after those in successful operation at Hanford, is being constructed for monitoring uranium in the Darex processing plant. An Am^{241} source of gamma rays, a cell constructed of fluorothene, a thin crystal of sodium iodide, and a photomultiplier detector constitute the unit. A chopper technique will be used to minimize electrical drift and unwanted gamma emission from the stream itself.

Colorimeter for Organic Process Streams. – A colorimeter that will record continuously the uranium concentration in organic process streams is being fabricated. An earlier model, which was tested in the Metal Recovery Plant, operated on aqueous streams only. The present model differs by having a channel that subtracts any contribution of the color of the solvent. Use of the instrument necessitates the installation of sampling lines from both the IAP and IAX streams of the Metal Recovery Process.

Interface-Level Controller. – An interface-level controller of the electrical conductivity type has been built for installation in an organic continuous column. The instrument will operate in the presence of an emulsion if continuous organic and continuous aqueous phases are present also. The controller indicates the presence of the emulsion phase.

The critically safe 8-in.-dia Head-End Aqueous (HA) columns of the Metal Recovery Plant will be provided with this type of controller when they are installed; should it fail, a float-type controller with differential transformer output will be installed as a replacement.

Flow-Rate Meter. – A prototype flow-rate meter that is based upon the measurement of the velocity of an introduced air bubble has been successfully demonstrated by the use of three different methods of detection: photoelectric, sonic, and electrical conductivity. This type of flow-rate meter is suited for the accurate measurement of low flow rates of highly radioactive solutions. Sonic detection can be used in a stainless steel system.

Air-Lift Metering Pump. – A flow-rate meter that is based upon the weighing of a fixed volume of liquid into which a known volume of air has been introduced at a known rate has been demonstrated in bench tests. This meter, combined with an air lift and pneumatic controller, is being developed into an air-lift metering pump.

Automatic, Electronic, Controlled-Potential Coulometric Titrator

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

The controlled-potential coulometric titrator[24] has been redesigned. One modified Philbrick USA-3, printed-circuit, operational amplifier has been used as a difference amplifier to replace both the solution-potential and the cathode-potential control amplifiers. This USA-3 amplifier drives a power transistor which controls the electrolysis current. The electrolysis current is supplied by a 55-v, d-c, silicon-diode voltage-doubler power supply. Provision is now made for reversing the

[24] M. T. Kelley and H. C. Jones, "Simplified Controlled-Potential Coulometric Titrators," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 14.

cell current in order also to perform oxidation titrations at a controlled potential. The transistor circuit has the advantage of simplicity, compactness, and low heat dissipation as compared with the thermionic tubes used in the previous instruments. A USA-3 amplifier has also been used as an integrating amplifier to replace the Philbrick K2-X and K2-P combination used in the previous instruments. All batteries have been eliminated in this instrument. The control-potential source is now a Zener(silicon, voltage-reference)-diode-regulated power supply which uses a silicon diode as a rectifier. Input biasing for the integrating amplifier is supplied by means of the Philbrick R-100A regulated power supply. The elimination of batteries makes this a completely a-c line-operated instrument.

Another feature of this instrument is overload protection for the current meter, with an optional provision for automatic cutoff. The cell-current meter, which is a 1-ma meter-relay, is shunted on four of its ranges by a silicon diode. The major portion of the cell current is carried by the diode until the current falls to a value such that the potential drop across the meter-relay and a series resistor is not sufficient to maintain forward conduction by the diode. At and below this point the meter-relay carries essentially all the cell current. This point is the full-scale value for each of three of the four linear current ranges and is an intermediate value for the fifth range, which is a "log current" range. When the current decreases sufficiently, the preset contacts of the meter-relay close, thereby actuating a relay which opens the cell circuit and thus terminates the integration process. Cell currents many times greater than the full-scale meter value cannot damage the meter. The meter also has calibrated ranges, with meter protection, when the automatic cutoff feature is not used.

A prototype of this instrument, which has the "log current" range but does not have the calibrated current meter ranges, is now in satisfactory operation. At the present time five of these instruments are being fabricated by the Instrument Department as model Q-2005.

A paper that describes this instrument in greater detail has been submitted to *Analytical Chemistry* for publication.

Improvements to the ORNL Model Q-1728, Velocity-Servo, Automatic, Potentiometric Titrator

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

The 6BN6 vacuum-tube gating circuit of the ORNL model Q-1728, velocity-servo, automatic, potentiometric titrator has been replaced by a transistor gating circuit. Readjustment of the original 6BN6 gate, which was required because of the instability of the type 6BN6 tube, was the most frequent service required for the titrator. An NPN switching transistor is driven by the cathode current through one-half of the multivibrator. A PNP transistor, driven by the NPN transistor, intermittently shorts to ground the output of a cathode-follower amplifier that carries the signal balancing the recorder pen. The output of the cathode follower is amplified by a grounded-grid amplifier and is returned to the recorder amplifier. This circuit is superior in performance to the original circuit because it is more stable and requires much less frequent adjustment. Three of these titrators have been modified and are in use. The first of the modified titrators has been in continuous duty for four months with no need for adjustment of the transistorized gate. The three 1.5-v batteries used for the Brown recorder in the titrator have been replaced by a 4.5-v Zener-diode-regulated power supply that uses a silicon diode as a rectifier. The elimination of these batteries makes this a completely a-c line-operated instrument. The maintenance manual and the Q-1728 series drawings for the titrator have been revised to incorporate these modifications.

Radio-Frequency Titrator

R. W. Stelzner

A radio-frequency titrator that operates at a frequency of 190 Mc was designed and constructed for the HRP Laboratory of the Analytical Chemistry Division. The design is based on a parallel-transmission-line oscillator that uses a type 955 vacuum tube in a simple triode circuit.[25] The transmission

[25] R. W. Stelzner and M. T. Kelley, *Radio-Frequency Oscillators for the Determination of Alkali*, ORNL-1742 (June 9, 1955).

lines are 8-in.-long sections of 0.5-in.-dia copper tubing spaced 1.5 in. between centers. The calculated Q of this circuit is approximately 4000. A holder for the titration vessel is placed between the parallel transmission lines and near the shorted end of the lines. A B+ voltage of approximately 150 v is applied to the circuit from an Oregon power supply. The grid current of the class C self-excited oscillator is measured as an empirical measure of concentration.

The instrument has been used in the development of analytical titration methods for thorium in which either disodium ethylenediaminetetraacetate or oxalic acid is the titrant. A double break is present in the titration curve for thorium when oxalic acid is the titrant.[26]

Controlled-Potential and Derivative Polarograph

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

The original prototype of the controlled-potential and derivative polarograph has been described.[27,28] Two additional polarographs, designated ORNL model Q-1988, are being fabricated by the Instrument Department of the Instrumentation and Controls Division.

The model Q-1988 polarograph will have a mechanical polarizing scan assembly in which motors, clutches, potentiometers, and mounting hangers of improved quality will be used. An electronic-scan and linear-compensator circuit has been designed for the prototype polarograph that does not use motor-driven potentiometers. It employs an operational amplifier to integrate a constant current and another amplifier as a voltage follower. Two electronic scan rates are available, 0.1 and 18 v/min. It has been found that GAP/R K2-X amplifiers are satisfactory for these applications. The following design improvements, which have been made to and tested in the original prototype polarograph, will be incorporated in the model Q-1988 polarographs. For both the potential-control and the current amplifiers, the combination of a K2-X and a K2-P operational amplifier has been replaced by a USA-3, printed-circuit, stabilized operational amplifier. The manufacturer has improved the model R-100 power supply, and the newer model R-100A will be used. The batteries originally used for initial-potential, span-potential, linear-compensator, and zero-set-potential sources have all been replaced by a-c line-operated, silicon-diode-rectified, Zener-diode-regulated potential sources. In order to prevent transient pulses of very short duration, such as switching transients, from being seen by the peak follower, an R-C filter network having a time constant of 0.03 sec has been inserted at the input to the cathode of the diode. It was found that the transients existing at the time of fall of a mercury drop caused some ringing of the derivative amplifier. The ringing was eliminated by the insertion of an R-C filter network having a time constant of 0.3 sec at the input terminal of the voltage-follower, operational amplifier in the parallel-T, R-C filter section. If neither the peak follower nor the parallel-T filter is in use, then zero-damped polarograms can be recorded since both of these added R-C networks are switched out of the signal bus. In the original design of the analog type of derivative computer, the feedback impedance in the operational amplifier was a resistor and the input impedance was a capacitor. This circuit tends to preferentially amplify the derivatives of the noise components of the signal because the relation between the output and the input voltages contains a frequency term. In order to minimize the derivative output that was due to a small 60-cps input arising from stray pickup, a parallel-T, R-C filter was used as a passive, 60-cps-rejection, coupling network to the derivative circuit. This filter is no longer required in the redesigned analog type of derivative computer; instead, the feedback impedance of the operational amplifier is a parallel-connected capacitor and resistor, and the input impedance is a series-connected capacitor and resistor. The relative time-constant values are chosen so that the computer will take the time derivative of low-frequency signals, such as the polarographic wave, but not the derivative of input-signal components of higher frequencies. For example, the 60-cps derivative output is less than the 60-cps input.

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[26] D. L. Manning, private communication to R. W. Stelzner, Sept. 1958.

[27] M. T. Kelley, H. C. Jones, and D. J. Fisher, "Controlled-Potential and Derivative Polarograph," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 17–18.

[28] M. T. Kelley, H. C. Jones, and D. J. Fisher, "Controlled-Potential and Derivative Polarograph," paper presented at 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 7–12, 1958 (to be published in *Anal. Chem.*).

Although it is not yet possible to make the derivative circuit completely attenuate D.M.E. drop frequencies while it takes an accurate derivative of the polarographic wave itself, a very considerable gain in signal-to-noise ratio has been achieved by this modification to the derivative-taking circuitry. Derivatives of the reduction waves of cadmium at concentrations of 10^{-6} *M* are significantly improved in form over those obtained with the original simple derivative-computer circuit.

Investigation of High-Sensitivity Polarography

W. D. Cooke[29] D. J. Fisher
M. T. Kelley

The variables that determine the useful sensitivity limit of polarography are being investigated. The study includes evaluations of the performance of the controlled-potential and derivative polarograph, as well as measurements of the nature and reproducibility of the electrochemical phenomena in the polarographic cell.

Fabrication and Design of Specialized Equipment for the Analysis of Radioactive Samples

H. C. Jones

Cell Caps and Positioning Block for Controlled-Potential Coulometric Titrators. – Cell caps of various designs have been constructed both for bench-top and for remotely controlled use with the controlled-potential coulometric titrators. The caps are made of Teflon, and each contains holes for a glass stirring rod, a reference electrode, an isolated working electrode, and a gas-inlet tube, and an opening through which the sample solution is introduced. Some of the caps have a 0.5-in.-deep circular groove on the lower side for insertion of the upper portion of the cell to assist in maintaining a blanket of inert gas over the solution.

For titrations by remote control a Lucite positioning block was made to hold the cell in position against the cell cap. A leveling-bulb-support clamp was used to hold the positioning block on a ring stand. A groove was cut lengthwise in one side of the ring-stand support. A set screw, located in the clamp and mated with the groove, allows the positioning block to be moved vertically by means of a master-slave manipulator without loss of its position beneath the cell cap. The positioning block is slotted in one side for the insertion of the cell and has a recessed top to hold the cell in position.

Sample Bottle and Capper for Surface-Area-Measuring Apparatus. – A sample bottle and a capper were designed and constructed for proposed use in remotely manipulated surface-area-measuring apparatus. The sample bottle is square in cross section and has a round top and a screw-type cap. The cap is sealed to the bottle by means of a gasket of sheet cadmium in order to retain a good vacuum seal at the extreme temperatures reached during the surface-area measurement. The sample bottle and cap are machined from brass stock. The sample-bottle cap is to be connected permanently to the vacuum system. The bottle that contains the sample is held in a spring-loaded adapter, which is mounted in a power-driven chuck. The chuck is pivoted to allow the bottle to be brought directly under the bottle cap. The adapter presses the bottle into the cap as the bottle is rotated by the chuck. The current drawn by the chuck motor is an indication of the torque necessary to seal the cap.

Oscillographic Chronopotentiometry

W. L. Maddox

A study of the chronopotentiometric method of analysis in which a cathode-ray oscilloscope is used for the observation of the potential-vs-time curves has been initiated. Constant current for the electrolysis is provided by a pentode power supply, which is a modification of that used by Schram[30] in an earlier investigation at ORNL. A DuMont model 401R oscilloscope has been received and tested. Preliminary findings indicate that the internal calibration signal of the scope provides a simple and practical means of measuring transition times of approximately 1 sec. These short times are expected to minimize errors from convection, which may occur during prolonged electrolysis. The potential-vs-time curves are recorded photographically with a time-base obtained from double exposure of the calibrating pattern over the signal trace.

[29] Research participant from Cornell University, Ithaca, N. Y.

[30] A. F. Schram, "Investigation of the Chronopotentiometric Method of Analysis," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 6.

Ratio Readout Recorder for the Spectrographic Determination of Oxygen in Metals

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

A readout instrument is being designed and fabricated for use in a spectrographic method for the determination of the amount of oxygen in certain metals. The purpose of this instrument is to continuously present on a potentiometric chart recorder the ratio of either the instantaneous or the integrated intensity of an oxygen emission line to that of an argon emission line. These two light beams from a spectrograph will be chopped, each at a different frequency, and the chopped beams will be optically directed onto a single multiplier phototube. The two signals will be electronically separated from the composite signal of the multiplier-phototube transducer, then rectified and either amplified linearily or integrated by operational amplifiers. The resulting voltages will be divided by the position servo of a potentiometric recorder so that the required information will be continuously presented on the recorder chart.

High-Resolution, High-Sensitivity, Scanning, Recording Flame Spectrophotometer

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

A new single-beam flame spectrophotometer is being designed and will be fabricated. The following components have been ordered for this work: Beckman oxygen-hydrogen flame source; Jarrell-Ash Ebert scanning spectrometer (catalog No. 82,000); types RCA 1P28, RCA 6217, and DuMont 6911 multiplier phototubes; Fluke model 404M d-c power supply; GAP/R model R-100A power supply; GAP/R models USA-3 and K2-X operational amplifiers; and a 10-mv Brown recorder. The spectrometer will scan at various selected rates from 2 to 500 Å/min from 2700 to 8700 Å in the first order and can be used manually down to 2000 Å. It has a linear reciprocal dispersion of 16 Å/mm, an aperture ratio of F/6.2, and a resolution of at least 0.2 Å in the first order. Slit widths of both 25 and 50 μ are provided. It is planned to chop the emission beam from the flame source in order to eliminate the effects of variable multiplier-phototube dark current, which is particularly troublesome with infrared-sensitive tubes. Because of the maximum use of unaltered commercial components, the fabrication cost of this instrument should be a relatively small percentage of the cost of the materials.

HRP LABORATORY (Y-12)

O. Menis H. P. House

Flame Photometric Determination of Silver

T. C. Rains I. B. Rubin

A procedure was devised for the flame photometric determination of microgram quantities of silver in solutions of uranyl sulfate. No separation is required when the uranium/silver weight ratio does not exceed 1000; the interference of uranium can be corrected for by application of the Chow-Thompson standard-addition technique.[31] For higher uranium/silver ratios or for samples containing sodium or nickel, which also interfere with the measurement of the radiant intensity of silver at a wavelength of 338 mμ, the silver must be separated from interferences. This is accomplished by internal electrolysis in which silver (and copper, if present) is deposited at a platinum cathode; cadmium is used as the anode. The silver and copper are then dissolved in nitric acid, and, after volatilization of excess acid, the silver is determined flame photometrically. Copper at a copper/silver weight ratio of 500 can be tolerated. As little as 1 μg of silver per milliliter in the final solution can be determined with a relative standard deviation of 10%.

Flame Photometric Determination of Aluminum in Thorium Oxide

T. C. Rains

A flame photometric method was outlined[32] for the determination of aluminum in thorium oxide by which the bulk of the thorium is extracted into a chloroform solution of 2-thenoyltrifluoroacetone (TTA) from an acetate medium at pH 1.5. Subsequently, the aluminum is extracted with TTA in 4-methyl-2-pentanone (hexone) at pH 6.0, and the radiant intensity of the AlO band is measured at 484 mμ. A major interference is fluoride, which is

[31] T. J. Chow and T. G. Thompson, "Flame Photometric Determination of Strontium in Sea Water," *Anal. Chem.* 27, 18 (1955).

[32] O. Menis *et al.*, "Flame Photometric Determination of Aluminum," *HRP Quar. Prog. Rep. July 31, 1957*, ORNL-2379, p 171.

required in the dissolution of thorium oxide. A procedure has been devised to overcome this interference and, at the same time, to eliminate the necessity for the prior extraction of thorium. The sample solution is saturated with ammonium carbonate, after which the aluminum is extracted with a 0.2% solution of 8-quinolinol in hexone, and the radiant intensity of the AlO band in the organic phase is measured at 484 mμ. The ammonium carbonate complexes the thorium and prevents its extraction. If iron(III) is present, thioglycolic acid is added prior to the extraction in order to reduce the iron(III) to iron(II) and thus prevent its interference. For aluminum within the concentration range of 2 to 10 ppm, the relative standard deviation is 5%.

Extraction and Flame Photometric Determination of Molybdenum

T. C. Rains I. B. Rubin

A method was investigated for the extraction and subsequent flame photometric determination of molybdenum. The molybdenum is separated from many interferences by extraction from 6 *M* hydrochloric acid either into hexone[33] or, preferably, into a 2-to-1 mixture of hexone and amyl acetate. Since molybdenum in the organic phase has no emission lines or bands suitable for use in flame photometry, its continuous emission is measured at 604 mμ, where it is at a maximum. Over the concentration range from 5 to 50 μg/ml, the radiant intensity at 604 mμ, corrected for background radiant intensity, was found to be a linear function of concentration and to be of magnitude sufficient for estimating the molybdenum concentration with an absolute error of no more than 1 μg/ml.

Flame Photometric Determination of Neodymium in Solutions of Uranyl Sulfate

I. B. Rubin T. C. Rains

A flame spectrophotometric method has been developed for the determination of microgram quantities of neodymium in solutions of uranyl sulfate. From work carried out by Rains and Dean,[34] it is indicated that a considerable increase in sensitivity can be attained by measuring the radiant intensity of the neodymium in an organic rather than an aqueous medium; consequently, neodymium is extracted from an acetate solution into a 0.1 *M* solution of TTA in hexone. As is shown in Fig. 4, virtually no neodymium is extracted from an acetate medium at a pH less than 2.5. Maximum extraction is achieved at pH ~5.5 from a 0.5 to 2 *M* acetate solution. The $pH_{1/2}$ value for neodymium increases with increasing acetate concentration; this indicates that some complexation with the acetate occurs.

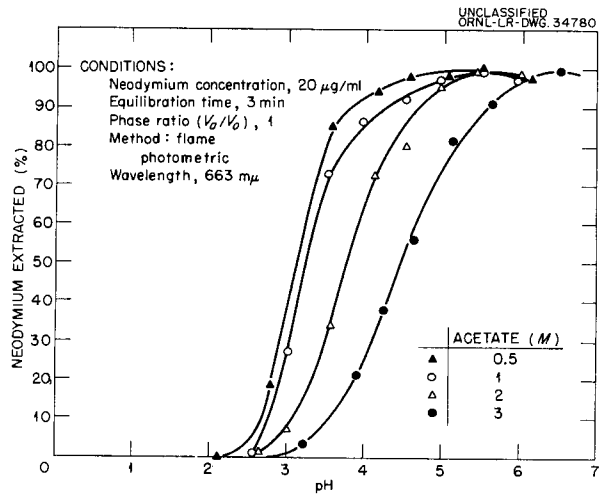

Fig. 4. Results of Extraction of Neodymium with 0.1 *M* TTA from Several Acetate Media as a Function of pH.

In the determination of neodymium, uranium, which would interfere with the extraction of neodymium by reacting with the TTA, is first removed by extraction from an acetate medium at pH 2 into 0.5 *M* solutions of TTA in chloroform. The pH of the aqueous phase is then adjusted to 5.5, and the neodymium is extracted, after which it is determined flame photometrically by measurement of the radiant intensity at 663 mμ (Fig. 5); an ORNL model Q-1457A high-sensitivity, recording, single-beam flame spectrophotometer is used. Over the neodymium concentration range of 4 to 20 μg/ml, the calibration curve is linear.

[33] I. Nelidow and R. M. Diamond, "The Solvent Extraction Behavior of Inorganic Compounds: Molybdenum(VI)," *J. Phys. Chem.* 59, 710 (1955).

[34] T. C. Rains and J. A. Dean, "Flame Photometric Determination of Lanthanum," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 59.

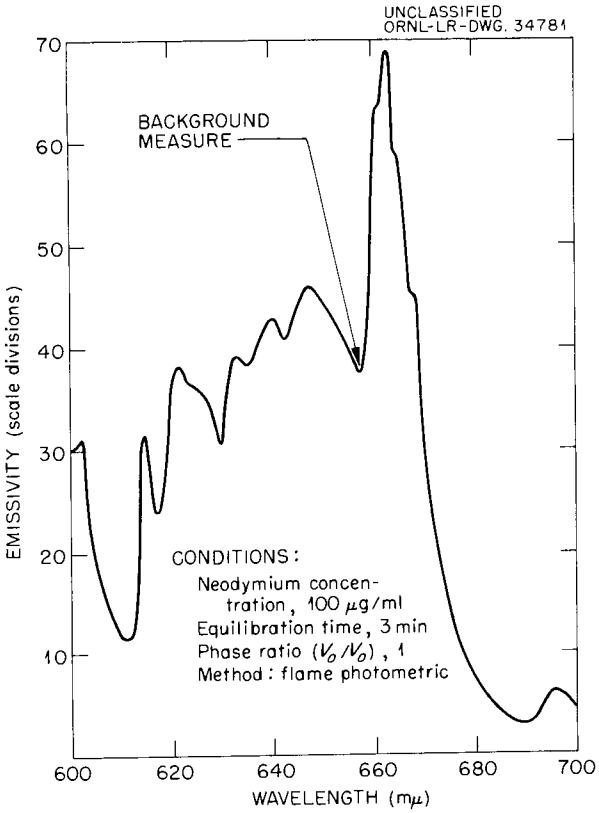

Fig. 5. Partial Emission Spectrum of Neodymium in a 0.1 *M* Solution of TTA in Hexone.

Determination of Iron in Solutions of Uranyl Sulfate and in Other Solutions

T. C. Rains

A rapid, sensitive method was developed for the extraction and subsequent determination of microgram quantities of iron in uranyl sulfate solutions that contained copper whereby the necessity for the removal of copper by electrodeposition is avoided. The method is also applicable to the determination of iron in dilute solutions of copper sulfate, phosphoric acid, sulfuric acid, or even hydrofluoric acid. The sample solution is made 6 *M* with hydrochloric acid, and the iron is then extracted into hexone.[35] Equilibrium is attained in 30 sec for solutions in which the hydrochloric acid concentration can vary from 4 to 8 *M*. After the extraction the iron is either re-extracted into water and determined colorimetrically by the α,α'-bipyridyl method or determined flame photometrically by aspiration of the organic phase into the flame and measurement of the radiant intensity at 372 mμ. For extremely low concentrations of iron (<2 ppm), the colorimetric method is more desirable because of its extreme sensitivity. The flame photometric method, however, is somewhat more rapid, since no re-extraction is required. By the introduction of the iron into the flame in an organic rather than an aqueous medium, the radiant intensity is enhanced at least tenfold. For iron in concentrations ranging from 2 to 10 μg/ml in solutions of uranyl sulfate and in other solutions, the relative standard deviation is of the order of 2%.

[35]H. Specker and W. Doll, "Photometrische Eisenbestimmung in Reinmetallen, Legierungen und NE-Erzen nach Abtrennung durch Verteilen zwischen zwei Lösungsmitteln," *Z. anal. Chem.* **152**, 178 (1956).

Extraction and Spectrophotometric Determination of Zirconium in Thorium Oxide

D. L. Manning G. Goldstein

A method was developed for the determination of microgram quantities of zirconium in slurries of thorium oxide that contain corrosion products of stainless steel and various additives in order to secure information for evaluating the corrosion rate of Zircaloy components of test loops. Zirconium is separated from thorium and minor components by the extraction of it from a 6 *M* hydrochloric acid solution into 0.5 *M* TTA in chloroform.[36] The organic phase is then backwashed with 10 *M* hydrochloric acid to remove traces of metals that may have accompanied the zirconium. After the organic material is removed by evaporation and oxidation, the residual zirconium is reacted with either of two chromogenic reagents, quercetin[37] (3,3′,4′,5,7-pentahydroxyflavone) or morin[38] (2′,3,4′,5,7-pentahydroxyflavone), both of which form yellow complexes in 1-to-1 ethyl alcohol–water solutions that are 0.5 *M* in hydrochloric acid. The zirconium can be determined colorimetrically by measurement of the absorbancy of either complex. The quercetin and morin complexes exhibit maximum absorbancy at wavelengths of 420 and 440 mμ,

[36]F. L. Moore, "Separation of Zirconium from Other Elements by Liquid-Liquid Extraction," *Anal. Chem.* **28**, 997 (1956).

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

[38]R. A. Geiger and E. B. Sandell, "Fluorometric Determination of Zirconium with Morin," *Anal. Chim. Acta* **16**, 346 (1957).

respectively; the molar absorbancy index of the quercetin complex is 28,000, whereas that of the morin complex is 50,000. Morin therefore provides somewhat greater sensitivity than quercetin. For 1-g samples of thorium oxide, 1 ppm of zirconium can be determined with morin, whereas with quercetin the lower limit of quantitative measurement is about 2 ppm. Over the range of 1 to 10 ppm of zirconium, the relative standard deviation is of the order of 3%.

For extremely low concentrations of zirconium (0.1 to 1 ppm), a fluorometric method is used in which the fluorescence of the morin-zirconium complex is measured. In this case the complex is developed in a 2 *M* hydrochloric acid solution that contains about 5 vol % ethyl alcohol. The relative standard deviation is about 10%.

Spectrophotometric Determination of Titanium in Thorium Oxide

I. B. Rubin T. C. Rains

The disodium-4,5-dihydroxy-*m*-benzenedisulfonate (Tiron) spectrophotometric method for the determination of titanium[39] has been modified to eliminate the interferences of chromium(VI), uranium, and molybdenum, which are often present in slurries of thorium oxide. The interference of microgram quantities of chromium(VI) is eliminated by reducing it to chromium(III) by the addition of a drop of concentrated hydrochloric acid to a hot perchloric acid solution of the sample. If milligram quantities of chromium(VI) are present, the major portion is removed by volatilizing it as chromyl chloride. Molybdenum, which interferes in concentrations as low as 0.08 μg/ml, is removed by a triple extraction from 6 to 7 *M* hydrochloric acid into hexone.[40] Traces of residual molybdenum can be masked with thioglycolic acid, but the inhibiting effect of this acid on the formation of the complex must be eliminated by heating the solution in a boiling water bath for 10 min. If, in addition to molybdenum, uranium is present, a single hexone extraction is made to remove essentially 90% of the molybdenum, after which the raffinate is passed through a column of Dowex 1 anion exchange resin in order to separate the uranium and residual molybdenum from titanium.[41] In this procedure iron is quantitatively removed from the solution; therefore a sample blank need not be prepared. The relative standard deviation of this procedure, for concentrations of titanium in the range of 2 to 10 ppm in slurries of thorium oxide, is of the order of 10%. For synthetic test samples the bias was found to be approximately +2%.

Polarographic Determination of Uranium in Thorium Oxide

R. G. Ball D. L. Manning

A polarographic method was applied to the determination of microgram quantities of uranium (~200 ppm), which was present as an additive in slurries of thorium oxide. The polarographic measurement of the uranium is made, without prior separation of the uranium, by recording the reduction wave of uranium(VI) in a supporting electrolyte of 0.1 *N* nitric acid. The half-wave potential is approximately −0.18 v vs the S.C.E. Of the impurities commonly present in thorium oxide slurries, only iron(III) interferes. This interference is eliminated by reduction with hydroxylamine prior to the recording of the polarogram. By the use of the ORNL model Q-1673 derivative polarograph and a standard-addition technique, from 200 to 500 ppm of uranium can be determined by this method with a relative standard deviation of about 3%.

Polarographic Determination of Mercury and Copper in Solutions of Uranyl Sulfate

R. G. Ball D. L. Manning

A polarographic method has been applied to the simultaneous determination of mercury and copper in solutions of uranyl sulfate. The reduction waves of these two elements coalesce unless a suitable complexing agent is added to the supporting medium. The waves can be resolved if either 0.25 *M* disodium ethylenediaminetetraacetate (EDTA)[42] or disodium nitrilotriacetate (NTA) is used as the complexing agent in a 0.9 *M* solution of sodium chloride at pH 9

[39] I. B. Rubin and T. C. Rains, "Spectrophotometric Determination of Microgram Quantities of Titanium in Thorium Oxide," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 61.

[40] I. Nelidow and R. M. Diamond, "The Solvent Extraction Behavior of Inorganic Compounds: Molybdenum(VI)," *J. Phys. Chem.* **59**, 710 (1955).

[41] K. A. Kraus and F. Nelson, "Anion Exchange Studies of the Fission Products," *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955* **7**, 113 (1955).

[42] A. D. Horton, P. F. Thomason, and M. T. Kelley, "Remote Control Determination of Corrosion Products and Additives in Homogeneous Reactor Fuel," *Anal. Chem.* **29**, 388 (1957).

as the supporting medium. The half-wave potentials of the reduction waves for mercury and copper in the presence of EDTA are 0.2 and 0.5 v vs the S.C.E., respectively, and in the presence of NTA are 0.1 and 0.4 v vs the S.C.E., respectively. The reduction waves of the two elements can therefore be readily resolved, and concentrations of each element as small as 4 μg/ml can be estimated with a relative standard deviation of 4%. In these media, iron(III) interferes with the determination of mercury; however, this interference can be eliminated by the use of a mixture of sodium citrate and ammonium carbonate as the complexing agent. In the sodium chloride–sodium citrate–ammonium carbonate medium, the $E_{1/2}$ for the mercury reduction is −0.06 v vs the S.C.E., whereas that for iron is −0.55 v. Concentrations of iron(III) as high as 300 μg/ml can be tolerated. Copper exhibits two reduction waves in this medium, $Cu^{2+} \rightarrow Cu^{+}$ at −0.21 v and $Cu^{+} \rightarrow Cu^{0}$ at −0.41 v vs the S.C.E. Iron(III) interferes with the latter reduction wave but, in this case, the wave at −0.21 v can be utilized for the estimation of copper. However, for the estimation of copper in low concentrations (~20 μg/ml), a supporting electrolyte that contains either EDTA or NTA is preferred because the sensitivity is about twice as great as it is for the chloride-citrate-carbonate medium. Uranium does not interfere in any of the media tested because it is not reduced within the range of potentials applied.

Polarographic Determination of Uranium in Tin

R. G. Ball D. L. Manning

In connection with a study of the solubility of uranium dioxide in molten tin, it became necessary to devise a method for the determination of small amounts of uranium in tin. The tin is dissolved in concentrated hydrochloric acid, and the solution is evaporated to near dryness. A small amount of concentrated nitric acid is then added to oxidize tin and uranium, after which over 99% of the tin is removed as the volatile $SnCl_4$ by repeated additions of concentrated hydrochloric acid and evaporation to a small volume. The uranium is then determined by derivative polarography in a 1 *N* hydrochloric acid medium; the U(VI) + $e \rightarrow$ U(V) reduction wave at −0.22 v vs the S.C.E. is used. The small quantity of residual tin does not interfere. By this method uranium in tin in concentrations ranging from 0.5 to 2 wt % was determined with a relative standard deviation of about 3%.

Anodic Stripping Polarography of Copper(II), Lead(II), and Cadmium(II)

R. G. Ball D. L. Manning

Anodic stripping polarography was applied to the determination of microgram and submicrogram quantities of copper(II), lead(II), and cadmium(II) in solutions of uranyl sulfate. The method of Nikelly and Cooke[43] by which a metal is deposited on an electrode and anodically removed under controlled conditions was utilized; the designs of the electrode and cell were modified slightly. By means of this method it is possible to determine copper(II) and lead(II) in concentrations ranging from 0.01 to 0.2 μg/ml with a relative standard deviation of ~10%. Cadmium can be determined in concentrations as small as 0.001 μg/ml (9×10^{-9} *M*) with a relative standard deviation of about 15%.

Determination of Chloride in Solutions of Uranyl Sulfate

R. G. Ball D. L. Manning

The coulometric stripping technique, introduced by Zittel *et al.*,[44] was further investigated as a means of determining microgram quantities of chloride in solutions of uranyl sulfate. For this application an ORNL high-sensitivity polarograph was substituted for the electronic coulometric stripper used by Zittel. When the microelectrode, which consists of a drop of mercury that is positioned at the end of a J-shaped capillary tube, is made the anode, any chloride in the solution is deposited on the surface of the anode as insoluble mercurous chloride. The mercurous chloride is then redissolved by scanning the potential at a constant rate in the negative direction. The current that flows during the dissolution period (stripping cycle) is a measure of the chloride and is proportional to the peak height of the recorded current-voltage curve.[43] A 0.1 *M* potassium nitrate–0.1 *M* citric acid solution is used as the supporting electrolyte; the current measurement

[43] J. G. Nikelly and W. D. Cooke, "Anodic Stripping Polarography," *Anal. Chem.* 29, 933 (1957).

[44] H. E. Zittel *et al.*, "Electronic Coulometric Stripper for the Determination of Submicrogram-to-Microgram Amounts of Halides," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 16.

is made on a final volume of 10 ml of solution. In this volume as much as 110 mg of uranium(VI), 60 μg of iron(III), and 30 μg of chromium(VI) do not interfere. By increasing the citric acid concentration to 0.5 *M*, as much as 600 mg of uranium(VI) can be tolerated. The tolerance level for chromium(VI) and iron(III) can be increased to 100 μg by reducing the chromium(VI) to chromium(III) with hydroxylamine sulfate and complexing the iron(III) with nitrilotriacetic acid. Other minor components, such as nickel, copper, and molybdenum, do not interfere in the concentrations normally encountered in uranyl sulfate solutions. From 2 to 20 μg of chloride in a final volume of 10 ml can be measured by this method with a relative standard deviation of about 15%.

Determination of Thorium

D. L. Manning

A radio-frequency oscillator[45] operating at 190 Mc/sec was utilized in ascertaining the end point in the direct titration of thorium in concentrations of approximately 3 mg/ml with either oxalic acid or EDTA. When the latter is used as the titrant, the end point is established by plotting the volume of titrant vs either the oscillator-grid current or the potential drop through a load resistor and extrapolating the two straight-line portions of the graph to their point of intersection. With oxalic acid as the titrant, however, two end points are observed, either of which can be used but the second is preferred because of the increased precision engendered by the larger volume of titrant. It has been postulated from these observations that the following step-wise reactions are involved in the titration of thorium with oxalic acid:

$$Th^{4+} + H_2C_2O_4 \longrightarrow Th(C_2O_4)^{2+} + 2H^+ \quad \text{(first end point)}$$

$$Th(C_2O_4)^{2+} + H_2C_2O_4 \longrightarrow Th(C_2O_4)_2\downarrow + 2H^+ \quad \text{(second end point)}$$

An advantage of the high-frequency titration procedure is elimination of the interference by substances ordinarily encountered in the visual titration of thorium when indicators are used. With this method 50 to 75 mg of thorium in a volume of 30 ml has been titrated with a relative standard deviation of approximately 1.5%. The titration can be conducted in the presence of as much as 200 mg of uranium(VI).

Determination of Chromium in High-Fired Thorium Oxide

I. B. Rubin T. C. Rains

The long time (often hours) required to dissolve refractory thorium oxide, calcined at 1200 to 1600°C, by standard methods in which nitric, perchloric, and hydrofluoric acids are used[46] is reduced to 30 min by dissolving the thorium oxide in hydrochloric acid containing a drop of hydrofluoric acid. Chromium is then determined by the diphenylcarbazide spectrophotometric method;[47] as proposed by Blundy,[48] ammonium hexanitritocerate rather than sodium bismuthate is used as the oxidizing agent. After the chromium is oxidized by being heated for 30 min with cerate in dilute sulfuric acid, excess ceric ion is reduced with sodium azide. Oxidation by the ceric salt is relatively independent of normal fluctuations in acidity in comparison with oxidation by bismuthate, which is dependent on the acidity.[49] Chromium in concentrations of 0.2 to 0.8 μg/ml in solutions that contain 200 to 800 μg of thorium per milliliter and other corrosion products of stainless steel can be determined by this method with a relative standard deviation of less than 5%.

Effect of Acetic Acid and pH on the Extraction of Thorium with TTA in Organic Solvents

G. Goldstein D. L. Manning

An extremely valuable method for the separation of thorium from other elements consists in the selective extraction of thorium from aqueous solutions with TTA in organic solvents. Acetic acid is reported to enhance the extractability;[50] a detailed study was therefore made of the effect of

[45] R. W. Stelzner and M. T. Kelley, *Radio-Frequency Oscillators for Determination of Alkali*, ORNL-1742 (June 9, 1955).

[46] T. C. Rains, "Preparation of Solid Thorium Oxide and Thorium Oxide Slurries for Analysis," Method No. 9 082200 (7-9-56), *ORNL Master Analytical Manual.*

[47] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2d ed., p 260, Interscience, New York, 1950.

[48] P. D. Blundy, *The Determination of Chromium by a Solvent Extraction Method*, AERE CE/M-219 (Feb. 1958).

[49] P. F. Urone and H. K. Anders, "Determination of Small Amounts of Chromium in Human Blood, Tissues, and Urine," *Anal. Chem.* 22, 1317 (1950).

[50] R. A. Day, Jr., and R. W. Stoughton, *Chemistry of Thorium in Aqueous Solutions. I. Some Organic and Inorganic Complexes*, ORNL-468 (Jan. 5, 1950).

acetic acid concentration and pH of the aqueous phase on the distribution ratio of thorium tracer when either a carbon tetrachloride or a hexone solution of TTA was used as the extractant. The results of these tests are presented graphically in Figs. 6 and 7 in which the log of the distribution ratio, D_a^o, is plotted vs pH for four aqueous solutions, the acetic acid concentrations of which range from 0 to 5.5 *M*. In general, the extractability of thorium at a fixed pH is shown to be increased by the addition of acetic acid up to a concentration of 1 *M*. At a pH greater than 1.0 an increase of the acetate concentration from 1 *M* to about 3 *M* tends to decrease the extractability of thorium. When the aqueous phase is made 5.5 *M* with acetic acid, however, the extraction of thorium by TTA in carbon tetrachloride is further increased; the reverse effect, that is, reduction of the extractability, is obtained if hexone rather than carbon tetrachloride is used as the solvent for TTA.

