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SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING APRIL 20, 1955

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ANALYTICAL CHEMISTRY DIVISION

SEMIANNUAL PROGRESS REPORT

for Period Ending April 20, 1955

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ABSTRACT

ANALYTICAL CHEMISTRY DIVISION – X-10 SITE

In the development of new ionic methods, major consideration has been given to the requirements of the Homogeneous Reactor Project. Ion-exchange–polarographic methods were prepared for the determination of chromium(III) and (VI) and of total chromium in HR fuels. Automatic coulometric titration methods were developed for the determination of chloride and of chromium in HR type samples. Satisfactory preliminary results were obtained with a new photometric end-point detector to be used in the barium perchlorate titration of sulfate in HR fuels. An ion-exchange–spectrophotometric method, which uses Aluminon reagent, is being evaluated for the determination of aluminum in HR fuels. Two satisfactory solvent-extraction procedures were developed for removing from thorium solutions substances that interfere in the Thoron colorimetric method for thorium. Polarographic methods are being investigated for the determination of technetium in Radioisotope Production Process solutions. A satisfactory precipitation separation followed by a polarographic determination of tin in copper-tin alloys was made. Cobalt was determined in aluminum-cobalt-manganese alloy by ion-exchange separation and potentiometric titration. The homogeneity of stainless steel–uranium dioxide plates with respect to uranium was measured by a solvent extraction–ferric sulfate volumetric titration of the uranium. The Warren Spectracord was used to obtain the ultraviolet absorption spectra of pertechnetate and perrhenate in perchloric acid media, of tetraphenylarsonium chloride in aqueous and in ethanolic solutions, and of thenoyltrifluoroacetone (TTA) in xylene; also, the visible absorption spectrum of the β-nitroso-α-naphthol complex of zirconium was measured. On the basis of the spectra obtained, spectrophotometric methods were suggested.

Analytical instrumentation research was related primarily to the development and adaptation of instruments for use in the High-Radiation-Level Analytical Facility. A remotely controlled falling-drop densimeter was put into operation for the determination of the densities of process feed solutions for the Thorex and metal recovery processes. Design of an improved remotely controlled turret assembly for the falling-drop densimeter was completed, and the turret is being fabricated. Development of a velocity-servo automatic potentiometric titrator that features a remotely operated titrant-delivery unit was completed. With this titrator, 6-mg samples of uranium were determined with a relative standard error of ±0.1%. Titrators of this design will be fabricated for use in the High-Radiation-Level Analytical Facility. An automatic coulometric titrator for Karl Fischer water titrations was designed and was found to be satisfactory. A new high-sensitivity recording polarograph, model Q-1673, which has unique filtering circuitry, is being fabricated; it can take both regular and derivative polarograms. A sample-bottle decapper is being built for operation by master-slave manipulators in the High-Radiation-Level Analytical Facility. It has positive action and is adaptable to bottles of various sizes. An inexpensive hand-operated sample-bottle decapper was designed. A method of modifying the focal range of monoculars and binoculars was tested. The Cenco-Lerner Lab-Jack is being motorized for the remote vertical positioning of light loads. Remotely controlled servo pipets were redesigned and are being fabricated; two capacities are available. A redesigned precision pipet elevator that is screw-operated was built and was found to be satisfactory. A filter photometer is being designed specifically for operation by master-slave manipulators. An automatic coulometric titrator for the analysis of HR fuels was built and tested; the titration current is stable, over long periods, to within 0.1%.

Radiochemical research on nuclear properties has included studies of the decay schemes and half lives of several radioelements, and the determination of the cross section of Pt^{196}. The 4π-coincidence method of measuring disintegration rates is discussed in some detail, and its use in calibrating a Pa^{233} standard is mentioned. A gamma spectrometer is being used in the analysis of samples from the Thorex process. A table that lists ORNL methods for measuring the activities of radioisotopes is in preparation. In the field of fission-product analysis, an indirect method for the determination of Sr^{90} is reported, and final evaluation of the TTA method for zirconium is almost completed. Further investigation of the electrodeposition of plutonium is in progress, and a method is proposed for the determination by

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gamma spectrometry of Am^{241} in plutonium. A method has been developed for separating radioiron from a fission-product mixture and determining its specific activity. Work is continuing on the analysis of fission products volatilized from reactor elements. Fission-product analyses of Thorex samples can be facilitated by use of an ion-exchange method for the removal of Pa^{233}. Electrodeposition is to be applied to the determination of radiocopper, radiotin, and radioantimony.

Neutron activation analysis has been applied to the determination of microgram or submicrogram quantities of the following: aluminum, magnesium, and titanium in nickel oxide; vanadium in titanium dioxide; chlorine, arsenic, and bromine in petroleum; and silicon in aluminum, nickel oxide, zirconium, and hafnium. In addition, contaminant elements were identified in enzyme solutions and in metals used as radioactive interstitial implants for cancer research. Also, activation analysis has been used to determine Cu^{63}/Cu^{65} isotopic ratios. Special studies included the determination of neutron-induced radioactivities in monkey blood and the investigation of the "self-shadowing" effect in cobalt. A discriminatory gamma counter has been built for the assay of radioelements. Extensive use of the activation analysis method for the determination of particle-size distribution is reported. Autoradiography has been used to determine the uniformity of plutonium oxide films electrodeposited on metal plates.

Spectrochemical research has resulted in new procedures for separating microgram quantities of rare earths from 20 g or more of thorium or its compounds, for determining 0 to 500 ppm of zirconium in thorium or its compounds, and for determining cobalt, mercury, tin, and cadmium in solution by the porous-cup technique. Progress is reported on the determination of silicon in thorium and its compounds. Attempts to separate thorium from rare earths with acetylacetone, disodium dihydrogen ethylenediaminetetraacetate, and cupferron are described.

New inorganic compounds that were prepared included the series from $LaMnO_3$ through admixtures of $LaMnO_3$ with $LaCrO_3$ to pure $LaCrO_3$. Crystal bar titanium was converted to $TiH_{1.99}$ and to $TiD_{1.98}$. In addition to several inorganic compounds of lithium, the following compounds were prepared: $H_3B^{10}O_3$, Ti_2O_3, $ThSi_2$, double and triple acetates of uranium, a series of low-bromide alkali-metal bromates, and diethoxyphosphinyl mercuric chloride. Most of these preparations were relative to work of the Physics and Chemistry Divisions.

Optical and electron microscopy studies have been chiefly of oxide films that were formed on metals of interest in reactor engineering. Microscopy was used in the investigation of the following: single crystals of lithium fluoride before and after their irradiation, the precipitate appearing at grain boundaries in Zircaloy, zirconium dioxide, plutonium dioxide, metallic iridium, the structure of welded Zircaloy, nickel-plated 24ST aluminum, cold-swaged and hot-forged Zircaloy, and pearlitic steels. Particle-size studies of a variety of materials, including thorium oxide calcined over a wide range of temperatures, were made. The development of new techniques of microscopy and an investigation of the nature of the growth of oxide films on Zircaloy are mentioned.

Forty-six new methods have been issued to the *ORNL Master Analytical Manual*; eighteen new manuals were issued.

Analytical service analyses are summarized in tabular form; special problems are discussed briefly. Ionic analyses were related primarily to the phase and corrosion studies for the HRT. Gamma spectrometry was the most important radiochemical technique used to determine identities and quantities of radioactive species. Recently observed half-life values are reported for seven gamma-emitting radionuclides. A new gamma scintillation spectrometer that eliminates the necessity of complete purification of the sample is in use. A summary is included of the extent of interest in activation-analysis service. Electrolytic and ion-exchange techniques have been used extensively in separations and purifications that were prerequisite to a number of wet-chemical analyses. A quality control program was initiated for the major colorimetric procedures used in the General Analyses Laboratory. A new vacuum-fusion apparatus was purchased and has been used to determine hydrogen, oxygen, and nitrogen in chromium-molybdenum-nickel alloys, titanium, zirconium, and thorium. An apparatus for the addition of known amounts of hydrogen, oxygen, and nitrogen to metals has been constructed for use in preparing standards for vacuum-fusion analysis. A micro Kjeldahl steam distillation apparatus was built to determine nitrogen in metallic elements and

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in alloys; results that have been obtained for thorium and zirconium agree remarkably well with the results by vacuum-fusion analysis. The status of work on the High-Radiation-Level Analytical Facility is indicated.

ANALYTICAL CHEMISTRY DIVISION – Y-12 SITE

The major problem of the HRP Analytical Chemistry Laboratory is the determination of contaminant elements that are present as corrosion products or as additives in solutions of uranyl sulfate and in slurries of thorium compounds. Procedures were developed and evaluated for the determination of barium in the presence of thorium, the dissolution of refractory pellets of aluminum oxide and of mixtures of thorium and titanium oxide, the determination of silver by flame photometry, the determination of palladium by α-furildioxime, and the removal of nitrate and ferric ions prior to the determination of zirconium by the chloranilic acid method.

In addition to these methods, studies relative to the estimation of nickel as the dimethylglyoxime complex in a solution of potassium persulfate and sodium carbonate were continued. Conditions were established for the electrodeposition of copper and nickel from solutions of uranyl sulfate. The determination of chromium(III) and (VI) in solutions of aluminum nitrate and nitric acid was investigated. Polarographic methods for oxygen in solutions of uranyl sulfate and for barium in the presence of thorium were tested. The concentration and characterization of impurities in compounds of thorium were investigated by means of conductivity and pH measurements. The separation and determination of titanium in the presence of thorium were studied. The spectrophotometric determination of ethylenediaminetetraacetic acid as the copper complex was investigated.

Relative to the work of the Raw Materials Group, methods have been modified and tested for the determination of uranium in the presence of iron, vanadium, and high concentrations of phosphate. The effect of uranium on the peroxide spectrophotometric method for vanadium was ascertained by means of the Warren Spectracord.

Work has been continued by the Methods Development Group on the determination of alkali and alkaline-earth elements by flame photometry, with special consideration to the interference of one element in the estimation of the others. Other work included the colorimetric determination of vanadium(IV) in solutions that contained vanadium(V), the determination of ammonia and carbonate in solutions of ammonium hydroxide that contained ammonium carbonate, the colorimetric determination of boron in low concentrations, the modification of the procedure for the colorimetric determination of cerium, and the separation of thorium from uranium prior to the determination of uranium by the fluorometric method.

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

A tabulation of the 88,148 determinations reported by the service groups is included; it indicates the distribution of work by divisions. The requirements of the Reactor Experimental Engineering and Materials Chemistry Divisions accounted for more than 80% of the service work.

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PRESENTATIONS OF RESEARCH RESULTS

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

OPEN-LITERATURE PUBLICATIONS

Author(s)	Title	Publications
Dean,[1] J. A., S. A. Reynolds	"Rapid Method for the Separation and Determination of Bismuth, Antimony, and Tin by Controlled Cathode Electroanalysis"	*Anal. Chim. Acta* 11, 390 (1954)
Handley,* T. H., E. L. Olson	"Neutron-Deficient Activities of Praseodymium"	*Phys. Rev.* 96, 1003 (1954)
Horton, A. D., P. F. Thomason, M. T. Kelley	"Indirect Polarographic Determination of Propylenediamine"	*Anal. Chem.* 27, 269 (1955)
Lyon, W. S.	"Decay of V^{49}"	*Phys. Rev.* 97, 121 (1955)
Lyon, W. S., J. E. Strain	"Decay of Rb^{86}"	*Phys. Rev.* 95, 1500 (1954)
Mahlman, H. A., G. W. Leddicotte, F. L. Moore	"Separation of Cobalt and Zinc by Liquid-Liquid Extraction"	*Anal. Chem.* 26, 1939 (1954)
Moore, F. L.	"Separation of Protactinium and Niobium by Liquid-Liquid Extraction"	*Anal Chem.* 27, 70 (1955)
Smith,* G. W., F. Nelson	"The Polarography of Thallium(III)"	*J. Am. Chem. Soc.* 76, 4714 (1954)
Smith, G. W., S. A. Reynolds	"Anion Exchange Separation of Tin, Antimony, and Tellurium"	*Anal. Chim. Acta* 12, 151 (1955)

[1]University of Tennessee.

ORAL PRESENTATIONS

Author(s)	Title	Presented At
Blosser, H. G., T. H. Handley,*,[2] M. K. Hullins	"Survey of (p,n) Reactions at 11.7 Mev"	1955 Annual Meeting, American Physical Society, New York, N. Y., Jan. 27–29, 1955
Feldman, C.	"The History and Anatomy of the Photographic Emulsion"	American Association of Spectrographers, Chicago, Ill., Nov. 9, 1954
Feldman,[2] C., J. Y. Ellenburg	"Contrast Changes of Eastman Kodak Spectrum Analysis No. 1 Emulsion During Storage and Their Effect on Observed Intensity Ratios"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 3, 1955 [also, *Spectrochim. Acta* (in press)]

[2]Speaker.