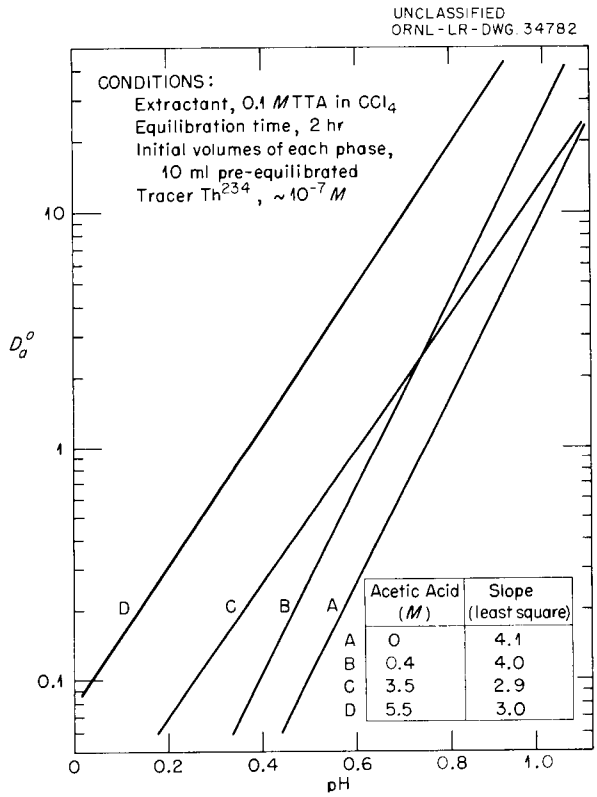

Fig. 6. Results of Extraction of Thorium from Acetic Acid Solutions with TTA in Carbon Tetrachloride. Effect of pH and acetic acid concentration on distribution ratio.

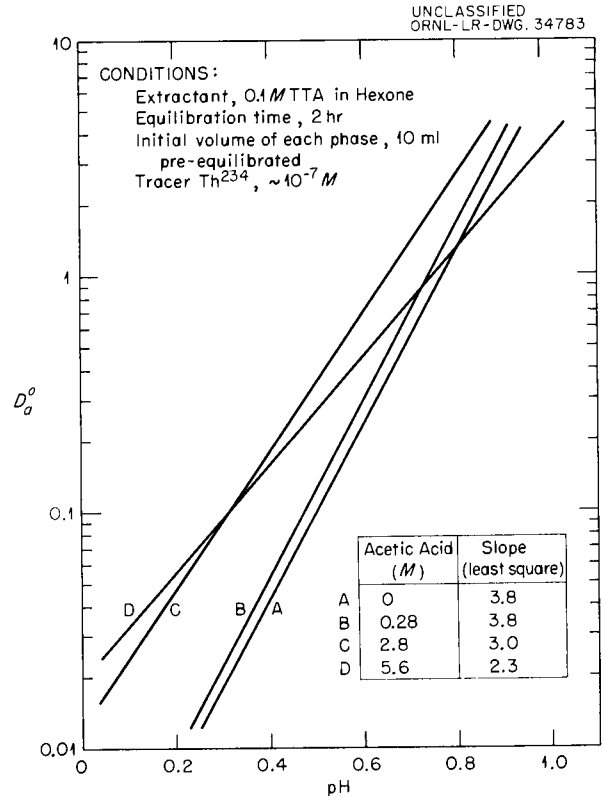

Fig. 7. Results of Extraction of Thorium from Acetic Acid Solutions with TTA in Hexone. Effect of pH and acetic acid concentration on distribution ratio.

From these data it is also possible to formulate the reactions on which the extraction of thorium is based. The conclusions reached as a consequence of this extraction study with TTA in carbon tetrachloride, based on distribution ratios as a function of pH, are summarized in Table 6.

When a hexone solution of TTA is used as extractant, the reactions are somewhat more complex and have not, as yet, been formulated. The distribution ratio of TTA is a function of acetic acid, hydrogen ion, and hexone concentrations in the aqueous phase. Acetic acid is also extracted and exists, in part, in the organic phase in the dimerized form. In general, this results in decreased extractability of thorium. The distribution ratio and also the solubility of the thorium-TTA chelate vary with the acetate concentration.

Table 6. Formulated Reactions on Which Extraction of TTA in Carbon Tetrachloride Is Based

HAc (*M*)	Reaction(s)	Equilibrium Constant, K_e	Remarks
0	$Th^{4+} + 4HT \rightarrow Th(T)_4 + 4H^+$	10.2	The distribution ratio is directly proportional to $[HT]^4$ and inversely proportional to $[H^+]^4$
1	$Th^{4+} + 4HT + HAc \rightarrow Th(T)_4 \cdot HAc + 4H^+$	42.4	A Th-TTA-HAc adduct is formed, which increases D_a^o
3.5	$Th^{4+} + HAc \rightarrow ThAc^{3+} + H^+$	0.28	The distribution ratio is inversely proportional to $[H^+]^3$ in the aqueous phase
	$ThAc^{3+} + 4HT \rightarrow Th(T)_4 \cdot HAc + 3H^+$	147	An additional species, the Th-TTA-HAc adduct, is formed which extracts; at equilibrium, residual thorium in the aqueous phase is present as $ThAc^{3+}$ rather than Th^{4+}
5.5	$ThAc^{3+} + 4HT + HAc \rightarrow Th(T)_4 \cdot 2HAc + 3H^+$	110	The distribution ratio is inversely proportional to $[H^+]^3$, and the principal species in the aqueous phase is still $ThAc^{3+}$ An additional extractable complex, $Th(T)_4 \cdot 2HAc$, is formed and so the distribution ratio is increased

Carbon tetrachloride is apparently preferable to hexone as the solvent for TTA since, for any acetate concentration, the distribution ratio with carbon tetrachloride is more favorable than that with hexone, as is shown in Figs. 6 and 7.

Separation of Aluminum and Lanthanum from Interferences

T. C. Rains

A further study was made of the extraction of aluminum[51] and lanthanum[52] with TTA in organic solvents for the purpose of separating these elements from thorium and other interferences prior to their determination. Effective separations of aluminum and lanthanum from thorium were attained by the selection of a suitable aqueous medium, optimum pH, organic solvent, and equilibration time.

The extraction rate of the aluminum–TTA chelate and also the distribution ratio are dependent upon the pH, concentration, and type of buffer used in the aqueous phase, and also on the organic solvent (chloroform or hexone). The extractability of the chelate by three organic solvents as a function of pH is shown in Fig. 8. This figure can be used as a guide in selecting the preferred solvent and pH for use in separating aluminum from specific interferences.

Data relative to the extraction of aluminum from various media with TTA in hexone as a function of pH and extraction time are presented in Table 7 and Fig. 9. From a dilute (0.5 *M*) acetate medium, no aluminum is extracted in 5 min at pH values below 2.8. Advantage is taken of this fact to remove thorium, which can be extracted rapidly with TTA in chloroform from this medium at pH 1.7.

[51] T. C. Rains, "Flame Photometric Determination of Aluminum," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 61.

[52] T. C. Rains and J. A. Dean, "Flame Photometric Determination of Lanthanum," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 59.

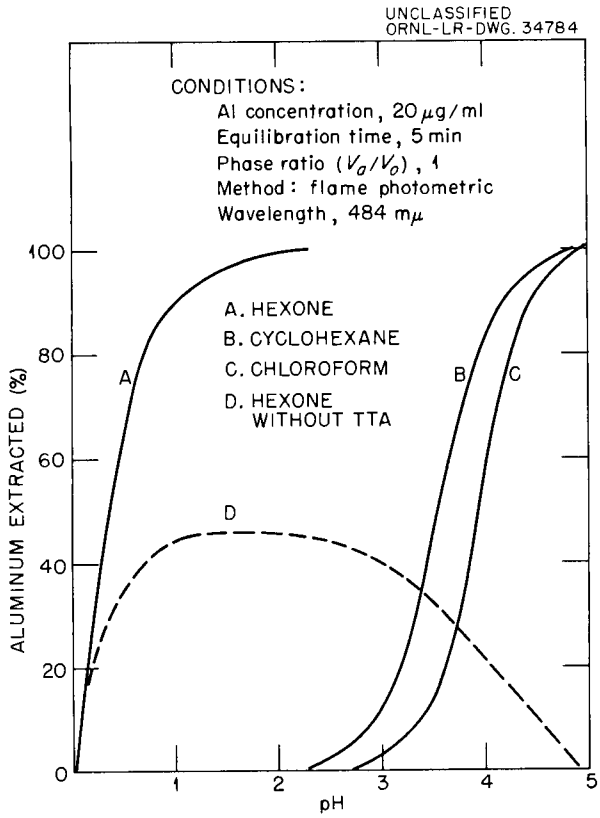

Fig. 8. Results of Extraction of Aluminum with 0.1 *M* TTA from a 2 *M* Trichloroacetate Buffered Medium. Effect of organic solvent as a function of pH.

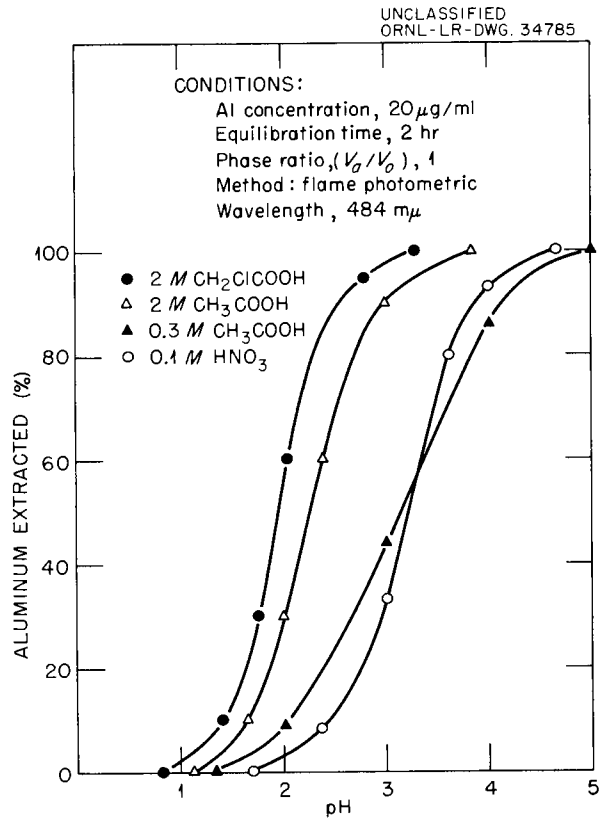

Fig. 9. Results of the Extraction of Aluminum with 0.1 *M* TTA in Hexone from Various Media as a Function of pH.

Table 7. Effect of Media and Equilibration Time on the Extraction of Aluminum with 0.1 *M* TTA in Hexone

Aqueous Media	Acid Concentration (*M*)	pH After 5 min for Aluminum Extracted			pH After 120 min for Aluminum Extracted		
		1%	50%	100%	1%	50%	100%
HNO_3	0.1	1.5	3.5	5.0	1.5	3.2	4.0
CH_3COOH	0.5	2.8	4.3	5.5	1.5	3.2	5.0
	2.0	1.5	4.2	5.5	1.0	2.3	4.0
	3.0	1.0	3.8	6.0	1.0	2.3	4.0
$CH_2ClCOOH$	0.5				1.5	2.0	4.0
	3.0	1.5	2.7	6.0	0.8	2.2	3.2
CCl_3COOH	2.0	0	0.5	2.0			

After the removal of the thorium, trichloroacetic acid is added, and the aluminum is rapidly extracted with TTA in hexone at pH 2. In a single 3-min extraction, 600 μg of aluminum can be extracted with 0.1 *M* TTA in hexone at phase ratios (V_a/V_o) as high as 25. The extraction is made at pH 2 to avoid extraction of the alkali elements which would interfere in the flame photometric determination of aluminum. A backwash of the organic phase with 0.1 *M* nitric acid is required to remove any extracted acetate and also traces of alkali metals.

Test results for the extraction of lanthanum with 0.1 *M* TTA in hexone and in chloroform from various media as a function of pH are presented in Fig. 10. With various aqueous media the extraction is dependent on the pH and also on the type of organic solvent used. When hexone is used as the solvent, equilibrium is attained in 10 min, whereas 2 hr is required to reach equilibrium when chloroform is used as the solvent. A procedure involving control of composition and pH of the aqueous phase and equilibration time, similar to that used with aluminum, can be applied to the separation of lanthanum from thorium and the alkali and alkaline-earth elements prior to its determination by flame photometry.

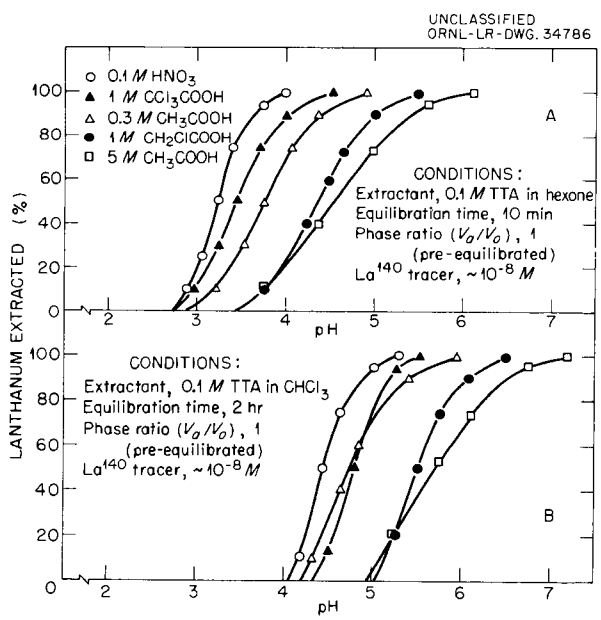

Fig. 10. Results of the Extraction of Lanthanum (La^{140}) with TTA as a Function of pH Under Equilibrium Conditions. Effect of solvent and composition of aqueous phase.

Papers that give the detailed procedures for the determinations of aluminum and lanthanum have been accepted for publication in *Analytical Chemistry.*

Separation of Fluoride and Chloride by Fusion Pyrolysis

R. H. Powell

A study of the fusion-pyrolysis method for the removal of fluoride from inorganic materials for analytical purposes[53,54] was continued in order to evaluate the usefulness and relative order of effectiveness of a variety of fluxes for different types of samples and to extend the application of this method to the separation of chloride. The fluxes studied, together with their characteristics, are listed in Table 8.

The selection of a flux is dependent upon the material to be analyzed. Of the fluxes studied, sodium bismuthate is the most effective for the removal of microgram quantities of fluoride from high-fired (1200 to 1600°C) thorium oxide and other refractory materials. It is even more effective than the sodium tungstate–tungstic oxide fusion mixtures previously reported[53] to be suitable for this purpose. A high-melting flux that is stable at high temperatures is required for the removal of chloride; of the fluxes tested for this purpose, sodium trimolybdate, which has a very low and reproducible chloride blank, was found to be the most suitable (see Table 9).

Both sodium bismuthate and sodium trimolybdate have certain shortcomings. The trimolybdate is not satisfactory for the removal of fluoride because small amounts of molybdenum are volatilized and interfere in the spectrophotometric titration of the fluoride. Molten sodium bismuthate creeps out of metal boats and damages the reactor tube. This does not occur when a silica boat is used, but, on cooling, the silica boat is cracked.

The low-melting fluxes, sodium dichromate, potassium dichromate, and sodium bisulfate, were found to be uniquely suitable for special materials.

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[53] R. H. Powell, "Removal of Fluoride from Inorganic Material by Pyrolysis," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957,* ORNL-2453, p 57.

[54] R. H. Powell and O. Menis, "Separation of Fluoride from Inorganic Compounds by Pyrolysis," *Anal. Chem.* 30, 1546 (1958).

Table 8. Characteristics of Fusion-Pyrolysis Fluxes

Fluxes	Melting Point (°C)	Pyrolysis Temperature Range (°C)	Comments
$NaBiO_3$	~800	825–1025	Effective for F^- and Cl^- in highly refractory materials
$NaVO_3$	630	700–1025	Slightly less effective than $NaBiO_3$
$Na_2WO_4 + WO_3$	~690	800–900	Slightly less effective than $NaBiO_3$ for CaF_2
$Na_2Mo_3O_{10}$	528	550–850	Interferes in determination of microquantities of F^-
$K_2Cr_2O_7$	398	450–600	Liberates F^- but not Cl^-
$KHSO_4$	210	250–300	Suitable for removal of Cl^- from organic materials

Table 9. Results of Recovery of Chloride by Fusion Pyrolysis

Flux: 16 g of $Na_2Mo_3O_{10}$

Sample		Chloride (μg)		
Composition	Weight (g)	Added[a]	Found	Net (per g of ThO_2)
$NaCl^b$		11	11	
$ThO_2{}^c$	5	0	6	1.2
	10	0	14	1.4
	10	0	16	1.6
	10	11	26	1.5
				Av = 1.4
				$S = 0.17$
				$V = 10\%$

[a]One milliliter of a standard solution of NaCl, 11 μg of Cl per milliliter.
[b]Corrected for 10-μg reogent blank.
[c]Ignited at 1600°C.

A dichromate flux is effective in the removal of fluoride from nonrefractory materials and salts, including sodium fluoride, but not from calcium fluoride. With this flux, by pyrolysis at less than 600°C, fluoride but not chloride is removed by volatilization; thus a method is provided for the separation of fluoride and chloride. Under the same pyrolytic conditions, it was demonstrated qualitatively that fluoride can be removed from Teflon without sublimation of the sample or contamination of the absorbing solution with organic decomposition products. Pyrolysis with sodium bisulfate as the flux was found to be satisfactory for removal of chloride from organic dyes. The reliability of this procedure was tested with reagent-grade trichloroacetic acid for which the chloride content was determined within 1%.

Separation of Ruthenium Metal by Fusion Pyrolysis

R. H. Powell

A fusion-pyrolysis method was devised for the separation of ruthenium metal that was deposited on stainless steel samples in HR corrosion studies. The ruthenium is separated by mixing the sample with sodium bismuthate and pyrolyzing the mixture

in moist oxygen at 1000°C,[55] whereby the ruthenium is volatilized as ruthenium tetroxide, RuO_4, and absorbed in a dilute solution of hydrochloric acid that is saturated with sulfur dioxide. The ruthenium is then determined spectrophotometrically by the β-nitroso-γ-naphthol method.[56–58] The method was evaluated by applying it to the estimation of quantities of ruthenium metal, the purity of which had been established spectrographically. The metal was recovered quantitatively, that is, within the experimental error of the spectrophotometric procedure, with a relative standard deviation of 3%. The method was then applied satisfactorily to steel samples that contained less than 100 μg of ruthenium.

Application of Gamma Counting to the Determination of Thorium Oxide

C. M. Boyd

A study was made of the applicability of a gamma-counting method for the determination of thorium oxide, particularly on fractions of slurry obtained in the measurement of particle-size distribution by gravity and centrifugal sedimentation methods.[59] The gamma emission of the daughter elements of natural thorium having energies within the range of 0.18 to 0.28 Mev is measured by means of a well-type scintillation counter with a thallium-activated sodium iodide crystal. Although the emissivity at different energy levels depends upon the extent to which the daughters are in equilibrium with the parent Th^{232}, this variable factor becomes unimportant if a portion of the same material that is contained in the samples under test is used for calibration purposes.

In sedimentation tests two samples, the settled and suspended fractions of oxide, must be analyzed for thorium. If the ratio of thorium oxide in these two fractions can be accurately determined, it is unimportant whether the absolute amounts are measured accurately. The gamma-counting method is adequate for this purpose in that the ratio can be established by this means with an error of approximately ±2%. It is, furthermore, fairly rapid, requiring no more than one-third of the time required by the conventional spectrophotometric method.

INORGANIC PREPARATIONS (X-10)

D. E. LaValle

The work for the Nuclear Physics and Neutron Diffraction Group of the Physics Division continued along much the same lines as in the past, that is, the preparation of anhydrous transition-metal halides with emphasis on materials for single crystal growth. These materials included ferrous and cobaltous bromides, ferric and chromic chlorides, and a large amount (~400 g) of manganous iodide, MnI_2. In addition, a preparation of 25 g of manganous deuteroxide, $Mn(OD)_2$, was made, and further experiments were carried out in attempts to produce the lower fluorides of molybdenum.

A series of solid solutions of $U^{233}F_3$ in CaF_2 and in BaF_2 was made for the Nuclear Physics and Low Temperature Group of the Physics Division.

The preparation of high-purity Li^6I for scintillation counter crystals in the work of the Basic Shielding and Reactor Physics Experiments Group of the Neutron Physics Division was resumed with emphasis on the removal of alkaline-earth-metal impurities.

For the High Temperature Reactions Group of the Metallurgy Division, the preparation of fused salts as solvents continued. Several 100-g quantities of anhydrous LiCl, $LiClO_4$, and the eutectics LiCl-KCl, LiBr-KBr were made for this purpose, in addition to smaller quantities of the alkali-metal and alkaline-earth-metal nitrates, lead chloride, and lead bromide. Smaller quantities (~25 g) of the anhydrous chlorides of zinc, magnesium, and copper(I) were also prepared. An attempt to make anhydrous $Ni(NO_3)_2$ by the method of Addison and Hathaway[60] was not successful.

The preparation of several pounds of high-purity MgO (total transition-element content <10 ppm)

[55] R. H. Powell, R. G. Ball, and D. L. Manning, "Pyrolytic Separation and Spectrophotometric Determination of Ruthenium," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 64.

[56] O. Menis and F. E. Jenkins, *Anal. Chem. Quar. Prog. Rep. Dec. 26, 1951*, ORNL-1233, p 77 (classified).

[57] O. Menis and F. E. Jenkins, "Colorimetric Determination of Ruthenium," *Anal. Chem. Quar. Prog. Rep. March 26, 1952*, ORNL-1276, p 82.

[58] O. Menis, C. K. Talbott, and M. L. Druschel, "Analysis of Uranyl Sulfate Solutions," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1953*, ORNL-1639, p 28.

[59] O. Menis, H. P. House, and C. M. Boyd, *Particle-Size Distribution of Thorium Oxide by a Centrifugal Sedimentation Method*, ORNL-2345 (Aug. 1957).

[60] C. C. Addison and B. J. Hathaway, "Gaseous Copper Nitrate," *Chem. Soc. (London) Proc.*, p 19 (Jan. 1957).

and of a series of barium aluminates of special composition was completed for the Nonmetals Group of the Solid State Division.

For the High Temperature and Structural Chemistry Group of the Chemistry Division, 100-g quantities of the anhydrous lithium halides and small quantities of Li^6Cl and CsF were prepared.

There were numerous simpler preparations relative to programs such as that of the 86-in. Cyclotron Nuclear Physics Group of the Electronuclear Research Division, and for the High Voltage Program and the Classification of Low-Lying Nuclear Energy Levels Group of the Physics Division.

IONIC ANALYSES (X-10)

P. F. Thomason

Determination of Europium by Controlled-Potential Coulometry

W. D. Shults, II

A method for the precise determination of milligram quantities of europium in the presence of other rare-earth elements has been developed. Two electrolyses at a mercury cathode vs a silver–silver chloride reference electrode are required: first, a reduction of europium(III) to europium(II) at a controlled cathode potential of –0.8 v, then a coulometric oxidation of the europium(II) back to europium(III) at –0.1 v. The reduction is complete, although current efficiency is less than 100%. The oxidation proceeds with 100% current efficiency, and therefore the quantity of current consumed during the oxidation is a measure of the amount of europium titrated. Either hydrochloric or perchloric acid can be used as the supporting electrolyte, and the acidity in either case can be between 0.1 and 1 *M* without deleterious effect. Nitrates and sulfates interfere. None of the rare-earth elements or other contaminants present in commercial-grade europium oxide interfere. The method has been used primarily to analyze high-grade europium oxide powder prior to its incorporation in neutron absorbers, and less frequently to analyze stainless steels that contain europium. The procedure for steels consists in dissolution of the steel in perchloric acid, fuming of the solution to assure higher valence states of the metal constituents, dissolution of the residue in 6 *M* hydrochloric acid, separation of chromium(VI) from the europium(III) by extraction into 10% triisooctylamine in xylene, neutralization of the excess acid with ammonium hydroxide before titration, and titration in the manner mentioned above. This controlled-potential coulometric method for europium is described in a paper which has been submitted for publication in *Analytical Chemistry*.

Determination of Uranium in Dissolver Solutions by Controlled-Potential Coulometry

B. B. Hobbs W. D. Shults, II

The application of controlled-potential coulometry to the analysis of various types of dissolver solutions is being studied. The ORNL "Mark III" electronic controlled-potential coulometric titrator was fabricated and evaluated. It has been established by studies made in the HRLAF that for the titration of 5-mg quantities of uranium(VI) the relative standard deviation of the method is 0.1% when the titration is made in normal bench-top fashion, 0.2% when it is made remotely, and 0.4% when the entire procedure (extraction of fission products and titration) is carried out remotely. A satisfactory procedure for the separation of uranium from major contaminants and fission products prior to its titration is being sought. The most promising procedure studied thus far is the extraction of uranium(VI) from an aqueous solution of dibasic aluminum nitrate into 5% triisooctylamine in xylene. The uranium is then removed from the organic phase with 1 *N* sulfuric acid–0.05 *M* perchloric acid solution, and the aqueous phase is drained directly into the titration vessel and electrolyzed at –0.35 v vs the silver–silver chloride electrode. The entire method (separation and coulometric determination) requires approximately 45 min and has a relative standard deviation of 0.2% when 10 mg of uranium is titrated. The procedure has been applied to nonradioactive dissolver solutions of stainless steel with similar precision. It is helpful in this case to reduce strong oxidants by the addition of a small quantity of hydroxylamine hydrochloride to the electrolyte in the cell before making the titration of uranium. The applicability of this method to other types of dissolver solutions and to radioactive samples is under study.

Determination of Uranium and Copper by Controlled-Potential Coulometry

W. D. Shults, II P. F. Thomason

An improved method for the determination of milligram quantities of uranium and copper by controlled-potential coulometric electrolysis has been developed. Two electrolyses are required, first a reduction of uranyl ion to uranium(IV) and of copper(II) to copper(mercury) at −0.3 v and then a reoxidation of only the copper(mercury) to copper(II) at +0.175 v. Mercury is the working electrode, 1 *N* sulfuric acid is the supporting electrolyte, and the reference electrode is silver–silver chloride. Copper is then calculated by means of Faraday's law from the quantity of current consumed during the oxidation, whereas uranium is calculated by difference from the quantity consumed during the reduction. This method is not sensitive to the uranium-to-copper ratio and is more rapid and more precise than the successive titration of these ions at different potentials; it is currently preferred for the analysis of HR fuel. A paper that describes the method was presented at the Southeastern Regional Meeting of the American Chemical Society on December 11, 1958, at Gainesville, Florida, and has been accepted for publication in *Analytical Chemistry*.

Polarographic Determination of Barium

H. E. Zittel

The work of Zlotowski and Kolthoff[61] indicated that barium could be determined polarographically if one of the tetraalkyl ammonium salts was used as the supporting electrolyte. They found that barium produced a wave at an $E_{1/2}$ of −1.94 v vs the S.C.E. in aqueous medium and that the $E_{1/2}$ shifted to a more positive value if an ethyl alcohol–water medium was used.

A study of this procedure was made; the best results were obtained when a 0.1 *M* solution of tetramethylammonium iodide in a 50 vol % solution of ethyl alcohol in water was used as the supporting electrolyte. The i_d/C ratio was constant over the barium concentration range from 10 to 200 μg/ml. Analysis of the waves indicated that the reaction is

$$Ba^{2+} + 2e \rightleftharpoons Ba \ .$$

It was found that the method is not usable in solutions of pH < 6 and that large amounts of potassium and sodium ions interfere. Beryllium ion also interferes if present in an amount comparable with that of barium.

Polarographic Study of Uranium(VI) in Acidic Media

H. E. Zittel

Herasymenko[62] was the first to study the polarography of uranium and noticed a three-step reduction wave in both neutral and acidic solutions. Harris and Kolthoff[63] investigated the polarographic behavior of uranium and from their results were able to explain the behavior of uranium at the D.M.E. They state that phosphate ion interferes markedly with the uranium wave in strongly acidic medium. Preliminary work done previously at this laboratory tended to both confirm and deny this observation. This study was undertaken to clarify the effect of the phosphate ion on the polarographic behavior of uranium. The effects of several mineral and organic acids were also studied.

It was found that, in the presence of the phosphate ion in acidic medium (phosphoric acid as the supporting electrolyte) the uranium reduction wave, U(VI) + 2*e* → U(IV), was composed of two waves. When perchloric acid was added in such amounts that the equivalent ratio of phosphoric to perchloric was ≧30:1, the two waves merged, with i_d values proportional, for practical purposes, to uranium concentration.

The effects of other acids, for example, nitric, sulfuric, hydrochloric, tartaric, oxalic, and hydrofluoric, were also studied. For all the acids the effect of pH change on i_d was the same, but effects of the anions were found to differ greatly among themselves. The effect of each anion on i_d is a function of the ease of complex formation

[61] I. Zlotowski and I. M. Kolthoff, "Polarographic Behavior of Alkaline Earth Metals. I. Barium and Strontium," *J. Am. Chem. Soc.* 66, 1431 (1944).

[62] P. Herasymenko, "Electroreduction of Uranyl Salts by Means of the Mercury Dropping Cathode," *Trans. Faraday Soc.* 24, 272 (1928).

[63] W. E. Harris and I. M. Kolthoff, "The Polarography of Uranium. III. Polarography of Very Weakly Acid, Neutral or Basic Solution," *J. Am. Chem. Soc.* 69, 446 (1947).

of the anion with either uranium(VI) or uranium(IV) and of the stability of the complex.

A careful study was carried out to determine the i_d/C value for the reaction, at the D.M.E., $U(VI) + 2e \rightarrow U(IV)$. It was found that the i_d/C value is not a true constant but varies both with pH and with uranium concentration. However, at uranium concentrations below 200 μg/ml, the i_d/C value is so close to a true constant that it may be considered so.

The results of this study are being correlated for oral presentation in the near future.

Amperometric Titration of Barium

H. E. Zittel F. J. Miller

The necessity for determining small amounts of barium in highly radioactive sample solutions led to a critical evaluation of available methods. Heyrovsky and Berezicky[64] demonstrated the feasibility of the amperometric titration of barium with sulfate but did no work at low concentrations of barium. Zlotowski and Kolthoff[61] studied the polarographic behavior of barium in aqueous and in ethyl alcohol–water solutions. None of the available methods met the requirements of the problem; therefore the following method, which is rapid and accurate, was developed. The test portion is dissolved in a supporting electrolyte composed of 0.1 *M* tetraethylammonium bromide in ethyl alcohol solution, the solution is titrated with a standard solution of lithium sulfate at a voltage of −2.0 v (the D.M.E. is the indicator electrode, and the S.C.E. is the reference electrode), and the diffusion current is measured by means of one of the three high-sensitivity polarographs developed at this laboratory (ORNL model Q-1160, Q-1338, or Q-1673). It was possible to determine barium in concentrations as low as 5×10^{-5} *M* with an error of less than 10%; for concentrations of $\sim 10^{-3}$ *M*, the error was <1%.

A study of interferences was carried out. It was found that sodium, chloride, fluoride, potassium, strontium, calcium, aluminum, and beryllium ions did not interfere if present in reasonable amounts. The lead ion did interfere, but it was found possible to titrate both the lead and barium together under the conditions given above. The lead was then measured by other means, and the barium was found by difference.

This work is described in a paper to be submitted for publication in *Analytical Chemistry*.

Polarography of Niobium in Ammonium Bifluoride

H. P. Raaen

The polarography of niobium in ammonium bifluoride, $NH_4F{\cdot}HF$, is of interest because liquid $NH_4F{\cdot}HF$ is being studied as a dissolvent for certain reactor fuels that contain niobium. It has been postulated that niobium exists only in the septivalent state when it is in solution in liquid $NH_4F{\cdot}HF$. This postulate suggests the possibility of the direct polarographic determination of niobium in liquid $NH_4F{\cdot}HF$ if the experimental difficulties associated with high temperatures (in the region of 150°C) and hydrofluoric acid can be overcome.

The experimental difficulties were overcome sufficiently well to permit a cursory evaluation of the polarography of niobium both in molten $NH_4F{\cdot}HF$ and in aqueous solutions of $NH_4F{\cdot}HF$. A Halocarbon oil in a stainless steel beaker that was set in a Glas-Col heater was a satisfactory constant-temperature bath for the electrolysis cell. It was possible by means of the recently developed ORNL model Q-1988 polarograph to use a platinum-wire reference electrode and a platinum-wire working electrode together in place of a saturated calomel reference electrode for the molten medium, which was of high resistance. These two reference-electrode systems were shown experimentally to give the same results when used for the determination at room temperature of cadmium in *n*-propanol, another system of high resistance. Several materials (Teflon, fluorothene, polystyrene, Lucite, polyethylene, and Saran) were evaluated for stability in molten $NH_4F{\cdot}HF$. Teflon proved to be the most stable, both dimensionally and chemically, and was used for the construction of the electrolysis cell. It was desired to use a D.M.E. as the indicator electrode. The rapid attack of molten $NH_4F{\cdot}HF$ on glass prevented use of a glass capillary. Attempts were made to fabricate from Teflon a capillary that simulated a glass capillary when used as a D.M.E. capillary. It was possible to obtain Teflon capillaries of short length (<3 mm, a limitation imposed by the maximum length of

[64] J. Heyrovský and S. Berezický, "The Deposition of Radium and Other Alkaline Earth Metals at the Dropping Mercury Kathode," *Collection Czechoslov. Chem. Communs.* 1, 19 (1929).

the drills) and as small as 3-mil ID by drilling Teflon rods into which wells (~4-mm ID) had already been drilled to serve as mercury reservoirs. These capillaries were unsatisfactory because of their short length (retraction of the mercury after the release of a drop caused molten $NH_4F{\cdot}HF$ to be drawn into the capillary), the nonspherical and varied shapes of drops, and irregular drop times and masses. It was difficult to obtain capillaries free of burrs and having an end surface perfectly perpendicular to the capillary opening. Two Teflon capillaries, each of ~8-in. length, were fabricated by the procedure of molding the Teflon about a 2- and a 3-mil-dia tungsten wire held taut and centered in the mold, and then withdrawing the wire. Although the difficulty caused by the retraction of mercury was minimized or eliminated, these capillaries were also unsatisfactory. By optical examination of the cross section of one of the capillaries (Fig. 11), it was shown that voids existed along the capillary and

Fig. 11. Cross Section of Unsatisfactory Teflon Capillary Intended for Use as a D.M.E. Capillary. 46X. Reduced 22%.

that the Teflon had not been molded to the surface of the wire. A platinum-wire indicator electrode was therefore used in lieu of a satisfactory Teflon D.M.E. capillary.

Molten $NH_4F{\cdot}HF$, and molten $NH_4F{\cdot}HF$ in which either niobium metal or niobium pentoxide was dissolved, were polarographed by means of platinum-wire working, indicator, and reference electrodes and of the ORNL model Q-1988 polarograph. The mole ratio of niobium to $NH_4F{\cdot}HF$ was about 1×10^{-4}. As a control experiment in which a metal of simple polarographic characteristics was used, molten $NH_4F{\cdot}HF$ that contained either dissolved cadmium metal or $CdCl_2{\cdot}2\frac{1}{2}H_2O$ was polarographed. The polarograms showed no reduction waves (or derivative peaks) that could be attributed to the reduction of forms of either niobium or cadmium. Reduction waves were obtained both in the absence and presence of niobium and cadmium, which indicated the presence of reducible impurities in the reagent-grade $NH_4F{\cdot}HF$.

Because the use of the platinum indicator electrode limited the investigation to applied potentials that were not more negative than about −0.8 v, a few experiments were made with a mercury-pool indicator electrode, whereby the negative potential was extended by about 0.1 v. The results likewise showed no reductions that could be associated with niobium.

The possibility of the polarographic determination of niobium in an aqueous solution of fused $NH_4F{\cdot}HF$ in which niobium was dissolved was investigated. The indicator electrode used was either a D.M.E. (glass capillary) or a mercury pool; the reference electrode was a platinum wire. Measurements were made at room temperature by means of the ORNL model Q-1673 polarograph since the aqueous solutions were not of high resistance; a Teflon electrolysis cell was used. The results were essentially the same as those obtained in the other experiments.

From this cursory study of the polarography of niobium in $NH_4F{\cdot}HF$, it is believed that in the supporting mediums described either the reduction occurs at a potential that is more negative than can be applied satisfactorily with the electrode systems used or the niobium does not exist in a polarographically reducible form. It is planned to investigate the polarographic behavior of niobium in other systems.

Study of Chemical Changes in UO_2-Al Reactor Fuel Elements During Heat Treatment at 600°C

H. Kubota

The studies that were described earlier[65] of chemical changes in UO_2-Al reactor fuel elements have been essentially completed. A reproducible scheme of analysis has been developed which is now being used in the analysis of two series of test plates. The major points of ambiguity, both in the analytical procedure and in the reaction, have been clarified.

The gasometric determination of metallic aluminum has been improved to give absolute values to within 1% when at least 0.2 g of aluminum is being determined. The positive bias of the gasometric over the gravimetric determinations that was reported last year has been eliminated.

The changes that take place within a completely reacted fuel plate can be represented by the reaction

$$3UO_2 + 16Al = 2Al_2O_3 + 3UAl_4$$

The initial products of the reduction of UO_2 are the lower intermetallics UAl_2 and UAl_3. Their presence in partially reacted plates has been confirmed by x-ray diffraction.

The results of the analysis of synthetic cores are depicted graphically in Fig. 12. The ratio of the uranium in the intermetallics to the total uranium is designated as degree of reaction (%). It is desirable to correlate degree of reaction with duration of heat treatment. Replicate cores that had been heat-treated for the same length of time, however, exhibited significant variation in the degree of reaction.

The results of the analysis of one series of fuel plates are given in Fig. 13. Fuel plates react more rapidly than synthetic cores under equivalent heat treatment, and the analytical results show a large gap between the as-fabricated and the 1.5-hr heat treatments at 600°C. Work is now under way to bridge this gap.

[65] H. Kubota, "Study of Chemical Changes in UO_2-Al Reactor Fuel Elements During Fabrication," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 10.

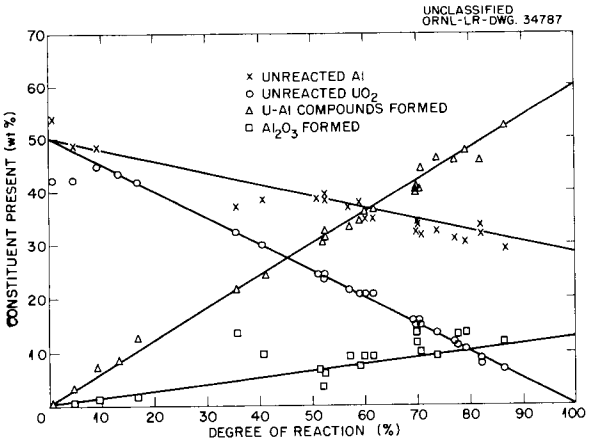

Fig. 12. Results of Constituent Analysis of Synthetic UO_2-Al Cores Reacted at 600°C.

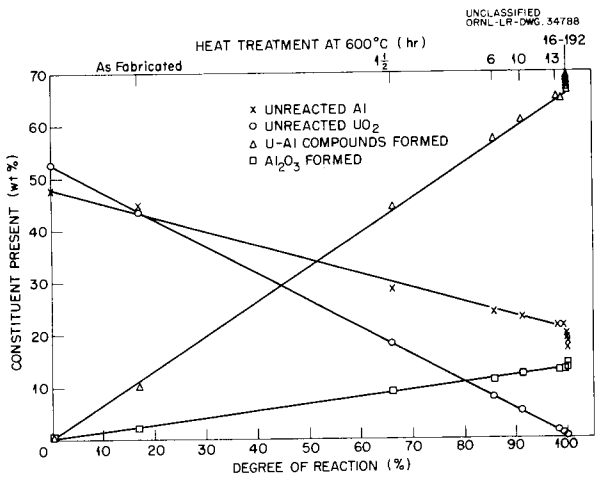

Fig. 13. Results of Constituent Analysis of 52.3 wt % UO_2–Al Fuel Plates Reacted at 600°C.

Determination of the Oxygen-to-Uranium Ratio of Uranium Dioxide

H. Kubota

Uranium dioxide almost invariably contains some oxygen in excess of the stoichiometric amount. Since many properties of the dioxide are a function of its composition, there is often a specific need to know the exact ratio of oxygen to uranium. Examination of the many methods available in the literature suggests that direct determination of the excess oxygen[66] is the most accurate method for determining the ratio.

[66] L. E. J. Roberts and E. A. Harper, *The Determination of Oxygen in Uranium Oxides*, AERE CR/R-885 (May 5, 1952).

Any oxygen in excess of the stoichiometric amount in UO_2 is held interstitially as the O^{2-} ion.[67] The oxygen can be held interstitially only if an amount of uranium(IV) equivalent to the interstitial oxygen is oxidized to uranium(VI). A determination of the uranium(VI) in UO_2, then, should provide a measure of the excess oxygen.

The test portion of UO_2 was dissolved in hot concentrated phosphoric acid under an argon atmosphere so that no change in oxidation states occurred. The uranium(VI) was determined polarographically in an aqueous medium containing 17 wt % phosphoric acid and 0.1 *M* perchloric acid. The polarography of uranium in phosphate systems has been studied in this laboratory [see "Polarographic Study of Uranium(VI) in Acid Media," this report] and elsewhere,[68] and the validity and reproducibility of the determination have been established.

The ratios of oxygen to uranium for test portions of −100 +325 mesh UO_2 reduced from $UO_3 \cdot H_2O$, one reduced in high-purity argon and the other in high-purity hydrogen, were determined to be 2.0172 ± 0.0013 and 2.0183 ± 0.0008, respectively. The excess oxygen increases with decreasing particle size. Pellets formed by sintering UO_2 granules at 1700°C in hydrogen showed the least amount of excess oxygen of all the samples of UO_2 studied.

Determination of Boron

H. Kubota

Studies of the determination of boron in various materials[69] have been continued, with special emphasis on separation procedures. When metallic cations are the interferences in the boron determination, their removal on a column of cation exchange resin has proved to be a simpler method of separation than the methyl borate distillation.

The volumetric determination of microquantities (10 to 100 μg) of boron was studied, and optimum conditions were established. It was also found that by the careful adjustment of the mannitol-to-borate ratio the free acid and mannitol-borate acid end-point breaks could be determined successively by means of an automatic titrator if the mannitol were added at the start of the titration.

Chelometric Titrations by Use of a Mercury Indicator Electrode

H. Kubota

Reilley *et al.*[70,71] have reported on the theory and application of a mercury indicator electrode for the potentiometric determination of a number of metal ions with ethylenediaminetetraacetic acid and its salts. The principle has been applied to the determination of certain metal ions, such as yttrium, magnesium, calcium, nickel, and bismuth, for which no really good volumetric method has been available. Successive titrations of yttrium and magnesium in the same solution have been performed by proper manipulation of the buffering system.

Reilley *et al.*[71] recommend manual titration; however, an ORNL autotitrator has been found to give good and reproducible titrations if the titrations are allowed to proceed at the slower feed speeds obtainable. A gold wire that has been dipped in mercury is used as the indicator electrode and an S.C.E. as the reference. A relative standard deviation of better than 1% is obtained when at least 0.1 mmole of metal ion is available for titration. In the titration of two ions successively the precision of the determination of the ion that is titrated second is usually poorer than the precision of the titration of that ion alone.

This titration shows great promise for the determination of a large number of metal ions. Work is being continued in investigating optimum buffer systems for the titration of mixtures.

Spectrophotometric Determination of Zirconium in Large Quantities of Thoria

A. D. Horton

Thorium oxide was dissolved in nitric, hydrochloric, or perchloric acid that contained a trace of hydrofluoric acid. Zirconium (10 to 150 μg) was extracted from 6 *M* nitric, hydrochloric, or

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[67] J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements*, p 139, Wiley, New York, 1957.

[68] T. Y. Chi, "Polarography of Uranium in Phosphoric Acid," *Hua Hsueh Hsueh Pao* 23, 79 (1957); [*Chem. Abs.* 52, 13483c (1958)].

[69] H. Kubota, "Determination of Boron," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 7.

[70] C. N. Reilley and R. W. Schmid, "Chelometric Titrations with Potentiometric End Point Detection," *Anal. Chem.* 30, 947 (1958).

[71] C. N. Reilley, R. W. Schmid, and D. W. Lamson, "Chelometric Titrations of Metal Ions with Potentiometric End Point Detection," *Anal. Chem.* 30, 953 (1958).

perchloric acid by a double extraction with 0.5 *M* thenoyltrifluoroacetone in xylene. Zirconium was stripped from the organic layer with 0.3 *M* hydrofluoric acid, and the extract was evaporated to dryness in the presence of nitric and perchloric acids to remove hydrofluoric acid and organic matter. The residue was dissolved in hydrochloric acid, and zirconium was determined spectrophotometrically by the method of Horton.[72]

Separation of Amsco from Tributyl Phosphate (TBP) and Quantitative Determination of Amsco by Vapor Chromatography

A. D. Horton

Very small amounts (2 to 25 mg) of Amsco were separated from large volumes (1 to 200 ml) of TBP and determined quantitatively. The TBP was hydrolyzed to a water-soluble organic salt by the method of Baldwin and Higgins,[73] that is, ethanolamine was added to the sample in the ratio of 5 moles of ethanolamine to 1 mole of TBP, the mixture was refluxed for 1 hr, and the salt was extracted into water from the Amsco; ethyl ether was used to extract Amsco from the aqueous phase. A known volume of the ether extract was injected into the dinonyl phthalate column of the vapor chromatograph, and the height of the first major peak of Amsco was compared with the height of the same peak on a standard Amsco elution curve (trace). The minimum quantity of Amsco that can be determined by this method is 2 mg.

Determination of Total Sulfates, Hydrogen Sulfide, Beryllium, and Lithium in Anhydrous Hydrofluoric Acid

A. D. Horton

Samples of anhydrous hydrofluoric acid to be analyzed for total sulfates were collected directly from the cylinder. Hydrogen sulfide was determined in a potassium hydroxide solution of the anhydrous hydrofluoric acid, which was given no further treatment. Beryllium and lithium were determined in samples related to studies of the solubilities of beryllium fluoride and lithium fluoride in anhydrous hydrofluoric acid.

Standard potassium iodate solution and potassium iodide were added to the sample that contained hydrogen sulfide. The solution was acidified with hydrochloric acid, and the excess iodine was titrated with a standard solution of sodium thiosulfate. One cylinder of anhydrous hydrofluoric acid that had been in use for several years was found to contain 0.25 wt % hydrogen sulfide.

Total sulfates, present initially as HSO_3F and H_2SO_4, were determined by evaporating the anhydrous hydrofluoric acid and other volatile constituents over a steam bath and then titrating the hydrofluoric acid–free residue with a standard solution of sodium hydroxide. The same cylinder that contained 0.25 wt % hydrogen sulfide contained only 0.005 wt % total sulfates.

Lithium was determined gravimetrically as the sulfate after the anhydrous hydrofluoric acid was evaporated off and the residue fumed with sulfuric acid. Lithium in small quantities was determined by flame spectrophotometry.

Beryllium was determined spectrophotometrically by the method of Luke and Campbell[74] after removal of the anhydrous hydrofluoric acid by evaporation and treatment of the residue with nitric and perchloric acids.

Coulometric Titration of Nickel in HR Fuel

A. D. Horton

Nickel was electrolyzed from an ammoniacal solution of HR fuel after the coulometric determination of copper and uranium in the fuel. The sample in the cell was neutralized with concentrated ammonium hydroxide solution, and an excess of 25% over the amount required for the neutralization was added. The solution was deaerated for 3 min and was pretitrated at –0.8 v vs the silver–silver chloride electrode. Nickel was then titrated at –1.2 v to a current background of 0.05 ma. The uranous hydroxide precipitate occludes a small amount of nickel. This tendency toward low results is overbalanced by a fairly high reagent blank. As a result, there is a positive bias of approximately 1%.

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[72] A. D. Horton, "Spectrophotometric Determination of Zirconium," *Anal. Chem.* 25, 1331 (1953).

[73] W. H. Baldwin and C. E. Higgins, "Determination of Equivalent Weight of Esters and Halides with Cation Exchange Resins," *Anal. Chem.* 30, 446 (1958).

[74] C. L. Luke and M. E. Campbell, "Photometric Determination of Beryllium in Beryllium-Copper Alloys," *Anal. Chem.* 24, 1056 (1952).

Ion Exchange–Spectrophotometric Determination of Fluoride in Dilute Sulfuric Acid

A. D. Horton

Fluoride ion was adsorbed on Dowex 1–X10 anion exchange resin that had been washed with ethyl alcohol and water and equilibrated with 0.5 *M* hydrochloric acid. Sulfate in the sample was adsorbed at the top of the column and displaced an equivalent of chloride from the resin. Fluoride, which has a distribution coefficient of about 3, was easily removed from the resin by elution with 0.02 *M* hydrochloric acid and was determined by the thoron color-diminution method of Horton, Thomason, and Miller.[75]

Analytical Investigation of the Vacuum Distillotion of TBP and Classification of the Degradation Products

A. D. Horton

It was proposed to distill TBP that had been used in the Thorex process in order to determine the nature of the degradation products that resulted from its irradiation and from its reaction with nitric acid. In order to make the data significant, pure untreated TBP was distilled first to determine whether or not it would undergo thermal degradation. The collection of the distillate was started at 82.5°C and 0.5 mm Hg. Five cuts were collected, and the temperature of the fifth cut was 89°C at 0.5 mm Hg. The distillation was discontinued because of a discoloration in the still pot and odors in the distillates, which indicated thermal degradation of TBP.

The classifications of the decomposition products as acids or as alcohols were made by the methods of Airan *et al.*[76] and Rice, Keller, and Kirchner,[77] respectively. Acids were extracted from the cuts into dilute solutions of sodium hydroxide, and the extracts were passed through Dowex 50 cation exchange resin. The organic acids were extracted from the water eluates into ethyl ether. Circular paper chromatography, in which an equivolume mixture of 5 *M* formic acid and 1-pentanol was the solvent, was used to indicate the presence of acids. Bromophenol blue was used as a developer. All cuts except the first contained acid residues. Alcohols were removed from the cuts by steam distillation and were extracted from the distillate into ethyl ether. After evaporation of the excess ether, the residues were heated with 3,5-dinitrobenzoyl chloride to form the 3,5-dinitrobenzoates of the alcohols. These were washed with a 2% solution of sodium carbonate, and the residues were recrystallized from ethyl alcohol. The characteristic orange color obtained when 1-naphthylamine is added to the 3,5-dinitrobenzoate of an alcohol was obtained only from the residue of the fourth cut.

Thermometric Titrations

F. J. Miller

Titration of Free Acid. – The study of the determination of free acid by thermometric titration has been concluded, and the results have been reported.[78] The systems studied were zirconium in hydrofluoric acid, uranyl ion in sulfuric acid, thorium in nitric acid, and uranyl ion in nitric acid. The method was found to be applicable to the determination of small amounts of free acid. Test solutions that contained quantities of free acid of the order of 0.1 meq were titrated with a relative standard error of ±1 to ±2% at the 95% confidence level; the relative standard error increased to about ±5% in the range of 0.01 meq. Free acid could not be successfully determined thermometrically in solutions that contained iron(II) or (III), aluminum(III), or uranium(IV). The results are discussed completely in ORNL-2489.[78]

Redox Titrations. – The thermometric redox titration of uranium(IV) with dichromate solution was investigated primarily to determine whether the thermometric method is applicable to redox titrations in solutions that contain ions deleterious to electrodes used in electrometric methods. A relative standard error of ±1% is attainable in the titration of quantities of uranium(IV) of the order of 5 mg. Less than 15 min is required to complete

[75] A. D. Horton, P. F. Thomason, and F. J. Miller, "Spectrophotometric Determination of Inorganic Fluoride," *Anal. Chem.* 24, 548 (1952).

[76] J. W. Airan *et al.*, "Identification of Organic Acids by Circular Paper Chromatography," *Anal. Chem.* 25, 659 (1953).

[77] R. G. Rice, G. J. Keller, and J. G. Kirchner, "Separation and Identification of 2,4-Dinitrophenylhydrazones of Aldehydes and Ketones, and 3,5-Dinitrobenzoates of Alcohols by Filter-Paper Chromatography," *Anal. Chem.* 23, 194 (1951).

[78] F. J. Miller and P. F. Thomason, *Thermometric (Enthalpymetric) Titration of Free Acid in the Presence of Certain Hydrolyzable Ions*, ORNL-2489 (June 13, 1958).

a titration. Fluoride ion can be tolerated in the solution if sufficient aluminum(III) is added to complex all the fluoride. The results of this study are given in a paper that has been submitted for publication in *Analytica Chimica Acta.*

Titration of Weak Acids. – The thermometric method has also been applied to the titration of acids that are somewhat difficult to titrate by more conventional methods. As an instance of this, boric acid has been titrated directly with a standard solution of sodium hydroxide by the use of an automatic thermometric procedure. Boric acid can be titrated either alone or in the presence of strong acids. Mannitol, if added to the solution of boric acid, sharpens the end point by improving the shape of the titration curve; however, this addition is not necessary to a good titration. Quantities of boric acid of the order of 0.2 meq can be titrated by the automatic thermometric procedure with a relative standard deviation of 1%. The results of this study have been described in a paper that has been accepted for publication in *Talanta.*

Precipitation Titration of Fluoride. – The precipitation titration of fluoride ion by means of a solution of lanthanum nitrate has also been studied. Early results indicate the feasibility of the titration, but the study has not been carried to a definite conclusion.

Determination of Halides

F. J. Miller

A study of the stoichiometry of the halide compounds of magnesium and of bismuth was initiated. Thus far, only the iodides have been studied.

The determination of magnesium iodide is complicated by its tendency to decompose in air. Special weighing bottles were used to transfer the test portion in a dry box under an inert atmosphere. The samples were dissolved in a solution of sodium hydroxide saturated with sodium sulfite. This solution was gradually neutralized with nitric acid until the magnesium hydroxide was dissolved, and it was then made up to a known volume. Magnesium was determined by titration with a solution of disodium ethylenediaminetetraacetate after a fuming with nitric acid to drive off all the iodide. Iodine in a separate aliquot was oxidized to the iodate with bromine, the excess bromine was reduced with formic acid in the presence of acetate buffer, sulfuric acid and potassium iodide were added, and the released iodine was titrated with thiosulfate.

Bismuth iodide is stable in air but tends to decompose readily when placed in solution. Consequently a special apparatus was devised that made possible the simultaneous decomposition and dissolution of the sample in nitric acid. The iodide was oxidized by the nitric acid to iodine. The iodine was evolved by heating the solution and passing an air stream through it; the iodine was trapped in a bubble tower in a solution of sodium hydroxide saturated with sodium bisulfite. The sodium hydroxide solution was made up to a definite volume, and the iodide content determined. The iodide was oxidized to the iodate with bromine, the excess bromine was reduced with formic acid in the presence of an acetate buffer, potassium iodide and sulfuric acid were added, and the released iodine was titrated with thiosulfate.

The solution of bismuth nitrate that remained in the flask was evaporated down in a platinum crucible, ignited to the trioxide at 900°C, cooled, and weighed as such.

Spectral Studies of Eu^{2+}, Eu^{3+}, and of $Li^6I(Eu)$ Scintillation Crystals

R. E. Biggers

For some time there has been considerable interest in anhydrous, $Li^6I(Eu)$ (0.025 to 0.1% Eu) scintillation crystals and in changes in their neutron-detection efficiency[79,80] with time after preparation. Such crystals are grown from molten Li^6I after the addition of $EuCl_3$. It is believed that Eu^{2+} is formed in the crystal-preparation process and is responsible to some degree for the scintillation properties. The valence-state distribution of europium in such crystals is being studied in several ways.

A nondestructive method is desirable so that the changes in the scintillation properties can be followed concurrently with the determinations of the valence-state distribution of europium as a function of time on a given crystal. Although considerable spectral work has been done on Eu^{3+}, very little has been done on Eu^{2+}. It is known,[81] however, that at wavelengths shorter than 4000 Å, solutions of Eu^{2+} absorb much more strongly than do

[79] R. B. Murray and J. Schenck, *Scintillation Response of LiI(Eu) Crystals to Monoenergetic Fast Neutrons,* ORNL CF-56-5-76 (May 11, 1956).

[80] R. B. Murray, *Fast-Neutron Spectrometer Development,* ORNL CF-56-11-5 (Nov. 2, 1956).

[81] H. N. McCoy, "Contribution to the Chemistry of Europium," *J. Am. Chem. Soc.* 58, 1580 (1936).

solutions of Eu^{3+}. Freed and Katcoff[82] have studied the absorption and fluorescence spectra of Eu^{2+} in crystals; however, with respect to the present study their work was qualitative, and they obtained the spectra by means of a spectrograph having photographic detection.

A vacuum-entry dry box has been set up for the handling of crystals and solid materials in a completely dry, inert atmosphere. A second small box has been set up for work with oxygen-free aqueous solutions in an inert atmosphere. Crystal holders have been constructed so that the absorption spectra of polished scintillation crystals or sections of crystals can be obtained in a dry, inert atmosphere by the use of a Cary model 14PM automatic recording spectrophotometer.

Pure compounds of Eu^{2+} and Eu^{3+} in oxygen-free organic and aqueous solutions are being studied. Considerable trouble has been encountered in obtaining sufficiently low oxygen concentrations for solvents used to dissolve pure Eu^{2+} compounds. Therefore, electrolytic techniques are being used for the preparation of standard solutions of Eu^{2+}; they are particularly useful for the preparation of solutions of low europium concentrations. When solutions thus prepared are kept in sealed cells, the Eu^{2+} appears to be very stable in perchloric acid solution. A detailed study is being made of Eu^{2+} spectra under numerous solution conditions, and the spectra should be available soon. Work with organic solvents has not been encouraging, primarily because of solubility limitations.

Destructive methods of analysis for Eu^{2+} and Eu^{3+} in the scintillation crystals are also being investigated; however, it is hoped that measurement of the spectral properties of the intact crystals will prove adequate for these determinations. The work will be continued.

Simultaneous Spectrophotometric Determination of Cerium and Plutonium Present as Mixtures of CeF_3, CeF_4, PuF_3, and PuF_4 in Fused $LiF\text{-}BeF_2$

R. E. Biggers J. H. Cooper[83]

In the study of fused-salt systems that contain plutonium, a method was needed for the accurate determination of total cerium and plutonium present as mixtures of the tri- and tetravalent fluorides in a fused eutectic of $LiF\text{-}BeF_2$. The examination of the absorption spectra of plutonium in all its possible valence states and of cerium in its two valence states indicated that, if the proper choice of valence states is made for the measurements, the system is almost spectrophotometrically ideal for a simultaneous determination of cerium and plutonium. Since neither a valence-state distribution nor a multicomponent analysis was required, a method by which each element could be determined in a definite and quantitatively reproducible valence state was satisfactory. The species most idealy suited for the simultaneous determinations were indicated to be PuO_2^{2+} and Ce^{4+}.

An intense and very narrow absorption peak is shown by PuO_2^{2+} at approximately 8350 Å. At this wavelength Ce^{3+} and Ce^{4+} show no absorbancy whatever. The spectrum of Ce^{4+} is characterized by a strong and very broad band that has a maximum at 3180 Å. However, the slope is such that the long-wavelength side of the band can be used without loss of sensitivity. Use of this side of the peak may be desirable for low Ce/Pu ratios, because PuO_2^{2+} shows gradually increasing absorbancy from 4000 to 3000 Å.

The absorption spectrum of Ce^{3+} is multibanded and lies entirely in the ultraviolet. The peaks are much sharper than is that of Ce^{4+} and occur at 2535, 2415, 2235, 2125, and 2930 Å; the absorbancy decreases in that order. The absorbancies of a Ce^{3+} sulfate solution (10 mg of Ce per liter) in 4 *M* sulfuric acid at the wavelengths shown are 2535 Å (2.17), 2415 Å (1.96), 2235 Å (1.05), 2125 Å (0.87), and 2930 Å (0.140). No absorbancy is exhibited by Ce^{3+} at wavelengths longer than 3300 Å.

In a medium that contains sulfate ion, complexes of plutonium sulfate and uncomplexed plutonium absorb light so strongly in the lower ultraviolet that the use of the ultraviolet region for the determination of small amounts of cerium in the presence of plutonium is excluded.

The problem has been approached from the point of view of finding suitable conditions under which dissolution of mixtures of CeF_3, PuF_3, CeF_4, and PuF_4 in the $LiF\text{-}BeF_2$ fused eutectic will be effected readily and under which both the plutonium and cerium will at the same time be quantitatively oxidized to their highest oxidation states. In this

[82] S. Freed and S. Katcoff, *The Absorption and Fluorescence Spectra of Bivalent Europium Ion in Crystals*, MDDC-1228 (declass. Aug. 14, 1947).

[83] High-Alpha Analytical Laboratory.

process it is obvious that the fluorides would have to be either removed or complexed sufficiently well to effect dissolution and to prevent any errors resulting from the presence of variable amounts of fluoride. Procedures of both removal and complexation have been investigated.

Previous work[84] on the determination of Pu^{3+} and Pu^{4+} in PuF_3-PuF_4 contained in fused NaF-BeF_2 has served as a starting point for the present work. The dissolution of the fluorides has been studied under numerous conditions of acidity, acid type, fuming methods, oxidant type, oxidant concentration, dissolution and fuming times, and fluoride volatilization and complexation. In addition, the fates of PuF_3 and CeF_3 have been studied individually by a fusion technique. The detailed results of these investigations involving about 16 different systems have been summarized[85] with regard to the advantages and disadvantages of each approach.

The procedure finally adopted consists in dissolution in boiling 5 vol % sulfuric acid–0.5 *M* boric acid; double fuming to remove fluorides as BF_3, H_2SiF_6, or HF; dilution of the residual liquid with dilute sulfuric acid; and oxidation of plutonium and cerium with Ag^{2+} (0.5 g of AgO). When the final solution is diluted to volume and allowed to stand for some time, the relatively large amount of Ag^+ formed precipitates from the solution as well-formed crystals of Ag_2SO_4, which readily settle, and not as the colloid or colloidal aggregates. In addition to the oxidation of the cerium, the PuF_3 or PuF_4 is quantitatively oxidized to PuO_2^{2+} under the above treatment. Spectra of the solution were obtained by means of a Cary model 14PM automatic recording spectrophotometer. A Beckman model DU spectrophotometer will not resolve the plutonium peak at 8350 Å.[86] Simultaneous equations were set up, and computations were made.

The attempted dissolution of the fluorides by fusion in potassium bisulfate–boric acid followed by oxidation with potassium pyrosulfate (Ag^+) yielded quantitative oxidation of plutonium fluorides to PuO_2^{2+}, but complete oxidation of Ce^{3+} to Ce^{4+} was never observed. Nitric acid is not suitable as a dissolvent since it has an absorption peak at 3000 Å. It could be used if subsequently removed by fuming with sulfuric acid but the amount of nitric acid–boric acid mixture necessary for dissolution would be larger than desired.

Procedures for separating cerium fluorides from plutonium fluorides in their mixtures have also been studied. Plutonium can be determined radiochemically and presents no problem, but the cerium separation is difficult. Samples have been dissolved in nitric acid–boric acid media, followed by fuming and dilution. Cerium separations were attempted by carrying on LaF_3. The analysis was then completed by dissolution of the cerium fluoride–lanthanum fluoride followed by reduction with excess Cr^{2+} and a conventional dichromate back titration. Even though the separations of cerium were complete, decontamination of the cerium fluoride–lanthanum fluoride from plutonium was never obtained, and errors in the titrimetric procedure resulted. The spectrophotometric procedure is preferred because the plutonium and cerium can be determined simultaneously and in less time than the separation procedure. No additional work is planned at the present time.

Simultaneous Spectrophotometric Determination of UO_2^{2+}, U^{4+}, and Cu^{2+} in 1 *M* Sulfuric Acid

R. E. Biggers

A rapid method has been developed for the accurate and precise determination of UO_2^{2+}, U^{4+}, and Cu^{2+} in acidic solutions obtained from a uranium-copper system that had been maintained in bombs at elevated temperatures and pressures. Measurements of the spectra of the pure species mentioned above show that the system is almost spectrophotometrically ideal over a wide concentration range for each species.

The measurement of a component present in an unusually lower concentration was facilitated by the use of long absorption cells.

The absorption spectrum of UO_2^{2+} in the low visible region (3500 to 5500 Å) is characterized by an 11-component band group with the central and

[84] R. E. Biggers and J. H. Cooper, "Determination of Plutonium(III) and (IV) in PuF_3-PuF_4 Mixtures Contained in Fused NaF-BeF_2," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 5–6.

[85] Memorandum from R. E. Biggers to P. F. Thomason, Aug. 4, 1958. Unpublished report is retained in reference files of P. F. Thomason, L. T. Corbin, R. E. Biggers, and J. H. Cooper.

[86] R. E. Biggers, "Spectrum of PuO_2^{++} in Sulfate Media – Resolution of the 8350-Å Absorption Peak of PuO_2^{++} into a Doublet," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 1–3.

highest absorption peak at 4195 Å. The absorption bands decrease in intensity toward longer wavelengths, and no absorption occurs at wavelengths longer than 5100 Å.

The spectrum of U^{4+} is multibanded; the most intense band occurs at 6516 Å and is also the most nearly ideal band for U^{4+} in the three-component system.

The absorption spectrum of Cu^{2+} shows one very broad band centered at 8100 Å and only very little absorption between 3300 and 6000 Å.

The molar absorbancy indexes a_M for this three-component system are given in Table 10. The matrix inversion for obtaining the simultaneous equations for this system was carried out by the use of the Oracle. The calculations were conventional. The absorption spectra are such that it is also possible to increase the number of components in the system, for example, by the addition of other actinides, such as plutonium, neptunium, or americium, in various valence states. The accuracy and precision of this rapid physical method compare very favorably with those of slower conventional chemical and separation procedures. No additional work is planned at the present time.

Preparation of Completely Deuterated Salts and Mineral Acids

R. E. Biggers

Some completely deuterated salts and mineral acids are needed in near-infrared absorption spectroscopic work, on plutonium and on plutonium solution kinetics, that is to be carried out in D_2O.

For the preparation of D_2SO_4, the method proposed by Shudde[87] has been found to be satisfactory. It consists in the slow vaporization of SO_3 from the pure stabilized γ-SO_3 (Sulfan B, General Chemicals Division, Allied Chemical & Dye Corp.) into scrubbers that contain pure D_2O. The SO_3 vapor is swept from the evaporators through an all-glass system by a stream of pure, dry helium. The method was scaled up and modified by making connections between each component with ball-and-socket joints and by increasing the temperature of the SO_3 vaporizer and trap to 42°C (automatically controlled). A 500-ml quantity of concentrated D_2SO_4, 36 *N* (99.9 at. % D), was prepared in a single experiment. The slow-vaporization procedure is very much superior to the methods[88–90] whereby liquid SO_3 is added directly to D_2O.

Procedures for the preparation of deuterated acids and other deuterated salts have been suggested.[89,90] Additional methods will be investigated.

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[87] R. H. Shudde, *The Preparation of Di-Deutero Sulfuric Acid*, NAA-SR-2158 (March 1, 1958).

[88] D. E. Glanville, *The Preparation of Deuterium Sulfate*, AERE C/R-2386 (Sept. 1957) [declassified version of HARD (B)/P-4 (Feb. 1956)].

[89] J. H. Freeman and C. E. C. Richards, *The Preparation of Deuterosulfuric Acid and Deuterochloric Acid and the Density of D_2SO_4 Solution*, AERE GP/R-2479 (Feb. 1958).

[90] R. E. Manson, *The Preparation of Deuterium Compounds*, CRE-480 (June 22, 1951).

Table 10. Molar Absorbancy Indexes (a_M) for the Analytically Important Absorption Bands of Uranium and Copper in 1 *M* H_2SO_4

Absorption Band Maximum (Å)	a_M			Ion of Greatest Absorption
	UO_2^{2+}	U^{4+}	Cu^{2+}	
4195	14.29	10.31	0.013	UO_2^{2+}
6516	0.091	50.09	3.046	U^{4+}
8100	0.194	7.219	12.22	Cu^{2+}

Measurement of Small Amounts of H_2O in D_2O by Near-Infrared Absorption Spectroscopy

R. E. Biggers

In preference to infrared absorption techniques,[91–96] a near-infrared technique has been used to determine H_2O in the concentration range from 0 to 10% in D_2O. Water (less than 5 vol %) in D_2O can be determined by infrared absorption spectroscopy;[97,98] however, near-infrared absorption spectroscopy has the following advantages. The absorptions resulting from overtone and combination frequencies of H_2O and D_2O in the near-infrared region are much less intense than those from the fundamental frequencies in the infrared region. Therefore in the near-infrared region much longer cells (of the order of centimeters) can be used; cells as long as 10 cm can be used for very low H_2O concentrations. Larger quantities of samples can be used since the lengths of cells for use in the infrared are of the order of a few hundredths of a centimeter. Construction of the cells is simpler and filling and cleaning are easier when the near-infrared is used. In addition, the path lengths can be measured with much greater accuracy than those of the short infrared cells. Furthermore there are no complications from window deterioration and dissolution when glass or quartz near-infrared cells are used, and the cells and windows are not so fragile.

The near-infrared spectrum of water has been obtained by previous workers[99,100] and by the present author; previous work is adequately summarized by Curcio and Petty.[101] Near-infrared absorption spectra of D_2O have been measured,[102–104] and the analytical applications have been discussed.[105]

When small amounts of H_2O are added to D_2O, the exchange reaction that produces HDO is instantaneous and practically complete; only when the concentration of H_2O is greater than about 8 vol % does unexchanged H_2O exist. It has been found,[105] and confirmed by the present work, that the near-infrared spectral character of H_2O is not observed as H_2O is added to D_2O. Instead a completely new absorption band, which is characteristic of HDO, is observed at 1.668 μ.

The experimental approach of the present work was similar to that previously proposed;[105] a detailed discussion of the experimental work has been written.[106] All absorption spectra were obtained with a Cary model 14PM automatic recording spectrophotometer. Cylindrical, ground-glass-stoppered quartz absorption cells (1- to 10-cm length) were used. By use of the suggested procedure,[105,106] 0.5, 2, 4, and 7 wt % H_2O in D_2O can be determined with respective approximate relative standard deviations of 7, 2, 1, and 0.7% when 1-cm absorption cells are used. For this length the lower limit of quantitative measurement

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[91] P. E. Shearin and E. K. Plyler, "Infrared Absorption of Mixtures Containing D_2O," *Phys. Rev.* 56, 845 (1939).

[92] F. P. Dickey and H. H. Nielsen, "The Infrared Spectrum of Heavy Water," *Phys. Rev.* 70, 109 (1946).

[93] F. P. Dickey and H. H. Nielsen, "The Infra-Red [Infrared] Spectrum of Heavy Water Vapor," *Phys. Rev.* 73, 1164 (1948).

[94] D. Williams and E. K. Plyler, "The Infra-Red [Infrared] Absorption of Heavy Acid Solutions," *J. Am. Chem. Soc.* 59, 319 (1937).

[95] M. Sohm, "Absorption of Light by Liquid H_2O and D_2O in the Infrared Spectral Region Between 5 μ and 27 μ" (translated), *Z. Physik* 116, 34 (1940).

[96] F. Matossi and H. Bluschke, "Infrared Reflection Spectra of H_2O, HDO and D_2O" (translated), *Z. Physik* 104, 580 (1937).

[97] V. Thornton and F. E. Condon, "Infrared Spectrometric Determination of Deuterium Oxide in Water," *Anal. Chem.* 22, 690 (1950).

[98] W. H. Stevens and W. Thurston, *The Determination of the D_2O Content of Heavy Water by Infra-red Spectrometry*, CRC-568 (March 1954).

[99] J. R. Collins, "Change in the Infrared Absorption Spectrum of Water with Temperature," *Phys. Rev.* 26 (2nd Series), 771 (1925).

[100] V. B. Evstigneev, "Heavy Water as a Solvent for Spectroscopic Investigations in the Near Infrared Region" (translated), *Doklady Akad. Nauk S.S.S.R.* 89, 105 (1953).

[101] J. A. Curcio and C. C. Petty, "The Near Infrared Absorption Spectrum of Liquid Water," *J. Opt. Soc. Am.* 41, 302 (1951).

[102] L. Kellner, "The Near Infra-Red Absorption Spectrum of Heavy Water," *Proc. Roy. Soc. (London)* **A159**, 410 (1937).

[103] G. Champetier, R. Freymann, and Yeon Ta, "The Absorption Spectrum of Heavy Water in the Near Infrared" (translated), *Bull. soc. chim. France* 5 (series 5), 929 (1938).

[104] W. C. Waggener, "Absorbance of Liquid Water and Deuterium Oxide Between 0.6 and 1.8 Microns. Comparison of Absorbance and Effect of Temperature," *Anal. Chem.* 30, 1569 (1958).

[105] J. Lecomte, M. Ceccaldi, and E. Roth, "Dosage isotopique de l'eau par mesure d'absorption dans l'infrarouge," *J. chim. phys.* 50, 166 (1953).

[106] An unpublished report, including a more detailed discussion of the experimental procedure, is retained in the files of R. E. Biggers and P. F. Thomason.

is ~0.2 wt % H_2O in D_2O. For less than 1 wt % H_2O, the use of longer absorption cells (up to 10 cm) results in a corresponding decrease in the lower limit; however, the relative standard deviations for correspondingly smaller weight percentages of H_2O are about the same.

Autoreduction of PuO_2^{2+} by Products of the Alpha-Particle Radiolysis of Water. Kinetics and Mechanisms[107]

R. E. Biggers

The work[108] on the autoreduction of PuO_2^{2+} by products of the alpha-particle radiolysis of water has been extended to include a number of additional parameters and has now been completed.[109] Ten additional autoreduction experiments have been carried out. Some of the parameters of these experiments are summarized in Table 11. Although the choice of systems may appear somewhat unusual, they were chosen to give basic information about the autoreduction phenomena in sulfate media, as well as the information primarily desired. The systems have been varied with respect to the following: media type; pH; total plutonium concentration at constant pH; and the ratio of per cent PuO_2^{2+} at the start of the reaction to total plutonium at fixed pH. The autoreductions have been allowed to proceed for a time sufficient for essentially complete reduction of PuO_2^{2+}. The plutonium in the starting solutions was present either completely or largely in the PuO_2^{2+} state. Plutonium not present as PuO_2^{2+} was present as Pu^{4+}

Space does not permit the graphical display of the linear and logarithmic time-dependent valence-state distribution for all the various systems studied. Typical examples are presented, and the relationships between the various parameters of the other systems are summarized briefly.

The radiation chemistry aspects of the autoreduction problem cannot be discussed herein. The general aspects of the radiation (x, γ, and α) chemistry of water and of the effect of accelerated light particles (protons, deuterons, and electrons)

[107] Abstracted from a paper presented at the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 13–18, 1958.

[108] R. E. Biggers and J. M. Chilton, "Autoreduction of PuO_2^{++} by Products of the Alpha-Particle Radiolysis of Water – Kinetics and Mechanisms," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 4–5; abstracted from ORNL CF-57-9-104 (July 8, 1957).

[109] A manuscript describing the entire work is now being prepared for publication.

Table 11. Some Parameters of the Plutonium Sulfate Systems Studied

Experiment No.	Medium	pH	Total Pu (mg of Pu per liter)	% PuO_2^{2+} at Start	% PuO_2^{2+} at End, of % PuO_2^{2+} Initially Present	Total Time* (hr)
1	0.3 *N* H_2SO_4	0.95	79.5	95.5	2.5	4414.2
2	0.3 *N* H_2SO_4, 1.26 *M* Li_2SO_4	0.95	114.7	96.7	2.3	4445.3
3	UO_2SO_4, 304 g of U per liter	1.55	58.1	38.2	3.3	957.2
4	UO_2SO_4, 304 g of U per liter	1.55	104.6	55.3	2.1	1505.9
5	UO_2SO_4, 304 g of U per liter	1.55	192.4	78.1	1.8	2105.4
6	UO_2SO_4, 310 g of U per liter	1.55	222	82.7	2.0	1429.0
7	UO_2SO_4, 304 g of U per liter	1.55	411.3	82.7	2.8	2297.7
8	UO_2SO_4, 304 g of U per liter	1.55	618.3	79.4	3.6	2297.8
9	UO_2SO_4, 304 g of U per liter	1.55	913.8	91.8	3.4	2469.1
10	UO_2SO_4, 212 g of U per liter	1.88	112.7	100.0	0.51	2592.7
11	UO_2SO_4, 121 g of U per liter	2.25	104.9	100.0	0.55	2572.4

*Time shown is the last time at which a % PuO_2^{2+} above 0 was obtained.

are well documented.[110,111] However, the up-to-date coverage[111] of alpha-particle radiation chemistry is rather brief and incomplete. A review was recently made of the alpha-particle radiation chemistry of aqueous media.[108].

Figure 14 shows the course of the autoreductions as evidenced by changes in the absorption spectra obtained during the course of the autoreduction of PuO_2^{2+} in 0.3 *N* sulfuric acid. In the UO_2SO_4 systems the minimum usable wavelength is about 5000 Å by the absorption of UO_2^{2+} at shorter wavelengths. The fairly sharp Pu^{4+} transition at 4805 Å can therefore not be used; instead, the 6750 Å and other less intense Pu^{4+} peaks are used. There were no peaks for Pu^{3+} and PuO_2^{+} visibly evident at any time during the autoreduction. The molar absorbancy index of Pu^{3+} is such that a rather small amount of it could be observed at 6000 Å if it were present; however, the spectrum of PuO_2^{+} is such that PuO_2^{+} in amounts equal to 5 to 10% of the total plutonium present could scarcely be observed in the presence of other valence states, particularly Pu^{4+}. Therefore the difference between the total plutonium and that found in the PuO_2^{2+} and the Pu^{4+} states may be accurately taken as PuO_2^{+} if no Pu^{3+} is evident at 6000 Å. If some Pu^{3+} is visibly present, calculations in which the four-component equation system is used will yield accurate results for the four valence states. Note in Fig. 14 that with increasing time the sharp PuO_2^{2+} doublet peak slowly disappears, and its disappearance results in increased absorption at the wavelengths where Pu^{4+} absorbs.

For the dilute H_2SO_4 system, Fig. 15 shows a linear relationship between the log of the PuO_2^{2+} concentration and time up to about 1700 hr, after which there is a definite break in the linearity. An expansion (not shown) of the 10-to-100% section indicates this somewhat more clearly. The "reaction" is obviously pseudo first order with respect to PuO_2^{2+} up to about 1700 hr.

A linear plot of the same data and, in addition, the complete valence-state distribution vs time are shown in Fig. 16. As is expected, Fig. 16 shows that the linear data plot of the first part of the reaction is curved (shown even more dramatically by experiments 10 and 11) and that a linear plot of the data forming the curved portion of Fig. 15 forms a straight line.

[110] S. C. Lind, *The Chemical Effects of Alpha Particles and Electrons*, 2d. ed., The Chemical Catalog Co., New York, 1928. American Chemical Society Monograph Series No. 2.