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Author(s)	Title	Presented At
Feldman, C., J. Y. Ellenburg[2]	"The Spectrochemical Determination of Boron in Carbon and Graphite"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 4, 1955 (submitted for publication in *Anal. Chem.*)
House,[2] H. P., J. M. Rogers	"Factors Involved in the Application of Flame Photometry to the Determination of Alkalies in Mixtures"	Southeastern Regional Meeting, American Chemical Society, Birmingham, Ala., Oct. 21–22, 1954
Leddicotte, G. W.	"Ion-Exchange Resins in Radiochemistry"	Analytical Chemistry Group, East Tennessee Section, American Chemical Society, Oak Ridge, Tenn., March 24, 1955
Leddicotte,[2] G. W., S. A. Reynolds	"Nucleonics in Analytical Chemistry"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb. 28–March 4, 1955
Manning,[2] D. L., J. C. White	"Differential Spectrophotometric Determination of Zirconium"	Southeastern Regional Meeting, American Chemical Society, Birmingham, Ala., Oct. 21–22, 1954
McCutchen, R. L.	"Use of Control Charts in Analytical Chemistry"	Southeastern Regional Meeting, American Chemical Society, Birmingham, Ala., Oct. 21–22, 1954 Tennessee Section American Society for Quality Control, Memphis, Tenn., Nov. 19, 1954 Analytical Chemistry Group, East Tennessee Section, American Chemical Society, Oak Ridge, Tenn., Feb. 24, 1955
Menis, O.	"Determination of Zirconium by the Chloranilic Acid Method"	Southeastern Regional Meeting, American Chemical Society, Birmingham, Ala., Oct. 21–22, 1954
Menis,[2], O., M. L. Druschel, C. D. Susano	"Spectrophotometric Determination of Nickel as the Dimethylglyoxime Complex"	Southeastern Regional Meeting, American Chemical Society, Birmingham, Ala., Oct. 21–22, 1954

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Author(s)	Title	Presented At
Rains,[2] T. C., O. Menis	"Spectrophotometric Determination of Palladium with α-Furildioxime"	127th National Meeting, American Chemical Society, Cincinnati, Ohio, March 31, 1955
Reynolds, S. A.	"Analytical Radiochemistry"	6th Annual Nuclear Sciences Seminar, Oak Ridge, Tenn., Nov. 30, 1954
		Frontiers in Chemistry Lecture, Wayne University, Detroit, Mich., Feb. 28, 1955
Ross,[2] W. J., J. C. White	"Determination of Water in Fluoride Salts"	Southeastern Regional Meeting, Americon Chemical Society, Birmingham, Ala., Oct. 21–22, 1954
Susono, C. D.	"Role of the Supervisor in an Analytical Chemistry Laboratory"	Southeastern Regional Meeting, American Chemical Society, Birmingham Ala., Oct. 21–22, 1954

TOPICAL REPORTS

Author(s)	Title	Report No.
Brooksbank, W. A., G. W. Leddicotte	"The Determination of Neutron Induced Activities in Animal Blood"	ORNL CF-55-2-87 (Feb. 15, 1955)
Harmon, T. G.	"To Determine the Thickness, Uniformity, and Bonding of Nickel Plated on 24 ST Aluminum"	ORNL CF-55-1-108 (Jan. 21, 1955)
Lyon, W. S., S. A. Reynolds	"Radioactivities in Cooling Water from the ORNL Low Intensity Test Reactor"	ORNL CF-54-9-99 (Sept. 16, 1954)
McCutchen, R. L.	"The Use of Control Charts in Analyticol Chemistry"	ORNL CF-54-10-45 (Oct. 7, 1954)
Reynolds, S. A.	"Preliminary Study of 'Cotton' and Thorium 'Backgrounds' in the Thorex Process"	ORNL CF-54-11-117 (Nov. 22, 1954)
Reynolds, S. A., T. H. Handley	"Radiochemical Studies of Aged 'Cotton' Product"	ORNL CF-55-2-63 (Feb. 10, 1955)
Reynolds,* S. A., R. Joseph	"Decay of Activity Induced in Nichrome Plates"	ORNL CF-54-10-132 (Oct. 26, 1954)
Shults, W. D., II, P. F. Thomason	"Coulometric Titration of Chloride and of Chromium in Homogeneous Reactor Type Solutions"	ORNL-1846 (March 11, 1955)
Susano, C. D., L. J. Brady	"Some Selected Methods for Determining Uranium and Vanadium in the Presence of Each Other"	ORNL CF-55-1-77 (Jan. 12, 1955)

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Thomason, P. F., L. A. Nutting,[3] U. Koskela, W. M. Byerly[4]	"The Salicylate Method for Determining Microgram Amounts of Uranium"	ORNL-1641 (Feb. 23, 1955)
Toomer, F. M.	"Particle Size Determination of Th-Sludge HNO_3"	ORNL CF-55-2-110 (Feb. 16, 1955)
	"Particle Size Determination of Thorium Oxide Samples by Electron Microscopy"	ORNL CF-55-3-29 (March 2, 1955)
Willmarth, T. E.	"Particle Size Determination of Caustic Dissolution Slurry of U-Al Alloy"	ORNL CF-54-11-11 (Nov. 1, 1954)
	"Particle Size Determination of UO_2 Sample, Submitted Oct. 28, 1954"	ORNL CF-54-11-32 (Nov. 8, 1954)
	"Particle Size Determination of Thorium Oxide Samples by Electron Microscopy"	ORNL CF-54-12-47 (Dec. 6, 1954)
	"Test Run of H-46"	ORNL CF-55-1-44 (Jan. 7, 1955)
	"Particle Size Determination of $(NH_4)_2C_2O_4 \cdot 2Th(C_2O_4) \cdot xH_2O$ Sample 3434-40"	ORNL CF-55-1-51 (Jon. 11, 1955)
	"Run-A-72"	ORNL CF-55-1-64 (Jan. 13, 1955)
	"Particle Size Distribution of Caustic Dissolution Slurries"	ORNL CF-55-1-158 (Jan. 26, 1955)
	"Study of the Oxide Films Formed on the Aperture Plate in the Thorium Loop"	ORNL CF-55-2-24 (Feb. 3, 1955)
	"Examination of PuO_2 in Bench Type Runs by Electron Microscopy and Diffraction"	ORNL CF-55-2-26 (Feb. 3, 1955)

[3]National Dairy Research Labs, Oakdale, Long Island, N. Y.
[4]Deceased.

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Author(s)	Title	Number(s)	Date
Cooper, J. H.	"Specific Gravity of Uranium and Plutonium Product Solutions, Direct Weighing Method"	9 043100	6-29-54
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	"Molybdenum Activity in Aqueous or Organic Solutions"	2 21501	2-26-54
	"Niobium Activity in Aqueous or Organic Solutions"	2 21551	3-1-54

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	"Tellurium Activity in Aqueous or Organic Solutions"	2 21841	3-5-54
	"Zirconium Activity in Aqueous or Organic Solutions"	2 21981	3-8-54
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Miller, F. J.	"Aluminum in the Presence of Thorium, Spectrophotometric Oxine (8-Hydroxyquinoline) Method"	9 0122020	2-19-54
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	"Chloride in Homogeneous Reactor Type Solutions, Coulometric Titration Method"	9 082211	2-8-55

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Shults, W. D., II	"Chromium in Homogeneous Reactor Type Solutions, Coulometric Titration Method"	9 082212	2-17-55
Stelzner, R. W.	"Dielectric Constant Meter, ORNL Model Q-946"	1 003070 9 003070	11-16-54
Wilson, G. R.	"Thorium, Spectrophotometric Thoron Method"	1 218710 9 00718710	3-26-54
Wolkowitz, W. J.	"Automatic Titrotor, Beckman Model K"	1 003020 9 003020	8-2-54
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	"Cobalt-58, Product Analysis Guide"	9 0733225	12-30-54
	"Indium-114m, Product Analysis Guide"	9 0733381	11-29-54
	"Selenium-75, Product Analysis Guide"	9 0733761	12-29-54
	"Strontium-85, Product Analysis Guide"	9 0733803	12-29-54
	"Yttrium-88, Product Analysis Guide"	9 0733962	12-29-54

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ANALYTICAL CHEMISTRY DIVISION - X-10 SITE

RESEARCH AND DEVELOPMENT

IONIC ANALYSES

P. F. Thomason

Spectrophotometric Determination of Aluminum in Homogeneous Reactor Fuels

A. D. Horton P. F. Thomason

Aluminum has been determined in Homogeneous Reactor (HR) fuels by passing a 9 *M* hydrochloric acid solution of the fuel through a column of Dowex 1 ion-exchange resin in the chloride form. Aluminum, nickel, and chromium(III) pass through the column, but uranium, chromium(VI), copper, cobalt, and zirconium are adsorbed. The effluent is evaporated to dryness, and aluminum in the residue is determined spectrophotometrically at a wavelength of 525 mμ with a buffered Aluminon reagent in accordance with the method of Luke.[1] The only anticipated interference is thorium. Interference by other additives and corrosion products that pass through the column has not been investigated. Development of this method is incomplete.

Polarographic Determination of Chromium(III) and (VI) and Total Chromium in Homogeneous Reactor Fuels

A. D. Horton P. F. Thomason

Considerable difficulty has been encountered in the polarographic determination of chromium in HR fuels. Chromium(III) must be separated from chromium(VI), uranium(VI), cobalt(II), and copper(II) because these metallic ions are major interferences in the polarographic determination of chromium(III).

Chromium(III) has been separated from interfering metals by passing a 9 *M* hydrochloric acid solution of HR fuel through a column of Dowex 1 ion-exchange resin in the chloride form. Chromium(III) passes through quantitatively and can be determined by evaporating the effluent to dryness, dissolving the residue, then diluting the solution to a known volume with a supporting electrolyte of 1.0 *M* NH_4OH–1.0 *M* NH_4Cl. Chromium(III) gives a poorly defined wave at an $E_{1/2}$ of –1.35 v vs the S.C.E. In a supporting electrolyte of 0.1 *M* pyridine–0.1 *M* pyridinium chloride, a wave is obtained at an $E_{1/2}$ of –0.95 v vs the S.C.E., but the wave definition is not satisfactory because of the interference of nickel, which gives a wave at an $E_{1/2}$ of –0.78 v vs the S.C.E.

Excellent results were obtained for chromium(VI) and for total chromium by use of Dowex 50 anion-exchange resin. To determine chromium(VI), the untreated HR fuel solution is passed through the column. The effluent, which contains the chromium(VI) as chromate, is collected in a 10-ml volumetric flask that contains three pellets (~300 mg) of sodium hydroxide. An aliquot of the known volume is analyzed polarographically for chromium(VI). Total chromium is determined by oxidizing chromium(III) to chromate by the addition of a small excess of potassium permanganate to the HR fuel solution and heating the solution to boiling. The solution is then passed through the Dowex 50 column as before, and chromate is determined polarographically. Chromium(III) is determined by the difference between the value for total chromium and the value for chromium(VI). Although the excess permanganate passes through the column, it does not interfere.

Well-defined waves are obtained at an $E_{1/2}$ of approximately –0.85 v vs the S.C.E. in the supporting electrolyte of approximately 0.75 *M* sodium hydroxide. Very small concentrations (~0.5 ppm) of chromium(VI) can be determined because of the large diffusion current that results from the chromium(VI) → chromium(III) reduction. Table 1 shows the results of polarographic analyses of solutions of chromium(VI) that was separated from interfering metallic ions by Dowex 50 cation-exchange resin.

Automatic Coulometric Titrations

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

Automatic coulometric titration methods were developed for the determination of chloride and of

[1] C. L. Luke, "Photometric Determination of Aluminum in Lead, Antimony, and Tin and Their Alloys," *Anal. Chem.* **24**, 1122 (1952).

[redacted]

TABLE 1. POLAROGRAPHIC DETERMINATION OF CHROMIUM(VI) AND TOTAL CHROMIUM IN SYNTHETIC HR FUELS

Supporting electrolyte, ~0.75 *M* NaOH
$E_{1/2}$ = −0.85 v vs the S.C.E.

Synthetic	Chromium(VI) Found (μg/ml)	Total Chromium Found (μg/ml)
A*	2.03	4.10
	1.99	4.10
	1.98	3.98
	1.94	3.99
B**		1.99
		1.96
		2.02
		1.94

*Chromium(III) present, 2.0 μg/ml; chromium(VI) present, 2.0 μg/ml.

**Chromium(III) present, 2.0 μg/ml.

chromium in HR type samples. This work[2] and the resulting methods[3,4] are described separately.

Photometric Titration of Sulfate

F. J. Miller

An accurate and precise sulfate determination will be required for the analysis of HR fuels. The barium perchlorate titration method of Fritz and Yamamura[5] appears to be suitable. However, they use visual indicator (Thoron) end-point detection, which will be difficult behind the barricade in the High-Radiation-Level Analytical Facility. A photometric end-point detector has been built that consists of a Welch Densichron, a light-tight brass box, Corning light filters to give a broad transmission band at 520 mμ, and a magnetic stirrer. The instrument is being evaluated for control use. Preliminary results show a very sharp change in optical density at the equivalence point.

Separation of Thorium from Rare Earths, Zirconium, and Phosphate and Spectrophotometric Determination of Thorium with Thoron Reagent

A. D. Horton P. F. Thomason

Two methods were investigated for freeing thorium solutions of substances that interfere in the Thoron colorimetric method for thorium. By the first method, zirconium is extracted from a strongly acidic solution of the sample into a thenoyltrifluoroacetone–carbon tetrachloride solution; then thorium is extracted from the aqueous phase at pH 1.5 ± 0.1 into thenoyltrifluoroacetone-xylene solution; and, finally, thorium is extracted from the organic phase into a strongly acidic aqueous solution. The second method is that of Banks and Byrd[6] by which thorium, the rare earths, zirconium, and phosphate are extracted from an acidic solution of the sample into mesityl oxide; then the rare earths, zirconium, and phosphate are extracted from the mesityl oxide into saturated aluminum nitrate solution; and, finally, thorium is extracted from the mesityl oxide layer into water. Both methods give comparable results, but the second method is much faster and the pH is not critical. The final extract, obtained by either method, is analyzed without further treatment by the Thoron method of Thomason *et al.*[7]

Polarographic Determination of Technetium

H. H. Miller

The polarographic method is being investigated for the determination of technetium[8] in radioisotope production process solutions. Technetium in the product solution, that is, the final process solution that contains the purified technetium, is determined by polarographing the technetium as pertechnetate (0.5 to 10 μg of technetium per milliliter) in a pH 10 buffer solution. The standard-addition technique is used. Technetium in process solutions that contain interfering ions and

[2] W. D. Shults, II, and P. F. Thomason, *Coulometric Titration of Chloride and of Chromium in Homogeneous Reactor Type Solutions*, ORNL-1846 (March 11, 1955).

[3] W. D. Shults, II, "Chloride in Homogeneous Reactor Samples, Coulometric Titration Method," Method No. 9 082211 (2-8-55), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and III.

[4] W. D. Shults, II, "Chromium in Homogeneous Reactor Samples, Coulometric Titration Method," Method No. 9 082212 (2-17-55), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols I and III.

[5] J. S. Fritz and S. S. Yamamura, *Rapid Microtitration of Sulfate*, ISC-540 (Nov. 12, 1954).

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

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

[8] H. H. Miller, "Polarography of Technetium," *Anal. Chem. Quar. Prog. Rep. Sept. 10, 1951*, ORNL-1129, p 11.

high levels of radioactivity is separated out by a sulfide precipitation; perrhenate ion is used as a carrier. The precipitate, which contains the technetium, is dissolved, and the solution is diluted to a known volume with pH 10 buffer. The polarographic behavior of the technetium-tetraphenylarsonium complex is being investigated.