[111] N. Miller, "Effects of Ionizing Radiation on Aqueous Media," *Revs. Pure and Appl. Chem. (Australia)* 7, 123 (1957).

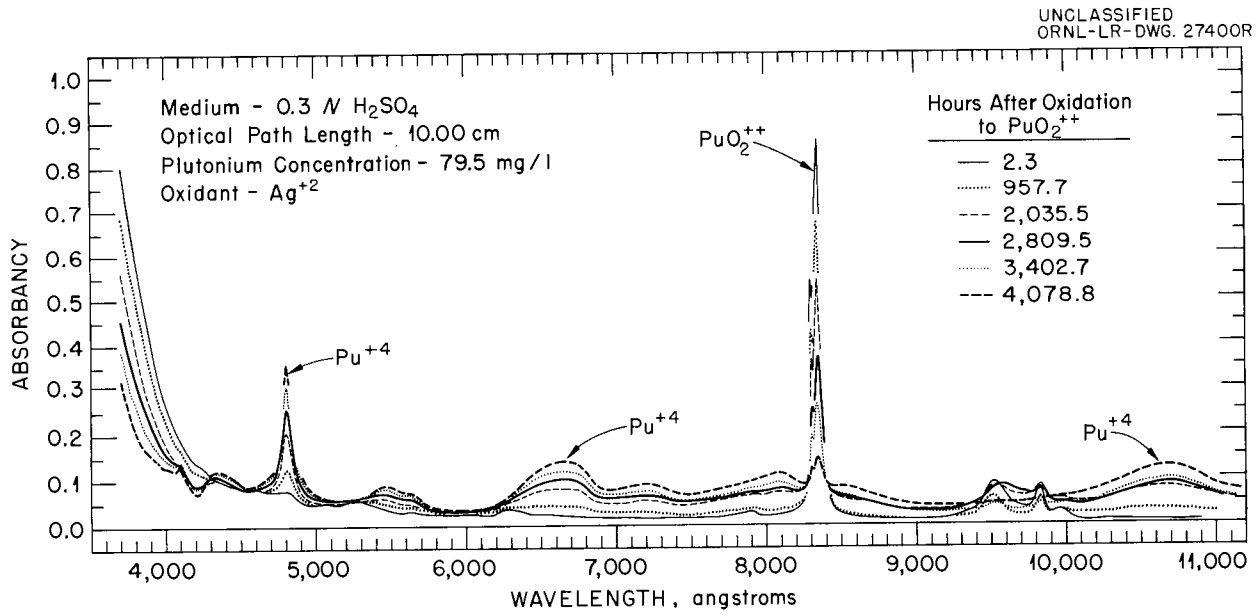

Fig. 14. Absorption Spectra of a Plutonium Solution, Showing Disappearance of PuO_2^{2+} and the Formation of Pu^{4+} with Increasing Time.

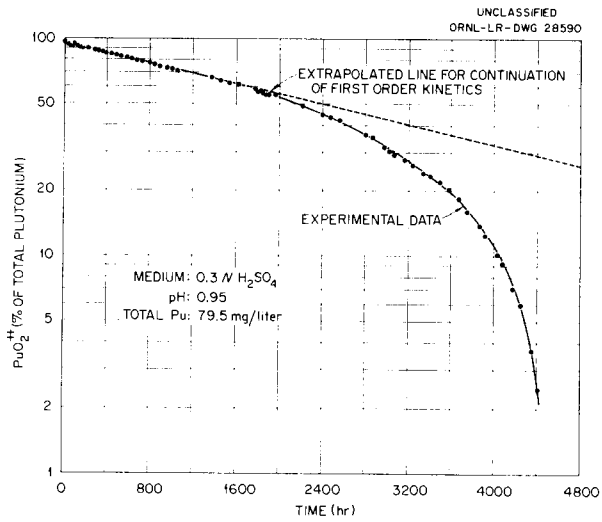

Fig. 15. Plot Showing the Decrease in the PuO_2^{2+} Concentration (Log Scale) with Increasing Time.

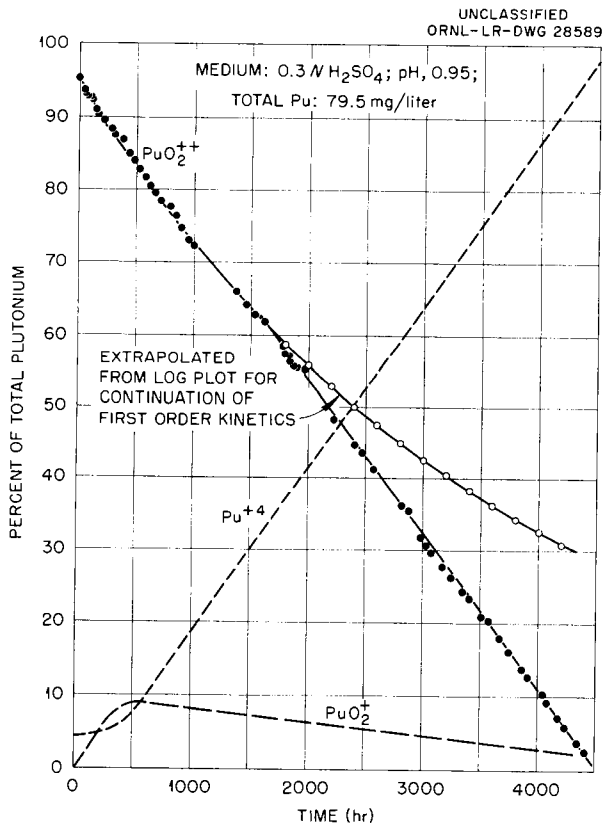

Fig. 16. Valence-State Distribution in a Plutonium Solution During the Course of the Autoreduction of PuO_2^{2+} to Lower Valence States.

As can be seen in Fig. 16, with no PuO_2^{+} present initially, PuO_2^{2+} is slowly reduced to PuO_2^{+} by active reducing species (e.g., H· and H_2O_2). After the PuO_2^{+} has reached a certain concentration level, it begins to disproportionate into Pu^{4+} and PuO_2^{2+} (the PuO_2^{2+} formed must be again reduced). With an initial Pu^{4+} concentration of 4.2%, the Pu^{4+} concentration begins to increase slowly, then much more rapidly, and finally increases over most of the reaction at a relatively constant rate. In the first step of the disproportionation reaction, Pu^{4+} and Pu^{5+} react to give Pu^{3+} and Pu^{6+}; this equilibrium reaction is then followed by the reaction of Pu^{3+} with Pu^{5+} to form $2Pu^{4+}$. The other possible reaction is $2Pu^{5+} \rightarrow Pu^{4+} + Pu^{6+}$. In either case the Pu^{3+} concentration never reaches an observable magnitude. The equilibrium reaction between all four valence states ($Pu^{4+} + Pu^{5+} \rightarrow Pu^{3+} + Pu^{6+}$) should actually lie toward the Pu^{4+} side because of the very strong sulfate complexation of Pu^{4+}.

The over-all mechanism consists in the reduction of Pu^{6+} to Pu^{5+} by the reducing agents, followed by the disproportionation of Pu^{5+} in such a manner that any Pu^{3+} formed rapidly disappears by subsequent reactions. The direct reduction of Pu^{6+} to Pu^{5+} and that of Pu^{4+} to Pu^{3+} by the reducing species formed by the radiolysis are possible reactions and most probably occur faster than the direct reduction of Pu^{5+} to Pu^{4+} and Pu^{3+}. In addition low concentrations of reducing agents, as in the present case, favor the disproportionation mechanism. Space does not permit a detailed analysis of the kinetics of even this one reaction. Since all four valence states can exist simultaneously, there are very many equilibriums, and many irreversible reactions are probably involved to some extent in the present systems. The direct reductions from one valence state to the next lower are possible by both H_2O_2 and free radicals of hydrogen. In addition, oxidation reactions of plutonium in all its valence states, with H_2O_2 and other radiolytic oxidizing fragments, and complexation reactions with H_2O_2 are possible. Furthermore, disproportionation and reproportionation reactions of the other valence states of plutonium, especially Pu^{4+}, are strong possibilities for certain stages of the over-all reactions for some systems studied.

In Fig. 16 the slopes for Pu^{4+} and PuO_2^{+} indicate that Pu^{4+} is being formed faster than it could all be formed from the disproportionation of Pu^{5+}.

This can be interpreted as a result of the direct reduction of Pu^{4+} to Pu^{3+} by reducing species; the Pu^{3+} then reacts very rapidly with Pu^{5+} to yield $2Pu^{4+}$ for each Pu^{4+} originally reduced, with the net conversion of Pu^{5+} to Pu^{4+}. The complete kinetic analysis for the system shown in Fig. 16 and all the other systems is extremely complex, and the end result of all the possible reaction paths must be interpreted only as the logical path which agrees with the observed valence-state distribution. It may not be a true picture since there are such a large number of reaction possibilities.

The general conclusions that can be drawn from all the autoreduction experiments are as follows. When the pH is maintained constant and the SO_4^{2-} concentration is increased, the Pu^{4+} concentration decreases from that present at the beginning of the autoreduction and then increases. This effect must be due to an oxidation reaction of the H_2O_2 that is formed by the alpha-particle radiolysis. Experiments carried out by varying the initial plutonium concentration show that as the plutonium concentration is increased Pu^{3+} can exist even though Pu^{6+} is present and show that the maximum Pu^{5+} concentration and duration of existence of Pu^{5+} decrease with an increase in the total plutonium concentration.

When the pH is increased, at approximately the same total plutonium concentration, toward the region of maximum stability of Pu^{5+}, the maximum concentration of Pu^{5+} is observed to increase, and no Pu^{3+} is observed as long as there is any Pu^{5+} or Pu^{6+} present. Calculations of the energetics for the experiments show that the H_2O_2 produced is by itself insufficient to account for the reductions observed.

The results of the present series of investigations and calculations have been compared; they show good agreement with the data known for americium[112–118] and with some recently reported data on the reduction of PuO_2^{2+} by products of the gamma-ray radiolysis of water.[119]

Calculations on the reaction energetics are all well within the accepted and expected limits and are in agreement with the postulated and possible mechanisms. In particular, the very recent work of Yakovlev and Kosyakov[120] on the autoreduction of americium shows very close agreement with the present work with regard to the type and general characteristics of the valence-state distribution plots.

At the present time no additional work on this phenomenon is planned or in progress. For the most part this is due to the very long time (4 to 6 months) required for a study of each experimental parameter or of part of each. To do otherwise would require a very large number of experiments at one time. A *complete* investigation from all interesting aspects would tie up personnel, a spectrometer, and large numbers of very expensive absorption cells for years. Unless a cooperative effort could be initiated between interested persons, each studying one or two parameters of a given system, further work on this phenomenon will probably have to be confined to americium, whose over-all reduction is approximately 50 times faster than that of plutonium.

MASS SPECTROMETRY (Y-12)

A. E. Cameron

The Referee Analysis Laboratory put two 6-in.-radius mass spectrometers into operation in the last year which had been constructed previously. The original tube in one of these has been replaced with

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[112] S. R. Gunn and B. B. Cunninghom, "The Heats of Formation of AmO_2^+ (aq.) and AmO_2^{++} (aq.) in 1 *M* $HClO_4$," *J. Am. Chem. Soc.* 79, 1563 (1957).

[113] L. B. Asprey and S. E. Stephanon, "The Autoreduction of Am(VI) and Am(V) in Dilute Acid," *Abstracts of Papers 118th Meeting of the American Chemical Society, Chicago, Ill., Sept. 3–8, 1950*, p 29Q (1950).

[114] L. B. Asprey and S. E. Stephanon, *The Auto-reduction of Am(VI) and Am(V) in Dilute Acid*, AECU-924 (Nov. 10, 1950).

[115] L. B. Asprey, S. E. Stephanon, and R. A. Penneman, "Hexavalent Americium," *J. Am. Chem. Soc.* 73, 5715 (1951).

[116] G. N. Yakovlev and V. N. Kosyakov, "Spectrophotometric Studies of the Behavior of Americium Ions in Solutions," *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955* 7, 363 (1955).

[117] G. R. Hall and T. L. Markin, "The Self-Reduction of Americium(V) and (VI) and the Disproportionation of Americium(V) in Aqueous Solution," *J. Inorg. & Nuclear Chem.* 4, 296 (1957).

[118] S. E. Stephanon, L. B. Asprey, and R. A. Penneman, *The Disproportionation of Americium(V)*, AECU-925 (1950).

[119] M. Pages, C. Ferradini, and M. Haissinsky, "Sur la réduction du sulfate de plutonyle par les rayons γ," *Compt. rend.* 245, 1128 (1957).

[120] G. N. Yakovlev and V. N. Kosyakov, *The Investigation on the Americium Chemistry*, Second United Nations Internatianal Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, Paper A/CONF. 15/P/2127 (1958).

an improved version that utilizes the source-chamber isolation valve of the type developed at KAPL. A 6-in.-radius, 180°, inhomogeneous-magnetic-field spectrometer was assembled and worked with during the year. The predicted dispersion, that is, equivalent to an ~30-in. geometrical radius, was attained. The spacing at the receiver slit between adjacent masses at mass 267 was measured to be 0.107 in. A recent revision of the pole-face geometry now takes better account of the fringing field, and focusing is improved.

Construction was begun in July of two mass spectrometers of the KAPL type, which uses two 12-in., 90°-deflection magnetic sectors in series. This type of instrument is particularly adapted to measurements of high abundance ratios at medium and high mass. The first of these two instruments will be in operation in January 1959, and it is estimated that the second will be ready in March 1959. Additional space was included in the pressurized clean laboratory to provide for this new equipment.

The service laboratory is now consolidated in Room 21 of Building 9735, with space for the installation of additional mass spectrometers. A 12-in.-radius, 60° instrument and a 6-in.-radius, 60° instrument are now being constructed.

Mass Spectrometry Research and Development

J. F. Burns

The 60°, 6-in.-radius mass spectrometer, which was used in the potassium work reported last year, has been modified to permit the analysis of gaseous samples. In addition, a ten-stage electron multiplier has been incorporated in the signal-detection system. It consists of the dynode assembly of a DuMont type 6292 multiplier phototube and is mounted in the same way that has been used successfully at other AEC installations. It was found to have a useful gain of 10^6 and is only slightly affected by short-time exposure to air.

The greater part of the time was devoted to a survey of the various fields to which the appearance potential technique, used in determining the heat of dissociation of nitrogen,[121] might be applied. Among these fields were the detection and identification of free radicals and other intermediate products in flames, photochemical processes, and the like; dissociation, ionization, excitation, and charge exchange phenomena induced by low-energy ion bombardment; processes leading to negative ion formation; and bond-energy measurements by electron bombardment. A fairly complete collection of the literature pertaining to these fields has been made. It is presently being analyzed so that a specific program, which will provide the greatest contribution to the knowledge and understanding of these related fields, can be set up. Experimental work will begin within a short time.

Thermal Diffusion

W. R. Rathkamp

The krypton thermal diffusion plant, which consists of 220 ft of $^7/_{16}$-in.-ID copper tubing surrounding a 0.020-in.-dia Nichrome heater wire, is now routinely producing Kr^{86} of 99.97% purity. This isotope of krypton will probably be chosen as the filling for gas discharge lamps to replace the cadmium now serving as the reference standard of length through the definition of the meter in terms of the 6438-Å line.

A new laboratory has been constructed to provide adequate facilities for extending the thermal diffusion work to other materials.

Eighteen large Calrod-heated columns, each 15 ft long, are being installed. It is expected that this system will make possible the separations of the light isotopes of krypton and the isotopes of neon and argon.

ORNL MASTER ANALYTICAL MANUAL

Authors of Methods (X-10 and Y-12)

H. P. Raaen (X-10) H. P. House (Y-12)

The *ORNL Master Analytical Manual* was one among seven handbooks and manuals that were displayed in the Special Reference Materials section of the United States Technical Information Center at the International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, August 1958. Two copies each of Sections 1 (*Ionic Methods*), 2 (*Radiochemical Methods*), 3 (*Spectrographic Methods*), and 5 (*Nuclear Analyses Methods*) were made available for examination by the delegates. Section 9 (*Process Methods*) has not yet been reprinted by the AEC Technical Information Service Extension.

Thirty-six new methods were issued to the *Manual* (see "Presentations of Research Results"), and

[121] J. F. Burns, *The Heat of Dissociation of Nitrogen and the Appearance Potential of Some Ions Formed in Fluorine and Hydrogen Fluoride by Electron Impact*, K-1147 (Oct. 8, 1954).

the Tables of Contents for three sections were revised to bring them up to date. The new methods represent a part of the research and development work of the Division. Eight new manuals were issued; of these, seven were issued to ORNL custodians.

OPTICAL AND ELECTRON MICROSCOPY (X-10)

T. E. Willmarth

H. W. Wright T. G. Harmon

Methods of Preparing Samples for Electron Microscopy

Replication of Crystals and Agglomerates of Thorium Oxide. – An improved method for replicating the surfaces of thorium oxide crystals and agglomerates for study in the electron microscope has been developed. A suitable dispersion of the material to be studied is prepared on a glass microscope slide, and then carbon is vaporized onto the preparation at a normal angle of incidence. The resulting film is crosshatched with a sharp point in squares of a size that just covers a ⅛-in.-dia, 200-mesh wire grid. The slide is then placed in a Petri dish, and enough concentrated sulfuric acid is flowed in to just cover the slide. To this is added 2 ml of 1% hydrofluoric acid solution. The acid mixture is warmed in a hood to a temperature at which the sulfuric acid fumes and is held at this temperature for approximately 3 hr, or until the squares of carbon film float free. Each freed film is picked up on a fine-mesh platinum screen and is transferred to a distilled water bath where it receives successive washings. Finally, the film squares are captured on 200-mesh, ⅛-in.-dia, copper grids and are shadowcast with germanium at a 30° angle. This technique has proved especially valuable in the study of the nature of thorium oxide produced from thorium oxalate. Direction of growth, shape characteristics, surface phenomena, and edge effects, difficult or impossible to perceive with particle preparations of the original material because of their opacity to the electron beam, can be observed and studied. An electron micrograph of a crystal of thorium oxide formed in a 0.001 *M* solution of oxalic acid and precipitated at 25°C from a thorium nitrate solution is shown in Fig. 17.

Electrolytic Stripping of Bulk Oxide Films from Stainless Steel. – The method of Willmarth *et al.*[122] for the electrolytic stripping of oxide films from stainless steel for use in electron microscopy and diffraction has been slightly modified for removing bulk oxide coatings of the type encountered on stainless steel samples from GCR test loops where weakly bonded, large oxide crystallites exist on the metal surface at the oxide-to-air interface. Such crystallites have a tendency to come off singly or in groups too small for collection and direct study. By introducing the additional step of vaporizing carbon onto their surfaces prior to their immersion in the electrolyte, such crystallites are held in position by the thin carbon film and float free in segments large enough for easy capture on electron microscope grids. These crystallites can be used for micrographs and transmission electron diffraction studies or can be mounted and studied by reflection electron diffraction. In the latter case, where multilayered oxide coatings are present, it is frequently desirable to identify the oxides present at both the oxide-to-metal interface and the oxide-to-air interface. This can be done by depositing a very thin carbon film, which offers little, if any, resistance to the penetration of electrons, and mounting the removed oxide-film segment in such a manner that it can be reversed and both sides presented to the electron beam without the necessity of breaking instrument vacuum.

Replication of Corroded Stainless Steel Surfaces. – The Faxfilm replica method, suggested by Ladd,[123] has been used, with slight modification, almost exclusively for electron microscopy studies of the corroded surfaces of metals exposed in the GCR test loops. This technique consists in placing a small drop of cellulose acetate–acetone solution on the surface of the material to be replicated and then placing a piece of cellulose acetate tape over the drop. The tape is pressed down with the ball of the thumb in order to spread the drop and to ensure intimate contact between the drop and the surface. After about 1 min, a free end of the tape is grasped with tweezers and stripped. The resulting negative replica is mounted flat in a holder, and a carbon film is vaporized on top at a normal angle of incidence. The sandwich of cellulose acetate and carbon is cut into segments to fit electron microscope grids and is placed in an acetone bath, carbon side up. The

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[122] T. E. Willmarth, F. D. McNeer, and B. I. Gary, *Chem. Quar. Prog. Rep. March 26, 1951*, ORNL-1088, p 78 (classified).

[123] W. L. Ladd, Ladd Research Inc., Roseyln Heights, N.Y., private communication to T. E. Willmarth, Sept. 11, 1957.

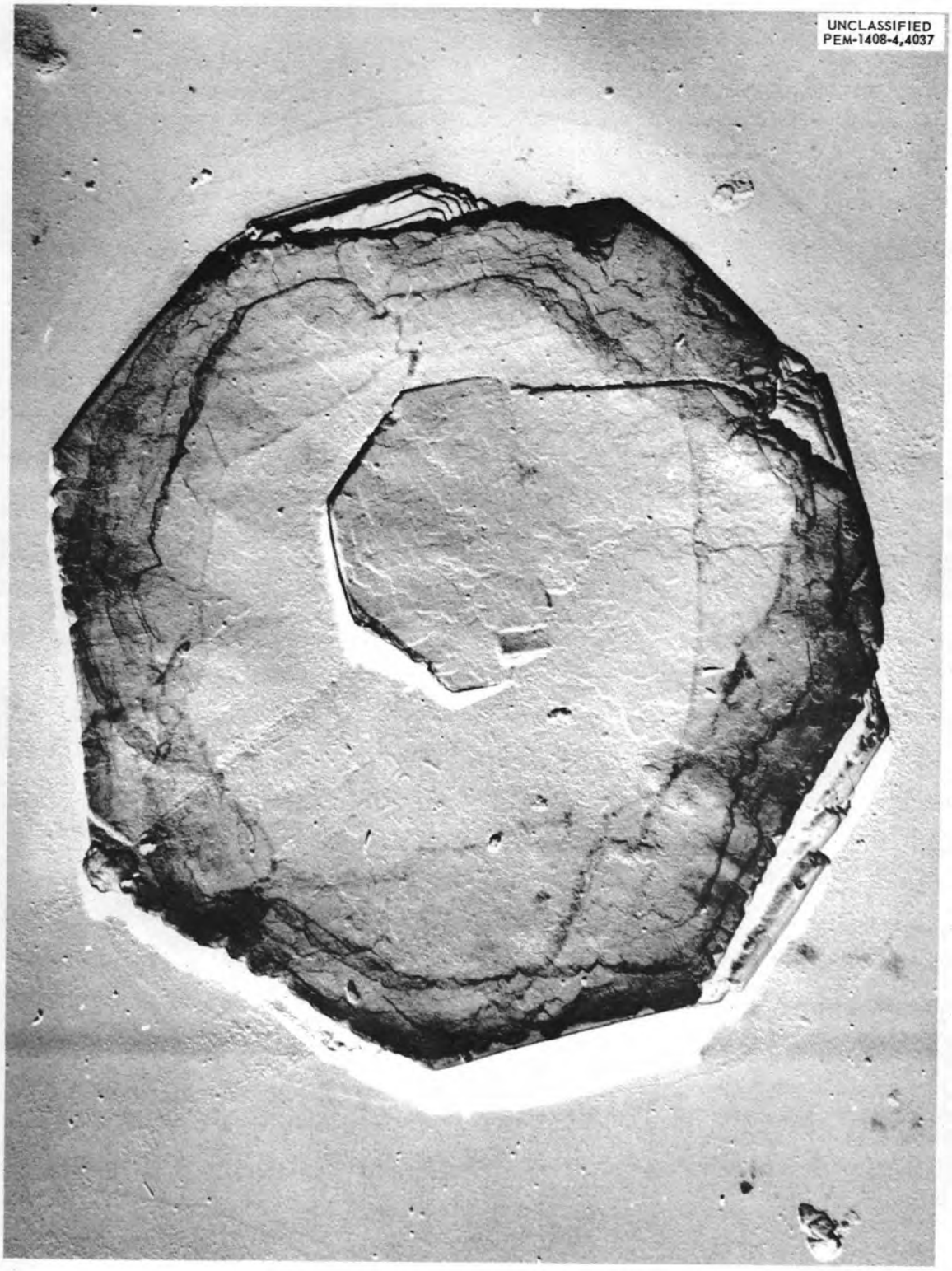

Fig. 17. Electron Micrograph of Thorium Oxide Crystal Precipitated from Thorium Nitrate Solution at 25°C by Means of 0.001 *M* Oxalic Acid. Carbon replica, germanium shadowcast; 12,000 X. Reduced 15.5%.

acetone dissolves the negative replica of cellulose acetate and thus allows the carbon positive-replica squares to float free. These are collected on grids and are shadowcast with germanium at a 30° angle. Such replicas have been found to duplicate minute surface details of the material under study. Frequently small segments of the oxide films adhere to the replica when it is stripped and remain with the final replica. Such oxides can then be successfully identified by transmission electron diffraction. The shadowcast germanium serves as a convenient, built-in standard. Figure 18 is an electron micrograph of the surface of type 316 stainless steel after it was exposed in an atmosphere of carbon dioxide at 1500°F.

Studies of Thorium Oxide

Microscopic studies were continued on the effect of size and shape of particles of thorium oxide on its rheological properties. In connection with this work, observations made by means of the TV-monitoring screen of the Cintel particle-size resolver with high, dry optics (4-mm objective; 10X ocular; screen magnification, 3200X) indicated that there were marked differences in the behavior of some thorium oxide preparations having particles in the size range below 1 μ when they were immersed in distilled water. Very obvious charge effects have been noted in particles appearing in the enlarged television image. Study is contemplated to determine whether a correlation exists between certain variables of preparation and the observed charge effects; the Cintel TV-monitoring screen will be used for preliminary observations, and Cine photomicrography for the permanent recording and more intimate slow-motion studies.

Examination of Thin Films, Corrosion Products, and Surface Structures

Corrosion test specimens and pipe sections from GCR test loops have been examined optically, and the surfaces have been replicated for observation in the electron microscope. Diffraction studies of corrosion films *in situ* and of stripped films have been made in order to identify surface constituents. Representative of this type of work was the finding of the high-temperature, isometric form of silicon dioxide (α-cristobalite) as a major component of surface films on test samples and pipe sections after initial test runs were made on the sections in an atmosphere of carbon dioxide at 1500°F. Subsequent investigation disclosed that a lower form of silicon dioxide was present, predominantly at grain boundaries in the original type 347 stainless steel pipe sections of the loop, as a result of sand-blasting treatment during fabrication. This form was changed to the high-temperature form during the run and was distributed throughout the system by convection currents.

A number of samples of aluminum foil that had been exposed at various positions in the plasma chamber of the DCX (Direct Current Experiment) machine were examined for the Sherwood Project. Black film deposits found on the foil were stripped from the aluminum base and were identified as carbon by transmission electron diffraction. Apparent corrosion of the aluminum strips was also noted, but corrosion products were not identified because controlled corrosion experiments have not been possible.

Study of Single Crystals of Germanium

Various sizes and shapes of single-crystal germanium platelets were prepared for use as detector elements for surface-barrier-type counters. Crystals were properly lapped in order to remove surface irregularities caused by the cutting operation and were acid-etched to remove scratches promoted by the polishing operation; the (111) faces of the crystal were covered with vaporized gold to a maximum thickness of 2000 Å. It was found that single crystals cut with a Cavitron, a high-frequency-sound cutting device, as well as crystals immersed in water and subjected to the high-frequency sound waves of a Brush hypersonic generator in order to clean etch products from the surface, were rendered useless as detectors. X-ray examination failed to disclose any lattice distortion, but optical investigation suggests the presence of submicro cracks at the crystal edges. Further electron microscopy studies will be made in which replica techniques are used.

Electron Microscopy of Biological Materials

The Biology Division is being assisted in preliminary explorations with the electron microscope to determine the nature and extent of radiation damage induced in the kidney tissues of mice that have received sublethal doses of radiation. Primary interest is in the blood-vessel walls which make up the glomerular coils. Radiation damage, as well as aging, indicated by the relative thickness of the walls, can be observed with the electron microscope

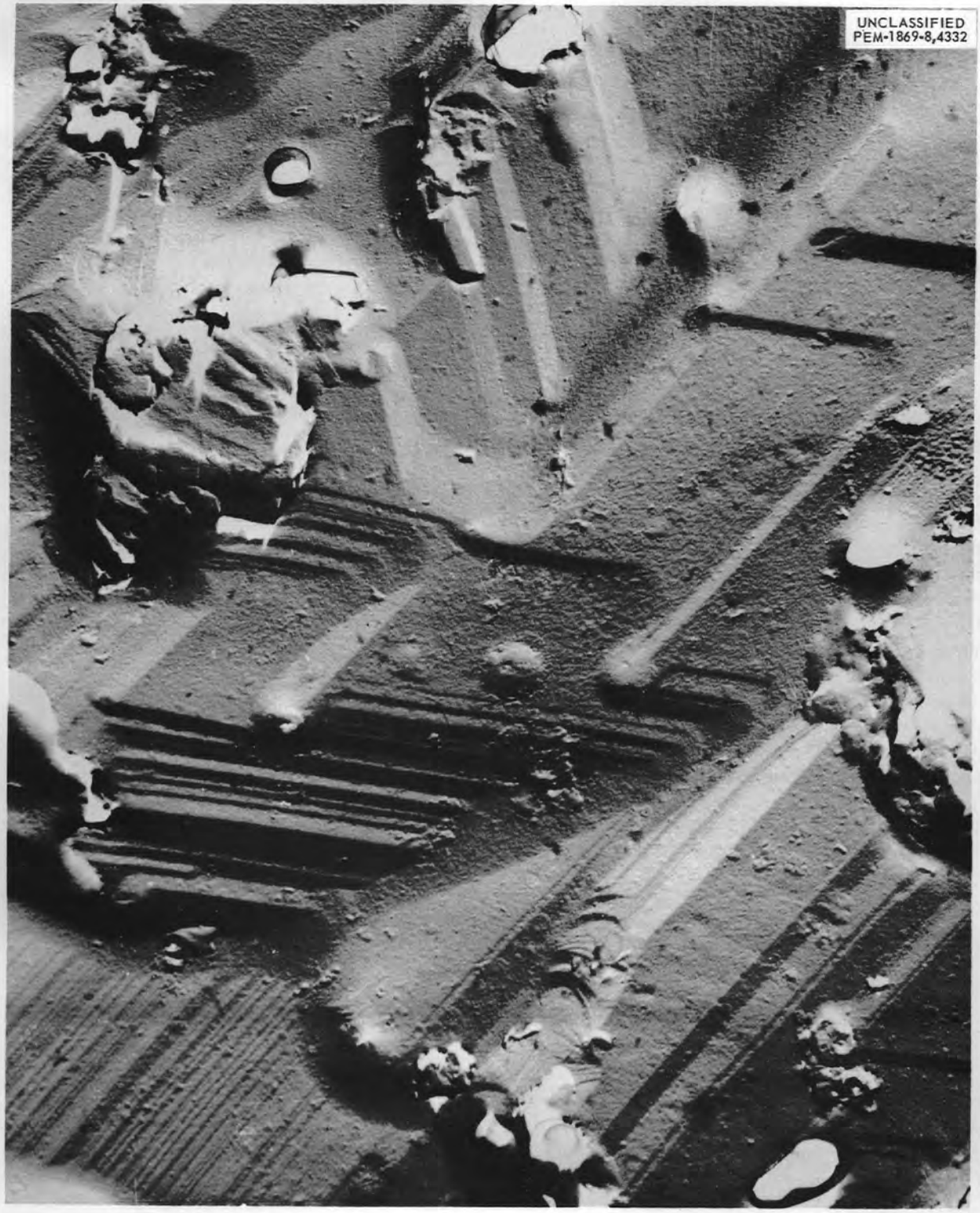

Fig. 18. Electron Micrograph of Surface of Type 316 Stainless Steel After Exposure in Carbon Dioxide Atmosphere at 1500°F. Faxfilm-carbon replica, germanium shadowcast; 24,000 X. Reduced 9%.

when extremely thin microtomed sections of the kidney tissue are used.

Instrumentation

The present EM-100 Philips electron microscope, which has a resolving power of approximately 50 Å, has been converted to an EM-100B type by the substitution of a new lens system that is capable of resolution of the order of 15 to 20 Å. A new EM-75B Philips electron microscope has been purchased for studying materials that do not require a resolution of less than 35 Å and for preliminary investigation and inspection of material which may require higher resolution.

QUALITY CONTROL

R. L. McCutchen (Y-12) B. J. Ginocchio (X-10)
C. D. Susano (Y-12)

The scope and operation of the Statistical Quality Control (SQC) program at X-10 remained essentially unchanged during 1958. Several innovations in the operation of the SQC program at Y-12,[124–126] however, were studied for improving the effectiveness of the work. Having determined as a result of this investigation[125–126] that certain modifications were necessary, operational changes were made in accordance with a plan previously formulated. While these operational changes do not relieve Quality Control of the responsibility for maintaining an effective departmental SQC program, they do enable each supervisor to recognize unsatisfactory conditions and to initiate prompt remedial action to eliminate them before the quality level of the work in his laboratory has been seriously affected.

The improvement in the quality level, defined as the per cent of control results outside the fixed control limits, for the Y-12 laboratories is apparent from the summary for 1958 given in Table 12, that is, 6% for 1958 as compared with 8% for 1957. (The values for 1957 represent actual experience rather than the estimation used in ORNL-2453.[127])

[124] M. T. Kelley, *Statistical Quality Control Report for the Analytical Chemistry Division January–March, 1958*, ORNL CF-58-4-120.

[125] M. T. Kelley, *Statistical Quality Control Report for the Analytical Chemistry Division January–June, 1958*, ORNL CF-58-7-125.

[126] M. T. Kelley, *Statistical Quality Control Report for the Analytical Chemistry Division January–September, 1958*, ORNL CF-58-10-94.

[127] R. L. McCutchen, B. J. Ginocchio, and C. D. Susano, "Quality Control," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 75.

Table 12. Summary of Distribution of Control Determinations by Laboratory for 1958

Laboratory	Determinations Evaluated for Control Purposes			Quality Level (%)*	
	Total Number	Outside Fixed Limits		1957	1958
		Number	Per Cent		
X-10					
Building 3019	7,272	603	8	5	8
Building 3508	457	52	11	11	11
Building 3550	855	65	8	5	8
Building 4500	1,252	81	7	4	7
Total	9,836	801	8	5	8
Y-12					
Building 9201-2	297	6	2	5	2
Building 9204-1	973	16	2	2	2
Building 9733-4	1,276	130	10	11	10
Total	2,546	152	6	8	6
Division total	12,382	953	8	6	8

*Per cent of control determinations outside fixed limits.

A year ago, when the quality level for the control work in the Division was estimated, a value of 10% was reported[127] for the laboratories at X-10. As shown in Table 12, the quality level in this case was actually 5% during 1957 rather than 10%. This serious discrepancy between actual and estimated quality level for the laboratories at X-10 is attributed to the technique that was used to calculate the estimate; a different, and apparently more valid, method was used to compute the values for 1958. The quality levels estimated for 1958 are 8 and 6%, respectively, for X-10 and Y-12; a quality level of 5% is considered to be satisfactory; the data for 1957 are compared in Table 12 with those for 1958. The higher percentage of unsatisfactory results noted for X-10 during 1958 is attributed to one or two programs in which some difficulty in maintaining the precision of the analyses was encountered. In general, the work in these laboratories is satisfactory.

In order to illustrate the scope of the control work in the laboratories the distribution of the 12,383 control results, by analysis, is presented in Table 13.

In addition to the activities usually associated with the operation of the SQC Program at Y-12, evaluations for about 30 sets of experimental data, derived from the toroid tests in the Reactor Experimental Engineering Division, were made. These data were analyzed by appropriate statistical techniques to ascertain the effect of concentration of thorium oxide in the slurry, particle-size distribution, and temperature on the activity rates of various metals and alloys. Since a basic lack of design was noted in all these toroid tests, a simply designed experiment was devised and submitted to the toroid group of REED for consideration. A method for expediting the evaluation of data obtained in future experiments was also suggested.

A statistical model was designed for the evaluation of experimental data that were secured in the Spectrographic Laboratory at Y-12 during the latter part of 1958. Inasmuch as nearly 5000 analyses were involved, the possibility of using the Oracle or the IBM-704 computor to make the necessary calculations was investigated. After the statistical model was modified slightly, arrangements were made to have these data evaluated by means of the IBM-704 computer. As a result of the problems encountered in this evaluation, it was decided that statistically designed experiments would be used in future investigations.

Table 13. Distribution of Control Results for 1958

Constituent	Distribution of Control Results			
	X-10		Y-12	
	Number	Per Cent	Number	Per Cent
Thorium	4990	50	407	16
Uranium	4400	45	713	28
Nickel	179	2	300	12
Iron	158	2	401	15
Chromium	110	1	285	11
Copper			121	5
Phosphate			97	4
Vanadium			97	4
Molybdenum			59	2
Nitrate			40	2
Aluminum			24	1
Sulfate			2	<0.1
	9837	100	2546	100

RADIOCHEMICAL ANALYSES (X-10)

S. A. Reynolds

Nuclear Properties

Neutron Activation Cross Sections at 195 kev (W. S. Lyon, R. L. Macklin[128]). – A Th^{228}-D_2O neutron source has been used to measure the neutron activation cross sections of several nuclides at 195 kev; the energy spread of the neutrons was about 50 kev. The cross sections of most of the nuclides have been measured previously at 25 kev.[129] For all the absolute gamma counting, a 3 × 3 in. crystal of thallium-activated sodium iodide was used. The values for the cross sections are referred to that for indium activated in spherical-shell geometry, the strength of the neutron source being determined in a large graphite-sphere neutron detector.[130] Some preliminary values are given in Table 14.

Measurement of Radioactivity

Liquid Scintillation Detection of Alpha and Beta Radioactivity (J. S. Eldridge). – The radiochemical determination of tritium and of other emitters of weak-beta activity is usually a difficult task because of the short range of weak-energy beta particles. A liquid scintillation spectrometer, the Packard Instrument Co. model 314 Tri-Carb, has been obtained for the measurement of weak-beta emitters. Basically, the model 314 is a refrigerated, double-coincidence type of liquid scintillation spectrometer, which has a two-channel pulse-height analyzer for the counting of radioactive nuclides in liquid scintillation samples.

The liquid scintillation method consists in the dissolution of a sample of radioactive material in

[128] Physics Division.

[129] R. L. Macklin, N. H. Lazar, and W. S. Lyon, "Neutron Activation Cross Sections with Sb-Be Neutrons," *Phys. Rev.* 107, 504 (1957).

[130] R. L. Macklin, "Graphite Sphere Neutron Detector," *Nuclear Instr.* 1, 335 (1957).

Table 14. Activation Cross Sections (σ_{act}) at 195 kev

Target Nuclide	σ_{act} (mb)	Target Nuclide	σ_{act} (mb)
Na^{23}	0.7	Ag^{107}	290
V^{51}	7	Pd^{108}	77
Mn^{55}	11	In^{115}	200
Cu^{63}	42	Sb^{122}	240
Cu^{65}	14	I^{127}	170
Ga^{71}	53	Ba^{138}	3
Ge^{74}	19	Ce^{142}	22
As^{75}	150	Pr^{141}	38
Zr^{94}	42	Sm^{152}	150
Zr^{96}	7	W^{186}	100
Ru^{96}	140	Au^{197}	320
Ru^{102}	190	Hg^{202}	32
Ru^{104}	28	U^{238}	120

a suitable solvent that contains a scintillator (a fluor) and then the detection of the light quanta emitted by the interaction of the alpha or beta particles and the fluor. Multiplier phototubes in a double-coincidence circuit detect the light quanta, which are converted to electronic pulses, amplified, and passed through a two-channel spectrometer for display on two scalers.