Separation and Polarographic Determination of Tin in Copper-Tin Alloys

H. H. Miller

When milligram amounts of tin are determined in copper-tin alloys, the copper and tin must be separated because copper interferes in most tin determinations. Jewsbury and Osborn[9] report that tin in macro quantities (~200 mg) is precipitated quantitatively from ammoniacal solution by ammonium benzoate. Copper is not precipitated under these conditions if it is complexed with ammonium acetate. Because of the limited amount of sample available (100 mg that contained 5 to 10% tin), it was necessary to adapt the method to the semimicro scale (1 to 10 mg of Sn). The copper-tin alloy was dissolved, and the tin was oxidized to tin(IV) with bromine water, then precipitated with ammonium benzoate from an ammonium acetate solution. A concentrated hydrochloric acid solution of the precipitate was diluted to a known volume in 1 *M* HCl–4 *M* NH_4Cl and polarographed. The standard-addition technique was used.

Ion-Exchange Separation and Potentiometric Titration of Cobalt in Aluminum-Cobalt-Manganese Alloy

H. H. Miller

The determination of cobalt in an aluminum-cobalt-manganese alloy that was estimated to contain about 0.5% cobalt and 0.5% manganese was requested; a relative standard deviation of 1% or better was desired. Cobalt in ammoniacal solution can be titrated potentiometrically with potassium ferricyanide solution; the precision is excellent. Aluminum precipitates from basic solution, and manganese in ammoniacal solution is titrated by potassium ferricyanide. Therefore aluminum and manganese had to be separated from cobalt. The separation was effected by placing a 9 *M* hydrochloric acid solution of the alloy on a chloride-form Dowex 1 resin column. Aluminum and manganese passed through the column and left cobalt adsorbed in a fairly narrow band at the top of the column. The cobalt was eluted with 0.1 *M* hydrochloric acid and titrated with potassium ferricyanide solution. The indicator electrode was a platinum wire, and the reference electrode was a saturated calomel electrode. The potential break occurred at 0.0 v vs the S.C.E.

Synthetic samples that contained approximately 0.40% cobalt were titrated; the standard deviation of the results was better than 1%. Seven portions from the same alloy sample were analyzed to determine the homogeneity of the alloy with respect to cobalt. The following results were obtained:

Sample No.	Cobalt in Alloy (wt %)
1	0.394
2	0.400
3	0.401
4	0.396
5	0.395
6	0.394
7	0.394

Volumetric Determination of Uranium in Stainless Steel–Uranium Dioxide Plates

P. F. Thomason

The previously reported polarographic method for the determination of uranium in stainless steel dissolver solution[10] is not sufficiently precise for the determination of the homogeneity of stainless steel–uranium dioxide (UO_2) plates. Separation of uranium from iron, nickel, and chromium in solutions of the plates followed by the precise ferric sulfate volumetric determination of uranium seemed to be the most promising method to check the homogeneity of the plates.

It was found that the stainless steel of the plate dissolved readily in concentrated hydrochloric

[9] A. Jewsbury and G. H. Osborn, "Some Further Analytical Applications of Ammonium Benzoate. An Investigation into the Uses and Limitations of Ammonium Benzoate for the Quantitative Estimation of Tin, Titanium, Zirconium, Thorium, Bismuth and Cerium, and for Their Separation from Other Elements," *Anal. Chim. Acta* 3, 642 (1949).

[10] P. F. Thomason, "Polarographic Determination of Uranium in Stainless Steel Dissolver Solution," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 1.

acid but that the UO_2 was practically insoluble. Nitric acid was added to dissolve the UO_2. Portions of the solution were made 1.5 *M* in $Al(NO_3)_3$ and were extracted twice with equal volumes of 12 vol % tributyl phosphate–isopropyl ether. The extracts were combined and were stripped three times with equal volumes of distilled water. The combined aqueous extracts that contained uranyl nitrate were then fumed with concentrated sulfuric acid to remove nitric acid. The ferric sulfate titration method[11] was used to determine the uranium.

Two synthetic samples that contained 77.50 mg of uranium per gram of stainless steel were analyzed by this method, and the uranium was recovered to within ±0.3%. The average relative standard deviation of the results of triplicate analyses of these two samples was 0.3%. The aqueous raffinates from the two synthetic samples and the stripped ether phases were analyzed fluorometrically for uranium. The total losses of uranium that occurred in the separation steps were found to be approximately 0.1%.

[11] J. H. Cooper, "Uranium, Potentiometric Ferric Sulfate Method," Method Nos. 1 219222 and 9 00719222 (8-3-53), *ORNL Master Analytical Manual.*

Simultaneous Spectrophotometric Determination of Technetium and Rhenium

W. J. Wolkowitz

A solution of ammonium pertechnetate was standardized gravimetrically by precipitation with tetraphenylarsonium chloride according to the procedure of Hillebrand and Lundell[12] for the gravimetric determination of rhenium. A 1×10^{-4} *M* solution was prepared and was made 1.1 *M* with $HClO_4$. The ultraviolet absorption spectrum of the solution was determined; the molar absorbancy indexes (Fig. 1, curve A) were found to be 2363

[12] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis* 2d ed., p 321, Wiley, New York, 1953.

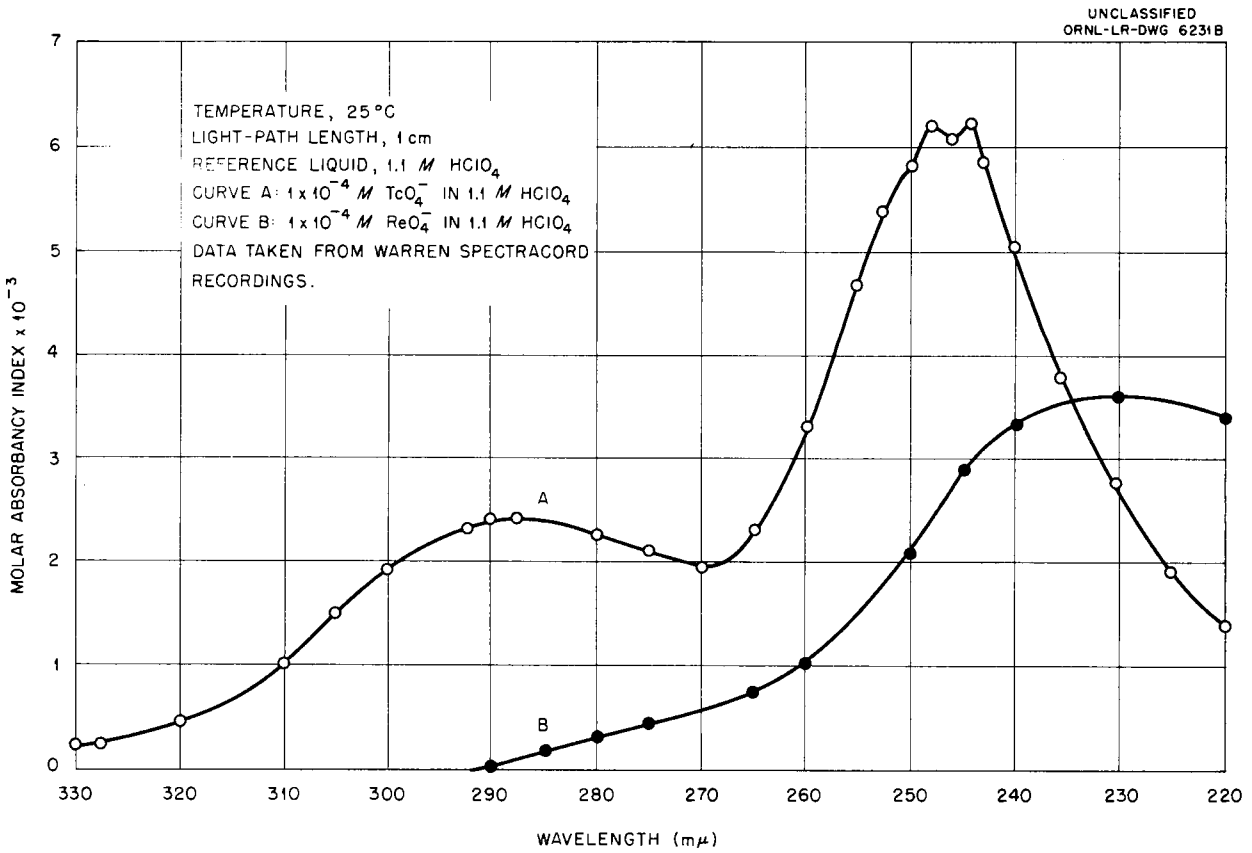

Fig. 1. Molar Absorbancy Index–Wavelength Curves for Pertechnetate and Perrhenate in Perchloric Acid Medium.

and 6200 for the 287.5- and 244.0-mμ wavelengths, respectively. This is in agreement with values published recently by Cartledge.[13] The concentration range investigated was 3.8 to 19.0 μg of technetium per milliliter.

The ultraviolet absorption spectrum of a 1×10^{-4} *M* solution of potassium perrhenate in 1.1 *M* $HClO_4$ was determined. As will be noted from the molar absorbancy index–wavelength curve (Fig. 1, curve B), perrhenate shows negligible absorption at 287.5 mμ. The absorbancies at 287.5 and 235.0 mμ can be used to determine technetium and rhenium simultaneously.

The molar absorbancy indexes of Fig. 1, curves A and B, were calculated from a continuous recording of wavelength vs transmittancy obtained by the Warren Spectracord.

Spectrophotometric Determination of Zirconium

W. J. Wolkowitz

Welcher[14] describes a spot test for the detection of zirconium in which a 2% ethanol solution of β-nitroso-α-naphthol is used. It was found that 1 ml of a 0.1% ethanol solution of β-nitroso-α-naphthol in 10 ml of a solution that contains 2.5 to 15 μg of zirconium per milliliter gives a red lake that exhibits an absorption peak at a wavelength of 486 mμ. The molar absorbancy index at this wavelength is 3570, the absorption obeys Beer's law, and the color is stable for at least 3 hr. The experimental work was done with a Warren Spectracord.

Spectrophotometric Determination of Tetraphenylarsonium Chloride

W. J. Wolkowitz

A method for the rapid determination of tetraphenylarsonium chloride, $C_6H_5AsCl{\cdot}2H_2O$, was needed because this reagent is used extensively in the recovery and purification of technetium. It was found that both aqueous and ethanolic solutions of tetraphenylarsonium chloride show sharp absorption peaks at wavelengths of both 270.5 and 263.6 mμ. The molar absorbancy index–wavelength curve for an aqueous solution of tetraphenylarsonium chloride is shown in Fig. 2. The molar absorbancy indexes are 2645 and 3182 for the 270.5- and 263.6-mμ wavelengths, respectively. The spectral absorbancy at 263.6 mμ was investigated, and Beer's law was found to hold in the concentration range 10 to 200 μg of tetraphenylarsonium chloride per milliliter. The molar absorbancy indexes of Fig. 2 were calculated from a continuous recording of wavelength vs transmittancy obtained by the Warren Spectracord.

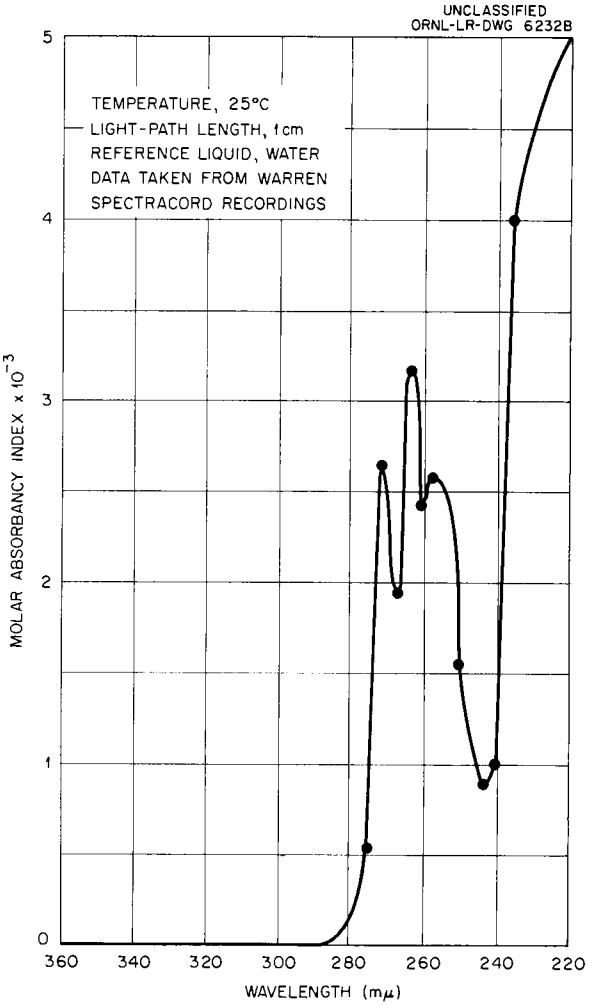

Fig. 2. Molar Absorbancy Index–Wavelength Curve for 1.32×10^{-4} *M* Aqueous Solution of Tetraphenylarsonium Chloride.

Spectrophotometric Determination of Thenoyltrifluoroacetone in Xylene

W. J. Wolkowitz

Thenoyltrifluoroacetone (TTA) is used commonly in the solvent extraction of zirconium and thorium;

[13] G. H. Cartledge, *The Inhibition of Corrosion by the Pertechnetate Ion*, ORNL-1833 (Dec. 30, 1954), p 7.

[14] F. J. Welcher, *Organic Analytical Reagents*, vol. III, p 323, Van Nostrand, New York, 1947.

therefore a method for the rapid determination of TTA was needed. The ultraviolet absorption spectrum of TTA in xylene showed that strong absorption occurs at a wavelength of 324 mμ. The molar absorbancy index (Fig. 3) at 324 mμ is 3680. Beer's law is obeyed in the concentration range 2 to 30 μg of TTA per milliliter of xylene. The molar absorbancy indexes of Fig. 3 were calculated from a continuous recording of wavelength vs transmittancy obtained by the Warren Spectracord.

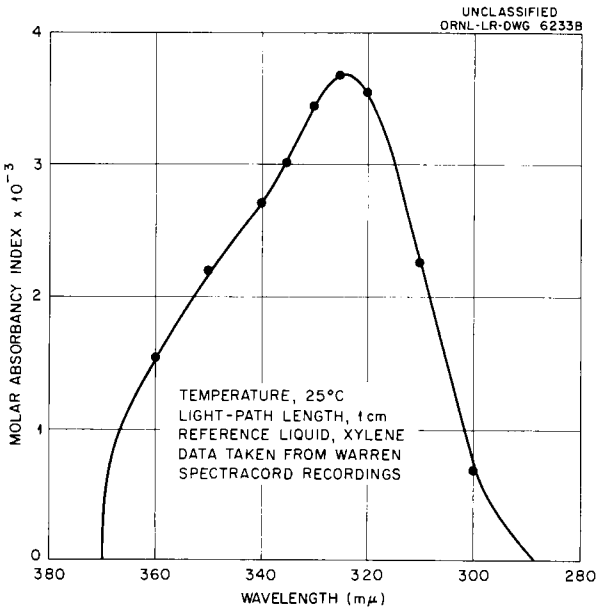

Fig. 3. Molar Absorbancy Index–Wavelength Curve for 4.87 × 15⁵ *M* Solution of Thenoyltrifluoracetone in Xylene.

ANALYTICAL INSTRUMENTATION

D. J. Fisher

Remotely Controlled Falling-Drop Densimeter

R. W. Stelzner M. T. Kelley
D. J. Fisher R. B. Quincy[15]

A remotely controlled falling-drop densimeter that consists of the following units was installed in the hot cell in Building 3019: remotely controlled sampling pipet, 0.1 ml (Dwg. D-20295) modified, pipet elevator (Dwg. D-11070), remote-control pipetter circuit (Q-1348-1r3), falling-drop densimeter (Q-1551) (timing unit), remotely controlled bottle decapper (Dwgs. D-8507 and D-8516), remotely controlled turret assembly,[16] Precision Scientific Co. thermostatted water bath, 30°C, Central Scientific Co. vacuum pump, and Sorenson & Co., Inc., voltage regulator. The densimeter is being used in the remotely controlled determination of the densities of process feed solutions for the Thorex and metal recovery processes. With the exception of the sample-bottle decapper and the turret assembly, the apparatus has performed satisfactorily. These units are undergoing redesign and construction (cf. "Sample-Bottle Decapper for High-Radiation-Level Analytical Facility" and "Remotely Controlled Turret Assembly for the Q-1551 Falling-Drop Densimeter," this report).

[15]Pilot Plant Control Laboratory.

Remotely Controlled Turret Assembly for the Q-1551 Falling-Drop Densimeter

R. W. Stelzner

A new design was developed for the remotely controlled turret assembly of the Q-1551 falling-drop densimeter to overcome the difficulties presented in the first model.[16] The assembly holds six "fall tubes." The fall tubes of the first model were held rigidly to the turret cover by a mounting ring and were rotated about an axis by a slow-speed Bodine motor. A machined bearing preserved the concentric alignment of the tubes about the vertical axis. Operation of the turret assembly in the determination of the densities of process feed solutions demonstrated that the Bodine motor could not deliver sufficient torque to overcome the radial thrust against the lubricated bearing surface. It was evident that the turret should be redesigned.

Each fall-tube assembly can be removed individually from the new model of the turret assembly by a master-slave manipulator for replacement of the oil or glass tube without the necessity of dismantling the entire turret. This is a feature that was not present in the older model.

The shaft of the new model of the turret assembly is mounted on a Timken roller bearing, which accepts the radial and axial thrusts that proved to be of disadvantage in the older model.

[16]M. T. Kelley, H. L. Hemphill, and N. D. Lee, "Fall-Tube Turret for Electronically Timed Falling-Drop Instrument for the Determination of Densities of Aqueous Solutions," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 7.

A ball bearing is mounted near the motor end of the shaft to maintain rigid axial alignment. The drive motor is a New England Gear Works gear motor, mounted axially, with a torque rated in inch-pounds; the Bodine motor is rated in inch-ounces. The slow-speed motor was selected because it should position the fall tubes accurately.

Most of the new turret is made of stainless steel; a few parts are of brass, aluminum, and Lucite. Stainless steel was selected because of its resistance to chemical corrosion and its ease of decontamination. In the first assembly, aluminum parts in the proximity of the oil were attacked by 1,1,1,1-tetrabromoethane, a component of the oil. The entire turret assembly can be dismantled for cleaning should decontamination be necessary.

The type 925 phototubes are enclosed in a brass cylinder that is mounted within the inner cylinder of the turret; they are in line with the light beams from the G-E 88 lamps. An adjustable lens assembly focuses the light at the center of the fall tubes so as to give a maximum signal from the interruption of the light beam by the drop.

A thermostatted water bath is used in conjunction with the unit to keep the temperature of the dropping oil at 30 ± 0.03°C. The water bath is to be mounted about 4 ft below the turret assembly; inasmuch as the water bath has a gravity return, electrical or pump failure would mean flooding. To prevent this occurrence, a standpipe is used to drain water off near the top of the turret. The standpipe was preferred to a ball-check valve because infrequent use of the check valve could cause it to function unreliably. The standpipe is not subject to this limitation.

The fall tubes are indexed in line with the light beams by a microswitch that removes the 120-v a-c line voltage from the drive motor and simultaneously applies a d-c voltage for braking the motor. The microswitch is actuated by an adjustable eccentric on a panel bearing assembly, which is mounted exactly 180 deg from the light beam. A full-sized microswitch is preferred instead of the midget variety used in the old model of the turret.

The base of the turret is to be fitted with three leveling screws; a circular bubble level-indicator will be embedded in the turret cover to aid in the alignment of the turret so that the drops fall along the vertical axis of the glass fall tube. Initial assembly and alignment of the turret assembly will be facilitated by the new type of construction. Detailed and assembly drawings of the turret have been prepared. The turret is being constructed in the Central Machine Shop.

Automatic Velocity-Servo Potentiometric Titrator

M. T. Kelley E. B. Wagner

A simplified model of a velocity-servo type of automatic potentiometric titrator has been reported.[17] This instrument was designed primarily for the titration of radioactive materials in the High-Radiation-Level Analytical Facility. However, it has proved to be adaptable and satisfactory for all types of potentiometric titrations.

The Special Analyses Laboratory of the Analytical Chemistry Division has used the new instrument for making a number of very successful titrations of uranium with ferric sulfate solution. The personnel titrated 6-mg samples of uranium with a relative standard error of ±0.1% (95% confidence level).

The titrator consists of two units, the control unit and a titrant-delivery unit, connected only by electrical cables. This arrangement permits the titrant-delivery unit to be placed in a hot cell and the control unit to be located at any convenient place outside the cell.

The new titrant-delivery unit, together with the master-slave manipulators, allows for complete remote control of the titration at the titrator control unit. The unit consists basically of a mechanical coupling between a synchro receiver and the plunger of a syringe which makes the movement of the syringe plunger proportional to the rotation of the synchro receiver. The titrant-delivery unit can be attached to an elevator; it can then be raised and lowered to facilitate the changing of samples in the titration vessel. Micro-Metric syringes of sizes from 0.5 to 5 cc/in. can be used easily with the unit.

A description of the titrator is being prepared for the *ORNL Master Analytical Manual.* It is planned to have several of the titrators fabricated for the High-Radiation-Level Analytical Facility and for the regular "cold" control laboratories.

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[17] M. T. Kelley, D. J. Fisher, and E. B. Wagner, "Simplified Model of Automatic Titrator with Velocity-Servo Control of Titrant Addition," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 6.

Automatic Coulometric Titrator for Karl Fischer Water Titrations

R. W. Stelzner D. J. Fisher
M. T. Kelley

An automatic coulometric titrator for the Karl Fischer determination of water with internally generated iodine was designed to be tested for routine use. A generating current of 50 to 300 ma is furnished by a 36-v battery supply. The compensating current of 4 to 34 ma is produced by a constant-current type 6AG7 vacuum tube that is powered by an electronic supply. Automatic cutoff of the generating current at a preset end-point potential is accomplished by use of a relay circuit that is actuated by voltage from a Leeds & Northrup model 7664 pH-millivolt meter.

Model Q-1673 Polarograph with Diode Filter

M. T. Kelley D. J. Fisher

The model Q-1673 polarograph with diode filter[18] is being fabricated by the Instrument Department. The specifications are as follows. The current range can be varied between 0 to 0.05 and 0 to 20 μa full scale. Various combinations of R-C, parallel-T–R-C, and diode filters are available for use in recording nonderivative polarograms. Provision is made for the attachment of a curve follower. The scan motor is reversible, both residual-current and linear compensators are included, and a Brown recorder is used. The polarograph also has a derivative-taking network. The current fluctuations that result from the rise and fall of the mercury drops can be filtered out completely with negligible distortion of the form of the polarographic wave.

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

C. L. Burros

A sample-bottle decapper is being built that will serve either to remove, discard, and replace a bottle cap or to hold a sample bottle, which has a diaphragm type of cover, while a sample is being removed with a hypodermic needle. The decapper holds a bottle in two half-cylindrical jaws that are mounted on a turntable, which is powered by a 4-rpm reversible motor. The bottle cap is held between another set of half-cylindrical jaws, which are fixed to a pivoted mechanical arm. After a bottle is positioned and clamped, the cap is removed by the simple operation of rotating the turntable counterclockwise.

Inexpensive Hand-Operated Sample-Bottle Decapper

D. J. Fisher

It has been found that very satisfactory hand-operated sample-bottle decappers can be fabricated rapidly from standard Walter rubber crucible holders that are used to hold Gooch crucibles in filter flasks. A handle is cut from $\frac{3}{8}$-in.-OD rod to the desired length, which is usually about 1 ft. Lucite or aluminum rod is suitable. The handle is fastened into the funnel-stem opening of the crucible holder by means of one screw.

Modification of Focal Range of Monoculars and Binoculars

D. J. Fisher

For use in the High-Radiation-Level Analytical Facility, monoculars and binoculars are needed that will focus over the object distance range of 4 to 11 ft. Standard oculars focus down to a minimum object distance of 15 to 20 ft. It has been found that the desired focal range is obtained by mechanically increasing the separation between the objective and eyepiece lenses. The quality of the image is satisfactory.

Motorized Lab-Jack

M. T. Kelley D. J. Fisher

An inexpensive elevating device is required for use in the High-Radiation-Level Analytical Facility for such purposes as positioning beakers under automatic titrators and vertically positioning other light loads. The Cenco-Lerner No. 19089 Lab-Jack is being adapted to this use. It is planned to actuate the jack from the rear by means of a 60-rpm reversible electric gear motor. The stroke of the jack will be about 6 in.

Remotely Controlled Sampling Pipets

M. T. Kelley D. J. Fisher

Redesigned remotely controlled sampling pipets for use in the High-Radiation-Level Analytical

[18] M. T. Kelley and D. J. Fisher, "New High-Sensitivity General-Purpose and Derivative Polarograph," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 9.

Facility are being built in the Central Machine Shop. The pipets are operated by a servo control, model Q-1348-1r3. A Teflon packing is used for the plunger. The assemblies of the 0.1- and 1.0-ml pipets are shown in Engineering Department drawings D-21064 and D-21065, respectively. The 0.1-ml pipet is for use with the Q-1551 falling-drop densimeter. The 1.0-ml pipet is intended for the preparation of quantitative sample dilutions. Both pipets will be mounted on elevators of the type shown in Engineering Department Dwg. No. E-19550. The samples will be received in samples bottles similar to those shown in Engineering Department drawings C-19250 and C-21576. A Buna "N" diaphragm is inserted in the top of the ring-type bottle cap. It is proposed to fit stainless steel needles to the sampling pipets in order to eliminate, whenever possible, the necessity of decapping the sample bottles to take a portion for analysis.

Pipet Elevator

M. T. Kelley D. J. Fisher

A precision screw-operated elevator is required for the High-Radiation-Level Analytical Facility. It is intended for use with the servo-operated pipet of the Q-1551 falling-drop densimeter and with the 1-ml servo-operated pipet. It can also be used to position the titrant-delivery unit of the velocity-servo automatic potentiometric titrators. The assembly of the elevator is shown on Engineering Department Dwg. No. E-19550. The range of operating height of the pipet adapter can be varied by a choice of pedestal tube spacers. The working stroke is 10 in. at a rate of 10 in. per minute. The elevator was designed to lift 8 lb at this rate. One elevator has been built by the Central Machine Shop and has been shown to meet or exceed the design specifications.

New Filter Photometer for Operation by Master-Slave Manipulators

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

A filter photometer is being designed for operation in the High-Radiation-Level Analytical Facility by master-slave manipulators. The photometer will utilize an interference filter, a Beckman DU lamp house with tungsten lamp backplate, a Welch Densichron probe, and a modified Coleman cuvette holder to carry the sample and reference solutions. The Densichron amplifying unit will be located in the instrument chase.

Automatic Coulometric Titrator for Homogeneous Reactor Fuels

R. W. Stelzner

An automatic coulometric titrator for the determination of chloride and chromium in HR fuels was developed for the Reactor Analyses Group. The generating current has a range of from 10 to 800 μa and a current stability of 0.1% over a range of cell resistance of from 0 to 10,000 ohms. The current is held constant over long periods of time (over 16 hr) by the use of a type 6SJ7 pentode in series with the coulometric cell. An adjustment of the control-grid bias of the 6SJ7 pentode by means of a bridge circuit permits a selection of an operating current in the range of the instrument. The current stability is increased by the use of an electronically regulated power supply based upon a type 6SL7 difference amplifier. A 6.3-v Sola Electric Co. constant-voltage transformer for the filament of the constant-current pentode further enhances the current stability of the instrument.

A Leeds & Northrup model 7664 pH-millivolt meter is an integral part of the instrument; it is used to indicate the potential difference of a suitable indicator electrode system and to furnish a voltage for the cutoff circuit. The voltage from the pH-millivolt meter is fed into the grid of an a-c–operated type 2D21 thyratron by means of a cathode follower stage. The cathode follower serves to isolate the thyratron from the cutoff circuit, thus avoiding difficulties arising from a feedback signal from the triggering of the thyratron. A ten-turn Borg Micropot ("cutoff adjust") in a bridge circuit produces an adjustable bucking voltage for the cutoff circuit. The adjustment of this calibrated dial from the front panel of the instrument permits selection of the end-point cutoff of the generating current at any value in the range of from 0 to 1400 mv or, by throwing a dpdt reversing switch, of from 1400 to 0 mv.