Self-absorption, which hampers the counting of alpha and beta particles from emitters in the solid phase, is greatly reduced when liquid scintillation techniques are used. In addition, 4π geometry is obtained in solutions since the disintegrating atom is completely surrounded by molecules of scintillator. In many cases the preparation of a sample for liquid scintillation counting consists simply in the pipetting of a portion of the test solution directly into a counting vial that contains a fluor dissolved in a suitable solvent.

Liquid scintillation methods have been applied to the detection of H^3, Ca^{45}, and Pu^{239}, and to the determination of P^{33} in the presence of P^{32}. The development of counting methods for other nuclides is in progress.

Instrumentation Analyses

Analysis of Radioactive Materials by Gamma Scintillation Spectrometry (J. S. Eldridge, T. H. Handley, W. S. Lyon, S. A. Reynolds). – Nondestructive analysis by gamma scintillation spectrometry[131] has been applied to a wider variety of samples, for example, liquids, charcoal traps, and metal parts from the HRT. Heath's catalog of gamma-ray spectra[132] has been most helpful in the analysis of materials having complex spectra. It has been possible to obtain for the Ecology Group of the Health Physics Division data on environmental samples that previously were unobtainable. Samples for analysis have also been submitted by the Solid State Division, University of Tennessee, and others. Some of this work was reported at the Gatlinburg Second Analytical Conference.[133]

Nondestructive Analysis of Fall-Out Activity (S. A. Reynolds, C. L. Burros,[134] J. H. Moneyhun[134]). – Gamma spectrometry and gross beta decay studies have been used to characterize and to estimate the age of the fission-product mixture (time since the explosion of a nuclear weapon) in a number of air-filter samples submitted by the Health Physics Division.

Two methods are available for the estimation of the age of fission-product material from its beta decay. One is the familiar Way-Wigner formula:[135]

$$A = Kt^{-1.2} ,$$

or

$$\frac{A_2}{A_1} = \left(\frac{t}{t + \Delta t}\right)^{1.2} ,$$

where

A = radioactivity of the fission-product mixture,
A_1 = radioactivity of the fission-product mixture at age t,
A_2 = radioactivity of the fission-product mixture at age $t + \Delta t$,
t = age of the fission-product mixture,
K = a constant.

From the second equation the following expression for t can be derived:

$$t = \frac{\Delta t \left(\frac{A_2}{A_1}\right)^{0.833}}{1 - \left(\frac{A_2}{A_1}\right)^{0.833}} .$$

Probably a more accurate estimate can be obtained from curves presented by Thornton and Houghton.[136] It is obvious that it is not practical to "date" material that is older than about three months unless the decay is followed for a long time. The accuracy of the dating depends upon the precision of the counting, as well as upon the validity of the assumptions made in the use of these methods. Values

[131] J. S. Eldridge *et al.*, "Analysis of Radioactive Materials by Gamma Scintillation Spectrometry," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 21.

[132] R. L. Heath, *Scintillation Spectrometry – Gamma-Ray Spectrum Catalogue*, IDO-16408 (July 1957).

[133] G. W. Leddicotte and W. S. Lyon, "Special Radiochemical Analysis in the Operation of ORNL Reactors," in *Proceedings of Second Conference on Analytical Chemistry in Nuclear Reactor Technology*, to be published by AEC.

[134] Low-Radiation-Level Analytical Laboratory.

[135] K. Way and E. P. Wigner, "The Rate of Decay of Fission Products," *Phys. Rev.* 73, 1318 (1948).

[136] J. K. Thornton and W. J. Houghton, *An Influence Function for the Beta Activity of Uranium(235) Fission Products*, NAA-SR-45 (Sept. 1, 1950).

for A_2/A_1, as a function of age, that are based upon Δt equal to one day, one week, and two weeks are given in Table 15.

An example of the use of the table follows. The weighted average value of A_2/A_1 ($\Delta t = 1$ week) for five filter samples was ~0.85. From the Thornton-Houghton (T-H) column in Table 15, the age was estimated to be 6 ± 1 weeks, whereas from the Way-Wigner (W-W) column, it appeared to be 7 ± 1 weeks. The "burst" dates that correspond to these estimated ages are March 4 and 11, 1958. According to AEC press releases, which were consulted after these estimates were made, the Russians conducted approximately nine nuclear weapons tests during February 23–March 22, 1958, six in the nine-day period ending March 22. Thus it is apparent that the estimated age of the fission products on the filters was consistent with the assumption that the fission products were formed by Russian nuclear weapons.

Analysis of Charcoal Traps for Fission-Product Gases (W. S. Lyon). – Many experiments have been performed by various groups in an effort to study the diffusion or flow of gases out of reactor fuel elements. One such experiment consisted in flowing air over fuel elements while they were being exposed to a high neutron flux and then passing this air through charcoal traps. This was done for many fuel elements. The decay of the radionuclides contained in these traps was followed by the use of a 3 × 3 in. gamma-ray crystal of thallium-activated sodium iodide and a 20-channel analyzer. In addition, some charcoal samples were burned, the resultant gases and residues were collected, and radiochemical analyses were made. The data confirmed the results obtained by nondestructive testing for the gamma-emitting nuclides. No attempt was made to assay routinely for activities having half lives less than a few hours. Typical spectra of a charcoal sample at several different decay times are shown in Fig. 19. The identifications of the gamma-ray photopeaks were confirmed by integration and decay plotting. The spectrum after 200 hr is shown in Fig. 20. Besides I^{131} and Te^{132}-I^{132}, Ba^{140}-La^{140} was also present. By fitting the 1.60-Mev gamma-ray peak to a known spectrum of Ba^{140}-La^{140}, it is possible to draw in the Ba^{140}-La^{140} contribution to the spectrum. This is indicated in Fig. 20.

By a similar matching and subtracting technique it is possible to obtain "pure spectra" for the various activities present; from these "pure spectra" the quantitative estimate of activity present is made. This is the technique that has been used very successfully on an almost routine basis to analyze a large number of such traps.

Table 15. Fission-Product Decay as a Function of Fission-Product Age

Δt = 1 Day			Δt = 1 Week			Δt = 2 Weeks		
t (days)	A_2/A_1 T-H*	A_2/A_1 W-W**	t (weeks)	A_2/A_1 T-H*	A_2/A_1 W-W**	t (weeks)	A_2/A_1 T-H*	A_2/A_1 W-W**
1	0.38	0.44	1	0.55	0.44	2	0.50	0.44
2	0.60	0.62	2	0.68	0.62	3	0.57	0.54
3	0.72	0.71	3	0.75	0.71	4	0.64	0.61
4	0.79	0.77	4	0.80	0.77	5	0.70	0.67
5	0.84	0.80	5	0.83	0.80	6	0.73	0.71
6	0.88	0.83	6	0.85	0.83	7	0.76	0.74
7	0.90	0.85	7	0.87	0.85	8	0.78	0.77
			8	0.88	0.87	9	0.80	0.79
			9	0.89	0.88	10	0.81	0.80
			10	0.90	0.89	11	0.82	0.82
						12	0.83	0.83
						13	0.84	0.84

*From Thornton and Houghton curves.

**From Way-Wigner formula.

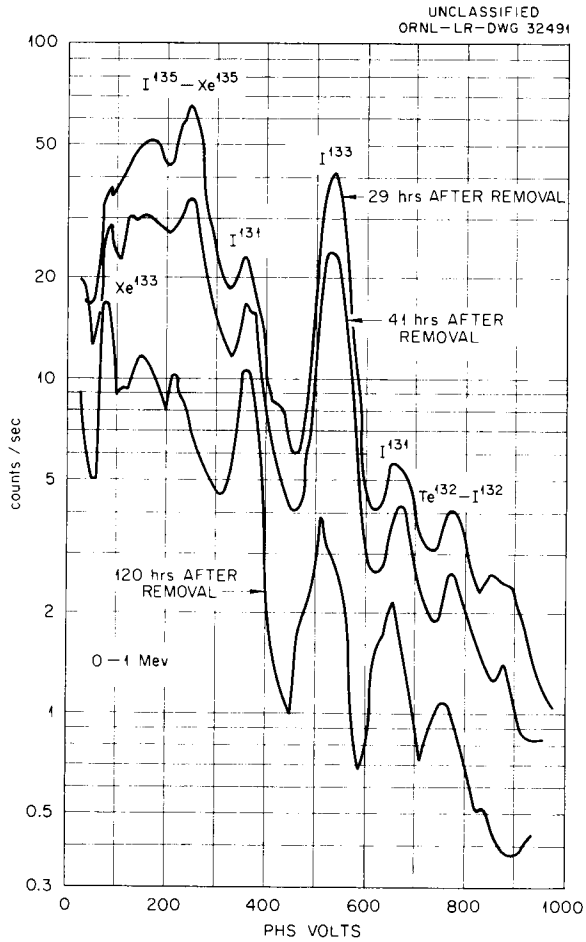

Fig. 19. Gamma-Ray Spectra of a Charcoal Sample at Different Decay Times.

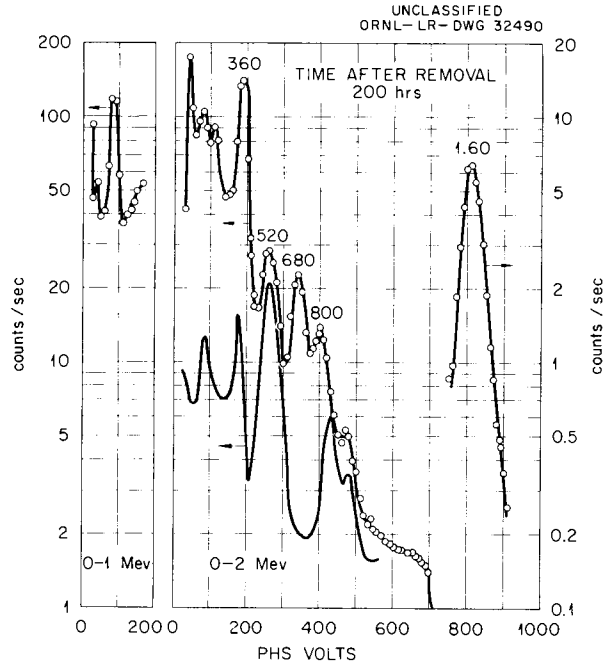

Fig. 20. Gamma-Ray Spectrum of a Charcoal Sample After 200 hr.

Fission Products

Isotopic Analysis: Ce^{141} and Ce^{144} (W. S. Lyon). – In the presence of each other Ce^{141} and Ce^{144} are determined by chemically isolating the cerium and then measuring the radiation from each cerium nuclide. The Ce^{144} is determined by counting the 3.0-Mev beta ray of Pr^{144}, and the Ce^{141} is determined by integrating beneath the 145-kev gamma-ray peak observed with a sodium iodide gamma-ray spectrometer. In the latter case, correction for contributions from Ce^{144} must be made. The gamma-beta branchings for the 145-kev gamma ray in Ce^{141} and the 134-kev gamma ray in Ce^{144} were determined.

A paper that contains further details of the method has been accepted for publication in *Nuclear Science and Engineering* and will appear in a forthcoming issue.

Radiochemical Determination of Y^{91} and Nd^{147} in Mixtures of Fission Products (J. S. Eldridge, W. S. Lyon). – Radiochemical determinations of Y^{91} and Nd^{147} have been found to be advantageous in the study of the behavior of rare-earth-element fission products in reactor solutions. A radiochemical procedure has been devised for the estimation of Y^{91} and Nd^{147}; it is based on a simple ion exchange separation in which citric acid is used as elutriant. The trivalent rare-earth elements (including yttrium) are separated from the other fission products and are used to charge an ion exchange column for their separation. Yttrium-91 elutes first; beta-counting experiments have shown that the eluted Y^{91} is free of other rare-earth activities. In the simple ion exchange procedure Nd^{147} may be accompanied by other rare-earth-element activities, mainly those of promethium and praseodymium. Gamma-ray spectrometry allows the differential measurement of Nd^{147} in the presence of many other activities. Such a

measurement, however, requires knowledge of the gamma branching in the decay of Nd^{147}. The fraction of beta events accompanied by each gamma ray in Nd^{147} has been determined. The electromagnetic-radiation energies and intensities found are *K* x rays, 0.51_4; 91.3-kev, 0.27_0; 277-kev, 0.00_8; 321-kev, 0.02_2; 400-kev, 0.01_3; 441-kev, 0.00_9; 533-kev, 0.13_4; and 688-kev, 0.00_7. By the use of a sodium iodide gamma-ray spectrometer, the number of 533-kev gamma rays from Nd^{147} is obtained. The absolute amount of Nd^{147} present is found by dividing the observed number of 533-kev gamma rays by the yield and the experimentally determined branching ratio.

Radiochemical Determination of Cesium (T. H. Handley, C. L. Burros). – A method has been developed for the radiochemical determination of cesium. Following scavengings with hydroxide and carbonate, cesium is separated from other fission products by precipitation with the organic reagent sodium tetraphenylboron. Good decontamination factors and chemical yields are obtained. After the separation, gamma-ray spectrometry is used to distinguish between Cs^{136} and Cs^{137}. A paper that describes the method has been accepted for publication in *Analytical Chemistry*.

Heavy Elements

Radiochemical Determination of U^{237} (F. L. Moore, S. A. Reynolds). – A radiochemical method for the determination of U^{237} has been developed. The method is based on the complexation of the uranyl ion in alkaline solution with hydroxylamine hydrochloride followed by scavenging with zirconium hydroxide and extraction of the uranium from hydrochloric acid solution with triisooctylamine-xylene. The technique has been applied successfully to the determination of U^{237} in HR fuel solutions. A paper that describes the method has been submitted for publication in *Analytical Chemistry*.

Determination of U^{232} in U^{233} (S. A. Reynolds). – Traces of U^{232} have been determined in U^{233} products of the Thorex Process. Alpha spectrometry made possible the estimation of the 5.3-Mev alpha radiation of U^{232} in an intensity about 0.001 of that of the 4.8-Mev alpha radiation of U^{233}. The growth of 2.6-Mev gamma radiation of Tl^{208}, a daughter of U^{232}, was followed by means of a scintillation spectrometer. Estimates by these independent methods agreed reasonably well. Other information was reported at the Gatlinburg Second Analytical Conference.[137]

Electronuclear Research Program

T. H. Handley

Work is continuing, in cooperation with members of the Electronuclear Research Division, on the investigation of neutron-deficient, rare-earth-element activities. Two oral presentations[138,139] of the work were given, and a paper has been submitted to *The Physical Review* for publication. Three other papers are being written and will be published in the open literature when they are completed. One of these papers gives details of chemical techniques used in this work and describes several improvements over previous techniques.

Solvent-Extraction Methods

Selective Liquid-Liquid Extraction of Iron with 2-Thenoyltrifluoroacetone–Xylene (F. L. Moore). – The extraction of iron(III) from 10 *M* nitric acid solution into a 0.5 *M* solution of 2-thenoyltrifluoroacetone in xylene has been found to be efficient and highly selective. Scrubbing the organic phase with 0.25 *M* hydrofluoric acid–0.25 *M* nitric acid increases the selectivity. Concentrated hydrochloric acid readily strips the iron from the organic phase. Excellent separation of iron is effected from the alkali, alkaline-earth, and rare-earth elements, and from ruthenium, zirconium, niobium, iodine, tin, antimony, cobalt, manganese, chromium, nickel, thorium, protactinium, and uranium. The technique has been applied successfully to the determination of the specific activity of iron in HR solutions. The extraction of iron(III) from 10 *M* nitric acid solution appears to be more highly selective than the currently popular techniques of ether extraction or anion exchange from hydrochloric acid solution. A paper that describes the method has been submitted for publication in *Analytical Chemistry*.

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[137] S. A. Reynolds, "Analysis for Low Concentrations of Uranium-232 in Uranium-233," in *Proceedings of Second Conference on Analytical Chemistry in Nuclear Reactor Technology*, to be published by AEC.

[138] K. P. Jacob *et al.*, *Electron Capture Decay of Tm^{168} and Tm^{166}*, a paper presented at the Meeting of the American Physical Society, Chicago, Ill., Nov. 28–29, 1958.

[139] B. Harmatz, T. H. Handley, and J. W. Mihelich, *Nuclear Spectroscopy of Odd Mass (161-173) Rare Earth Nuclides*, a paper presented at the Meeting of the American Physical Society, Chicago, Ill., Nov. 28–29, 1958.

Experimental Method for the Study of Diffusion and Extraction Across a Liquid-Liquid Interface (T.W. Martin[140]). – The prototype apparatus shown schematically in Fig. 21 offers a promising new experimental approach to the study of diffusion and extraction across the interface between certain aqueous-organic systems, the processes being uncomplicated by diffusion control in the adjacent bulk phases. The method may also prove to indicate effectively the factors that influence the behavior and "structure" of the interface. The apparatus is operated in the following way. The substance (labeled with a radioactive tracer) being extracted is dissolved in the 1-ml, static, aqueous phase, which is so positioned that the aqueous surface formed at the bottom of the 0.25 × 0.001 in. Teflon slit is oriented lengthwise across the width of the rim and ~0.006 in. above the wheel. Individual organic drops, falling at a rate of 1 to 5 drops/sec, are dropped on the Teflon rim, which spins at 10 to 200 rpm. Each drop is squeezed past the slit where it makes brief contact with the aqueous phase before being almost entirely dragged away from the slit, wiped off, and collected at the bottom of the wheel. The product of the activity of the extracted substance per milliliter of extract by the drop rate is a measure of the apparent extraction rate, a parameter which is sensitive to the concentration of constituents involved in the extraction process.

[140] Research participant from Vanderbilt University, Nashville, Tenn.

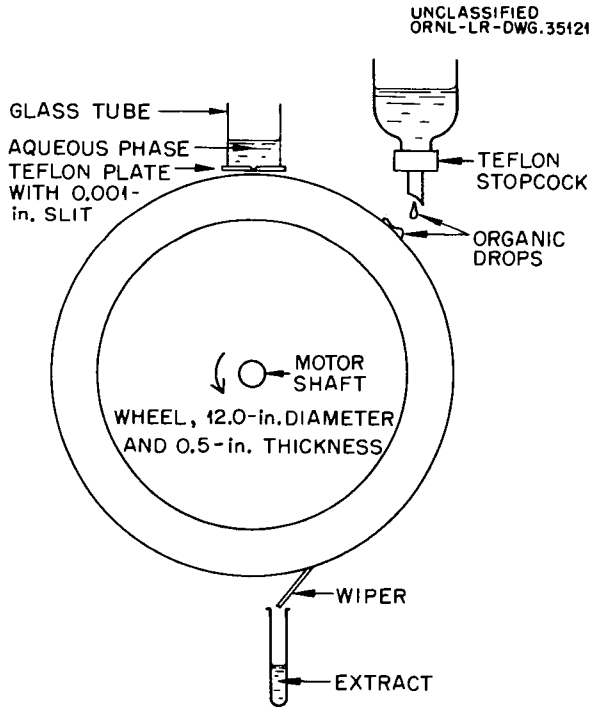

Fig. 21. Schematic Cross Section of "Steady-State" Interfacial Extraction Apparatus.

In a study, made at 100 rpm, of the simultaneous extraction of radioactive iron(III) and cesium(I) from a 1 *M* nitric acid–water solution with pure tributyl phosphate (TBP), the ratio of cesium activity to iron activity in the extract was 0.80 ± 0.02 compared with the original value 1.18 ± 0.03 for the aqueous phase alone. The total activity per milliliter in this extract was $\sim 10^{-3}$ times that of the aqueous phase, but it was ~10 times more than is extracted by TBP in a single equilibrium extraction with the same volume. These data indicate that a "stable" interface with diffusive flow across it was achieved and that a differential extraction rate in favor of iron(III) over cesium(I) was observed. Furthermore, the ratio of cesium activity to iron activity in the extract differed markedly from the equilibrium value of 2.0 for this phase, which is good evidence that the extraction depends on irreversible processes. When the organic phase is a mixture of TBP and kerosene, the apparent extraction rate of iron(III) is dependent on the concentrations of iron(III), nitric acid, and TBP. For example, the rate is approximately 50 times greater when pure TBP is used than when pure kerosene is used under similar conditions. These qualitative results indicate the feasibility of determining the form of the kinetic rate expression and of testing the mechanism of extraction processes by this approach.

Further details of this preliminary investigation are contained in a paper that has been submitted for publication in *Nature*; the paper will probably be published in January 1959. A more comprehensive investigation of the potentialities of the instrument is being carried out by the author at Vanderbilt University.

Y-12 Radiation Excursion

S. A. Reynolds J. S. Eldridge

Members of the Group began to assist the Health Physics Division and other organizations on the afternoon of the accidental radiation excursion at

Y-12.[141,142] Assistance was also afforded by members of the Nuclear Analyses, Radioisotopes-Radiochemistry, and Pilot Plant Laboratory groups. Analyses included the estimation of the number of fissions that had occurred during the accident[142] and estimation of fast- and slow-neutron intensities, based on activities induced in various materials.[141]

RAW MATERIALS LABORATORY (Y-12)

L. J. Brady

Use of Gold Plates in the Preparation of 3 M Sulfuric Acid Solutions of Plutonium for Gross Alpha Counting

L. J. Brady J. M. Peele

When attempts were made to determine the plutonium content of aqueous raffinate solutions that were 3 *M* in sulfuric acid by the method of gross alpha counting,[143] the precision of the results was poor. On careful examination of the stainless steel plates after they were flamed, it was discovered that unusually large amounts of residues had been left on the plates. It was concluded that the sulfuric acid concentration of these samples was sufficiently high to cause severe attack of the stainless steel plates and that the residues of the corrosion products were left on the plates after evaporation of the samples. In order to correct this without making a separation of the plutonium from sulfuric acid by precipitation or extraction methods, the samples were evaporated and flamed on gold plates. The excess sulfuric acid was thus evaporated without attacking the gold, and very little residue remained on the plates.

The relative standard deviation of the results obtained with the gold plates was 1% as compared with 5% for the steel plates. The average number of counts per minute per milliliter for samples on the stainless steel plates was 13% lower than that for samples on gold plates. This lowering of the count rate is interpreted as indicating that the residue of metallic oxides produces a significant attenuation of the alpha particles.

Determination of the Hydrogen Content of Paraffin

L. J. Brady E. C. Lynn

The hydrogen content of six samples of paraffin, taken at random from a large batch of paraffin that was intended for use in criticality studies, was determined in quadruplicate in order to ascertain the precision of the results and the homogeneity of the paraffin with respect to the hydrogen content. A conventional combustion method was used in which approximately 50 mg of sample was burned in an atmosphere of oxygen in the presence of a copper oxide catalyst. The water produced during combustion was collected in a drying tube filled with magnesium perchlorate and was weighed.

The results obtained by application of the variance ratio or "F" test to the six series of test results indicated that there was no significant difference in the reproducibility of the results for the six samples. Furthermore, the average values reported for the hydrogen content of the separate samples were found to be essentially the same when the Student's "t" test was applied to the test results. The hydrogen content of the paraffin was found to be 14.56%; the relative standard error of the results was 0.3% at the 95% probability level. It was concluded that, within the limitations imposed by the relative standard deviation of the method (0.7%), the paraffin from which the six samples were taken is homogeneous with respect to the hydrogen content.

Dibenzoylmethane Method for the Determination of Uranium

L. J. Brady J. R. Lund

The dibenzoylmethane colorimetric method for uranium, reported recently by Horton and White,[144] has been adapted, with some simplification, for use in the Raw Materials Laboratory. The simplified method has the following advantages: (1) greater sensitivity than the methods used previously (molar absorbancy index with dibenzoylmethane = 18,000; with ascorbic acid = 1330; with thiocyanate = 2000), (2) greater stability of the color complex and chromogenic reagent, (3) improvement in visual detection of color complex, whereby the analyst can save time by eliminating from further processing those samples

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[141] *Accidental Radiation Excursion at the Y-12 Plant, June, 1958, Preliminary Report*, Y-1199 (June 25, 1958).

[142] *Accidental Radiation Excursion at the Y-12 Plant, Final Report*, Y-1234 (July 28, 1958).

[143] R. L. Walker, "Gross Alpha," Method Nos. 9 002301 and 0 0733000 (9-30-53), *ORNL Master Analytical Manual*.

[144] C. A. Horton and J. C. White, "Separation of Uranium by Solvent Extraction with Tri-*n*-Octylphosphine Oxide, Direct Colorimetric Determination with Dibenzoylmethane," *Anal. Chem.* 30, 1779 (1958).

in which no color is visually detectable, (4) applicability of the fluorometric method to the same organic extract prepared for the colorimetric determination, which is particularly useful in those cases where the uranium concentration is found to be too low for determination by the colorimetric method, (5) solubility of organophosphorus extractants that contain uranium in cyclohexane solutions of TOPO, thus making possible the determination of uranium by the method outlined above and the avoidance of the time-consuming wet ashing of the sample, and (6) ease of removal of the ethyl alcohol solutions from the surface of the absorption cells as compared with the solution of ammonium thiocyanate, which was formerly used in the determination of uranium.

REACTOR PROJECTS LABORATORY (Y-12)

J. C. White

Studies of Extractions with Tri-*n*-octylphosphine Oxide

J. C. White

Investigations were continued on the analytical applicability of tri-*n*-octylphosphine oxide[145] (TOPO) as a reagent for the separation of metals by solvent extraction. The fundamental extraction characteristics of tin and cerium in TOPO-cyclohexane solutions were ascertained, and further studies were made in elucidating the stoichiometry of the extracted species. In addition, the ultraviolet spectra of the metal-TOPO adducts were found to be sufficiently unique and intense to serve as means for the direct determination of the metal species involved.

Reports on the extraction of zirconium[146] and thorium[147] have been issued. The statuses of current investigations are summarized briefly below.

Tin (W. J. Ross). – Tin is readily extracted from acidic chloride solutions with TOPO in cyclohexane; for example, the loading capacity of 1 mmole of TOPO for tin is 60 mg. As much as 54 mg of tin is extracted in one equilibration from 3 to 5 *M* chloride solutions at a 1:1 phase ratio. The extraction coefficient is at a maximum (> 1000) in 3 *M* hydrochloric acid, but falls to 360 in 1 *M* hydrochloric acid and to as low as 15 in 7 *M* hydrochloric acid. Even greater extraction is achieved by increasing the chloride concentration of a 1 *M* hydrochloric acid solution by the addition of lithium chloride to the aqueous phase. Equilibrium is generally attained in less than 5 min and is essentially unaffected when the phase ratio (V_a/V_o) is increased from 1 to 20. The extracted species is postulated to be $SnCl_4 \cdot 2(TOPO)$ regardless of the initial oxidation state of the tin. No divalent tin was observed in the organic phase. The presence of nitric or perchloric acid is detrimental to the extraction of tin from chloride solutions. Sulfuric acid in concentrations as high as 5 *M* does not affect the extraction; however, in the absence of chloride, tin is extracted only very slightly from acidic sulfate solutions.

In order to facilitate the investigation of the extraction characteristics of tin, an ultraviolet spectrophotometric method was developed that is based on the absorbancy of the stannic chloride species in 8 *M* hydrochloric acid at 222 mμ. This absorbancy varies linearly with respect to the concentration of tin; the molar absorbancy index is 13,000. This method for the determination of tin in chloride solutions that do not contain any interfering ions is performed much more rapidly and conveniently than are existing colorimetric or polarographic methods.

Cerium(IV) (W. J. Ross). – Cerium(IV) is extracted from nitric acid by TOPO in cyclohexane and to a lesser degree from sulfuric acid and hydrochloric acid. Complete extraction is not attainable, however, since cerium(IV) is partially reduced during equilibration to the nonextractable cerium(III). In nitrate solutions the degree of extraction (and reduction) is not appreciably affected when the concentration of nitric acid is varied from 1 to 10, so that 97% of 20 mg of cerium is extracted in 1 min by 0.5 mmole of TOPO at a phase ratio of 1:1. The extraction is impaired slightly as a result of increased reduction of cerium(IV) when the V_a/V_o ratio is increased above 2 or when neutral nitrate salts are present. The loading capacity of 1 mmole of TOPO for cerium(IV) is 70 mg; the molar ratio of TOPO to cerium in a saturated organic phase is 2. Sulfate impairs the extraction of cerium(IV) from nitric acid, whereas the presence of hydrochloric acid in concentrations greater than 1 *M* produces

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[145] J. C. White, "Methods Development Group," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 64.

[146] J. C. White and W. J. Ross, *The Use of Tri-n-octylphosphine Oxide in the Solvent Extraction of Zirconium*, ORNL-2498 (April 1958).

[147] W. J. Ross and J. C. White, *The Use of Tri-n-octylphosphine Oxide in the Solvent Extraction of Thorium from Acidic Solutions*, ORNL-2627 (Nov. 1958).

rapid reduction of cerium(IV) and drastically inhibits its extraction.

In all tests pertaining to the extraction of cerium, the amount of cerium that remained in the aqueous phase was determined spectrophotometrically. Nitrate was removed by adding sulfuric acid to portions of the aqueous phase and heating them to fumes, after which any cerium(III) that was present was reoxidized to cerium(IV) with argentic oxide. The orange cerium(IV) species in 1 *M* sulfuric acid absorbs light in the near ultraviolet region, and this absorbancy exhibits a linear relation to the concentration of cerium at 318 mμ where the molar absorbancy index is 5300 when it is measured vs water.

Uranium (W. J. Ross). – The absorbancy of the adduct of uranium and TOPO in chloride systems was made the basis of a rapid method for the determination of uranium in cyclohexane solutions of TOPO. Uranium(VI) is extracted readily from hydrochloric acid solutions. The adduct, $UO_2Cl_2 \cdot 2(TOPO)$, exhibits maximum absorbancy of light in the ultraviolet region at 234 mμ. Beer's law is followed at this wavelength where the molar absorbancy index is 5200 when the absorbancy of the uranium solution is measured vs a corresponding concentration of the acid-TOPO adduct. This method has been applied successfully to the determination of uranium in solutions that contained chloride and both chloride and sulfate solutions that also contain thorium. Thorium is extracted by TOPO; however, the thorium-TOPO adduct does not absorb light in the ultraviolet region.

Thorium (W. J. Ross). – The extraction of thorium from 1 *M* hydrochloric acid into TOPO in cyclohexane is enhanced by the addition of aluminum chloride to the aqueous phase. Extraction coefficients in excess of 1000 are obtained in systems that are 1 *M* in hydrochloric acid and 2 to 3 *M* in aluminum chloride. The beneficial effect of nitrate in the extraction of thorium was also demonstrated in systems that contain sulfuric or phosphoric acid. Milligram amounts of thorium can be extracted completely from solutions that are less than 0.1 *M* in sulfate and/or phosphate if the solutions are 1 *M* with respect to nitric acid and 1 *M* in sodium nitrate. Thorium is readily back-extracted by 0.3 *M* sulfuric acid. Trivalent rare-earth elements are not extracted from nitrate solutions by TOPO; consequently, the latter two characteristics of thorium were successfully applied to the determination of thorium in monazite sands by a rapid and simple procedure. The species that is extracted is $Th(NO_3) \cdot x(HNO_3) \cdot 3(TOPO)$, where the coefficient x increases with increasing concentration of nitric acid in the aqueous phase.

Niobium and Tantalum (C. A. Horton). – Work was continued on the behavior of niobium and tantalum in several media before, during, and after their extraction with TOPO in cyclohexane. Analyses were made by equilibration of their radioactive isotopes Nb^{95} and Ta^{181}, admixed with the normal isotopes, with TOPO in cyclohexane and by determination of the activities of the organic phases. Tartrate, oxalate, citrate, lactate, fluoride, peroxide, thiocyanate, and catechol were added to the solutions to prevent hydrolysis of niobium and tantalum in hydrochloric acid. Similar complexers were required for other inorganic acid media except for 10 *M* sulfuric acid, in which the metals were in solution indefinitely.

In Fig. 22 the effects of the concentrations of hydrochloric acid and of the organic complexing acid used on the extraction of niobium, added as potassium niobate, are shown.

Niobium is also extracted, without precipitation, from hydrochloric or sulfuric acid stabilized with thiocyanate, or from catechol-stabilized solutions. In 6 *M* sulfuric acid, the degree of extraction of niobium approaches 98% but decreases somewhat as the sulfuric acid concentration approaches 8 *M*, above which a third small niobium-rich organic phase forms.

In Fig. 23 is shown the degree of extraction of tantalum from hydrochloric acid that contained lactic acid or fluoride ion to stabilize the solution and sulfuric acid to prevent hydrolysis. Fluoride, as compared with lactic acid, drastically hinders the extraction of tantalum.

Nitric Acid (R. A. Zingaro[148]). – It has been found[145] that nitric acid is readily extracted by TOPO in cyclohexane solution and that the mole ratio of acid to TOPO at saturation is greater than 1 when the concentration of nitric acid in the extracted solution exceeds 2 *M*. This work was undertaken to ascertain the nature of the extraction of free nitric acid by TOPO and also to determine the effect of temperature on the extraction of acid.

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[148] Summer employee from Texas A & M.

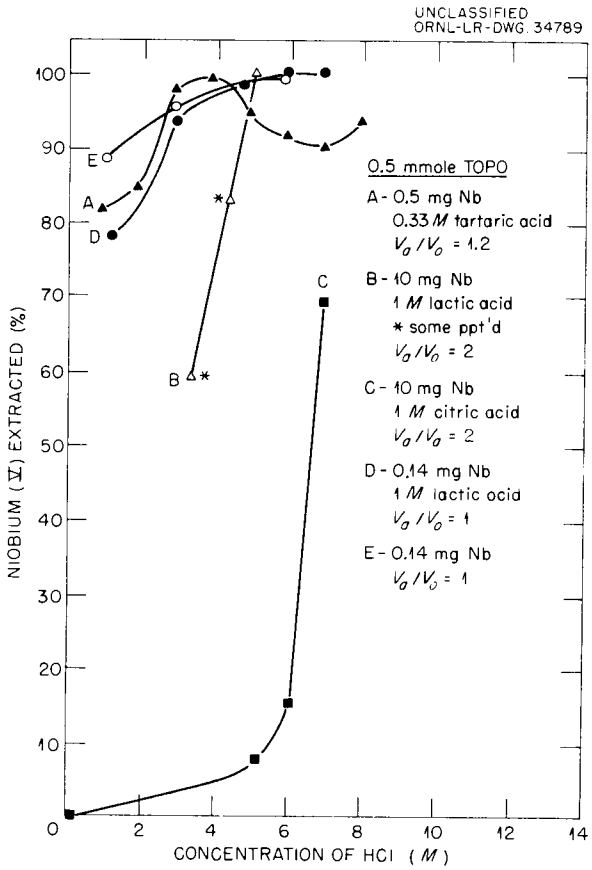

Fig. 22. Results of Extraction of Niobium from Hydrochloric Acid by TOPO.

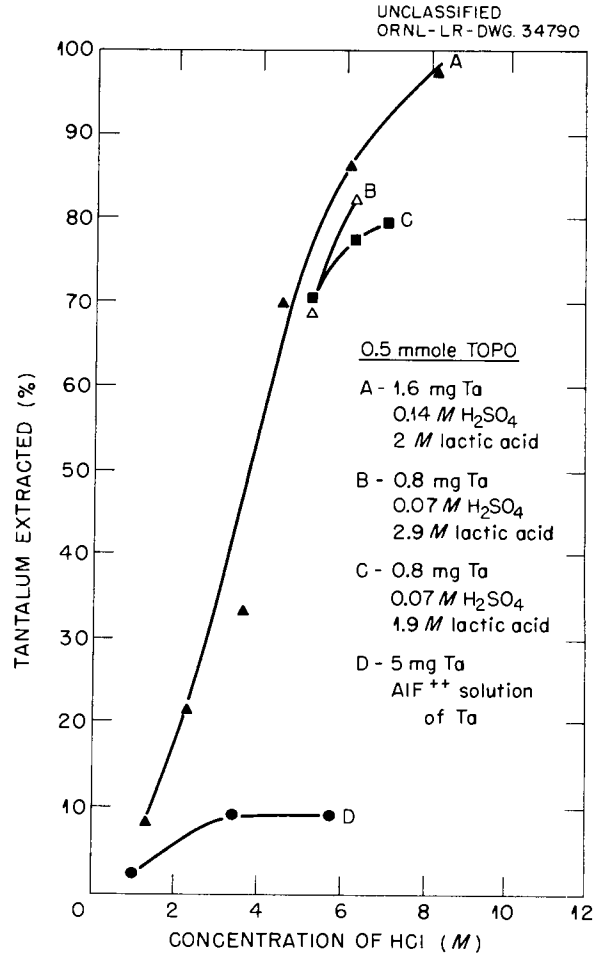

Fig. 23. Results of Extraction of Tantalum from Hydrochloric Acid by TOPO.

Studies of the effect of temperature on liquid-liquid extraction are important from both a theoretical and a practical point of view. Large differences in temperature coefficients can be used as a basis for enhancing the degree of separation of different species and accelerating the rate of equilibration. From equilibrium constants at different temperatures, useful thermodynamic values, such as the heat of transfer between phases, can be calculated.

In this investigation the extraction of aqueous nitric acid solutions by TOPO-cyclohexane solutions was studied at a constant ionic strength of 2 M nitric acid at 12.4, 25, and 35°C. Equal volumes of the two phases were equilibrated by rapid shaking in glass separatory funnels in a bath at the appropriate temperature. The minimum time required for equilibration was determined by titration of control samples at each temperature. One hour was found to be more than adequate, but a minimum of 2 hr of shaking was used at 35°C, and 8 hr at the lower temperatures. After equilibration, test portions were withdrawn from each phase and titrated; phenolphthalein was the indicator used. The organic solutions were dissolved in ethyl alcohol and titrated in this solvent. Thus, a direct value of the nitric acid concentration in each phase was obtained. The concentration of free TOPO had to be determined by difference on the basis of the postulation of the nature of the extracted species. This parameter is the most questionable of all the parameters.