A rough determination of the value of the generating current is obtained from a 0- to 1-ma meter mounted on the front panel. A more precise reading is made by the use of a Rubicon Pointerlite potentiometer to measure the voltage drop across a 1000-ohm precision resistor in the 6SJ7 plate

circuit. By use of a dummy cell, that is, a 3.3-K resistor, the generating current can be adjusted to the desired value at the start of a titration without current flow through the coulometric cell. When the titration is started by throwing the "standby-titrate" switch to "titrate," the dummy cell is switched out of the circuit, and it is replaced by the coulometric cell; at the same time, a Standard timing clock is started. The titration (and the clock) is stopped automatically at the desired end-point potential, and the dummy cell is switched back into the pentode circuit.

An R-C time-delay circuit is available for use in titrations that involve slow reactions for which the end-point potential is reached prematurely. After the generating current is stopped at a false end point, a 20-sec delay occurs before current can again flow through the coulometric cell. This delay permits a time interval for the chemical reaction to take place.

An improved polarizing-current circuit that uses a type 5651 voltage regulator tube is a part of this titrator. The circuit permits a constant polarizing current of from 0 to 7.5 μa with a stability of better than 1% during a 10-hr period of time.

RADIOCHEMICAL ANALYSES

S. A. Reynolds

The portion of the work of the Radiochemical Analyses Group that is being reported in the open literature is increasing. For this reason, a minimum of descriptive detail appears in this report.

Nuclear Properties

Sc^{47} and Y^{91} (W. S. Lyon, B. Kahn[19]). The results of work on the decay schemes of Sc^{47} and of Y^{91} will appear in *The Physical Review.*

Decay Schemes of Several Nuclides (W. S. Lyon, T. H. Handley). Papers submitted for publication in *The Physical Review* have included information on Ho^{167}, Ca^{47}, the long-lived isomer of Al^{26}, and the neutron-deficient activities of terbium.

Half Lives of Several Nuclides (H. W. Wright, E. I. Wyatt,[20] S. A. Reynolds). The least-squares method was applied to decay data of a number of radionuclides to determine their half lives. These results will be included in a forthcoming open-literature publication.

Cross Section of Pt^{196} (W. S. Lyon). The thermal-neutron activation cross section of Pt^{196} was found to be 0.7 ± 0.1 barn. The experimental details have been reported to members of the Homogeneous Reactor Project.[21]

Measurement of Radioactivity

4π-Coincidence Method of Absolute Beta Disintegration Rate Determination (W. S. Lyon). Electronic equipment is now available and is being used to make 4π beta-gamma coincidence measurements. The method is believed to be the most accurate one yet devised for absolute measurements of disintegration rates.

The arrangement used is to place the 4π chamber that contains the sample to be assayed directly on top of the 3 × 3 in. sodium iodide gamma-ray spectrometer. The pulse-height selector on the spectrometer is then set to one gamma photopeak (usually the most energetic) in the sample to be assayed, and the slit width is opened to 10 v. Pulses from the differential discriminator of the spectrometer and the pulses from the 4π beta counter are introduced into a variable delay circuit, where the delay times are matched. The beta and gamma pulses then go into the coincidence circuit and out to either the beta or the gamma recorder. Coincident events are recorded on a coincidence recorder. Since the 4π beta counter has approximately 100% counting efficiency, the method is exceptionally useful for radionuclides that are accompanied by highly converted gamma rays.

The product of the observed beta counting rate times the gamma counting rate divided by the coincidence counting rate (after backgrounds and random coincidence corrections have been subtracted) is equal to the absolute disintegration rate of the sample. The method has been applied to a variety of radionuclides, including K^{42}, Sc^{47}, Ca^{47}, Co^{60}, and Ce^{141}. If there are approximately 100% beta-counting efficiency and a fairly clean gamma peak, many difficulties that are present in ordinary external beta–integral gamma coincidence counting are avoided.

[19] U.S. Public Health Service.

[20] Radioisotope Production Analyses Group.

[21] H. F. McDuffie and H. S. Pomerance, "Thermal Neutron Cross Sections of Platinum Isotopes," memo to J. A. Swartout (March 15, 1955).

Calibration for Measurement of Pa^{233} (W. S. Lyon). By use of the 4π-coincidence method, a sample of Pa^{233} was assayed and was used to obtain scintillation counter efficiencies for protactinium-233.[22]

Instrumental Methods

Analysis of Thorex Solutions by Gamma Spectrometry (H. W. Wright). The analysis of samples from Thorex process streams by gamma spectrometry is currently under way.[23] The results are to be compared with the results of radiochemical analyses of the same samples in order to evaluate the method. A report will be issued later.

Miscellaneous Analyses by Gamma Spectrometry (W. S. Lyon). Among the types of material examined for gamma components were activated stainless steels, reactor fuels, unidentified residues from loop experiments, and activated rare-earth materials.

Radioisotope Analysis

Table of Radioisotope Methods (S. A. Reynolds, W. S. Lyon, E. I. Wyatt[24]). A table that summarizes ORNL methods for the standardization and routine measurement of radioisotope products is in preparation. The information will be presented at the May meeting of the Beta and Gamma Ray Measurements and Standards Subcommittee of the National Research Council, and it will appear subsequently in the open literature.

Fission Products

Analysis of Biological Samples for Sr^{90} (T. H. Handley). Because of the presence of large amounts of phosphorus, calcium, and strontium (from bone) in biological samples, the results of radiochemical methods for strontium in biological samples were uncertain, and the method was time-consuming. Therefore an indirect method was used. A cation-exchange column was used to separate Y^{90} from the large amount of other material present. A radiochemical procedure for Y^{90} was then followed. For calculation, it was assumed that the daughter Y^{90} was in equilibrium with its parent Sr^{90} and that the amount of Sr^{90} present was therefore equal to the Y^{90} determined.

Extraction of Zirconium into Thenoyltrifluoroacetone (TTA)-Xylene (F. L. Moore). Further studies have been made on the extraction of zirconium into thenoyltrifluoroacetone (TTA)-xylene. A method has been developed for the rapid determination of Zr^{95} in fission-product solutions. Details will be published soon in the open literature.

Heavy Elements

Electrodeposition of Plutonium (F. L. Moore, G. W. Smith). A series of plutonium electrodeposits of 100-$\mu g/cm^2$ density on 0.5-in.-dia nickel foils is being prepared for the Physics Division. A low-geometry alpha counter has been set up and calibrated for the determination of the amount of plutonium on the foils. Preliminary preparations[25] from synthetic solutions have indicated that the electrodeposits are of adequate uniformity and adherence.

Gamma Spectrometric Determination of Am^{241} in Pu^{239} (S. A. Reynolds, F. L. Moore). Americium-241 decays approximately 40% by emission of 0.06-Mev gamma radiation.[26] No significant amount of such radiation is emitted by plutonium isotopes.[27] Measurement of the 0.06-Mev gamma radiation therefore furnishes a very sensitive method for the determination of Am^{241} in plutonium products. One product has been analyzed by this method and was found to contain 0.26% Am^{241} in terms of alpha activity, or 50 ppm by weight. Of several plutonium products examined qualitatively, all but one have been shown to contain Am^{241}. A conservative estimate of the sensitivity of the method permits the prediction that as little as 1 ppm of Am^{241} could be determined. A

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[22] W. S. Lyon, *Analytical Division Counter Efficiency for Beta and Gamma Counting of Pa^{233}*, ORNL CF-54-12-159 (Dec. 23, 1954).

[23] H. W. Wright, "Analysis of Thorex Solutions by Gamma Spectrometry," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 11.

[24] Radioisotope Production Analyses Group.

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

[26] H. Jaffe, T. O. Passell, C. I. Browne, and I. Perlman, "Gamma and X-Radiation in the Decay of Am^{241}," *Phys. Rev.* 97, 142 (1955).

[27] J. M. Hollander, I. Perlman, and G. T. Seaborg, "Table of Isotopes," *Revs. Mod. Phys.* 25, 469 (1953), esp. p 608–9.

systematic study of the method will be made, and the results will be given in a topical report.

Reactor Analyses

Determination of Specific Activity of Fe^{59} in Fuel Elements (G. W. Smith). In order to determine the extent of contamination by stable iron of MTR-irradiated fuel elements obtained from the Solid State Division, a method was developed for the determination of Fe^{59} specific activity. The iron is removed from the bulk of the fission products by ether extraction. It is then stripped into an aqueous phase, and the aqueous phase is divided. Total iron is determined in one portion. Iron-59 is determined in the other portion by addition of iron carrier, double acid-sulfide precipitation, hydroxide precipitation, and a series of ether extractions with back-extractions into water, until pure Fe^{59} is shown to be present as indicated by no change in count upon correction for yield of carrier. The extent of stable iron contamination after irradiation is estimated by comparing the experimental value for Fe^{59} with the value for Fe^{59} calculated from total iron, neutron flux, irradiation time, and cross section.

The significant results obtained on several fuel elements are given in Table 2.

The data show that the major part of the iron in the fuel elements results from contamination of the fuel elements after their removal from the MTR. The check analysis of the Inconel was considered satisfactory. A few more samples may be analyzed following attempts by the Solid State Division to reduce the contamination by stable iron.

Determination of Volatile Fission Products from Fuel Elements (G. W. Smith). In joint work with the ANP group of the General Electric Co., methods are being developed for determining fission products volatilized from irradiated fuel elements. The in-pile tests to date have included the irradiation of fuel elements in the LITR and the collection of volatile fission products from the cooling air by means of charcoal traps and scrubbers. The collection efficiency of traps and scrubbers is being tested.

Isotopes of iodine, tellurium, xenon, molybdenum, and other volatile fission products from samples of cooling air have been identified by their gamma spectra. Argon-41, produced in the LITR by (n,γ) reactions on the naturally occurring argon in the air stream, was also identified. The counting efficiency of the "Xenon" spectrometer,[28] which is on loan from the Solid State Division, was determined by calibration with known amounts of pure isotopes of gamma energies as great as 1.3 Mev. The disintegration rates of many of the volatile nuclides were determined with an accuracy of a factor of 2 or better. These experimentally determined disintegration rates agreed with values calculated by General Electric Co. personnel.

Because the "Xenon" spectrometer is only temporarily available, the ANP group of the

[28] W. A. Brooksbank and S. A. Reynolds, "Xenon Experiment – ANP," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 12.

TABLE 2. ACTIVITIES OF Fe^{59} IN FUEL ELEMENTS

Fuel Elements	Fe^{59} (d/min per 500 μl**) Calculated	Found	Stable Iron Contamination (%)
1	3.85×10^3	Low	High
2	4.53×10^3	$\leqslant 200$	$\geqslant 95$
3	3.28×10^3	$\leqslant 300$	$\geqslant 90$
4	7.21×10^3	$\leqslant 70$	$\geqslant 99$
5	2.66×10^4	7.63×10^3	71
Inconel*	4.29×10^4	4.03×10^4	6 (?)

*Analyzed to check the method; no fuel element present.

**500-μl aliquot of final extract.

General Electric Co. is contemplating purchase of a spectrometer. Various types, including multichannel devices with liquid scintillation detectors, are being considered.

Cyclotron Research

(p,2p) Cross Sections of Ni^{58} (W. S. Lyon, F. Green[29]). The determination of the (p,2p) cross sections of Ni^{58} is essentially complete, and results will be published in *The Physical Review.*

Ion Exchange and Chromatography

Protactinium Decontamination in Thorex Solutions (G. W. Smith). In continuation of the study reported previously,[30] ion-exchange batch and column experiments were carried out with Dowex 1 resin, protactinium, and fission-product tracers. A simple tentative method that requires about 4 hr of elapsed time was developed for the anion-exchange decontamination of protactinium from fission products in Thorex feed solutions. The thorium, rare earths, and part of the ruthenium, zirconium, and niobium are eluted in 9 *M* hydrochloric acid solution from a Dowex 1 resin column. The remainder of the ruthenium, zirconium, and niobium is eluted with an 8 *M* HCl–0.3 *M* oxalic acid solution; this elution leaves essentially all the protactinium on the column. Following the protactinium decontamination, the fission products can be determined with the gamma scintillation spectrometer by means of their respective gamma activities. When Thorex feed solutions become available, the method will be tested by use of solutions upon which routine radiochemical analyses have been made.

Electrodeposition

H. W. Wright S. A. Reynolds

Preliminary investigations are under way to determine the effectiveness of electrodeposition methods for the determination of radiocopper, radiotin, and radioantimony. The work on radiocopper is following the pattern of an investigation reported earlier,[31] which was interrupted because of other problems.

[29]Electronuclear Research Division.

[30]G. W. Smith, "Protactinium Decontamination in Thorex Solutions," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954,* ORNL-1788, p 15.

ACTIVATION ANALYSES

G. W. Leddicotte

Discriminatory Gamma Counter

W. A. Brooksbank S. A. Reynolds[32]
G. W. Leddicotte

A previous report[33] describes the use of a gamma scintillation spectrometer in activation analysis. However, because use of this instrument for the measurement of the gamma spectrum of an irradiated sample in the range of 0.040 to 2.0 Mev requires at least 30 min, it is not suitable for the determination of radioelements that have half lives of 30 min or less. A discriminatory gamma counter (Fig. 4) that uses the principles of the gamma scintillation spectrometer has been built. The counter measures the disintegration rates of the specific gamma radiations emitted by the sample and discriminates against gamma radiations of higher or lower energies. Secondary effects, especially Compton distributions that arise from radiations of higher energy than those discriminated against, are also counted. However, these effects are usually minor, and a correction can be made for them. The analytical data can be recorded in one of three ways: as a collection of counts by means of the scalers, as a Brown recording of continuous decay, or as a spectrum scan.

Examples of uses of the counter in the determination of radioelements of short half lives are given below. The counter has also been used successfully in the rapid assay of the radioactivity associated with individual long-lived radioelements that have been separated from an irradiated sample by a radiochemical procedure. In this application, the counter can minimize the effects of radioactive impurities, particularly in those analyses in which only a small amount of the radioelement of interest has been separated from large amounts of a radioactive matrix element(s).

[31]D. J. Coombe and S. A. Reynolds, "Activity Analyses by Electrodeposition. Copper," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954,* ORNL-1717, p 14.

[32]Radiochemical Research and Development Group.

[33]G. W. Leddicotte, J. E. Strain, and W. A. Brooksbank, "Determination of Microgram and Submicrogram Quantities of Elements by a Combined Neutron-Activation–Gamma-Spectrometer Technique," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954,* ORNL-1788, p 16.

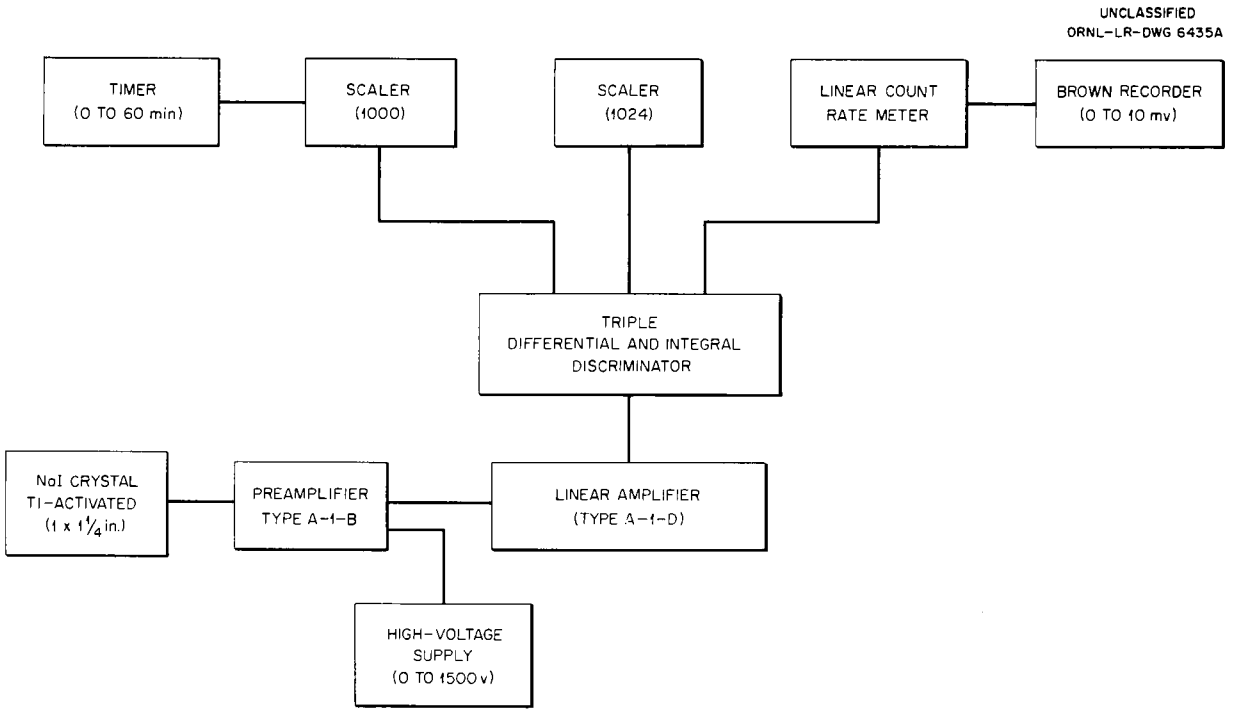

Fig. 4. Block Diagram of Discriminatory Gamma Counter.

Determination of Microgram Amounts of Vanadium in Titanium Dioxide

W. A. Brooksbank

Microgram amounts of vanadium can be determined in titanium dioxide by the nuclear reaction $V^{51}(n,\gamma)V^{52}$ (3.76 m). Because the half life of V^{52} is too short to permit the use of radiochemical separations, it is necessary to employ the discriminatory gamma counter, described above, in a method of nondestructive analysis. In this method, the counter is used to preferentially measure the 1.50-Mev gamma radiations from V^{52}. Interferences from the 0.32- and 0.91-Mev gammas of Ti^{51} (5.8 m) are negligible. However, if a sample contains aluminum as a contaminant, a correction must be made for the interference due to the Compton distribution effects of the 1.80-Mev gamma radiations from the induced Al^{28} (2.3 m). This correction can be accomplished by measuring only those gamma radiations of energies above 1.50 Mev at different counting times and then solving the simultaneous linear equations: $A_t = A^{Al} + A^V$ (total activity at ony time t = Al^{28} activity + V^{52} activity); $A_{t1} = A^{Al}(e^{-\lambda_1 t_1}) + A^V(e^{-\lambda_1 t_1})$ [total activity at some later time $t_1 = A^{Al}$ (at that later time) + A^V (at that later time)]. The term $e^{-\lambda_1 t_1}$ is simply the fraction of each activity at time t_1 and is calculated from the half life of the element(s) of interest. The equations can then be solved for the radioactivity due to V^{52} at time t. The comparator-sample technique is used; a known weight of vanadium as NH_4VO_3 is irradiated and processed in the same manner as the unknown sample.

When aluminum is present as an impurity, it is possible to determine vanadium in amounts greater than 10 μg only. The absence of aluminum permits the determination of amounts as small as 0.5 μg. The conditions for establishing these limits of detection were based upon 3.0-min irradiations in the ORNL Graphite Reactor. Vanadium can also be determined in other materials, such as nickel oxide and petroleum, by this method.

Determination of Microgram and Submicrogram Amounts of Aluminum, Magnesium, and Titanium in Nickel Oxide

W. A. Brooksbank

The nuclear reactions $Al^{27}(n,\gamma)Al^{28}$ (2.3 m), $Mg^{26}(n,\gamma)Mg^{27}$ (9.6 m), and $Ti^{50}(n,\gamma)Ti^{51}$ (5.8 m) can be used in activation analysis assays for

microgram and submicrogram amounts of aluminum, magnesium, and titanium, respectively, in nickel oxide. Because the half lives of Al^{28}, Mg^{27}, and Ti^{51} are too short to permit the use of radiochemical separation procedures in their determination, a nondestructive method of analysis that employs the discriminatory gamma counter, described above, was used. The elements were determined by irradiating the nickel oxide in the ORNL Graphite Reactor for short periods. The irradiated material was placed in the counter, and either the 1.80-Mev gamma radiation from Al^{28}, the 0.84-Mev gamma radiation from Mg^{27}, or the 0.32-Mev gamma radiation from Ti^{51} was measured; the comparator-sample technique was used. Interference from nickel was negligible. Limits of detection for the elements were: Al, 0.34 μg; Mg, 8.0 μg; and Ti, 15.0 μg. These limits can be lowered by use of the high neutron flux of the LITR. The same techniques of analysis can be used to determine these elements in materials other than nickel oxide.

Determination of Microgram and Submicrogram Amounts of Americium

W. A. Brooksbank

Microgram and submicrogram amounts of americium in such materials as AMEX process solutions can be determined by neutron activation analysis. The sample is irradiated, and the 0.053-Mev gamma radiation emitted in the decay of Am^{242m} in the nuclear reaction

$$Am^{241}(n,\gamma)Am^{242m} \xrightarrow[16.0\ h]{\gamma} Am^{242}$$

is measured by means of a gamma scintillation spectrometer. The comparator-sample technique is used. Interference from the 0.0597-Mev gamma radiation of Am^{241} is negligible. Quantities of americium as small as 10^{-3} μg have been determined by this method.

Determination of Nonmetals in Petroleum

J. E. Strain[34] W. A. Brooksbank
L. C. Bate

Determination of Chlorine. The nuclear reaction $Cl^{37}(n,\gamma)Cl^{38}$ (38.5 m) has been used to determine microgram and submicrogram amounts of chlorine in petroleum. The petroleum sample and a comparator sample are irradiated in the ORNL Graphite Reactor, and then the gamma spectrum of the induced Cl^{38} is measured directly by means of a gamma scintillation spectrometer. The photopeak area of either the 1.60- or the 2.15-Mev gamma radiation is integrated. Quantities of chlorine as small as 0.05 μg have been determined by this method.

Simultaneous Determination of Arsenic and Bromine. Microgram and submicrogram amounts of arsenic and bromine have been determined simultaneously in petroleum by the respective nuclear reactions $As^{75}(n,\gamma)As^{76}$ (26.8 h) and $Br^{81}(n,\gamma)Br^{82}$ (35.9 h). The petroleum sample and comparator samples are irradiated in the ORNL Graphite Reactor; then the gamma spectra of the induced As^{76} and Br^{82} are measured directly by means of a gamma scintillation spectrometer. The photopeak areas of the 0.550-Mev gamma radiation from As^{76} and of the 0.547- and 0.766-Mev gamma radiations from Br^{82} are integrated. Because the As^{76} peak occurs at 0.550 Mev and that peak is superimposed upon the 0.547-Mev peak of Br^{82}, the ratio of the bromine peaks to each other must be used to calculate the contribution of the 0.547-Mev Br^{82} to the composite photopeak area at 0.550 Mev. The difference is related directly to the amount of As^{76} in the sample. Amounts of arsenic and bromine as small as 0.02 and 0.008 μg, respectively, have been determined by this method.

Proper interpretation of the photopeak areas is essential in the spectrometric method. Another method, which employs the discriminatory gamma counter, described above, is being studied.

Identification of Contaminant Elements in Interstitial Implants

W. A. Brooksbank

Contaminant elements in metals used to make radioactive interstitial implants ("seeds") for use in cancer research were identified by activation analysis. Copper and gold wires, as well as chromium-plated copper and gold wires, were irradiated in the LITR. The radioelements induced into the stable isotopes of the contaminant elements were separated by a modification of Handley's method[35] and were identified by gamma

[34] U.S. Navy.

[35] T. H. Handley, "General Qualitative Analysis Scheme for Preliminary Examination of Radioisotope Products for Radioactive Impurities," Method Nos. 2 0913 and 9 0732009 (1-6-55), *ORNL Master Analytical Manual.*

spectrometry and decay measurements. Radionuclides of silver, tin, antimony, cobalt, and chromium (possibly a contaminant of the copper) were identified.

Identification of Contaminant Elements in Enzyme Solutions

W. A. Brooksbank

Neutron activation analysis has been used to identify contaminant elements in enzyme solutions. The solutions were irradiated in the ORNL Graphite Reactor. The radioelements induced into the stable isotopes of the contaminant elements were separated by a modification of Handley's method[35] and were identified by means of gamma spectrometry and decay measurements. Sodium was present in concentrations of the order of 1 to 2 ppm; radionuclides of lead, rhenium, arsenic, palladium, chromium, and silicon were indicated to be present.

Determination of Neutron-Induced Radionuclides in Monkey Blood

W. A. Brooksbank G. W. Leddicotte

Activation analysis techniques were applied to the assay of blood samples from monkeys used in a recent Tower Shielding Facility experiment. The radionuclides that were induced in their blood when they were irradiated during the experiment were determined. The results have been reported.[36]

Determination of Microgram Amounts of Silicon

W. T. Mullins G. W. Leddicotte

Microgram amounts of silicon have been determined in aluminum oxide, nickel oxide, zirconium, and hafnium by the nuclear reaction $Si^{30}(n,\gamma)Si^{31}$ (2.7 h). The samples were irradiated in either the ORNL Graphite Reactor or the LITR for at least 5.0 hr and were then processed by an isotopic-carrier method. A Geiger-Mueller counter was used to measure the Si^{31} radioactivity. The comparator-sample method of analysis was used. Amounts of silicon as small as 4.0 μg have been determined by this method. Silicon can be determined in other materials by the same method.

[36] W. A. Brooksbank and G. W. Leddicotte, *The Determination of Neutron Induced Activities in Animal Blood*, ORNL CF-55-2-87 (Feb. 15, 1955).

Determination of Relative Abundances of Cu^{63} to Cu^{65}

J. E. Strain[34] G. W. Leddicotte

Two rapid and sensitive methods can be used to determine the relative abundance of Cu^{63} to Cu^{65} in a mixture of these isotopes. One method is nondestructive and employs the nuclear reactions $Cu^{63}(n,\gamma)Cu^{64}$ (12.8 h) and $Cu^{65}(n,\gamma)Cu^{66}$ (5.1 m). The irradiated sample is put directly into a well-type gamma scintillation counter, and the decays of both the copper radioisotopes are followed by means of a photographic record of the data that appear on the recorders of the counters and timing devices. The other method employs the $Cu^{63}(n,\gamma)Cu^{64}$ reaction only; the Cu^{64} is electrodeposited and is measured by means of a gamma scintillation counter. The comparator-sample technique is used in each method.

Self-Absorption Effects in Neutron-Irradiated Materials

J. E. Strain[34] G. W. Leddicotte

Certain elements, when exposed to a neutron flux, absorb thermal neutrons very readily. For such elements, a neutron-flux differential exists during irradiation. In this phenomenon of "self-shadowing" or self-absorption, the neutron flux inside the sample (especially in the comparator sample) may be much less than that on the surface. This effect has been investigated for cobalt. The bias of the results is high if pure cobalt is used as a comparator sample. Self-absorption in cobalt can be minimized by dispersing the cobalt in magnesium fluoride. Additional work on cobalt is under way, and other elements of similar neutron-absorption characteristics will be studied.

New Applications of Activation Analysis

G. W. Leddicotte

Inquiries have been received regarding the suitability of activation analysis for the determination of microgram and submicrogram quantities of the following elements in the materials indicated: sulfur and phosphorus in chromium, phosphorus in aluminum and in aluminum oxide, thorium and uranium in river mud, rhenium in metals and alloys, and contaminant elements in water.

Particle-Size Distribution

R. E. Druschel G. W. Leddicotte
H. H. Miller[37]

The apparatus for the determination of particle-size distribution in thorium oxide slurries by activation analysis[38] has now been incorporated into a multiple-analysis unit. The method will be described in detail in a topical report.

Autoradiography

Uniformity of Electrodeposited Plutonium Oxide (W. A. Brooksbank, G. W. Leddicotte). The uniformity with which plutonium oxide can be electrodeposited upon metal surfaces was studied by an autoradiographic technique. A photographic plate (Eastman nuclear track plate, type NTA) of 50-μ emulsion thickness was placed in contact with the plutonium oxide deposit for 1 min. After the exposure, the plate was developed as described by Yagoda.[39] The uniformity of plutonium oxide deposits on metal plates of 3- and 5-in. diameters was examined in this way and also by measurement of the photographic density of the autoradiographs by means of a densitometer. Applications of the autoradiographic method to other alpha-particle-distribution studies are being made.