It can be assumed that TOPO extracts nitric acid according to the following reaction:

$$(1)\quad H^+_a + NO_{3_a}^- + nTOPO_o \longrightarrow HNO_3 \cdot nTOPO_o \quad .$$

On the basis of studies of solvent extraction processes in general, n is expected to be a small

integer. However, in the event that more than 1 mole of nitric acid is extracted per mole of TOPO or if a polymerization process should be involved, n may be smaller than unity. Another assumption, that TOPO exists as the monomer in cyclohexane solution, is subject to subsequent verification. An equilibrium expression for Eq. 1 can be written in the following form:

$$(2) \qquad K = \frac{(HNO_3 \cdot nTOPO)_o}{(H^+)_a (NO_3^-)_a (TOPO)_o^{\,n}} .$$

The constant can be written in terms of the extraction coefficient, E_a^o, where

$$(3) \qquad E_a^o = \frac{(HNO_3 \cdot nTOPO)_o}{(H^+)_a}$$

$$= \frac{\text{total } HNO_3 \text{ in organic phase}}{\text{total } HNO_3 \text{ in aqueous phase}} .$$

Furthermore, since the ionic strength of all solutions is 2 M and since only those extraction coefficients will be considered for which the total concentration of acid extracted is less than 0.05 M (NO_3^- concentration, ~2 M), equilibrium quotients are calculated by use of the following approximate form for the equilibrium quotient:

$$(4) \qquad K \approx \frac{E_a^o}{2(TOPO)_o^{\,n}} .$$

The form of Eq. 4 is such that a plot of log E_a^o vs log of concentration of TOPO should yield a straight line of slope n. Such plots were made by use of experimentally determined values of E_a^o and by calculating $(TOPO)_o$, that is, the concentration of uncomplexed organic reagent, by difference. A series of plots were obtained for values of $(TOPO)_o$ calculated from $n = 0.5$, 1, and 2. The only correlation obtained was for $n = 1$. A plot of E_a^o vs $(TOPO)_o$ for $n = 1$ is shown in Fig. 24 at the various temperatures studied. The lines have been drawn with a slope of unity. It is clear that the extraction coefficients decrease slightly with falling temperature, although the three uppermost points at 12.4°C are well above those at 25°C. This may be due in part to experimental error [$(H^+) \cong 0.001$ in this region], but these points also would fall on a much steeper slope and indicate a dependency on

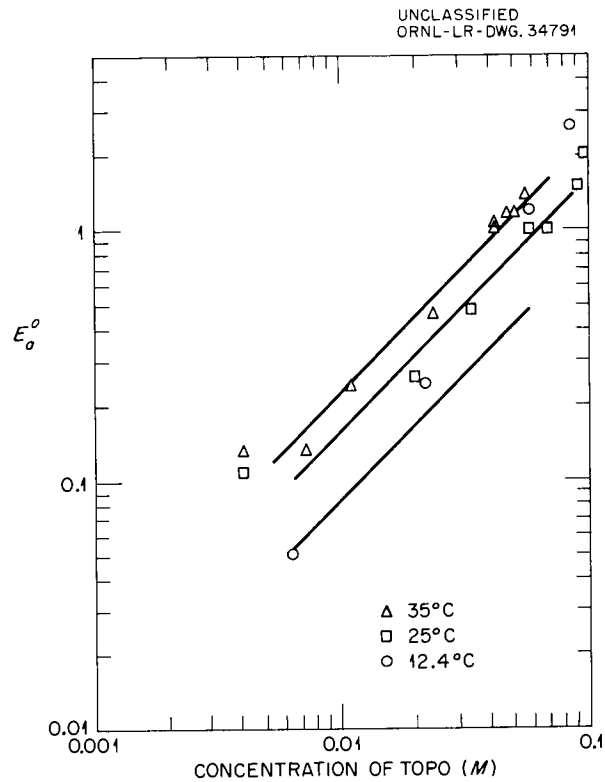

Fig. 24. Variation of Extraction Coefficient of Nitric Acid as a Function of Concentration of TOPO.

$n > 1$. The 12.4°C data were plotted with $(TOPO)_o$ values obtained by assuming formation of a $2TOPO:1HNO_3$ complex. These points fell on a line of slope 0.5. This indicates that the equilibrium probably involves both species; neither alone is satisfactory. Also, the lowest points on the 25 and 35°C curves are well out of line, but in this region the hydrogen ion concentration is sufficiently high that the organic reagent is essentially 100% complexed, and values of the organic reagent concentration, calculated by difference, are subject to very large error. However, in the region of $(H^+)_a \sim 0.005$ to 0.4 M and $(TOPO)_o \sim 0.01$ to 0.05 M, the points are reasonably consistent with first-power dependency on the organic reagent concentration.

In Table 16 values of K are given that have been calculated by the use of Eq. 4. Values have been calculated only for those points where the analytical error is not greater than 2% and where the value of the concentration of the uncomplexed organic reagent, calculated by difference, is subject to small error.

Table 16. Extraction of Nitric Acid by TOPO

Molarity						E_a^o	K
$[H^+]_i$	$[H^+]_a$	$[H^+]_o$	$[H^+]_a + [H^+]_o$	$[TOPO]_i$	$[TOPO]_i - [H^+]_o$		
				At 35°C			
0.1966	0.166	0.039	0.205	0.05	0.011	0.235	10.7
0.0787	0.057	0.026	0.083	0.05	0.024	0.456	9.5
0.0157	0.0076	0.0081	0.0157	0.0625	0.0544	1.065	9.8
0.0157	0.0076	0.0079	0.0155	0.050	0.042	1.063	12.6
0.00629	0.0030	0.0035	0.0065	0.0625	0.0595	1.167	9.8
0.00629	0.0031	0.0032	0.0063	0.053	0.0498	1.165	11.7
						av	10.7
				At 25°C			
0.393	0.310	0.080	0.390	0.10	0.020	0.258	6.5
0.197	0.137	0.066	0.203	0.10	0.034	0.482	7.1
0.080	0.042	0.042	0.084	0.10	0.058	1.00	8.6
0.0157	0.0056	0.0101	0.0157	0.10	0.0899	1.80	10.0
0.0063	0.0022	0.0044	0.0066	0.10	0.0956	2.00	10.5
						av	8.5
				At 12.4°C			
1.975	1.88	0.0937	1.974	0.10	0.0063	0.0498	4.0
0.3950	0.318	0.0782	0.396	0.10	0.0218	0.245	5.6
0.1975	0.133	0.0649	0.1979	0.10	0.0351	0.488	7.0
0.0765	0.0343	0.0419	0.0762	0.10	0.0581	1.22	10.5
0.0790	0.0371	0.0419	0.0790	0.10	0.0581	1.13	5.3
						av	7.3

The average value for K, when all experimental values were used, was 11.6 at 35°C, 9.1 at 25°C, and 7.3 at 12.4°C (values at very low acid concentrations at the last temperature were excluded). The trend toward lower values of K with decreasing temperature is apparent. An approximate value for ΔH of 1.3 kcal/mole was calculated from the slope obtained by plotting log K vs $1/T$. The small value for ΔH is to be expected in view of the very moderate effect of temperature on the equilibrium.

One of the ways in which an indication of the stoichiometric nature of the extracted species can be obtained is to plot the molar ratio of total reagent to acid concentration in the organic phase against the aqueous acidity. The limiting values of the $(TOPO)_o/(HNO_3)_o$ are 1.10 at 12.4°C, 1.00 at 25°C, and 0.88 at 35°C. The formation of a 1:1 $TOPO:HNO_3$ complex is strongly suggested, but the formation of species in which both more and less than 1 mole of nitric acid is extracted per mole of TOPO is also involved. The latter conclusion is based on the limiting value of 0.88 for the ratio of reagent to nitric acid concentration and the slope of > 1 for the experimental points obtained for dilute acid concentrations at 12.4°C (Fig. 24).

Although the following picture is admittedly speculative, it appears likely that at the aqueous-organic interface the TOPO molecules are oriented with presumably polar $^-O{-}P^+$ grouping toward the phase possessing the high dielectric. The polar $^-O{-}P^+$ tails may actually extend across the interface and into the aqueous phase. The extraction of the nitric acid molecules would then involve bonding of the proton to the negative end of the $^-O{-}P^+$ dipole. The nitrate ion would have to be carried

into the organic phase in order to maintain electrical neutrality. This mechanism is summarized as follows:

$$H_3O^+_a + NO_3^-{}_a + \overset{-}{O}-\overset{+}{P}R_3{}_o \rightleftharpoons H_2\overset{-}{O}\text{---}\overset{+}{H}\text{---}\overset{-}{O}-\overset{+}{P}R_3{}_{ao} + NO_3^-{}_a \rightleftharpoons H_2O_a + (NO_3H-O-PR_3)_o$$

In the middle term the subscript *ao* suggests the species which is formed at the phase boundary. Clearly, the formation of the indicated complex should be reflected by a shift in the phosphoryl stretching frequency. Such an observation has been made in recent studies by Horton.[149]

These studies suggest many other areas of research to be undertaken for a basic understanding of the phosphine oxide extraction process. Among these are physicochemical investigations of TOPO solutions to establish the nature of the molecular species relative to their aggregation, measurements of the interfacial tension of organic-aqueous solutions, isolation and structure studies of the pure adducts, and kinetic studies on the rate of transfer across the interface.

Coextraction of Mineral Acids (W. J. Ross and R. A. Zingaro). – The relative extractability of various mineral acids by TOPO in cyclohexane has been described previously.[145] Continued investigation of the extractability of nitric acid and sulfuric acid reveals that the degree of extraction of the more extractable acid (nitric acid) is enhanced when the concentration of the less extractable acid (sulfuric acid) is increased in the aqueous phase. In 1 *M* nitric acid–1 to 9 *M* sulfuric acid systems, the extractability of nitric acid increases as the concentration of total acid in the aqueous phase increases. Only 0.05 mmole of sulfuric acid is extracted from the mixed-acid systems by 1.5 mmole of TOPO in cyclohexane when the concentration of sulfuric acid in the aqueous phase exceeds 7 *M*.

Solubility of TOPO in Cyclohexane (R. A. Zingaro). – In order to study the extraction of metallic ions by TOPO dissolved in cyclohexane as a function of temperature, a knowledge of the solubility of TOPO in this solvent at various temperatures is desirable. Such information will make it possible to avoid the use of solutions that would be supersaturated at lower temperatures and will also indicate the magnitude of concentrations to be used so as to minimize the effects of large deviations from unity in the activity coefficient of the solute. In this study, values for the solubility and density of saturated TOPO-cyclohexane solutions have been determined at 6.5, 11, 25, and 35°C. Eastman white-label-grade cyclohexane was used without further purification. The TOPO used in these experiments was carefully purified. Eastman white-label material was treated with a solution of potassium permanganate in order to oxidize contaminating phosphinous acids to the phosphinic acids as follows:

$$R_2POH \xrightarrow{O} R_2\overset{O}{\overset{\|}{P}}-OH$$

Following removal of all manganese compounds by successive treatment with oxalate, sulfuric acid, and hydrochloric acid, the petroleum ether solution of TOPO was slurried with activated alumina to remove the phosphinic acids. The final product, recrystallized from petroleum ether at –20°C, contained a maximum of 0.07% phosphinic acids, as indicated by titration and its ultraviolet spectrum, and melted at 53.5°C.

Solutions were prepared by saturating cyclohexane with TOPO at a temperature higher than that at which the determination was to be made. The saturated solution was then equilibrated by shaking in a constant-temperature bath. Each sample was withdrawn through a cotton filter into a calibrated pipet and was weighed in a tared glass-stoppered sample bottle. The solution was then evaporated at a temperature below the boiling point of the solvent, and final traces of cyclohexane were removed *in vacuo* at a temperature above its boiling point. The 11 and 25°C baths had a temperature fluctuation of ±0.05°C; the 35°C bath, ±0.2°C. Measurements at 6.5°C were made in an equilibrium mixture of cyclohexane at its freezing point (6.5°C). The cyclohexane slush was maintained at its equilibrium temperature by immersion in a second insulating bath of frozen cyclohexane whose temperature was controlled by immersion in, or removal from (depending on its temperature), a third outer ice-water bath. The temperature fluctuation at this

[149] C. A. Horton, unpublished studies.

temperature was ±0.1°C. At least four samples were measured at each temperature. The maximum deviation within a series of measurements was 0.5%.

Attempts to make measurements at 45°C led to results that were not reproducible since efforts to obtain equilibrium at this temperature were unsuccessful.

The densities and compositions of saturated TOPO-cyclohexane solutions are given in Table 17. To test the ideality of the solutions, log N_2 (N_2 = mole fraction of TOPO) has been plotted against $1/T$; the results are shown in Fig. 25.

It is readily observed from Table 17 that the solubility of TOPO in cyclohexane increases 4½ times as the temperature increases from 6.5 to 25°C. Concurrently, there is a regular increase in density, although the change is rather small. In fact, a value of 0.8 for the density of saturated TOPO-cyclohexane solutions can be used without introducing any serious error. As the temperature is increased from 25 to 35°C, the solubility of TOPO increases only very slightly and, as is shown in Fig. 25, falls completely out of line with the values at the lower temperatures. This suggests that the solubility is approaching a maximum or limiting value at this temperature. It is also to be noted that there is a slight decrease in density at 35°C compared with the value at 25°C.

The experimentally determined points in Fig. 25 have been connected by a solid line. For an ideal solution, a plot of log N_2 vs $1/T$ should yield a straight line whose slope is $-\Delta H_f/4.575$, where ΔH_f is the heat of fusion of the solute. The upper limit of this line should be at $N_2 = 1$ (log $N_2 = 0$) at the melting point of the solute. The dashed line in Fig. 25 connects the experimental points at 11 and 25°C and has been extrapolated to $N_2 = 1$. The point on this line at which log $N_2 = 0$ corresponds almost to the experimentally determined melting point of TOPO. This suggests that these solutions approach ideal behavior in the temperature range from 11 to 25°C. From the slope of the

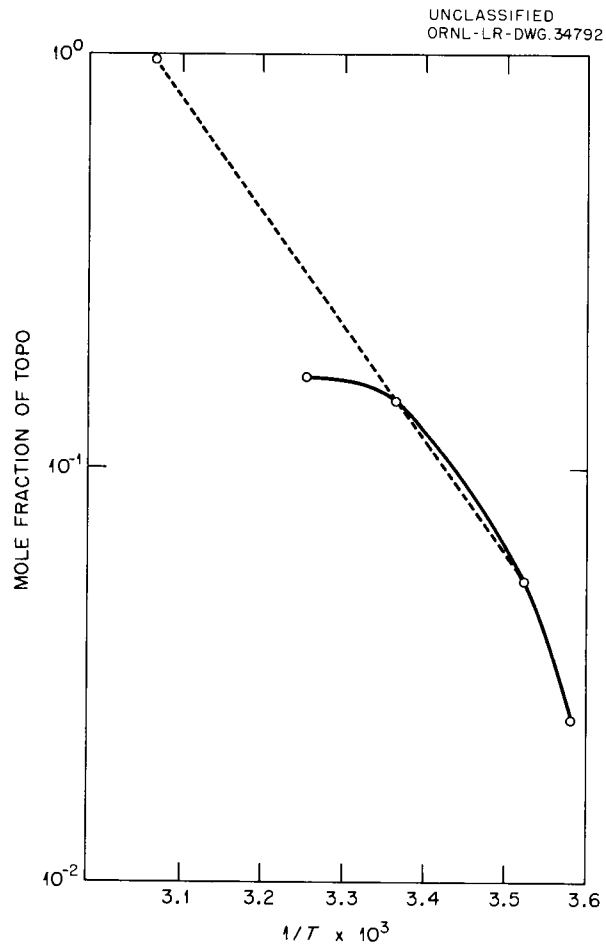

Fig. 25. "Ideality" of TOPO-Cyclohexane Solutions (T in °K).

Table 17. Densities and Solubilities of Saturated TOPO-Cyclohexane Solutions at Various Temperatures

Temperature (°C)	Density (g/ml)	Solubility of TOPO		Weight Per Cent of TOPO	Mole Fraction	
		Grams/Liter	Moles/Liter		TOPO	Cyclohexane
6.5	0.7711	81.42	0.2107	10.56	0.02505	0.9749
11.0	0.7912	164.9	0.4253	20.78	0.05402	0.9458
25.0	0.8057	356.1	0.9222	44.20	0.1471	0.8530
35.0	0.7977	360.8	0.9334	45.24	0.1690	0.8310

dashed line, an approximate value of 12.1 kcal/mole is calculated for the heat of fusion of TOPO.

Infrared Examination of TOPO Metal and Acid Adducts (C. A. Horton). – In continuation of work reported previously,[145] infrared spectra were studied for several films formed by evaporation of TOPO in cyclohexane extracts obtained after equilibration with aqueous acids or acids containing metal ions. In all cases of the metal adducts and acid extractions in concentrations above 4 *M*, the phosphoryl stretching vibration of the phosphorus compound, some observed at 8.37 μ in cyclohexane or at 8.75 μ as a solid film, disappeared and new bands appeared between 8.95 and 9.5 μ. No position of the assumed shifted phosphoryl vibration in this region could be correlated with known properties of the metal ion or the assumed weight of the adduct per mole of TOPO. Each extract from sulfuric acid or nitric acid showed one or more of the bands typical of sulfate or nitrate in the spectra of inorganic salts. Extracts of chromium from hydrochloric acid, of uranium(VI) from hydrochloric or nitric acids, of molybdenum(VI) from hydrochloric or sulfuric acids, and perhaps of hafnium from nitric acid showed new bands in the 10.6- to 11.2-μ region attributed to MO^{2+}-type groups or MO^{x+} groups bound to TOPO.

Examination of solutions of the adducts as extracted in cyclohexane in the near-infrared region, 1 to 2.6 μ, did not furnish any additional information on the type of complex formed because of the strong, many-banded absorption of cyclohexane. Thus a few extracts were examined by the use of a carbon tetrachloride solution of the TOPO. The spectra of TOPO in carbon tetrachloride and of extracts from equilibration with 3 *N* hydrochloric acid, 3 *N* hydrochloric acid plus uranyl ion, or 3 *N* nitric acid plus uranyl ion were all similar in the 0.8- to 2.6-μ region and compared favorably with the spectrum of *n*-octane except for the absence of a strong band at about 1.12 μ and the presence of new weak bands at about 1.2 μ.

Determination of Nitrate in Cyclohexane Solutions of TOPO (W. J. Ross). – Nitrate in a metal or acid adduct of TOPO absorbs light in the ultraviolet region and exhibits maximum absorbancies at 197 and 274 mμ. Beer's law is followed at both wavelengths; the molar absorbancy indexes are 5200 and 10, respectively. The absorbancies at these two wavelengths have been applied to the determination of nitrate in cyclohexane solutions of TOPO that do not contain any other constituent that also absorbs light in these regions.

Spectrophotometric Determination of Iron in TOPO Extracts

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

The extraction of iron(III) from 6 *M* hydrochloric acid into cyclohexane solutions of TOPO and the subsequent spectrophotometric measurement of the iron(II)–*o*-phenanthroline complex in the organic medium was utilized as a basis for a method of increased sensitivity for the determination of iron. After the iron has been extracted by a 2-min equilibration with 0.1 *M* TOPO in cyclohexane, the *o*-phenanthroline complex is developed in the organic medium according to the method reported[150] for the determination of iron in di(2-ethylhexyl) phosphoric acid extracts. In this procedure the color of the complex of the iron that is contained in a test portion of the extract is developed by the addition of glacial acetic acid, which accelerates the color development, and of solutions of hydroquinone and *o*-phenanthroline in ethyl alcohol. The solution is then diluted to a volume of 10 ml with isopropyl alcohol, and after 30 min the absorbancy of the complex is measured at 510 mμ. The relative standard deviation of the method is about 2% over the iron concentration range from 0.2 to 5 μg/ml.

Because the iron is favorably extracted from hydrochloric acid solutions, a substantial concentration of the iron can be effected by carrying out the extraction at high V_a/V_o phase ratios. Ross and White[151] have reported an extraction coefficient of several hundred for the extraction of centigram quantities of iron from 6 *M* hydrochloric acid into 0.1 *M* TOPO in cyclohexane. In this investigation much higher coefficients were determined for the extraction of iron in the concentration range suitable for spectrophotometric measurement. When the concentration of iron in the 0.1 *M* solutions of TOPO was limited to 1 mg/ml, extraction coefficients of approximately

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[150] A. S. Meyer, Jr., and B. L. McDowell, "Spectrophotometric Determination of Iron in Hydrocarbon Solutions of Di(2-ethylhexyl) Phosphoric Acid with *o*-Phenanthroline," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 70.

[151] W. J. Ross and J. C. White, *The Solvent Extraction of Iron with Tri-n-octylphosphine Oxide*, ORNL-2382 (Sept. 26, 1957).

5000 were measured for V_a/V_o ratios from 1 to 500. Therefore quantitative extraction can be obtained in a single equilibration at phase ratios as high as 100.

The method is remarkably insensitive to common anions that interfere with the determination in aqueous solutions. Concentrations of fluoride or phosphate of 0.5 *M* and nitrate of 0.05 *M* cause virtually no interference in this determination. These concentrations of anions correspond to 40-, 5000-, and 12-fold increases in the tolerances for fluoride, phosphate, and nitrate, respectively, over that reported[152] for the determination in aqueous solution.

In addition to the elements that have been reported[152] to interfere with the determination in aqueous solutions, all other elements[153] that are extracted from 6 *M* hydrochloric acid solution by TOPO were also tested as interferences. Although, with respect to interference by metal ions, the method offers little general improvement in selectivity over the aqueous determination, it is sufficiently flexible to be used in elimination of specific interfering constituents.

Four different modes of interferences have been observed: competition for the TOPO between iron and other constituents having high extraction coefficients, absorbancy by constituents that yield colored extracts, absorbancy by colored or insoluble complexes formed by the reaction of an extracted contaminant and *o*-phenanthroline, and incomplete formation of the iron complex due to competition between the iron and an extracted component that forms colorless complexes with *o*-phenanthroline.

Special techniques that have been investigated as means of eliminating these interferences are (1) adding masking agents to the aqueous phase prior to extraction, (2) backwashing the organic phase after extraction to remove partially extractable interferences that have been extracted with the iron, and (3) increasing the concentration of *o*-phenanthroline in the solution on which the absorbancy measurements are made in order to completely complex the iron, as well as the interfering constituent. Quantities of iron of less than 100 μg have been successfully determined in the presence of approximately 20 mg of zinc and tin(IV), both of which are extracted by TOPO and interfere with the *o*-phenanthroline determination. This was accomplished by adding ammonium citrate to the aqueous phase to mask the interference of tin(IV) and by adding a sufficient quantity of *o*-phenanthroline to the extract to complex the iron, as well as the zinc. Another potential technique, which has not been investigated, is the addition of masking agents to the final solution before the addition of the *o*-phenanthroline. If none of these techniques prove successful in the elimination of some interference that has been extracted along with the iron, it should be possible after separation of the phases to effect a separation of the iron and interfering constituent by reducing the iron(III) to iron(II), which is not extracted by TOPO, and transferring the iron to an aqueous solution by contacting the organic phases with a fresh portion of 6 *M* hydrochloric acid.

Determination of Oxides in Fluoride Salts

A. S. Meyer, Jr. G. Goldberg

The determination of trace amounts of oxides by measurement of the oxygen that is evolved on fluorination of oxides with bromine trifluoride has been applied to fluoride salts. In accordance with the recommendations proposed by Sheft and coworkers,[154] fluorination is carried out by use of the molten addition compound of bromine trifluoride and potassium fluoride, $KBrF_4$. The reaction can be conducted at a temperature as high as 450°C without the generation of excessive pressures of bromine trifluoride. The addition compound, $KBrF_4$, has been found to be suitable for the quantitative evolution of oxygen when applied to the fluoride salts of yttrium, beryllium, zirconium, magnesium, and uranium and to mixtures of these salts with fluorides of the alkali metals.

Approximately 35 g of $KBrF_4$ is prepared in each nickel reaction tube by the addition of potassium fluoride to an excess of bromine trifluoride and subsequent removal of the excess bromine trifluoride by distillation. After the metal components of the apparatus have been prefluorinated to remove

[152] G. F. Smith and F. P. Richter, *Phenanthroline and Substituted Phenanthroline Indicators*, The G. Frederick Smith Chemical Co., Columbus, Ohio, 1944.

[153] J. C. White, *Extraction of the Elements with Trioctylphosphine Oxide from Acidic Solutions*, ORNL CF-56-9-18 (Sept. 1956).

[154] I. Sheft, A. F. Martin, and J. J. Katz, "High Temperature Fluorination Reactions of Inorganic Substances with Bromine Trifluoride Addition Compounds," *J. Am. Chem. Soc.* 78, 1557 (1956).

oxide contaminants from the system, the reactor is cooled to room temperature, and the sample (usually 200 mg) is added while a flow of helium is maintained to prevent contamination by atmospheric gases. The reactor, which is isolated from the system by means of a nickel diaphragm valve, is evacuated to remove noncondensable gases and moisture from the sample and is then heated for 2 hr at 450°C. After the evolution of oxygen is complete, the reactor is cooled to room temperature and opened to the measuring system. The oxygen is transferred to the measuring system by means of the automatic Toepler pump through fluorothene cold traps, which are cooled to the temperature of liquid nitrogen to remove bromine trifluoride and its volatile reaction products. The oxygen is determined by measuring its pressure with a differential manometer when it is confined in a calibrated volume above the mercury in the Toepler pump. The range of oxygen that can be measured is from 0.02 to 10 mg, a range which can be readily altered by changing the volume of the confining space.

The realtive standard deviation, which is about 5%, was established by the analysis of samples of pure oxides. Quantitative recovery of oxygen from fluoride salts is indicated by the fact that negligible quantities of oxygen were evolved during additional reaction periods of 2 hr. Typical results of analyses of various materials are shown in Table 18.

The method has also been applied to the determination of oxygen in zirconium metal but is not suitable for the analysis of yttrium metal because of a slow reaction rate. Halides other than fluorides can also be analyzed; however, the bromine trifluoride is rapidly depleted as a consequence of the oxidation of the less electronegative halides.

The rapid evolution of oxygen even from magnesium oxide, which is reported[154] to react only with acidic addition compounds, such as $BrF_2 \cdot SbF_5$, is attributed to the use of the addition compound in large excess. With an excess of the addition compound a large number of samples can be analyzed before the reagent is depleted, and, because of the

Table 18. Results of Determination of Oxygen in Oxides and Fluorides

Sample Composition	Sample Weight (g)	Oxygen (%)	
		Calculated	Determined
Y_2O_3	0.0103	21.2	21.0
	0.0102		21.4
BeO	0.099	63.9	62.0
ZrO_2	0.0100	26.0	27.4
	0.0100		26.5
MgO	0.0047	39.7	39.3
	0.0057		38.7
YF_3	0.250		0.114
	0.250		0.122
YF_3-LiF	0.250		0.065
	0.250		0.068
YF_3-MgF_2-LiF	0.200		0.027
	0.200		0.021
MgF_2	0.125		3.7
	0.125		3.5
BeF_2	0.250		0.83
	0.200		0.88
NaF-ZrF_4-UF_4	0.200		0.35
	0.200		0.38

reduced reaction period, the blank correction, which is usually in the range of 30 to 50 μg of oxygen, is minimized.

The method is highly selective for oxygen and is subject to interference only by nitrogen and by rare gases that may be entrained. With modifications to the apparatus, both nitrogen and oxygen can be determined separately in the evolved gases.

Determination of Yttrium and Magnesium in $LiF-MgF_2-YF_3$

J. P. Young R. F. Apple

A potentiometric method for the determination of both yttrium and magnesium in $LiF-MgF_2-YF_3$ (57.8-20.2-22.1 mole %) was developed and evaluated. These elements form stable complexes with disodium ethylenediaminetetraacetate (EDTA) and can be determined in the same sample by direct titration by applying the technique of Reilley and Schmid,[155] who use a modified mercury electrode. The electrode system is essentially an amalgamated gold wire as the indicator electrode and an S.C.E. as the reference electrode. Yttrium, which forms the more stable complex, is first titrated at a pH of 4.0 ± 0.4; then the pH is increased to 9.7 ± 0.3 and magnesium is titrated. When the titrations are performed with 0.01 *M* EDTA, at least 5 mg of yttrium and 1 mg of magnesium should be present in order to obtain a satisfactory change in potential at the end point. Of the many cations that could interfere with these determinations, only those of iron, nickel, and chromium were evaluated since these metals constitute the bulk of the corrosion products present in the sample. The sum of the concentrations of these corrosion materials in $LiF-MgF_2-YF_3$ rarely exceeds 1000 ppm. This method is unaffected by concentrations of iron, nickel, and chromium up to 1500 ppm by weight. Macroamounts of these cations definitely interfere, however.

Approximately 400 μg of fluoride can be present in the test portion of the sample solution without affecting either determination. The titrations can be performed in either a nitrate or sulfate medium; large concentrations of chloride affect the response of the mercury electrode. The relative standard deviation of the method is about 1%. Based on standards, the results of these determinations are accurate to within ±2%. This method is being used for the routine determination of yttrium in yttrium oxide and yttrium fluoride and of yttrium and magnesium in $LiF-MgF_2-YF_3$; it is much more rapid than gravimetric methods.

Spectrophotometry of Molten Fluoride Salts

J. P. Young

An instrument suitable for spectrophotometric studies of molten fluoride salts is being developed. Although spectrophotometric investigations of molten nitrate and chloride salts have been successfully performed,[156,157] little work of a similar nature has been carried out with molten fluoride salts because of their high melting points and highly corrosive nature. Spectrophotometric examination of molten fluoride salts should provide information relative to the degree and mode of complex formation in molten fluoride salts; kinetics of various corrosion processes; identification and determination of relatively unstable oxidation states of various metals [chromium(II)]; and the mechanism of the reaction between uranium tetrafluoride and the structural metals iron and chromium.

A container, or cell, is being constructed that will be compatible with molten fluoride salts at high temperatures (400 to 700°C) and will also permit optical investigations of the melt. The cell is designed so that it can be inserted into a commercial spectrophotometer, such as the Beckman model DU or the Cary model 14. In order to attain sufficient transmission of light through the sample, it is estimated from data obtained with molten chloride salts[156] that the light path through the molten salt should be less than 0.3 cm. A reflectance cell, a transmission cell, and a pendant-drop arrangement were considered. In the initial spectral studies the mixture of LiF-NaF-KF (46.5-11.5-42.0 mole %) which melts at 459°C was used.

Reflectance Cell. – In a reflectance cell a suitable reflecting material that can be immersed in the fluoride melt is required. The results of various tests, which were made to determine the compatibility of polished metal surfaces with LiF-NaF-KF, are shown in Table 19. All specimens tested

[155] C. N. Reilley and R. W. Schmid, "Chelometric Titrations with Potentiometric End Point Detection," *Anal. Chem.* 30, 947 (1958).

[156] D. M. Gruen, "A Preliminary Spectrophotometric Study of Complex Ions in Fused Salts," *J. Inorg. & Nuclear Chem.* 4, 74 (1957).

[157] C. R. Boston and G. P. Smith, "Visible and Ultraviolet Absorption Spectra of $NiCl_2$ Dissolved in Fused LiCl-KCl Mixtures," *J. Phys. Chem.* 62, 409 (1958).

Table 19. Compatibility of Various Polished Metal Surfaces with LiF-NaF-KF at 550°C

Metal	Period of Immersion (hr)	Condition of Surface After Immersion
Inconel	4	Reflectance lost immediately; surface badly etched
Nickel	5	Considerable loss of reflectance; surface etched
Gold-plated nickel	24	Considerable loss of reflectance; surface covered with microscopic blisters
Gold	40	Considerable loss of reflectance; surface showed macrocrystalline growth
Platinum	40	Some loss of reflectance; surface slightly white

suffered at least some loss in reflectance upon immersion in molten LiF-NaF-KF. Platinum appears to be by far the best material of those tested, but it is not completely inert to the molten LiF-NaF-KF. During these compatibility tests it was noted that a sediment was sometimes present in the molten LiF-NaF-KF. Any insoluble material, whether lighter or heavier than the liquid phase, that is formed or is present in the melt will pose serious problems in obtaining useful spectra with a reflectance cell arrangement. Because of the lack of a suitable mirror and of the other problems associated with the reflectance cell, this line of investigation has been discontinued.

Transmission Cell. – In order to carry out spectrophotometric studies of molten fluoride salts with a transmission cell, a transparent window material must be found that is inert to the molten salts at high temperatures. Diamond appears to meet these requirements, and a transmission cell with diamond windows has been constructed at Battelle Memorial Institute.[158] The expense and size considerations of transparent diamond windows are serious limitations, however. Synthetic crystalline aluminum oxide was found to be badly attacked by molten LiF-NaF-KF within 1 hr. Crystalline magnesium oxide, on the other hand, was found to be very inert to molten LiF-NaF-KF when in contact with this mixture for 20 hr at 550°C. The results of further compatibility tests indicated that this window material is likewise compatible with nickel fluoride in molten LiF-NaF-KF. It is also expected that this oxide will be compatible with such salts as chromium fluoride and iron fluoride. Uranium tetrafluoride in molten LiF-NaF-KF does react with magnesium oxide. This window material is completely transparent to light over the range of wavelengths from the infrared down to approximately 320 mμ, but it absorbs light completely below 300 mμ.

A transmission cell was fabricated from crystalline magnesium oxide; ultrasonic machining techniques were used. Also, the fabrication of a heated cell compartment that is designed for use with the Cary model 14 recording spectrophotometer is almost complete. A drawing of the proposed apparatus is shown in Fig. 26. The furnace is composed of two quartz plates wound with platinum wire which are so positioned in a solid, nonmetallic, insulating block that the cell of crystalline magnesium oxide can be placed between the heaters. The furnace is surrounded by insulation and is enclosed in a copper container, which is water-cooled. The whole assembly is suspended in proper position from the top cover of the sample compartment in the Cary instrument. Suitable light ports allow complete transmission of the available light through the heated cell compartment.

Pendant Drop. – The arrangement under consideration consists of a pendant drop of molten fluoride salt contained in a platinum ring.[159] This type of confinement would eliminate the corrosion problems that are associated with polished metal mirrors and transmission-cell windows. A relatively simple

[158] G. G. Cocks, J. B. Schroeder, and C. M. Schwartz, BMKI-1185, p 13 (classified).

[159] L. L. Merritt, Jr., private communication to J. P. Young, May 1958.

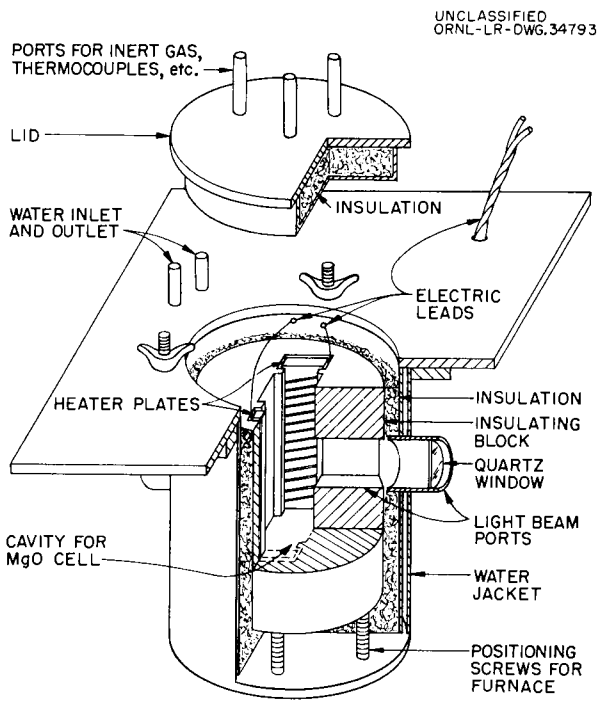

Fig. 26. High-Temperature Cell Compartment for the Cary Model 14 Recording Spectrophotometer.

optical design was suggested[160] in which the pendant drop of molten fluoride is suspended at the focal point of some suitable lens system. Any optical effect of the lens-shaped drop of liquid is minimized and possibly eliminated by such a design. Since the optical arrangement of the Cary model 14M spectrophotometer makes use of a beam of light that is focused in the sample compartment, the optical design of this instrument is somewhat similar to the design proposed above. By use of the Cary instrument it was found possible to obtain well-defined spectra of various metal-borax glass beads. These beads were confined in a platinum ring of approximately 5 mm diameter. Further studies are under way to evaluate the usefulness of a pendant drop of sample for accurate spectral measurements.

With the heated cell compartment described above, it should also be possible to obtain the spectral response of pendant drops of molten fluoride salts with the Cary spectrophotometer. A series of quick and relatively simple screening tests will be made in this manner, which should prove valuable in making a critical evaluation of the general analytical usefulness of spectrophotometric measurements of molten fluoride salts.

[160] K. L. Vandersluis and W. F. Peed, private communication to J. P. Young, June 1958.

Determination of Fluoride in Yttrium Metal

J. P. Young R. F. Apple

A colorimetric method for the determination of microgram amounts of fluoride in yttrium metal is being evaluated. This method is a modification of the classical Willard and Winter distillation[161] to give a separation of fluoride from yttrium and a bleaching by fluoride of the color of the thorium-thoron complex[162] in order to provide a determination of fluoride in the distillate. On the basis of the limited number of results obtained to date, the method appears to be satisfactory. The relative standard deviation of the method is less than 3%. The accuracy and sensitivity of the method are being checked; it is probable that this method will be useful for the determination of less than 10 ppm of fluoride in yttrium metal.

Ultraviolet Spectrophotometric Determination of Cerium

J. C. White R. F. Apple

An ultraviolet spectrophotometric method for the determination of cerium was developed specifically for application to mixtures of fluoride salts, such as NaF-ZrF_4-UF_4 (50-46-4 mole %). After dissolution of the salt mixture in an H_3BO_3-HNO_3-H_2SO_4 solution, a test portion that contains 0.5 to 5 mg of cerium is treated with sufficient ammonium hydroxide to precipitate cerium and the insoluble hydrous oxides of other metals, in this case, the hydrous oxides of zirconium and of uranium. The hydroxides are then redissolved in 7 *M* hydrochloric acid, and the acidic solution is extracted with 0.05 *M* TOPO in cyclohexane. Zirconium, uranium, and iron are extracted, whereas cerium remains in the aqueous phase. The oxidation state of the cerium in 7 *M* hydrochloric acid is entirely trivalent. The absorbancy of the aqueous phase is then measured at 253 mμ vs water as a reference.

[161] H. H. Willard and O. B. Winter, "Volumetric Method for Determination of Fluorine," *Ind. Eng. Chem. Anal. Ed.* **5**, 7 (1933).

[162] A. D. Horton, P. F. Thomason, and F. J. Miller, "Spectrophotometric Determination of Inorganic Fluoride," *Anal. Chem.* **24**, 548 (1952).

The method is rapid and precise; the relative standard deviation is 1% when the Cary model 14M spectrophotometer is used to measure the absorbancy. One particular advantage of the method is that the effect of the oxidation state of cerium, which is an important factor in most colorimetric methods for cerium, is simply eliminated by the use of 7 *M* hydrochloric acid, which reduces cerium(IV) to cerium(III) and also serves as the optimum medium for the separation of the main interfering ions by extraction with TOPO.

A paper that describes this work has been submitted for publication in *Talanta.*

Determination of Boron in Nitrate Solutions

W. J. Ross

The carminic acid method for the determination of boron[163] has been extended to acidic nitrate solutions through the development of a method for removing nitrate, as well as interfering cations, without the accompanying loss of boron. With this modification the method was applied to the determination of low concentrations (<50 ppm) of boron in nickel-base alloys that contain in excess of 100 times as much iron, chromium, and molybdenum, dissolved in aqua regia. Molybdenum(VI) and iron(III) are readily extracted from diluted solutions of aqua regia by TOPO[164] and are thus separated from boron, nickel, and chromium(III). The relatively small interference of chromium(III) is additive and is compensated by the application of "spiking" techniques. Boron in 1- to 2-ml test portions is subsequently freed from nitrate by reducing the nitrate to oxides of nitrogen with formic acid and expelling the volatile oxides of nitrogen under reflux conditions that prevent the loss of boron by volatilization. When the boron concentration of the nitrate-free solution is less than 20 μg/ml, the boron–carminic acid chromophore is formed *in situ* by the addition of the required reagents through the reflux condenser.

A similar procedure was used to determine boron in concentrations as small as 5 μg/ml in solutions of uranyl nitrate, $U^{233}O_2(NO_3)_2$. A separation step was included whereby uranium is removed from the nitrate solution by extraction with TOPO.[164] The remaining steps, decomposition of nitrate and development of the boron–carminic acid color, can then be performed without taking precautions to avoid hazards or possible loss of fissionable material.

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

[164] J. C. White, W. J. Ross, and C. A. Horton, "Extraction of Elements from Acidic Solutions with Tri-*n*-octylphosphine Oxide (TOPO) in Cyclohexane," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 64.