SPECTROCHEMICAL ANALYSES

C. Feldman

Rapid Separation of Microgram Quantities of Rare Earths from Gram Quantities of Thorium (Nitrated Cellulose–Batch Adsorption Method)

J. Y. Ellenburg C. Feldman

Microgram quantities of rare earths cannot be determined spectrochemically in the presence of thorium. It is therefore necessary to isolate and concentrate the rare earths before the spectrochemical determinations. Because the rare-earth contents of the thorium preparations that are usually dealt with are very small and may become smaller and because spectrographic sensitivity limits are usually absolute in nature, it is evident that the separation procedure must be applicable to large samples if necessary.

A batch separation procedure has been developed[40] that is a modification of the Kember[41] procedure employing a nitrated cellulose column and an ether–nitric acid elution. Whereas the column procedure is limited as to sample size and is time-consuming, the batch procedure is unlimited as to sample size and can be carried out in 30 min. The thorium in the sample is converted to $Th(NO_3)_4 \cdot 4H_2O$, which is dissolved in a minimum quantity of concentrated nitric acid, and sufficient diethyl or di-*n*-propyl ether is added to make the solution 12.5 vol % in ether. Approximately 2 g of slightly nitrated cellulose is then added to the solution, and the mixture is agitated for 5 min. Tracer studies with $Eu^{151,154}$ have shown that the rare earths are quantitatively adsorbed onto the cellulose during this agitation. The mixture is then filtered through a sintered-glass filter and washed with the nitric acid–ether mixture. The rare earths are desorbed from the cellulose by treatment with dilute nitric acid (pH 2.0). The resultant solution may contain 0.1 to 1 mg of thorium; this can be extracted from the solution at pH 1.0 with a 0.5 *M* solution of thenoyltrifluoroacetone (TTA) in xylene. The rare earths can then be isolated in a pure state by extraction with the same reagent at pH 4.5.

Separation of Gram Quantities of Thorium from Microgram Quantities of Rare Earths and Other Contaminants [Thenoyltrifluoroacetone (TTA) Extraction Method]

J. Y. Ellenburg D. E. Fornwalt
C. Feldman

Hyde and Tolmach[42] have shown that thorium can be extracted from aqueous solutions of pH 1.0 by 0.2 *M* solutions of TTA in benzene. Since the only other likely contaminants of thorium which are extracted at that pH are zirconium, iron, and scandium, this appeared to afford another method of separating thorium from most of its impurities,

[37] Ionic Analyses Group.

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

[39] H. Yagoda, *Radioactive Measurements with Nuclear Emulsions*, p 56–63, Wiley, New York, 1949.

[40] C. Feldman, "Separation of Rare Earths from Thorium by Adsorption on Cellulose, Batch Method," Method Nos. 1 00705 and 9 00650 (3-23-55) *ORNL Master Analytical Manual.*

[41] N. F. Kember, *The Extraction of Thorium Nitrate with Ether Containing Nitric Acid in the Presence of Activated Cellulose and the Application of this Process to the Analysis of Monazite Sands and Urano-thorianite*, CRL-AE-23 (Sept. 1948).

[42] E. K. Hyde and J. Tolmach, *TTA Extraction of Dilute Solutions of Thorium Nitrate and Uranyl Nitrate*, ANL-4248 (no date).

including the rare earths. Optimum conditions were found for performing this separation on the gram scale. Compared with the batch cellulose procedure, the TTA extraction has the advantage of yielding a solution in which all contaminants other than zirconium, iron, and scandium can be determined. However, because the major component, thorium, is extracted, the procedure cannot conveniently be used for samples that contain more than 5 g of thorium. A sample of this size will permit spectrochemical determination of the major rare earths usually present in purified thorium (e.g., 1 ppm of lanthanum, >25 ppm of neodymium, >15 ppm of cerium, 1 ppm of yttrium).

In a typical analysis, 0.5 g of thorium as the nitrate is dissolved in 500 ml of solution at pH 1.0. This solution is transferred to a 1-liter extraction flask of the type illustrated in Fig. 5, and 500 ml of a 0.5 *M* solution of TTA in benzene is added. The solutions are heated to 70°C to accelerate the extraction. The contents of the flask are then agitated vigorously with a high-speed stirrer for 10 min, and the extraction is repeated with a fresh portion of TTA solution.

Rare earths can be recovered quantitatively and freed of residual thorium by coprecipitation on ferric hydroxide, redissolution in a small volume, and re-extraction of thorium and iron under the above conditions.

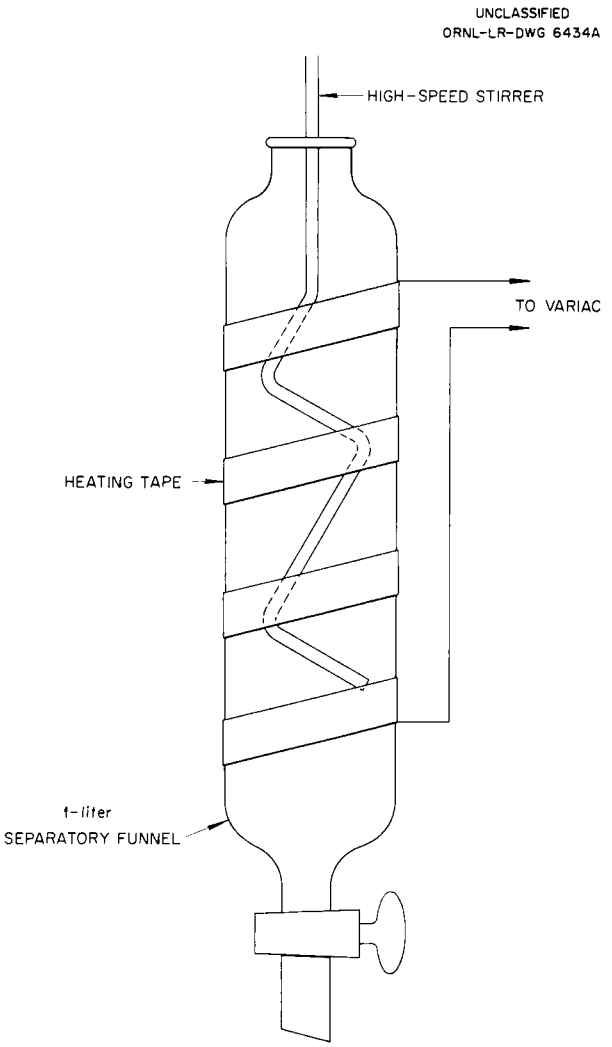

Fig. 5. Heated Flask for Thenoyltrifluoroacetone (TTA) Extractions.

Spectrochemical Determination of Traces (ppm Range) of Zirconium in Thorium and Its Compounds

D. E. Fornwalt

The 0 to 1000 ppm of zirconium often found in purified thorium cannot be determined spectrochemically without prior chemical separation from the thorium. This separation can be effected by preparing a chloride solution of the thorium in 1:1 hydrochloric acid and extracting the zirconium into a 0.5 *M* solution of TTA in xylene.[43] The solution is then agitated at 70°C for 10 min. The zirconium can be recovered by shaking the organic layer with an approximately 1 vol % aqueous solution of hydrofluoric acid. This solution can then be concentrated and the zirconium determined spectrochemically.

Attempts to Separate Thorium from Rare Earths with Acetylacetone, Disodium Dihydrogen Ethylenediaminetetraacetate, and Cupferron

J. Y. Ellenburg C. Feldman

Reports of the properties of metallic acetylacetonates by Steinbach[44] and by Staniforth[45] suggested that these compounds might be used to separate thorium from the rare earths. However, attempts to separate thorium(IV) from lanthanum(III) by extraction with acetylacetone at 20 and 55°C and at pH values from 0.5 to 3.5 gave

[43] W. M. Latimer, "Extraction of Zr by TTA," *Progress Report for July 1947*, BC-68, p 5.

[44] J. F. Steinbach, *Acetylacetone as an Analytical Extraction Agent* (Thesis, University of Pittsburgh), NYO-6347 (1953).

[45] R. A. Staniforth, *Chelate Compounds of the Rare Earth Metals* (Thesis, Ohio State University, 1943).

negative results in nitrate, chloride, and sulfate solutions. By complexing thorium with disodium dihydrogen ethylenediaminetetraacetate, it was possible to increase the pH of a solution of thorium to 10 without precipitating the thorium; addition of cupferron to this solution causes precipitation of thorium at any pH. However, lanthanum behaves in the same manner; therefore no separation is obtained.

Spectrochemical Determination of Traces (ppm Range) of Silicon in Thorium Dioxide

J. Y. Ellenburg C. Feldman

Attempts to determine traces (ppm range) of silicon in thorium dioxide with a sifter electrode[46] have been suspended pending acquisition of an Ebert spectrograph. It has been found that excellent precision can be obtained in this determination by completely burning a 2-mg sample of thorium dioxide (ThO_2) in a carbon arc, with boron oxide (B_2O_3) used as an internal standard. However, contamination from atmospheric dust is so severe a problem with a 2-mg sample that efforts are presently being made to use a carrier-distillation technique, which employs gallium sesquioxide (Ga_2O_3) as the carrier and germanium dioxide (GeO_2) as the internal standard.

Development of Analytical Curves (Porous-Cup Technique)

M. M. Murray A. J. Estepp D. E. Fornwalt

Analytical curves were developed for determining the metals listed in Table 3 by the porous-cup method.

INORGANIC PREPARATIONS

D. E. LaValle

Special Preparations

D. E. LaValle

In further preparations of ternary oxides of the general formula $LaMO_3$ for the Nuclear Physics and Neutron Diffraction Group of the Physics Division, the series from $LaMnO_3$ through admixtures of $LaMnO_3$ with $LaCrO_3$ to pure $LaCrO_3$ were made in 50-g quantities.

For the same group, two 40-g sections of crystal bar titanium were converted, one[47] to $TiH_{1.99}$ and the other[47] to $TiD_{1.98}$. Ten grams of B^{10} as the element was oxidized to $H_3B^{10}O_3$, and a 75-g quantity of anhydrous $MnCl_2$ was prepared. Also, several attempts were made to prepare Ti_2O_3 by the reaction of Ti with TiO_2 at high temperatures[48] (1600°C) in an induction furnace. Because of the limited inductive capacity of the charge, however, the best product was only about 90% Ti_2O_3.

For the Low Temperature Nuclear and Solid State Physics Group of the Physics Division, the following double and triple acetates of uranium

[46] J. Y. Ellenburg and C. Feldman, "Determination of Traces (ppm Range) of Silicon in Thorium Dioxide," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 26.

[47] T. R. P. Gibb, Jr., and H. W. Kruschwitz, Jr., "The Titanium-Hydrogen System and Titanium Hydride. I. Low-Pressure Studies," *J. Am. Chem. Soc.* **72**, 5365 (1950).

[48] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, p 909–11, F. Enkee, Stuttgart, Germany (1954).

TABLE 3. SPECTRAL LINES AND CONCENTRATION RANGES FOR NEW POROUS-CUP ANALYTICAL CURVES

Subject Metal	Concentration Range (ppm)	Spectral Lines	Internal Standard Metal	Concentration (ppm)	Spectral Lines
Co	5–200	3405 3409	V	50	3185
Hg	15–125	2536	In	1000	2560
Sn	25–200	3262	Co	75	3409 3489
Cd	30–500	3261	Co	75	3405 3409 3462

were prepared in the quantities indicated:

50 g of $Mn(UO_2)_2(C_2H_3O_2)_6 \cdot 12H_2O$,

100 g of $Co(UO_2)_2(C_2H_3O_2)_6 \cdot 7H_2O$,

200 g of $NaMn(UO_2)_3(C_2H_3O_2)_9 \cdot 10H_2O$,

100 g of $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 9H_2O$.

The triple acetate $NaCu(UO_2)_3(C_2H_3O_2)_9 \cdot 9H_2O$ was prepared in a 10-g quantity by use of depleted uranium that contained 99.998% U^{238}.

A series of low-bromide (<25 ppm) alkali-metal bromates are being prepared in 50-g quantities for the Nuclear Chemistry Group of the Chemistry Division. A stock quantity of $NaBrO_3$ was purified sufficiently by recrystallization, and $CsBrO_3$ was prepared in the pure form by the reaction of Cs_2SO_4 with purified $Ba(BrO_3)_2 \cdot H_2O$. Anhydrous lithium bromate, $LiBrO_3$, was also prepared, but its high solubility prevented sufficient purification by ordinary methods.

Miscellaneous preparations included 2 g of $ThSi_2$ (ref. 49) for the Spectrochemical Analyses Group of the Analytical Chemistry Division, and 15 g of diethoxyphosphinyl mercuric chloride[50] for the Scintillation Spectrometry and Instrument Development Group of the Physics Division.

Miscellaneous Preparations and Purifications

R. H. Sampley

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

Purified	Prepared
LiI	LiI
LiCl	Li^6I
HI	Li_2CO_3
$(NH_4)_2CO_3$	$Li_2^6CO_3$
$EuCl_3$ (< lb quantity)	$LiI \cdot 3H_2O$
	$Li^6I \cdot 3H_2O$
	HI
	$PbCO_3$ (< lb quantity)
	$2\ PbCO_3 \cdot Pb(OH)_2$ (< lb quantity)
	$Pb(ClO_4)_2 \cdot 3H_2O$ (saturated solution)
	Mo from MoO_3 (< lb quantity)

OPTICAL AND ELECTRON MICROSCOPY

T. E. Willmarth

F. M. Toomer T. G. Harmon
J. M. Smith

Qualitative Analysis by Electron Microscopy

The electron microscope was used to study the nature of the precipitate formed at grain boundaries in Zircaloy and the nature of the surface of single crystals of lithium fluoride before and after they were irradiated. In collaboration with the Metallurgy Division, electron micrographs were made of the pearlite in 1.0% manganese steels transformed at 620 and 690°C, 1.5% manganese steels transformed at 601 and 650°C, 1.8% manganese steel transformed at 660°C, and iron carbide steels transformed at 550, 600, and 660°C. The structure of zirconium-indium alloys was also observed.

Particle-Size Studies

The optical and electron microscopes were used to determine particle-size distribution in the following: caustic slurries of uranium-aluminum alloys, uranium dioxide, plutonium dioxide exposed in a titanium reactor, zirconium dioxide, zirconium dioxide treated with cold 4 *M* hydrochloric acid, zirconium dioxide treated with hot concentrated hydrochloric acid, sodium chloride crystals, metallic iridium, aluminum oxide slurries, polystyrene particles, lead sulfide, thorium sludge treated with nitric acid, thorium oxide calcined at 650, 750, 900, and 1300°C, Pilot Plant product thorium oxide that was sized by the hydroclave technique, ore-leach pulp that contained uranium, and ion-exchange resins.