SPECTROCHEMICAL AND X-RAY ANALYSES

C. Feldman (X-10) J. A. Norris (Y-12)

Ammonium Bisulfate as Fusion Agent for $NaF-ZrF_4-UF_4$ Fuels and Other Substances

C. Feldman (X-10)

As an acid fusion agent, ammonium bisulfate has the following advantages over potassium pyrosulfate: it melts at a lower temperature (146.9°C vs >300°C); it can be kept molten or boiled for prolonged periods without solidifying provided that a tight watch glass is used; if the watch glass is removed, the salt can be volatilized completely; and it does not attack platinum, Pyrex, or fused-quartz vessels.

When the impurities in a refractory sample are to be concentrated for spectrographic analysis, it is usually impossible to begin by fusing the sample. The large quantities of fusion salt thus introduced cannot be eliminated in the wet way without the simultaneous elimination of some of the trace elements to be determined (alkali and alkaline-earth metals). Since ammonium bisulfate can be completely volatilized after the fusion, however, it is free from this disadvantage. Where its presence is not objectionable, as when the subsequent analysis is to be chemical rather than spectrographic, the evaporation may be omitted.

The fused-salt mixture $NaF-ZrF_4-UF_4$ is quickly converted to a mixture of Na_2SO_4, $ZrOSO_4$, and UO_2SO_4 by fusing 10 parts of NH_4HSO_4 with 1 part of the fluoride mixture in a platinum dish. The fusion can be started on a hot plate at ~375°C and, if speed is essential, completed with the aid of a Meker burner. A quartz or Pyrex beaker may be used with fluoride samples if the impurities thus introduced into the melt will not be harmful.

For spectrographic analysis the sulfate mixture that remains after the evaporation of the ammonium bisulfate is dissolved in 10 *N* nitric acid, and the uranium and zirconium are extracted with tributyl phosphate. The remaining aqueous solution is analyzed spectrographically by the porous-cup technique.

Effect of Concentration of Sulfuric or Perchloric Acid on Intensity Ratios in the Porous-Cup Technique

M. M. Murray C. Feldman
(X-10)

Identical mixtures of trace elements were dissolved in 2, 5, and 10% solutions of sulfuric acid and of perchloric acid. Seventeen ratios of metal intensity to internal-standard intensity were measured in quadruplicate porous-cup exposures of each solution. The intensity ratio of each line pair measured in the 2% sulfuric acid solution agreed to within less than 10% with its value in the 2% perchloric acid solution. On changing from 10% sulfuric acid to 10% perchloric acid, half these line pairs showed intensity-ratio changes of less than 10%; the others changed by amounts ranging from 20 to 100%. Results for the 5% acid solutions were intermediate. Extrapolation indicated that intensity ratios given by 1% solutions of these acids should be identical.

Investigation of Porous-Cup Electrodes by Use of the Photoelectric Spectrometer

Z. Combs J. J. Mundzak J. A. Norris
E. H. Waters R. E. Weekley
(Y-12)

The use of photoelectric instead of photographic methods of recording spectral intensities requires closer control of spectral background in order to prevent distortion of the calibration curve at low signal-to-noise ratios. In Fig. 27 the variation of background (noise) with exposure time, that is, the time required for the emission from the internal-standard element to reach a predetermined intensity, is shown for the following conditions:

Electrode	United Carbon Products Co. type 1994 in water-cooled electrode holder
Element and line	Pr 4222
Solution	50% HCl with 25 μg of Sr per ml
Excitation, high-voltage a-c spark	
capacitance	0.016 μf
inductance	300 μh
resistance	1 ohm in secondary
number of breaks	2 per half cycle
r-f current	7.5 amp
Exposure	30 v on Sr 4215 capacitor
Electronics	Baird-Atomic direct reader

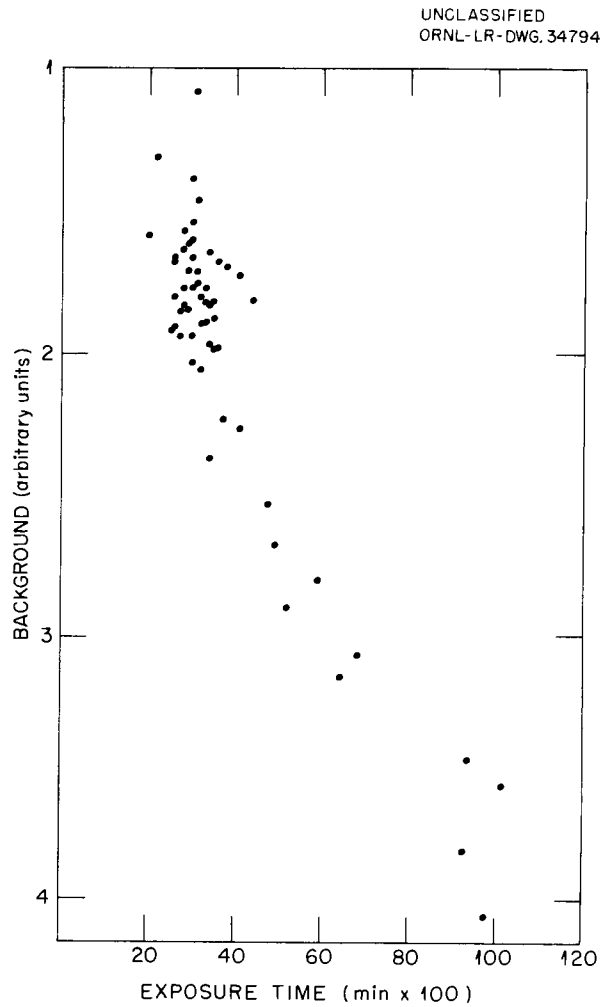

Fig. 27. Relationship of Background to Exposure Time in Photoelectric Determination of Rare Earths.

The exposure-time variation for 20 or more of four different types of porous-cup electrodes, taken under the conditions given above for Fig. 27, is shown in Fig. 28.

The data of Figs. 27 and 28 were taken from an experiment carried out to compare electrode types. A preliminary analysis of these data (one element) indicates considerable difference in the porosity of electrodes; the best precision can be expected with National Carbon type 4048 electrodes when two exposures are made on an electrode and discarded, following which any one of four succeeding exposures can be used for analytical purposes. The complete data for six other elements are being analyzed by means of standard statistical techniques with computation by the IBM-704 computer.

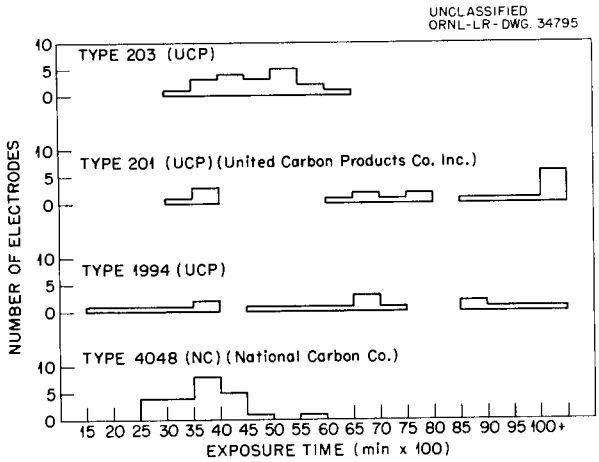

Fig. 28. Histograms Showing Variation of Exposure Time for Four Types of Porous-Cup Electrodes.

Determination of Rare Earths in Other Rare Earths and in Yttrium Oxide

Z. Combs J. J. Mundzak J. A. Norris
E. H. Waters R. E. Weekley
(Y-12)

The preparation of Lu_2O_3-base standards for the determination of other rare earths in the oxides of lutetium isotopes completed the stock of standards of the rare-earth-element group. Presently available are standards with the oxides of yttrium, lanthanum, cerium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, ytterbium, and lutetium as the base materials. If 1-mg samples are used for analysis, the concentration range of the other rare earths in the various bases is, in general, as follows:

Rare Earth	Concentration Range (ppm)
Y_2O_3	40 to 800
La_2O_3	40 to 800
Ce_2O_3	1000 to 8000
Pr_2O_3	400 to 4000
Nd_2O_3	1000 to 4000
Sm_2O_3	1000 to 4000
Eu_2O_3	40 to 800
Gd_2O_3	40 to 800
Tb_2O_3	500 to 2000
Dy_2O_3	200 to 4000
Ho_2O_3	200 to 4000
Er_2O_3	40 to 800
Tm_2O_3	40 to 800
Yb_2O_3	20 to 400
Lu_2O_3	40 to 800

Photoelectric Determination of Rare Earths in Rare-Earth Mixtures

Z. Combs J. J. Mundzak J. A. Norris
E. H. Waters R. E. Weekley
(Y-12)

The determination of the rare earth scandium oxide has been added to the regular analysis of rare-earth mixtures developed by this laboratory and adapted for photoelectric recording.[165] The rare earths and ranges for which calibration curves are available are listed below. With current equipment, any eight rare earths can be determined simultaneously.

Rare Earth	Concentration Range (μg/ml)
Sc_2O_3	20 to 600
Y_2O_3	20 to 1000
La_2O_3	20 to 800
Ce_2O_3	50 to 1000
Pr_2O_3	50 to 2000
Nd_2O_3	50 to 1500
Sm_2O_3	20 to 1000
Eu_2O_3	10 to 500
Gd_2O_3	25 to 800
Tb_2O_3	50 to 1000
Dy_2O_3	50 to 2000
Ho_2O_3	20 to 1000
Er_2O_3	20 to 1000
Tm_2O_3	50 to 2000
Yb_2O_3	20 to 1000
Lu_2O_3	20 to 1000
Th_2O_3	50 to 1000

Spectrochemical Determination of Oxygen in Metals

R. E. Weekley (Y-12)

Work has been under way to adapt the method of Fassel and Tabeling[166] for the routine spectrographic determination of oxygen in metals. By the use of a 3.4-m Jarrell-Ash Ebert spectrograph in the second order of a 7500-line/in. plane grating, the intensity ratio of the line pair, oxygen 7771.9 Å

[165] J. A. Norris and C. E. Pepper, "Quantitative Spectrochemical Analysis of Rare-Earth Mixtures," *Anal. Chem.* **24**, 1399 (1952).

[166] V. A. Fassel and R. W. Tabeling, "The Spectrographic Determination of Oxygen in Metals – I. Plain Carbon Steels," *Spectrochim. Acta* **8**, 201 (1956).

and argon 7891.1 Å, has been correlated with the oxygen content of both plain carbon and alloy steels in the range from 0.0020 to 0.0800% oxygen. The analytical curve (Fig. 29) was derived by the use of standard samples supplied by the National Bureau of Standards, the Jones and Laughlin Steel Co., and this Division. The data were corrected for residual oxygen by the method of Duffendack and Wolfe.[167] The curve is plotted as log of intensity ratio vs log of "corrected oxygen concentration," which is defined as the product of the oxygen concentration (ppm) of a 1-g sample by the sample weight (g). This procedure is desirable because, unless the analytical curve has unit slope, which in general will not be the case, division of the measured intensity ratio by the sample weight is not a valid normalizing procedure. The relative standard deviation is about 10% in the low (0.002 to 0.010%) range and about 5% in the high (0.010 to 0.080%) range of oxygen content.

The present evidence indicates that the major sources of residual oxygen, which causes a significant blank, are the O-ring seals, chamber inleakage, and gradual desorption of oxygen from the Pyrex separator. In this connection a mass spectrometric assay has been made of the off-gas from a Neoprene O-ring, both at ambient and elevated temperatures. A plot of relative mass intensity vs temperature is given in Fig. 30. Vacuum pretreatment of the electrodes at 900°C for periods of up to four days, followed by cooling under argon pressure, has been found to be ineffective in removing the source of the blank. The gas purification train described originally[166] has been found to be unnecessary since tank argon with less than 5 ppm of oxygen-containing contaminants (determined by mass spectrometry) is commercially available.

[167] O. S. Duffendack and R. A. Wolfe, "Analysis of Caustic Liquors for Traces of Impurities," *Ind. Eng. Chem. Anal. Ed.* 10, 161 (1938).

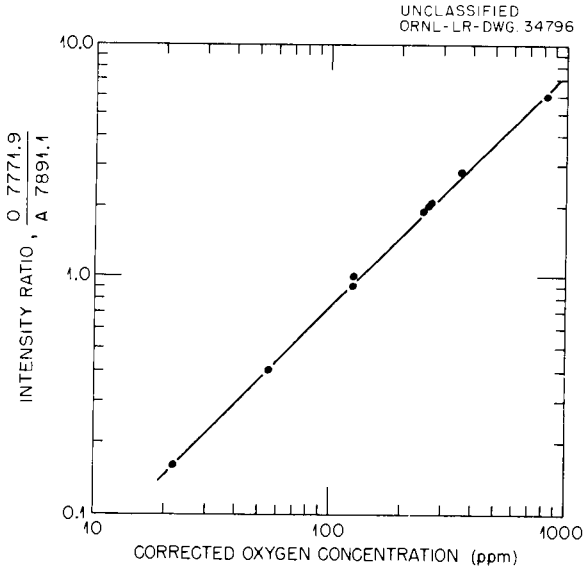

Fig. 29. Analytical Curve for the Spectrographic Determination of Oxygen in Steel. (Experimental conditions given in context.)

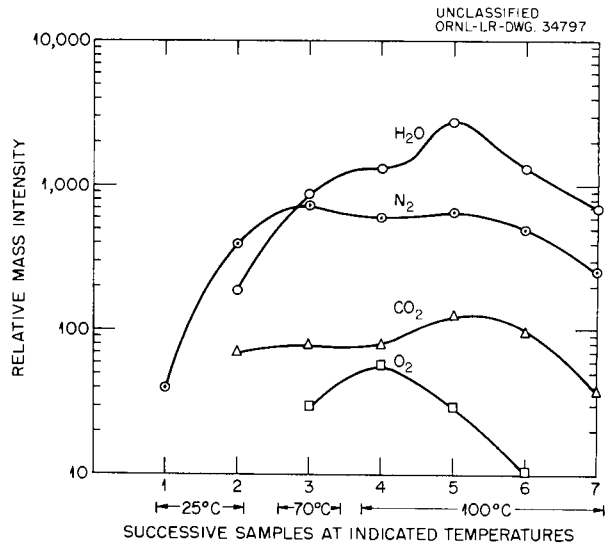

Fig. 30. Results of the Mass Spectrometric Assay of Off-Gas from Neoprene O-Ring.

Spark Exposures in a Helium Atmosphere Without the Use of a Chamber

C. Feldman (X-10)

By means of a hollow counter-electrode, helium was introduced into the analytical gap of porous-cup exposures at the rate of 10 liters/min. In Table 20 a comparison of net line intensity (L), background intensity (B), and line/background ratio (L/B) for four lines is given between these exposures and conventional exposures in still air. In all cases the L/B ratio is considerably greater in the helium exposure. Most of this effect is due to reduction of background by helium, but net line intensities are also greater in helium than in air.

Table 20. Effect of Helium Atmosphere on Porous-Cup Spectra

L = line intensity
B = background intensity

Spectral Line	L (He) / L (Air)	B (He) / B (Air)	L/B (He) / L/B (Air)
Fe(II) 2410	1.41	0.48	3.1
Co(I) 2411	1.60	0.48	3.9
Co(II) 2587	1.26	0.51	2.4
Mn(II) 2939	1.42	0.27	5.7

Real improvements in sensitivity are thus possible by this method.

In the helium exposures a 1% sulfuric acid solution that contained 7.5 ppm iron, 25 ppm cobalt, and 1.0 ppm manganese was exposed in a bevel-bottom (United Carbon Products Co. type 201) porous cup. In the air exposures the counter electrode was a $\frac{1}{8}$-in.-dia, graphite, flat-topped rod. Electrical excitation was a 0.0025-μf, 0.040-mh, 2.75-rf-amp discharge (six breaks per half cycle) furnished by a Jaco Varisource.

Use of Triisooctylamine for Extraction of Zirconium

C. A. Pritchard (X-10)

The extraction of zirconium from a 9 N hydrochloric acid solution into a 20% solution of triisooctylamine in xylene was found at times to be less efficient than stated by Moore.[168] It appeared on investigation that the ability of this reagent (prepared from Union Carbide Products Co. commercial-grade triisooctylamine) to extract zirconium diminishes on standing. Full efficiency for zirconium extraction is obtained only with a freshly prepared mixture.

[168] F. L. Moore, "Liquid-Liquid Extraction of Uranium and Plutonium from Hydrochloric Acid Solution with Tri(iso-octyl)amine," *Anal. Chem.* 30, 908 (1958).

X-Ray Fluorescence

H. Dunn (X-10)

A procedure has been developed for the determination of niobium, zirconium, and uranium in the presence of each other where the ratio of any two of the metal concentrations is no greater than 1:5. When large amounts of uranium are present (e.g., in uranium-niobium-zirconium fuels), uranium is extracted from one test portion before niobium and zirconium are determined. Uranium is determined in a second test portion. Yttrium is used as an internal standard in all cases.

The Lucite solution containers first used in this work have been found to crack under x rays and have been replaced by polystyrene containers. Scotch mending tape (No. 8310) has been found to be more chemically stable than Scotch cellophane tape, especially toward nitric acid solutions. The former is therefore preferred for sealing the opening in this cell.

The conversion of a General Electric XRD-5 x-ray instrument for use in x-ray absorption analysis is 80% complete.

High-Radiation-Level Spectrographic Laboratory

W. R. Musick A. H. Marshall
(X-10)

It was found that the use of 1000 ppm of zinc in solutions of rare-earth elements exposed by the porous-cup technique minimized the effects of lanthanum on the working curves of gadolinium, dysprosium, and samarium. A gas chamber was designed for use inside the Jaco No. 1930 excitation stand located in this facility.

SERVICE ANALYSES

A summary of the service analyses made by the laboratories of the Analytical Chemistry Division is given in Table 21.

ACTIVATION ANALYSES (X-10)

G. W. Leddicotte

Activation analysis has been used to determine submicrogram and microgram amounts of elements in such materials as metals, alloys, minerals, petroleums, water, and biological specimens. The method has also been used to determine particle-size distributions in thorium oxide, thorium oxalate, and mixtures of the oxides of thorium and uranium.

GENERAL SERVICES (Y-12)

L. J. Brady

Counting Laboratory

J. M. Peele

The Counting Laboratory was put into operation in May 1958, with a staff consisting of a supervisor and one analyst. The counting equipment originally provided was a model 117 proportional alpha counter and a Geiger-Mueller counter. This equipment has been supplemented by two proportional-type alpha counters and a single-channel gamma scintillation spectrometer.

The staff of the Counting Laboratory has analyzed 564 samples during the year. The major portion of these samples was submitted by the Chemical Technology Division for plutonium determination in connection with their liquid-liquid extraction studies on synthetic solutions that simulated reactor waste materials. Slightly more than half these samples were in aqueous solutions of nitric acid. Since these samples contained sufficient quantities of sodium nitrate to partially mask the alpha activity, a preliminary separation of the plutonium by extraction with thenoyltrifluoroacetone (TTA) was necessary. The remaining samples were various organic extracts of plutonium which were diluted with an inert solvent. The plutonium concentration of these solutions was determined by gross-alpha counting.

The gamma scintillation spectrometer was put into operation in September and has been used in the determination of the gamma activity of various fluoride-salt mixtures to which radioactive isotopes had been added and in the determination of the residual gamma activity in metallic fuel containers. This work was carried out for the Reactor Projects Division.

Miscellaneous Analyses Laboratory

E. C. Lynn J. R. Lund

During the year the staff of the Miscellaneous Analyses Laboratory analyzed approximately 5200 samples, which originated in a number of different ORNL divisions and at Y-12 and were of various types. Acidic solutions and solids, related to studies of the application of ion exchange columns to the the recovery of uranium from slag from reduction-bomb liners, were analyzed for uranium, nitrate, and sulfate. Studies by the Chemistry Division of isotopic enrichment by means of chemical-exchange reactions were continued during this period, and were the source of approximately 50% of the samples submitted to this laboratory. Concentrated solutions of sulfuric acid from the Nitrox system were analyzed for nitrate. Specification testing of ferrous and nonferrous metals and alloys continued throughout the period, and a number of samples of paint and ink that were to be used for marking metals were analyzed for chloride.

From studies related to reactor waste disposal and conducted by the Ceramics Research Group, samples of lime and shale were submitted for complete chemical analysis, and the fluoride content of aqueous solutions that had been used to leach ceramic materials fired at different temperatures was determined. The fluoride content of the leach solution indicated the degree of solubility of the ceramic material.

Other analyses conducted by the staff of the Miscellaneous Analyses Laboratory included the determination of hydrogen in paraffin; chemical composition and electrical conductivity of water samples; water and sulfur content of transformer oils; boron on targets used in the cyclotron; and viscosity, specific gravity, and acidity of vacuum-pump oils that had been subjected to radiation for various periods of time.

Raw Materials Laboratory

J. R. Lund E. C. Lynn

Approximately 7100 samples were analyzed by the staff of the Raw Materials Analytical Chemistry Laboratory during the year. Most of them were derived from studies of solvent extraction processes in which

Table 21. Summary of Analytical Service Work

Group Making Analyses	Number of Persons		Number of Results Reported																																
			For ORNL																					For Others											
	Scientists	Technicians	Analytical Chemistry	Applied Nuclear Physics	Biology	Chemical Technology	Chemistry	Development	Education	Electronuclear Research	Engineering and Mechanical	Finance and Materials	Health Physics	Homogeneous Reactor Project	Instrumentation and Controls	Isotopes	Metallurgy	Neutron Physics	Operations	Physics	Reactor Experimental Engineering	Reactor Projects	Solid State	Armour Research Foundation	Army Package Power Reactor	General Electric Company	K-25	Miscellaneous	North Carolina State College	ORINS	Paducah	University of Tennessee	Y-12	Totals
Activation Analyses* (X-10)	5	6	579			2,286	86			7			69	11	3	9	235	15	4432	58	493	590	315			10	8	34					16	9,256
General Services (Y-12)																																			
Counting Laboratory	1	1				532																48													580
Miscellaneous Analyses Laboratory, and Raw Materials Laboratory*	3	10				19,312	3634						31			105	156	86			704	159						217					761	25,165
HRP Laboratory* (Y-12)	12	10																			101,000														101,000
Ionic Analyses* (X-10)	10	0	52			524	991			20		33	61	41		7	270	6		55	189		5												2,254
Mass Spectrometry Analyses* (Y-12)	3	3	924		76	1,044	1005					100	30		26	2,008	3,623			111	49	10,360	36					102		18			1320	20,832
Optical and Electron Microscopy* (X-10)	3	3	44		51	892	137	35	106				376			18	340	4			866													2,869
Process Analyses (X-10)																																			
High-Alpha Analytical Laboratory	2	3				8,436	268						122			113		123	2		20		16											9,100
Pilot Plant Control Laboratory	6	9				33,371							21	1,290		2			2627												1		37	37,349
Process-Development Analytical Laboratory	3	6	6			25,323	145						73			18	33		96	2	22	140	12					109						25,979
Special Analyses Laboratory	10	9		418		18,065	33						2592			604	4,264		1063		866	136	449											28,490
Radiochemical Analyses* (X-10)	5	1				686	10						1528	133	4	64		5	18	9	418		24		42	603	1				13	62	104	3,724
Radioisotopes-Radiochemistry Laboratory (X-10)	3	17				9,012	498						2574	57		17,885		618	88		757		270			1482		330						33,571
Reactor Analyses Laboratory (X-10)	7	9				218	34							14,795		54					308		100	25		3			72				11	15,620
Reactor Projects Laboratory* (Y-12)	11	3				231											1,966				923	11,066						126						14,312
Spectrochemical and X-Ray Analyses* (X-10)	7	2	8		3	2,804	344				2	2	28	1,432	50	41	792	32	140	51	940	72	249											6,990
Spectrochemistry Laboratory* (Y-12)	4	1				6,546	1521									4,742	1,436				2,644	356						746					1177	19,168
Totals	95	93	1613	418	130	129,282	8706	35	106	27	2	135	7505	17,759	83	25,670	13,115	889	8466	286	110,199	22,927	1476	25	42	2098	9	1664	72	18	14	62	3426	356,259

*These groups also do research and development work.

organophosphorus compounds or high-molecular-weight amines were used as extractants.

During the earlier part of the year the application of hydrometallurgical processes to the separation of uranium from domestic ores was studied. A major part of the work consisted in the analysis of both organic and aqueous solutions of the ores for uranium and for vanadium, iron, molybdenum, and other metals that are commonly associated with uranium in ores found on the Colorado Plateau.

Later in the year more attention was centered on the application of solvent extraction to the separation of thorium from acid leach liquors. Volumetric, gravimetric, and colorimetric methods for the determination of thorium were applied in the analysis of these solutions. Adequate separation procedures were required in order to separate thorium from other metals and from anionic components that otherwise would interfere in the determination.

In order to compare the results of tests conducted on a pilot-plant or laboratory-bench scale with those obtained in actual mill operation, samples were taken by personnel of the Chemical Technology Division from a number of points in the flow streams of ore-processing mills on the Colorado Plateau during normal operations. These samples were analyzed in the Raw Materials Analytical Chemistry Laboratory; then the results were compared by members of the Chemical Technology Division with data from pilot-plant tests. The information thus gained enables the chemical engineer to predict the operational conditions necessary when laboratory or pilot-plant equipment and processes are scaled up for mill operations.

In addition, physical measurements were made on various acid leach liquors and on solutions of organic extractants in kerosene. Traces of water were determined in the latter samples by coulometric titration. Traces of calcium (5 to 10 ppm) in 0.5 *M* sodium nitrate solutions were determined flame photometrically by recording the radiant intensities at 423 mμ and comparing them with the intensities of solutions that contained known amounts of calcium in the same media.

HIGH-RADIATION-LEVEL ANALYTICAL FACILITY (HRLAF) (X-10)

J. E. Morton

During 1958, minor modifications were made to the HRLAF and to the equipment used in it. Audible alarms were added to the remote-area monitoring system to supplement the warning lights. Changes were made in the air system of the hydraulic lift in order to prevent exhaust air from blowing dust and possible contamination out of the sample-cart trench. Standpipes were installed in all the electrical floor outlets to protect the cables from damage during cleaning operations. Folding gates were placed across the west side of the loading dock to provide access, completely within the classified area, to the dock. Radiation hazards from contaminated vacuum lines were eliminated by lead shields placed over the vacuum-line valve stems on the faces of the cells. A demountable hood was installed in one of the cells to prevent corrosion of manipulators and equipment by acid fumes. Several types of plastic cell-floor coverings were tested, including Cocoon, vinylite, and polyethylene, and Cocoon was selected as the material for completely lining three cells.

Efforts were continued to reduce manipulator down time. A preventive maintenance schedule was set up, and six manipulators were completely overhauled. Protective rubber boots and plastic sleeves were put on manipulator arms where needed. Repairs on tong springs were almost eliminated by the relocation of the springs on the tongs and by the substitution of lock washers for Truarcs as spring fasteners. The master-hands were improved by the installation of a heavy, single finger-cable in place of the double finger-cables and by the replacement of the webbed finger-links and thumb-links with solid metal links. Down time for the repair of broken inner finger-cables was reduced by the practice of removing the differential assembly containing the broken cables and replacing it with a spare assembly. Cable repairs were then made at the manipulator shop.

HRP LABORATORY (Y-12)

O. Menis

H. P. House C. K. Talbott F. L. Layton

During 1958 the staff of the HRP Laboratory made 101,000 determinations on 14,900 samples, approximately the same number of samples analyzed last year; the number of determinations increased 20%. Most of the samples were solutions of uranyl sulfate only; uranyl sulfate solutions that contained the sulfates of copper, lithium, magnesium, or sodium; and slurries of thorium dioxide. The following materials were analyzed less frequently: 1 *M* and 5% solutions of nitric acid, 1 *M* sulfuric acid, 1 *M* deuterium sulfate, steam condensate, hydrogen

peroxide, organic dyes, and inks. The methods commonly used for the various determinations are summarized below:

Method	Constituent
Titrimetric	
visual indicator	Th, SO_4^{2-}, free acid, U, $C_2O_4^{2-}$
colorimetric	U^{4+}, Bi, F, Ce
potentiometric	Cl^-, Br^-, I^-, free acid
Spectrophotometric	Fe, Ni, Cr, Cr^{6+}, Al, Co, Cu, Ti, Zr, Si, As, Sb, Pt, Ru, Au, NO_3^-, PO_4^{3-}, O_2, W, Mo, Mn
Flame photometric	Ba, Ca, Na, K, Li, Cs, Nd, Ag, B
Polarographic	Sn, Zn, Hg, Pb, U
Gasometric	H_2, O_2, CO_2
Electrogravimetric	Cu
Gravimetric	Th
Beta counting	Tc

The solutions of uranyl sulfate were most frequently analyzed for uranium, copper, sulfate, iron, nickel, chromium, and chloride and occasionally for the other elements that are listed above, of which the most common were the alkali, alkaline-earth, and transition elements. The hydrogen-ion concentration of a large number of these solutions was also measured, and the dissolved oxygen, hydrogen, and carbon dioxide were determined.

Thorium oxide and other compounds of thorium were analyzed for thorium and for impurities similar to those that are found in solutions of uranyl sulfate. Slurries of thorium oxide were analyzed for dissolved oxygen, hydrogen, and carbon dioxide and also for a number of additives, as well as for corrosion products of stainless steel and other components of test loops. The densities and zeta potentials of a number of thorium oxide slurries were determined. Measurements were also made of of the particle-size distribution in slurries of aluminum oxide and of titanium oxide. Thermogravimetric analyses were also made on a variety of solid samples, principally mixtures of thorium oxide with other metallic oxides.

Iron, nickel, chromium, and free acid were determined in nitric and in sulfuric acid solutions. The densities of some of these solutions were also measured. Other work included the determinations of conductance, pH, uranium, sulfate, and chloride on samples of steam condensate; the establishment of the concentration of solutions of hydrogen peroxide; and the evaluation of the chloride content of a number of organic dyes and inks. Fusion pyrolysis was used to separate chloride, fluoride, and ruthenium from a number of samples prior to their determinations.

IONIC ANALYSES (X-10)

P. F. Thomason

The major portion of the service work of the group was for the Chemistry Division relative to their research in high-temperature solubilities, HR fuels, and fundamental ion exchange studies. Work for the Chemical Technology Division was concerned with their studies in reactor-fuel reprocessing. Service work for the Metallurgy Division supported their studies in the development of alloy-type fuel elements. For the Reactor Experimental Engineering Division the work was relative to their corrosion studies. The majority of the methods that were used are contained in the *ORNL Master Analytical Manual.* New methods that were developed to support the service work have been either published or submitted for publication in *Analytical Chemistry.*

LOW-RADIATION-LEVEL ANALYTICAL LABORATORY (X-10)

C. L. Burros

Interim Low-Radiation-Level Analytical Laboratory

C. L. Burros J. H. Moneyhun
S. A. Reynolds[1]

The engineering drawings for the modification of Building 0907 for use as the Low-Radiation-Level Analytical Laboratory were completed and were accepted on May 9. The contract was awarded to Vickers Construction Co., which began construction on September 11, with 90 days thereafter to complete the job.

The following instruments have been ordered for the Interim Low-Radiation-Level Analytical Laboratory: a gamma scintillation spectrometer (200-channel), an alpha range analyzer, an alpha proportional counter, a low-background beta counter,

[1]Radiochemical Analyses Group.

two gamma scintillation counters, and a Geiger-Mueller counter.

Standard radiochemical procedures have been adapted for the analysis of samples of low activity. Modifications to the procedures include a step for concentrating small quantities of activity from large volumes of samples, such as samples of river water. Volume reduction can be effected by evaporation, precipitation, or ion exchange. The precipitation and ion exchange methods are used in preference to evaporation because they are faster and more selective and are subject to fewer losses. In the precipitation method ferric nitrate is added and the hydroxides are precipitated together with the ferric hydroxide. The ferric hydroxide precipitate serves a twofold purpose: it acts as a scavenger and it increases the settling rate of the other precipitates. Wyatt[2] and Smith[2] have done most of the work on the modifications of the radiochemical methods. The modified methods have been included in the *ORNL Master Analytical Manual.*[3-8]

River water and silt have been analyzed by radiochemical methods and by gamma spectrometry. The method for the determination of yttrium in river water and silt was devised by Handley.[1] A number of filter samples taken from air monitors were analyzed by gamma scintillation spectrometry.

MASS SPECTROMETRIC ANALYSES (Y-12)

J. R. Sites

During the past year the Analytical Mass Spectrometry Group has continued to make quantitative analyses for the relative abundances of isotopes in various elements and for impurities in very nearly pure gases. The gaseous species baked out during the GCR component tests have been continuously monitored throughout each experiment. Several samples of separated stable isotopes of greater than 99.9% isotopic purity have been reported.

During its first full year in the Analytical Chemistry Division, the Analytical Mass Spectrometry Group has made 20,832 analyses on 2713 samples.

PROCESS ANALYSES (X-10)

L. T. Corbin

High-Alpha Analytical Laboratory

J. H. Cooper

The major portion of the work done by the High-Alpha Analytical Laboratory was for the Chemical Technology Division, relative to plutonium-producer-blanket studies and to studies of the transuranic elements. The High-Alpha Analytical Laboratory assisted the Health Physics Division in preparing 250 pellets of neptunium oxide for radiation dosimetry studies.

In their study of the solubility of plutonium fluoride in mixed-fluoride salts, the Chemistry Division requested determinations of cerium, barium, and lithium in the presence of plutonium. Barium was determined by the standard sulfate precipitation method without prior separation from plutonium. Lithium was separated from plutonium and determined on the flame spectrophotometer. The separation was accomplished by adsorbing plutonium from a 7 *M* nitric acid solution onto an anion exchange resin. The effluent solution of lithium was free enough of alpha activity to be analyzed on a flame spectrophotometer. Plutonium interferes in the spectrophotometric determination of cerium and must be removed. Chemical separation was obtained by precipitating cerium as the fluoride after oxidation of plutonium to the sexivalent state. The cerium tetrafluoride was dissolved, and the absorbancy of the cerium(IV) was measured.[9]

In studying the transuranic elements, the Chemical Technology Division required analyses for neptunium and plutonium in the same solutions. Existing methods of determining the two elements were not satisfactory. However, the two were

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[2]Radioisotopes-Radiochemistry Laboratory.

[3]E. I. Wyatt and D. K. Smith, "Low Concentrations of Strontium and Barium Activities in Water," Method No. 2 21802 (10-14-58), *ORNL Master Analytical Manual;* TID-7015, sec 2.

[4]E. I. Wyatt and D. K. Smith, "Low Concentrations of Ruthenium-106 in Water," Method No. 2 21732 (10-13-58), *ibid.*

[5]E. I. Wyatt and D. K. Smith, "Low Concentrations of Cerium or Trivalent Rare-Earth Elements in Water," Method Nos. 2 21182 and 2 21994 (7-28-58), *ibid.*

[6]E. I. Wyatt and D. K. Smith, "Low Concentrations of Rare-Earth-Element Activity in Water," Method No. 2 21993 (7-30-58), *ibid.*

[7]E. I. Wyatt and D. K. Smith, "Low Concentrations of Cesium-137 in Water," Method No. 2 21193 (6-27-58), *ibid.*

[8]E. I. Wyatt and D. K. Smith, "Low Concentrations of Cobalt-60 in Water," Method No. 2 21221 (7-2-58), *ibid.*

[9]M. E. Smith, *Spectrophotometric Determination of Cerium in Plutonium,* LA-1995.

determined by alpha-energy analysis of a gross-alpha mount of the sample solution. Americium was determined in the presence of plutonium by a gross-alpha count of a solution of the sample in 7 M HNO_3 after it was passed through an anion exchange resin column. The plutonium was adsorbed on the resin, whereas the americium passed through.

Pilot Plant Control Laboratory

C. E. Lamb

The major portion of the 37,349 analyses done by the Pilot Plant Control Laboratory was for the Chemical Technology Division, Operations Division, and HRP. The sections of the Chemical Technology Division submitting the majority of samples were Thorex Process, Volatility Process, Thorium Oxide Preparation, and Metal Recovery Process.

The analyses for the Metal Recovery Process were made on samples taken by the Metal Recovery Section during the processing of materials from the following programs: Tank Farm, Americium Recovery, Sand, Paducah Ash, Underground Safety Shot Recovery, HRT Recovery, and Hanford Assistance.

At the request of the Thorium Oxide Preparation Section, equipment has been set up for the determination of particle-size distribution in thorium oxide and thorium oxalate[10] slurries.

Special samples of U^{233} were prepared[11] in the HRLAF for the Thorex Pilot Plant from highly radioactive solutions that contained mostly protactinium and fission products. The U^{233} solution was decontaminated from an activity of ~250 r/hr at 3 in. to an activity of ~1 mr/hr at 1 in. The solutions were decontaminated for subsequent mass analysis by the Argonne National Laboratory.

Plutonium in UF_6 products from the Volatility Process was determined by adding a hydrolyzed portion of the sample to an excess of a saturated solution of boric acid. The uranium and plutonium were removed from fluoride interference by means of a hydroxide precipitation. The precipitate of the hydroxides of uranium and plutonium was dissolved in nitric acid, uranium was removed from the solution by means of the lanthanum fluoride method,[12] and total plutonium was determined by the thenoyltrifluoracetone extraction method.[13]

Process-Development Analytical Laboratory

G. R. Wilson

The Chemical Technology Division, which submitted 97% of the work done by the Process-Development Analytical Laboratory, requested several analyses that required new or modified analytical procedures. The concentrations of the oxides of nitrogen were determined,[14] by visible and infrared spectrophotometry, in off-gas samples submitted by the Darex and Waste Disposal Development Groups. By the same methods the concentration of nitrous oxide was determined in xenon for the Isotopes Division. Boron was determined volumetrically in samples that contained thorium, aluminum, and uranium, after it was separated by ion exchange. Boron was also determined colorimetrically with the reagent curcumin. Niobium was determined colorimetrically by means of hydroquinone and sulfuric acid.[15,16] In samples that contained uranium and/or zirconium, the niobium was extracted into hexone prior to the colorimetric determination. X-ray apparatus, developed by the Chemical Technology Division, is being used to determine the settling rates of thorium oxide slurries at various temperatures.

Special Analyses Laboratory

W. R. Laing

New types of samples have necessitated changes and refinements in some of the existing analytical methods, as well as the development and use of new methods. A total of 28,490 analyses were made.

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[10] L. C. Bate, *Proposed Pipette Method of Particle Size Analysis of Thorium Oxalate*, memorandum to C. E. Lamb, Sept. 16, 1958.

[11] M. J. Gaitanis, *Preparation of Special Samples of U-233*, memorandum to W. T. McDuffee, Oct. 10, 1958.

[12] R. L. Walker, "Plutonium, Lanthanum Fluoride Method," Method Nos. 2 31620 and 9 008620 (5-19-53), *ORNL Master Analytical Manual;* TID-7015, sec 2.

[13] R. L. Walker, "Total Plutonium, Thenoyltrifluoracetone Extraction Method," Method Nos. 2 31621 and 9 008621 (5-18-53), *ibid.*

[14] W. D. Shults, II, "Determination of Oxides of Nitrogen," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 12.

[15] G. R. Waterbury and C. E. Bricker, "Separation and Spectrophotometric Determination of Microgram Amounts of Niobium," *Anal. Chem.* 30, 1007 (1958).

[16] H. Kubota, "Determination of Niobium," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 9.

The method for boron[17] was refined considerably and now gives greater precision and accuracy, as well as a saving in time. Boron has been determined in the range from 20 ppm to 94% in samples of stainless steel, stainless steel–uranium alloys, INOR-8, boron carbide, amorphous boron, and uranium-aluminum alloys.

In the field of vacuum fusion, yttrium metal was analyzed for oxygen and nitrogen. Niobium was analyzed for nitrogen by both vacuum-fusion and micro-Kjeldahl methods; both gave good results. Samples of irradiated reactor-construction materials were analyzed for hydrogen by the equilibrium pressure method.

Surface-area measurements were made on samples of soil and on powders of stainless steel, germanium, copper, and cupric oxide, as well as on the usual samples of ThO_2, UO_2, UO_3, U_3O_8, UF_4, and UO_2F_2.

Uranium hexafluoride and fused salts of UF_4-ZrF_4-NaF were analyzed for uranium by the potentiometric ferric sulfate method.

In some of the new work, solutions of mercury that contained mercury at a concentration of 800 mg/ml and thorium at concentrations of 3 to 200 μg/ml were analyzed for thorium by extraction of the thorium into hexone followed by a colorimetric determination. Gallium, selenium, germanium, tellurium, and antimony were determined in resin-column eluates. Cores of UO_2-Al fuel plates, prepared by powder metallurgy, were analyzed for U^0, UAl_4, UO_2, Al_2O_3, and Al^0. Carbon was determined in solutions of uranyl sulfate in heavy water. A large number of resin samples from the LITR water-purification columns were tested for residual and total capacities. Approximately 300 samples of corn, beans, other garden plants, grasses, and soils were analyzed for calcium, sodium, magnesium, potassium, and phosphorus.

Equipment was installed to measure the yield stress and the modulus of rigidity of thoria slurries. Solutions of lithium fluoride and beryllium fluoride in 60 to 100% hydrofluoric acid were analyzed for hydrofluoric acid, lithium, and beryllium. Spot tests were run on a group of 120 specimens of nickel, stainless steel, Hastelloy, Monel, and Inconel for identification purposes. Metal hydrides were analyzed for hydrogen by combustion in a stream of oxygen. The rates of combustion of various samples of irradiated graphite were determined by their reactions with air at several temperatures.

RADIOCHEMICAL ANALYSES (X-10)

S. A. Reynolds

Over 70% of the service analyses made by the Radiochemical Analyses Group were performed for three ORNL divisions. For Health Physics many gamma spectrometric determinations of fission products and other activities were made in a variety of materials, including water, soil, plant ash, and air-borne particles. Work for Chemical Technology included analyses of HRT Chemical Plant samples for radionuclides. Analyses were performed for Reactor Experimental Engineering, the results of which permitted deduction of the behavior of radioelements in HRT fuel.

RADIOISOTOPES-RADIOCHEMISTRY LABORATORY (X-10)

E. I. Wyatt

R. R. Rickard H. A. Parker

The radioisotope product work has continued at about the same level as in 1957. Most of the radiochemical separations were relative to the HR, the Volatility Pilot Plant, and the Fission Product Pilot Plant. Adaptation of existing analytical methods to the determination of trace quantities of fission products in river water has been completed and the adapted methods incorporated in the *ORNL Master Analytical Manual.*

A satisfactory method of leaching iodine trapped in charcoal beds has been developed. A mixture of equal volumes of 30% hydrogen peroxide and 58% ammonium hydroxide will remove the iodine from the charcoal. Chromatographic studies have shown that the iodine is in the iodide form after it is removed from the charcoal. Two leachings will remove 80% of the iodine, whereas three leachings will remove more than 90%. The removal of iodine by means of several other reagents was attempted without success. Among them were concentrated sulfuric acid, carbon tetrachloride, and glacial acetic acid plus hydrogen peroxide, and aqueous solutions of sodium hypochlorite and sodium bicarbonate, sodium nitrite

[17] F. M. Hill, "Boron (Borate), Potentiometric Mannitol–Sodium Hydroxide Titration Method," Method Nos. 1 211220 and 9 00711220 (6-25-57), *ORNL Master Analytical Manual;* TID-7015, sec 1.

plus a weak acid, sodium persulfate, tetraethylammonium iodide, and sodium bisulfite. A strong solution of nitric acid will remove iodine but a closed system is required in order to prevent losses. Nitric acid will also remove barium and strontium.

The half lives of Ga^{72}, Hg^{203}, and Ru^{106} were determined by means of a high-pressure gamma ionization chamber. The half life of Ga^{72} was found to be 14.12 ± 0.02 h. The decays of Hg^{203} and Ru^{106} were followed for more than three half lives, and values of 46.0 ± 0.2 d and 363.9 ± 0.2 d, respectively, were obtained.

A paper entitled "Radiochemical Determination of Fission Ruthenium in Aqueous Solutions (a Nondistillation Technique)" was presented by R. R. Rickard at the 133rd meeting of the American Chemical Society and will be published in the January issue of *Analytical Chemistry*.

A nondestructive method of estimating the Np^{237} content in uranium fluorination ash has been developed in which the gamma scintillation spectrometer is used. The method will be described in a paper being prepared for publication in the open literature.

REACTOR ANALYSES LABORATORY (X-10)

U. Koskela L. G. Farrar

The HRT supplied about three-fourths of the samples analyzed by the Reactor Analyses Laboratory during the past year; this service took about two-thirds of the time. The rest of the samples came primarily from supporting work for the HRP.

HRT Service

U. Koskela L. G. Farrar

Samples from the first HRT precritical run were received on December 16, 1957. Analytical service was provided for six more runs that have been completed through September 15, 1958. Practically all the hot analyses were performed within the HRLAF. Most of the methods used are described in the *ORNL Master Analytical Manual*. During the earlier prepower operations of the HRT, the uranium was determined potentiometrically.[18] However, a rapid increase in radioactivity in the samples necessitated changing over to a coulometric[19] determination for both copper and uranium. Nickel[20] can be determined along with the copper and uranium. It is hoped that equipment will be available for the next power operations.

Determination of pH

J. L. Mottern U. Koskela

The ORNL disposable, microelectrode assembly for pH determinations[21] has been used for both pH and pD determinations in the HRLAF. The assemblies are still made by members of the Laboratory. The results of experiments with Leeds & Northrup fused-capillary electrodes were reported previously.[22] Recently Leeds & Northrup has put on the market "The L & N Miniature pH Electrode Assembly."[23] The results of preliminary tests with two-month-old HRT fuel indicate that this electrode might possibly be used in high-radiation fields.

Determination of Dissolved Oxygen in Water

R. E. Corcoran

The method described previously,[24] with minor adaptations, has been applied successfully to the analysis of HRT feed-water samples. As little as 2 ppb of dissolved oxygen was determined in some samples. A study of the method was made by Surak.[25] On a recommendation resulting from this study, the sample size used for titration was

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[18] J. H. Cooper, "Uranium, Potentiometric Ceric Sulfate Method," Method Nos. 1 219221 and 9 00719221 (3-25-54), *ibid.*

[19] L. G. Farrar, P. F. Thomason, and M. T. Kelley, "Controlled Potential Coulometric Determination of Uranium and Copper in Homogeneous Reactor Fuels," *Anal. Chem.* 30, 1511 (1958).

[20] A. D. Horton, L. G. Farrar, B. B. Hobbs, and W. D. Shults, *The Coulometric Titration of HRT Fuel in the High-Radiation-Level Analytical Facility (HRLAF); Determination of Cu, U, and Ni*, a paper presented at the Second Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29–Oct. 1, 1958.

[21] H. L. Hemphill, "Disposable Microelectrode Assembly for pH Determinations," Method Nos. 1 001003 and 9 001003 (12-16-54), *ORNL Master Analytical Manual*; TID-7015, sec 1.

[22] U. Koskela and J. Slessinger, Jr., *Anal. Chem. Semi-ann. Prog. Rep. April 20, 1956*, ORNL-2070, p 30 (classified).

[23] Data sheet E-96(3) 60-658, Leeds & Northrup Co., 4907 Stenton Ave., Philadelphia 44, Pa.

[24] R. E. Corcoran, "Determination of Dissolved Oxygen in Water," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 55.

[25] Research participant from Marquette University, Milwaukee, Wis.

increased from 100 to 500 ml. This was accomplished by replacing the 250-ml tall-form beaker, used as the titration vessel, with a 32-oz wide-mouth bottle. This bottle was fitted with a rubber stopper through which the electrodes and buret tip were inserted. A larger magnetic stirring bar was used, and the titration was performed, as before, by electrometric titration of liberated iodine with a standard solution of sodium thiosulfate.

REACTOR PROJECTS LABORATORY (Y-12)

J. C. White W. F. Vaughan

A total of 10,378 samples, twice as many as last year, was analyzed in the Reactor Projects Laboratory. Most of these samples were fused fluoride salts, either single fluorides or mixtures of the fluorides of uranium, sodium, lithium, potassium, rubidium, magnesium, yttrium, beryllium, thorium, zirconium, cerium, chromium, nickel, iron, and cesium. Analyses were made primarily for corrosion products (nickel, chromium, iron, molybdenum, niobium, titanium, and copper) contained in the fused salts. Approximately 10% of these salts were analyzed for the major constituent also, in order to determine the composition of the salt. Gravimetric, volumetric, and spectrophotometric methods were used.

Numerous samples of Inconel and related materials were analyzed to ascertain their exact composition before they were used in fluoride-salt corrosion studies.

A large number of graphite samples were received that had been milled from the surfaces of graphite rods which had been impregnated with $LiF\text{-}BeF_2$ and then soaked for 800 hr in $LiF\text{-}BeF_2\text{-}UF_4$. The graphite was analyzed to determine the depth of penetration of fluoride-salt mixture into the graphite rods. In order to make precise evaluations of the concentrations of uranium and beryllium, it was necessary to dissolve the entire sample of graphite (0.4 to 3.5 g). The samples were dissolved in a nitric-perchloric acid solution to which sodium chlorate was added at frequent intervals to aid in oxidation. A period of 4 to 10 hr was necessary to effect dissolution. Uranium was determined by the spectrophotometric dibenzoylmethane method;[26] beryllium was determined by the differential spectrophotometric *p*-nitrobenzeneazo-orcinol method.[27]

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[26] C. A. Horton, "Uranium(VI), Tri-*n*-octylphosphine Oxide (TOPO) Extraction–Spectrophotometric Dibenzoylmethane Method," Method Nos. 1 219213 and 9 00719213 (2-6-58), *ORNL Master Analytical Manual;* TID-7015, sec 1.

[27] D. L. Manning, "Beryllium, Differential Spectrophotometric *p*-Nitrobenzeneazo-orcinol Method," Method Nos. 1 211011 and 9 00711011 (2-10-56), *ibid.*

PRESENTATIONS OF RESEARCH RESULTS

The Analytical Chemistry Division sponsored a Second Conference on Analytical Chemistry in Nuclear Reactor Technology at Gatlinburg, Tennessee, on September 29–October 1, 1958. The committee consisted of C. D. Susano (Chairman), D. J. Fisher, O. Menis, S. A. Reynolds, and P. F. Thomason. Sixty-four papers were presented, augmented by panel discussions.

There were 329 registrants: 132 from Oak Ridge, 71 from other AEC installations, 75 from industrial plants and laboratories, 25 from universities and colleges, 4 from Canadian and United Kingdom atomic energy installations, and 22 with miscellaneous affiliations. Many of those in attendance from industrial plants, commercial laboratories, and universities are also engaged in AEC-related projects.

In order to make the information presented at this conference generally available, the proceedings will be published, as were the proceedings of the first conference (TID-7555). The third conference in this series is scheduled for October 26–28, 1959.

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.

PUBLICATIONS

Articles

Author(s)	Title	Publication
Blosser, H. G., C. D. Goodman, T. H. Handley*	"Measurements of (n,α) Cross Sections at 14 Mev"	*Phys. Rev.* 110, 531 (1958)
Brooksbank, W. A., Jr.,[1] G. W. Leddicotte, J. A. Dean[2]	"Neutron Activation Analysis of Aluminum-Base Alloys"	*Anal. Chem.* 30, 1785 (1958)
Farrar, L. G., P. F. Thomason, M. T. Kelley	"Controlled Potential Coulometric Determination of Uranium and Copper in Homogeneous Reactor Fuels"	*Ibid.*, p 1511
Feldman, C.	"Spectrochemical Analysis of Reactor Materials"	*Proceedings, First Conference, Analytical Chemistry in Nuclear Reactor Technology*, TID-7555 (Aug. 1958), p 227
Feldman, C., J. Y. Ellenburg[3]	"Certain Rare Earths in Purified Thorium and Uranium Preparations. Chemical Isolation and Spectrographic Determination"	*Anal. Chem.* 30, 418 (1958)
Fisher, D. J.	"Falling-Drop Timing Circuit with Automatic Reset"	*Ibid.*, p 308
Fisher, D. J., M. T. Kelley	"Screw-Operated Elevator"	*Hot Laboratory Equipment*, 2d. ed., April 1958; compiled by L. G. Stang, Jr., GPO, Washington, p 236 (paper No. 4.54)
	"Servo-Controlled Pipetters"	*Ibid.*, p 168 (paper No. 4.10)

[1]Now associated with Structures and Mechanical Laboratory, Army Ballistic Missile Agency, Redstone Arsenal, Ala.

[2]University of Tennessee, Knoxville.

[3]Now associated with Southern Research Institute, Birmingham, Ala.

Author(s)	Title	Publication
Fisher, D. J.,* M. T. Kelley,* E. B. Wagner	"Automatic-Recording Potentiometric Velocity Servo Titrator"	*Ibid.*, p 285 (paper No. 5.22)
Fisher, D. J., R. W. Stelzner, M. T. Kelley	"Falling-Drop Densimeter"	*Ibid.*, p 280 (paper No. 5.20)
Fisher, D. J.,* E. B. Wagner, M. T. Kelley*	"Filter Photometer"	*Ibid.*, p 290 (paper No. 5.24)
	"Motorized Lab-Jack"	*Ibid.*, p 235 (paper No. 4.53)
Goldberg, G., A. S. Meyer, Jr., J. C. White	"Small-Volume Five-Centimeter Absorption Cell"	*Anal. Chem.* 30, 1163 (1958)
Goldstein, G., D. L. Manning, O. Menis	"Spectrophotometric Determination of Molybdenum as the Quercetin Complex in an Alpha-Benzoinoxime-Chloroform-Ethyl Alcohol Medium"	*Ibid.*, p 539
Horton, C. A., J. C. White	"Separation of Uranium by Solvent Extraction with Tri-*n*-octylphosphine Oxide. Direct Colorimetric Determination with Dibenzoylmethane"	*Ibid.*, p 1779
Kahn, B.,[4] S. A. Reynolds	"Determination of Radionuclides in Low Concentrations in Water"	*J. Am. Water Works Assoc.* 50, 613 (1958)
Kelley, M. T.	"Equipment-Transfer Drawer"	*Hot Laboratory Equipment*, 2d. ed., April 1958; compiled by L. G. Stang, Jr., GPO, Washington, p 362 (paper No. 7.22)
Kelley, M. T.,* J. H. Edgerton,[5] H. G. Davis,* L. C. Henley	"Filter for Flame Spectrophotometer"	*Ibid.*, p 42 (paper No. 1.23)
Kelley, M. T., D. J. Fisher	"Instrumental Methods of Derivative Polarography"	*Anal. Chem.* 30, 929 (1958)
Kelley, M. T.,* E. B. Wagner, W. L. Maddox,* H. C. Jones,* D. J. Fisher*	"Remotely Operated Filter Photometer"	*Ibid.*, p 1711
Leddicotte, G. W., W. T. Mullins, L. C. Bate, J. F. Emery	"The Determination of Trace Elements in Reactor Materials by the Methods of Neutron Activation Analysis"	*Proceedings, First Conference, Analytical Chemistry in Nuclear Reactor Technology*, TID-7555 (Aug. 1958), p 192
Mann, C. K.,[6] J. C. White	"Extraction of Chromium with Trioctylphosphine Oxide from Acidic Solutions of Alkali Metal Salts"	*Anal. Chem.* 30, 989 (1958)
Menis, O., T. C. Rains, J. A. Dean[2]	"A Study of the Flame Emission Characteristics of Lanthanum in an Aqueous-Alcoholic Medium"	*Anal. Chim. Acta* 19, 179 (1958)

[4]Massachusetts Institute of Technology, Graduate House No. 518A, Cambridge.
[5]Now associated with Lockheed Aircraft Corp., Marietta, Ga.
[6]Florida State University, Tallahassee.

Author(s)	Title	Publication
Menis, O., D. L. Manning, R. G. Ball	"Automatic Spectrophotometric Titration of Fluoride, Sulfate, Uranium, and Thorium"	*Anal. Chem.* 30, 1772 (1958)
Moore, F. L.	"Liquid-Liquid Extraction of Uranium and Plutonium from Hydrochloric Acid Solution with Tri(iso-octyl)amine"	*Ibid.*, p 908
	"Radiochemical Determination of Ionium in Uranium Fluorination Ash"	*Ibid.*, p 1020
	"Radiochemical Determination of Neptunium-239 and Plutonium-239 in Homogeneous Reactor Fuel and Blanket Solutions"	*Ibid.*, p 1368
	"Metals Analysis with Thenoyltrifluoracetone"	*Solvent Extraction in the Analysis of Metals*, A.S.T.M. STP No. 238, A.S.T.M., Philadelphia (Dec. 1958)
Powell, R. H.,[7] O. Menis	"Separation of Fluoride from Inorganic Compounds by Pyrolysis"	*Anal. Chem.* 30, 1546 (1958)
Raaen, H. P., P. F. Thomason	"Separation of Pa^{233} and U^{233}"	*Nuclear Science and Technology (Extracts from Reactor Science and Technology, Vol. 4, Issues 1 to 4, Mar.–Dec. 1954)*, TID-2505 (Del.) p 211–18
Reynolds, S. A.	"Radioactivity Associated with Uranium, Thorium, and Plutonium"	F. R. Bruce, J. M. Fletcher, and H. H. Hyman (eds.), *Progress in Nuclear Energy Series, "Process Chemistry,"* vol II, Pergamon Press, London, 1958, p 562–72
Robinson, M. T., W. A. Brooksbank,[1] S. A. Reynolds,* H. W. Wright,* T. H. Handley*	"The Behavior of Fission Products in Molten Fluoride Reactor Fuels"	*Nuclear Sci. Eng.* 4, 288 (1958)
White, J. C.	"Solvent Extraction"	*Proceedings, First Conference, Analytical Chemistry in Nuclear Reactor Technology*, TID-7555 (Aug. 1958), p 240
	"The Use of Tri-*n*-Octylphosphine Oxide in Analytical Chemistry"	*Solvent Extraction in the Analysis of Metals*, A.S.T.M. STP No. 238, A.S.T.M., Philadelphia (Dec. 1958)
Willmarth, T. E.	"Electron Microscopy at the Oak Ridge National Laboratory"	*Norelco Reptr.* 5, 8 (1958)
Young, J. P., J. R. French, J. C. White	"Microdetermination of Zirconium in Sulfuric Acid Solutions with Pyrocatechol Violet"	*Anal. Chem.* 30, 422 (1958)

[7]Now associated with Applied Research Institute (Armour Research Foundation), Union of Burma, Rangoon, Burma (American Embassy).

Author(s)	Title	Publication
Young, J. P., J. C. White	"The Extraction of Zirconium with Tri-*n*-Octylphosphine Oxide and Its Direct Determination in the Organic Phase with Pyrocatechol Violet"	*Talanta* 1, 263 (1958)

Reports

Author(s)	Title	Report No.
Emery, J. F., G. W. Leddicotte	"Aluminum Determination in Reactor Cooling Water"	ORNL CF-58-9-20 (Sept. 9, 1958)
Miller, F. J., P. F. Thomason	"Thermometric (Enthalpymetric) Titration of Free Acid in the Presence of Certain Hydrolyzable Ions"	ORNL-2489 (June 13, 1958)
Powell, R. H.,[7] O. Menis	"Separation of Fluoride from Refractory Materials by Fusion-Pyrolysis"	ORNL-2512 (April 28, 1958)
Reynolds, S. A.	"Analysis of APPR-1 Demineralizer Contents"	ORNL CF-58-2-2 (Feb. 6, 1958)
Ross, W. J., J. C. White	"The Use of Tri-*n*-Octylphosphine Oxide in the Solvent Extraction of Thorium from Acidic Solutions"	ORNL-2627 (Nov. 5, 1958)
Susano, C. D., H. P. House, M. A. Marler (eds.)	"Proceedings, First Conference, Analytical Chemistry in Nuclear Reactor Technology"	TID-7555 (Aug. 1958)
White, J. C., W. J. Ross	"The Use of Tri-*n*-Octylphosphine Oxide in the Solvent Extraction of Zirconium"	ORNL-2498 (April 10, 1958)

New Methods Issued to *ORNL Master Analytical Manual*[7a]

Author(s)	Title	Number(s)	Date
Botts, J. L.	"Carbonate, Acid Dissolution—Direct Gravimetric Method"	1 220007 9 00720007	4-10-58
Brady, L. J.	"Tantalum, Gravimetric Acid Hydrolysis Method"	1 218250 9 00718250	1-30-58
Ginocchio, B. J.	"Uranium, Automatic Potentiometric Ferric Sulfate Method"	1 219224 9 00719224	2-24-58

[7a]The *ORNL Master Analytical Manual* is being made available in reprint form, designated TID-7015, from the Office of Technical Services, Dept. of Commerce, Washington 25, D. C. The following sections are now available at the prices indicated:

Section	Section Title	Price
1	Ionic Methods	$9.00
2	Radiochemical Methods	$6.50
3 and 5	Spectrographic Methods and Nuclear Analyses Methods	$4.50

Section 9, "Process Methods," is yet to be reprinted.

Author(s)	Title	Number(s)	Date
Goldstein, G.	"Molybdenum, Spectrophotometric α-Benzoinoxime–Ethanol–Quercetin Method"	1 215011 9 00715011	2-26-58
Horton, C. A.	"Uranium(VI), Tri-*n*-Octylphosphine Oxide (TOPO) Extraction–Spectrophotometric Dibenzoylmethane Method"	1 219213 9 00719213	2-6-58
Kubota, H.	"Aluminum, Modified Gravimetric Oxine (8-Hydroxyquinoline) Method"	1 210252 9 00710252	2-26-58
Laing, W. R.	"Aluminum in the Presence of Zirconium, Ion-Exchange Separation–Spectrophotometric Ammonium Aurintricarboxylate (Aluminon) Method"	1 210212 9 00710212	4-10-58
	"Nickel, Volumetric Cyanide Method"	1 215470 9 00715470	4-10-58
	"Titanium, Colorimetric Disodium-1,2-dihydroxybenzene-3,5-disulfonate (Tiron) Method"	1 219013 9 00719013	4-10-58
Laing, W. R., H. G. Davis	"Hydrogen, Nitrogen, and Oxygen in Metals, Vacuum-Fusion Method"	1 213793 1 215693 1 215893	7-2-58
McDowell, B. L.	"Cerium, Spectrophotometric Disodium-1,2-Dihydroxybenzene-3,5-Disulfonate (Tiron) Method"	1 211811 9 00711811	2-7-58
Meyer, H. C.	"Zirconium, Amperometric Cupferron Titration Method"	1 219820 9 00719820	4-10-58
Miller, F. J.	"Cobalt, Potentiometric Potassium Ferricyanide Method"	1 212221 9 00712221	3-11-58
	"Sulfate, Automatic Titration Method (Photometric End-Point Detection)"	1 218171 9 00718171	2-25-58
	"Sulfate (Sulfur), Volumetric Barium Perchlorate–Thoron Method"	1 218174 9 00718174	2-27-58
	"Uranium(IV) and Uranium(VI) in Fluoride Melts"	1 219273 9 00719273	2-27-58
	"Free Acid in Aqueous Solutions of Hydrofluoric Acid and Zirconyl Fluoride, Thermometric Titration Method"	1 220005 9 00720005	2-13-58
Roemer, A. F., Jr., L. J. Brady	"Fluorophotometer, ORNL Modified Model R"	1 003081 9 003081	1-30-58
Rubin, I. B.	"Standardization of Solutions of Disodium Dihydrogen Ethylenediaminetetraacetate, Spectrophotometric Cupric Sulfate Titration Method"	1 00440 9 00440	3-13-58
Susano, C. D.	"Care and Use of Glass Volumetric Apparatus"	1 001002 9 001002	3-11-58
Talbott, C. K.	"Magnesium, Eriochrome Black T Spectrophotometric Method"	1 214711 9 00714711	6-4-58
	"Sulfate in Uranyl Salt Solutions, Volumetric Barium Chloride–Alizarin Red S Method"	9 082202	4-8-58
Vaughan, W. F.	"Neutralization Number of Insulating Oils"	1 2300032	2-20-58
	"Water in Insulating Oils, Extraction Method"	1 2300033	2-20-58

Author(s)	Title	Number(s)	Date
Walker, R. L.	"Surface Area of a Powdered Solid, Nitrogen Adsorption Method"	1 102 9 00602	1-15-58
Wyatt, E. I., D. K. Smith	"Low Concentrations of Cerium and Trivalent Rare-Earth-Element Activities in Water"	2 21182 2 21994	7-28-58
	"Low Concentrations of Cesium-137 in Water"	2 21193	6-27-58
	"Low Concentrations of Cobalt-60 in Water"	2 21221	7-2-58
	"Low Concentrations of Ruthenium-106 in Water"	2 21732	10-13-58
	"Low Concentrations of Strontium and Barium Activities in Water"	2 21802	10-14-58
	"Low Concentrations of Rare-Earth-Element Activities in Water"	2 21993	7-30-58
Young, J. P.	"Zirconium, Spectrophotometric Pyrocatechol Violet Method"	1 219812 9 00719812	2-10-58

ORAL PRESENTATIONS

At Meetings of Professional Societies

Author(s)	Title	Presented at
Bate, L. C.,[8] G. W. Leddicotte	"An Evaluation of the Particle-Size Distribution of Multicomponent Systems"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
Berg, R. H.,[9] L. C. Bate, G. W. Leddicotte[8]	"Particle-Size Distribution of ThO_2 by Electronic Sizing"	*Ibid.*
Biggers, R. E.,*[8] J. M. Chilton	"Stability of the Valence States of Plutonium in Concentrated Uranyl Sulfate Solutions. Autoreduction of PuO_2^{++} by Products of the α-Particle Radiolysis of Water, Kinetics and Mechanisms"	133rd Meeting, American Chemical Society, San Francisco, April 13–18, 1958
Boyd, C. M. (presented for S. Berg, Porcelaen Fabrik Denmark, Lyngby, Denmark)	"New Methods for Determining Particle-Size Distributions by Examining Gravitational and Centrifugal Sedimentation" (a condensation of several papers)	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
Boyd, C. M., O. Menis, H. P. House[8]	"Particle-Size Determination of ThO_2 by a Sedimentation Method"	*Ibid.*
Brooksbank, W. A., Jr.,[1] J. E. Strain, G. W. Leddicotte[8]	"A Neutron Absorptometer for Laboratory and Flowing Stream Analyses"	Symposium on Instrumental Methods of Analysis, Instrument Society of America, Houston, May 12–14, 1958

[8]Speaker.
[9]Coulter Industrial Sales Co., Elmhurst, Ill.

Author(s)	Title	Presented at
Chilton, J. M.,[8] R. E. Biggers*	"Spectrophotometric Determination of Plutonium Valence States in Sulfate Systems"	133rd Meeting, American Chemical Society, San Francisco, April 13–18, 1958
Dean, J. A.,[8,2] W. A. Brooksbank, Jr.,[1] G. W. Leddicotte	"Activation Analysis of Aluminum Base Alloys: A Study of Precision and Accuracy"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, March 3–7, 1958
Eldridge, J. S., W. S. Lyon[8]	"Radiochemical Determination of Y-91 and and Nd-147 in Fission Product Mixtures"	Southeastern Regional Meeting, American Chemical Society, Gainesville, Fla., Dec. 11–13, 1958
Eshelman, H. C.,[10] J. A. Dean,[8,2] O. Menis, T. C. Rains	"Extraction and Flame Spectrophotometric Determination of Aluminum"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, March 3–7, 1958
Feldman, C.	"Spectral Excitation of Solutions in Electrical Discharges and Flames"	43rd Annual Meeting, Optical Society of America, Detroit, Oct. 9–11, 1958
Feldman, C.,[8] W. R. Musick	"Spectrochemical Analysis of Radioactive Samples in a Remote-Control Facility"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gotlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
Fisher, D. J.	"Applications of Operational Amplifiers to Controlled Potential and Derivative Polarography"	*Ibid.*
	"Instrumentation for Chemical Analysis Developed by the Analytical Instrumentation Group at ORNL"	Meeting of Southern Indiana Section, American Chemical Society, Indiana University, Bloomington, April 1, 1958
Goldstein, G., D. L. Manning,[8] O. Menis	"Spectrophotometric Determination of Cobalt with 1(2-Pyridylazo)-2-Naphthol and Separotion from Interfering Ions. Application to Thorium Oxide"	134th Meeting, American Chemical Society, Chicago, Sept. 7–12, 1958
Harmatz, B., T. H. Handley,* J. W. Mihelich[8]	"Nuclear Spectroscopy of Odd Mass (161-173) Rare Earth Nuclides"	Meeting of the American Physical Society, Chicago, Nov. 28–29, 1958
Horton, A. D.,[8] L. G. Farrar, B. B. Hobbs, W. D. Shults	"The Coulometric Titration of HRT Fuel in the High-Rodiation-Level Analytical Facility (HRLAF); Determination of Cu, U, and Ni"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
Jacob, K. P., J. W. Mihelich,[8] B. Harmatz, T. H. Handley*	"Electron Capture to Levels in the Two Even-Even Isotopes Er^{168}-Er^{166}"	Meeting of the American Physical Society, Chicago, Nov. 28–29, 1958

[10]Southwest Louisiana Institute, Lafayette.

Author(s)	Title	Presented at
Jones, H. C.	"Applications of Semiconductor Devices to Potentiometric and Coulometric Titrations"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
Kahn, B.,[4] D. W. Moeller,[11] T. H. Handley, S. A. Reynolds[8]	"Analysis for Radionuclides in Aqueous Wastes from an 'Atomic' Plant"	National Meeting, American Society for Testing Materials, Boston, June 23–27, 1958
Kahn, B.,[4] S. A. Reynolds[8]	"Some Methods for the Determination of Radionuclides in Water in Low Concentrations"	Nuclear Science and Engineering Congress, Chicago, March 17–21, 1958
Kelley, M. T.	"Analysis Instrumentation for Nuclear Application"	Symposium on Instrumental Methods of Analysis, Instrument Society of America, Houston, May 12–14, 1958
Kelley, M. T.,* H. L. Hemphill, D. J. Fisher*[8]	"Servo-Controlled Pipetter for Precise Delivery of Microliter Drops"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
Kelley, M. T., H. C. Jones, D. J. Fisher[8]	"Controlled-Potential and Derivative Polarograph"	134th Meeting, American Chemical Society, Chicago, Sept. 7–12, 1958
Kelley, M. T.,[8] H. C. Jones, D. J. Fisher	"Electronic Controlled-Potential Coulometric Titrator"	*Ibid.*
Kelley, M. T., R. W. Stelzner,[8] D. J. Fisher	"Instrumentation for the Remote Determination of Density by the Falling-Drop Method"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
Koskela, U.,[8] L. G. Farrar, J. E. Attrill, J. L. Mottern	"Analytical Service for the HRT"	*Ibid.*
Kubota, H.	"The Volumetric Determination of Microgram Quantities of Boron"	*Ibid.*
Kubota, H.,[8] J. G. Surak[12]	"Determination of Fluoride by Conductometr Titration"	133rd Meeting, American Chemical Society, San Francisco, April 13–18, 1958
Leddicotte, G. W.	"Activation Analysis"	Gordon Research Conference on Analytical Chemistry, New Hampton, N. H., Aug. 11–15, 1958
	"Activation Analysis"	Informal lecture meeting at Robert A. Taft Sanitary Engineering Center, U. S. Public Health Service, Cincinnati, Dec. 12, 1958

[11] Now associated with U. S. Public Health Service, Robert A. Taft Sanitary Engineering Center, Cincinnati.
[12] Temporary summer employee from Marquette University, Milwaukee.

Author(s)	Title	Presented at
Leddicotte, G. W.,[8] L. C. Bate	"The Determination of Oxygen in Metals and Alloys by Neutron Activation Analysis"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, March 3–7, 1958
Leddicotte, G. W.,*[8] L. C. Bate,* R. E. Druschel	"The Determination of Particle Size Distributions by Neutron Activation Analysis"	*Ibid.*
Leddicotte, G. W.,[8] W. A. Brooksbank, Jr.,[1] J. E. Strain	"Neutron Photometry as a Nondestructive Analysis Method"	133rd Meeting, American Chemical Society, San Francisco, April 13–18, 1958
Leddicotte, G. W., W. S. Lyon[8]	"Special Radiochemical Analysis in the Operation of ORNL Reactors"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
Leddicotte, G. W.,*[8] H. H. Miller,[13] R. E. Druschel, M. T. Kelley,* L. C. Bate*	"Particle Size Distribution Analysis of Radioactive Materials"	Symposium on Instrumental Methods of Analysis, Instrument Society of America, Houston, May 12–14, 1958
Leddicotte, G. W.,*[8] W. T. Mullins,* L. C. Bate,* J. F. Emery,* R. E. Druschel, W. A. Brooksbank, Jr.[1]	"The Use of Neutron Activation Analysis in Analytical Chemistry"	Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, Sept. 1–13, 1958
Leddicotte, G. W.,[8] S. A. Reynolds	"Neutron Activation Analysis"	Seminar, Laboratory of Nutrition and Endocrinology, National Institute of Health, USPHS, Bethesda, Md., Feb. 10, 1958
	"Nondestructive Methods of Analysis for Radioactive Nuclides"	133rd Meeting, American Chemical Society, San Francisco, April 13–18, 1958
Maddox, W. L.,[8] M. T. Kelley	"A Gamma Absorptiometer for Laboratory Analysis of the Heavy Elements"	Symposium on Instrumental Methods of Analysis, Instrument Society of America, Houston, May 12–14, 1958
McCutchen, R. L.	"The Use of Control Charts in Analytical Chemistry"	Mid-Atlantic Conference, American Society for Quality Control, New York, Feb. 28, 1958
McDowell, B. L., A. S. Meyer, Jr., R. E. Feathers, Jr., J. C. White (presented by J. P. Young)	"Spectrophotometric Determination of Traces of Nickel with 4-Isopropyl-1,2 Cyclohexanedionedioxime"	134th Meeting, American Chemical Society, Chicago, Sept. 7–12, 1958
Menis, O., T. C. Rains,[8] D. L. Manning, G. Goldstein, I. B. Rubin	"Determination of Al, Zr, Mo, U, and Ti in ThO_2 Slurries"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958

[13] Now associated with USAEC, Isotope Applications Branch, Office of Industrial Development, Washington, D. C.

Author(s)	Title	Presented at
Moeller, D. W.,[8,11] G. W. Leddicotte, S. A. Reynolds	"Radionuclides in Reactor Cooling Water – Identification, Source, and Control"	Nuclear Science and Engineering Congress, Chicago, March 17–21, 1958
Moore, F. L.	"Metals Analysis with 2-Thenoyltrifluoroacetone"	National Meeting, American Society for Testing Materials, Boston, June 23–27, 1958
Rathkamp, W. R.	"Separation of Isotopes of Argon and Krypton by Thermal Diffusion"	Gordon Research Conference on Chemistry and Physics of Isotopes, Meriden, N. H., July 7–11, 1958
Reynolds, S. A.	"Analysis for Low Concentrations of Uranium-232 in Uranium-233"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
	"Analytical Radiochemistry"	Annual Naval Reserve Nuclear Science Seminar, ORINS, Oak Ridge, Tenn., Dec. 10, 1958
	"Half-Lives of Various Nuclides"	Meeting of Subcommitte on Radioactivity Measurements and Standards, National Research Council, Argonne National Laboratory, Lemont, Ill., May 9, 1958
	"Radiochemical Analysis"	Informal lecture meeting at R. A. Taft Sanitary Engineering Center, U.S. Public Health Service, Cincinnati, Nov. 20, 1958
Rickard, R. R.,[8] E. I. Wyatt	"Radiochemical Determination of Fission Ruthenium in Aqueous Solutions (A Non-Distillation Technique)"	133rd Meeting, American Chemical Society, San Francisco, April 13–18, 1958
Ross, W. J.,[8] A. S. Meyer, Jr., J. C. White	"Extraction and Determination of B in Fluoride Salts"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
Shults, W. D.,[8] P. F. Thomason	"Controlled Potential Coulometric Titration of Copper and Uranium"	Southeastern Regional Meeting, American Chemical Society, Gainesville, Fla., Dec. 11–13, 1958
Stelzner, R. W.	"Applicotions of Radio-Frequency in Reactor Analyses"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
Thomason, P. F.,[8] L. T. Corbin, M. T. Kelley	"Methods Used at ORNL to Assay Uranium in Fuel Elements and Homogeneous Reactor Fuel"	Symposium on Reactor Fuel Measurement Techniques, Kellogg Center, Michigan State University, East Lansing, June 18–20, 1958

Author(s)	Title	Presented at
White, J. C. (presented by G. E. Boyd)	"New Developments in the Analysis of the Alkali Metals"	133rd Meeting, American Chemical Society, San Francisco, April 13–18, 1958
White, J. C.	"The Sampling of Molten Fluoride Salts and their Analysis for Uranium"	Symposium on Reactor Fuel Measurement Techniques, Kellogg Center, Michigan State University, East Lansing, June 18–20, 1958
	"The Use of Tri-*n*-Octylphosphine Oxide in Analytical Chemistry"	National Meeting, American Society for Testing Materials, Boston, June 23–27, 1958
White, J. C., R. F. Apple[8]	"The Spectrophotometric Determination of Ce in Fluoride"	2nd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Sept. 29, 30, and Oct. 1, 1958
White, J. C., B. L. McDowell,[8] A. S. Meyer, Jr.	"Spectrophotometric Determination of Iron by Formation and Measurement of Its *o*-Phenanthroline Complex in Organic Media"	Southeastern Regional Meeting, American Chemical Society, Gainesville, Fla., Dec. 11–13, 1958
Young, J. P.,[8] J. C. White	"The Extraction of Titanium Thiocyanate with Tri-*n*-octylphosphine Oxide and Its Direct Colorimetric Determination in the Organic Phase"	134th Meeting, American Chemical Society, Chicago, Sept. 7–12, 1958

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Lecturer	Lecture Title	Presented at
Cameron, A. E.	"Geological Age Determinations by Isotopic Measurements"	Savannah River Section of the American Chemical Society, Aiken, S. C., Sept. 25, 1958
	"Geological Age Determinations by Isotopic Measurements"	Vanderbilt University, Nashville, Tenn., Feb. 27, 1958
	"Geological Age Determinations by Isotopic Measurements"	West Virginia University, Morgantown, June 12, 1958
	"Geological Age Determinations by Isotopic Measurements"	Catholic University of America, Washington, D. C., March 21, 1958
Leddicotte, G. W.	"Radioactivation Analysis"	School of Chemistry, University of Alabama, University, Nov. 12, 1958
Reynolds, S. A.	"Analytical Radiochemistry"	Southwestern Louisiana Institute, Lafayette, Jan. 16, 1958

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