Photomicrographic, Metallographic, and Autoradiographic Studies

The following were studied by optical microscopy, and the observations were reported: welded Zircaloy bombs, cold-swaged and hot-forged Zircaloy bar stock, Zircaloy welding rod, nickel-plated 24ST aluminum, and a plugged, type 347 stainless steel tube from a high-pressure loop that contained rare-earth sulfates. Autoradiographs were made of the inner surface of a

[49] G. F. Hardy and J. K. Hulm, "Superconducting Silicides and Germanides," *Phys. Rev.* 89, 884 (1953).

[50] R. B. Fox and D. L. Venezky, "Mercuration of Dialkyl Phosphonates," *J. Am. Chem. Soc.* 75, 3967 (1953).

plutonium-coated Zircaloy tube and of a filter on which uranium and fission products were deposited.

Methods Development and Special Problems

Work has been done to develop the following: an improved method for removing oxide films from zirconium, from Zircaloy, and from titanium for electron microscopic examination; a method for producing thin carbon films of extensive surface area; and a reliable nonstaining etch for Zircaloy and titanium to be used where the surfaces of these metals are to be replicated for electron microscopy. Also, an anodic stain method to be used in the study of grain-boundary precipitation in Zircaloy has been evaluated. An experiment, which uses microscopy and electron diffraction, is now in progress to determine the nature and mechanics of oxide film growth on Zircaloy in air after various times and at various temperatures. This work is preliminary to a study of the process of formation and of the nature of Zircaloy films that are formed in acidic solutions.

Corrosion Studies

The nature of the metallic oxide films and corrosion products formed during exposure of metals to solutions and slurries of interest in reactor development continues to be a subject for study. Oxide films formed on type 347 stainless steel in the presence of chromate ion were studied; the results were similar to those given previously.[51] Electron microscopic studies of replicated surfaces of coatings formed in such a manner at the oxide-solution interface indicate that chromate ion in the solution produces a tough, seemingly impermeable layer of closely bonded, triangular-shaped crystals that are randomly oriented. Lattice spacings calculated from electron and x-ray diffraction patterns of this material did not match any of the indexed spacings of known metallic oxides. Of interest is the observation that the Fe_2O_3 layer, which is usually formed at the oxide-solution interface under the same temperature conditions when chromate ion is absent, was now found beneath this unidentified top layer. This would suggest that diffusion of ferric ion for reaction at the oxide-solution interface has been curtailed by the growth of this new layer.[52] Electron microscopy of oxide films that were stripped from a type 347 stainless steel aperture in a thorium oxide loop indicated that the material at the oxide-solution interface was a thick, closely bonded layer of thorium oxide aggregates of uniform size. The presence of these aggregates, which ranged in diameter from 0.2 to 0.4 μ, suggests the possibility that the characteristics of thorium oxide slurries under thorium oxide loop conditions are dependent upon the exposed surface areas of primary aggregates rather than upon the nature of the secondary particles. It was also observed that the plating out of the thorium oxide seemed to be preferential in relation to the contours of the metal surface on which it impinged.[53]

An electron diffraction and microscopic study of oxide films stripped from Zircaloy test bombs that were exposed to uranyl sulfate solutions at 250°C showed the presence of a striated double-layer film composed of two phases of zirconium dioxide. The metastable tetragonal phase was found at the oxide-metal interface, and the stable monoclinic phase at the oxide-solution interface. Other corrosion films and products that were studied included the bulk oxide formed on type 347 stainless steel in a loop that contained uranyl sulfate and neodymium sulfate, type 347 stainless steel exposed[54] for 2265 hr to a solution of 15 g of UO_2SO_4 per milliliter of 0.006 *M* sulfuric acid at 320°C, Zircaloy exposed to a phosphoric acid solution at 250°C, type 347 stainless steel exposed for 200 hr to 0.05 *M* phosphoric acid at 250°C, and the deposit formed on a nickel calorimeter during high-temperature operation *in vacuo*.

ORNL MASTER ANALYTICAL MANUAL

Authors of Methods

H. P. Raaen H. P. House

Forty-six new methods have been issued to the *ORNL Master Analytical Manual*; they are listed in the section of this report entitled "Presentations of Research Results." Eighteen new manuals were issued. The lists of methods yet to be written for the *Manual* were revised to bring them up to date.

[51] T. E. Willmarth, "Corrosion Studies," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 28.

[52] T. E. Willmarth, *Test Run of H-46*, ORNL CF-55-1-44 (Jan. 7, 1955).

[53] T. E. Willmarth, *Study of the Oxide Films Formed on the Aperture Plate in the Thorium Loop*, ORNL CF-55-2-24 (Feb. 3, 1955).

[54] T. E. Willmarth, *Run-A-72*, ORNL CF-55-1-64 (Jan. 13, 1955).

SERVICE ANALYSES

A semiannual summary of the service analyses made at the X-10 laboratories of the Analytical Chemistry Division is given in Table 4.

IONIC ANALYSES

P. F. Thomason

Most of the service work of the Ionic Research and Development Group continued to be for the Chemistry Division relative to their phase and corrosion studies for the HRT. The methods that were used have been discussed previously.[1]

RADIOCHEMICAL ANALYSES

S. A. Reynolds

Most of the service work of the Radiochemical Analyses Group was done for the Chemical Technology, Health Physics, and Operations Divisions and for the ANP Group of the General Electric Co. Gamma spectrometry was the most important technique employed in determining identities and quantities of radioactive species. Some of the samples submitted by the Health Physics Division required separation of small quantities of radioelements from the products of the wet-ashing of biological material. Radionuclides of more than routine interest that were assayed or studied included $As^{73,74}$, Cd^{109}, I^{125}, I^{129}, Ce^{139}, and Ir^{192}. Further details are given in this report (cf. "Radiochemical Analyses").

ACTIVATION ANALYSES

G. W. Leddicotte

The extent of interest that has been shown by the Oak Ridge plants and outside organizations in activation analysis service is summarized in Table 5. The difference in number between the inquiries and the request for analyses that have been received from outside organizations can be explained, in part, by the normal time lag required for submission of samples. The following elements were determined in a variety of materials: antimony, arsenic, copper, cobalt, calcium, zinc, phosphorus, boron, iron, chromium, silver, gold, chlorine, bromine, aluminum, vanadium, thorium, titanium, zirconium, hafnium, cadmium, silicon, tungsten, sodium, potassium, rubidium, cesium, strontium, tin, mercury, uranium, selenium, indium, tantalum, nickel, manganese, molybdenum, magnesium, lanthanum, and gallium. In addition to this work, the particle-size distribution was determined in a large number of thorium oxide samples.

GENERAL ANALYSES LABORATORY

J. H. Edgerton

General Analyses

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

A variety of wet-chemical analyses, characterized by difficult separations that resulted from unusual sample compositions, were completed for the Chemistry, Chemical Technology, Health Physics, Metallurgy, Operations, and Solid State Divisions. Electrolysis, ion exchange, and extraction proved to be the most effective separation methods. Calcium was separated from lead and magnesium was separated from cadmium by electrolysis; deposition at a mercury cathode was used in the analysis of steels, Inconel, thorium alloys, and uranium alloys. Both cation- and anion-exchange resins were utilized for the separation of uranium and boron from aluminum.

Separations and colorimetric determinations of aluminum, chromium, iron, magnesium, nickel, silicon, sulfate, titanium, and uranium were made on various alloys and solutions. Polarographic analysis was applied to the determination of sulfur, cadmium, lead, uranium, and tin. Gravimetric methods were employed in analyses for aluminum, calcium, germanium, lead, magnesium, nickel, niobium, cadmium, silicon, silver, thorium, tin, and zinc. The automatic potentiometric titrator was used in the determination of boron, bromide, chloride, manganese, silver, and uranium. Barium, boron, and vanadium, as well as calcium in the presence of large quantities of lead nitrate, were determined by flame photometry.

A quality control program has been established for the colorimetric determination of chromium, iron, nickel, and uranium.

[1] P. F. Thomason, "Ionic Analyses – Development Group," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1951*, ORNL-955, p 65.

TABLE 4. SUMMARY OF ANALYTICAL SERVICE WORK AT X-10 FOR THE PERIOD ENDING APRIL 20, 1955

	Number of Personnel		ORNL Divisions Requesting Analyses																	Others Requesting Analyses						
	Technical	Nontechnical	Analytical Chemistry	ANP Project	Biology	Chemical Technology	Chemistry	Electronuclear Research	Engineering and Mechanical	General Office	Health Physics	HRP	Instrumentation and Controls	Metallurgy	Operations	Physics	REED	Solid State	Stable Isotopes	Director's Division	General Electric	K-25	Y-12	Pratt & Whitney	Others	Total Determinations
Group Making Analyses			Number of Determinations																							
Activation Analyses*	5	5	620	36	63	393	96	14			22			182	870	25	5		5				12			2,343
General Analyses	7	6		1335		667	128		42		597	5		2116	478	111		116								5,595
Ionic Analyses*	7	1	38			78	561							35	23	47										782
Laboratory and Semi-Works Control	3	8				13,376	44					8		285	23	7										13,743
Optical and Electron Microscopy*	3	1	154			741	208				20	197		196	6			44								1,566
Pilot Plant Control	7	13				19,849											302									20,151
Plutonium Isolation Laboratory	4	3				4,204	32	13			10	64					8								18	4,349
Radiochemical Analyses*	7	1			8	81	8	28			63			33	60	10	29	44	16	4	166					550
Radioisotope Production Control	3	18				3,009	82				479				7733	190	226	18			249	72		10		12,068
Reactor Analyses	2	4	1			103	90					100					822									1,116
Special Analyses	4	5				5,780												4								5,784
Spectrochemical Analyses*	5	0		26		266	112		2	7	7		2	400	77	41	46	10								996
Totals	57	65	813	1397	71	48,547	1361	55	44	7	1198	374	2	3247	9270	431	1438	236	21	4	415	72	12	10	18	69,043

*These groups also do research and development.

TABLE 5. SUMMARY OF ACTIVATION ANALYSIS SERVICES

Period	Inquiries from Outside Organizations	Requests for Analyses	
		From Oak Ridge* Plant Sites	From Outside Organizations
Prior to September 1, 1954	333	264	110
September	3	17	2
October	4	13	1
November	4	11	1
December	10	15	8
January 1955	12	13	5
February	13	15	4
March	15	18	7
	394	366	138

*Same as number of inquiries.

Vacuum-Fusion Analyses

H. G. Davis J. H. Edgerton

A new vacuum-fusion apparatus was purchased from National Research Corp., Cambridge, Massachusetts, and installed. It features a high-temperature furnace of the Guldner type and mercury cutoffs instead of stopcocks. The furnace can maintain temperatures as high as 2400°C for long periods of time. The mercury cutoffs eliminate contamination by stopcock grease and leakage. A Toepler pump is used to transfer the gases into a calibrated McLeod gage, where they are measured. The new apparatus extends the limits of detection of hydrogen, nitrogen, and oxygen. It has been used in the analysis of chromium-molybdenum-nickel alloys and of titanium, zirconium, and thorium.

A micro Kjeldahl apparatus was constructed to determine nitrogen in metals for the purpose of comparing the results with those obtained by vacuum-fusion analysis. Results of the analysis of thorium and zirconium agree remarkably well with the results by vacuum-fusion analysis. The use of Nessler's reagent and spectrophotometric measurements of the ammonia in the Kjeldahl distillate permits the determination of nitrogen in the concentration range of 1 to 10 ppm.

There are no vacuum-fusion standards available for such metals as thorium, titanium, and zirconium; hence it was necessary to construct an apparatus for the preparation of standards of hydrogen, nitrogen, and oxygen. The apparatus consists of a furnace, calibrated volume, McLeod gage, diffusion pump, and a means of admitting a small amount of the particular gas to a calibrated volume.

Because of the low carbon content of alloys, a preliminary investigation of the low-pressure-combustion vacuum-fusion method for the determination of carbon was made.[2] This technique is very precise and can be used to detect as little as 1 μg of carbon in a 0.5-g sample. An apparatus is being considered for construction and subsequent use in conjunction with vacuum-fusion analysis.

RADIOISOTOPE PRODUCTION ANALYSES

E. I. Wyatt

The half lives of several radionuclides were determined; the data are presented in Table 6. Three samples of Se^{75}, two of Rb^{86}, and one each of the other radionuclides listed were studied. With the exception of Pr^{143}, each sample was scanned for gamma-emitting impurities by means of the gamma scintillation spectrometer both before and after the period of observation; none were found.

[2] J. H. Edgerton and H. G. Davis, *Investigation of Vacuum Fusion and Other Equipment for the Determination of Oxygen, Hydrogen, Nitrogen, and Carbon in Non-Ferrous Metals and Alloys*, ORNL CF-54-9-16 (Sept. 2, 1954).

TABLE 6. OBSERVED HALF LIVES OF SOME GAMMA-EMITTING RADIONUCLIDES

Radionuclide	Period of Observation (days)	Half Life (d)	Instrument Used	Reaction Used to Produce the Radionuclide
Co^{56}	436	78	High-pressure gamma chamber	$Fe^{56}(p,n)Co^{56}$
Fe^{59}	245	45	High-pressure gamma chamber	$Fe^{58}(n,\gamma)Fe^{59}$
Se^{75}	414	121	High-pressure gamma chamber	$Se^{74}(n,\gamma)Se^{75}$
Rb^{86}	58	19.0	Gamma scintillation counter	$Rb^{85}(n,\gamma)Rb^{86}$
In^{114m}	260	49.5	High-pressure gamma chamber	$In^{113}(n,\gamma)In^{114m}$
Ba^{131}	48	12.0	Gamma scintillation counter	$Ba^{130}(n,\gamma)Ba^{131}$
Pr^{143}	38	13.7	Geiger-Mueller counter	(Fission)

A new gamma scintillation spectrometer, built by the ORNL Instrument Department, is in use. It consists of a regulated high-voltage power supply, a linear amplifier, a differential-integral pulse-height selector, a 1024 scaler, and a detector made up of a well-type sodium iodide crystal sealed onto a Dumont 6292 photomultiplier tube. The resolution of the detector is about 10% for Cs^{137}. This spectrometer is being used currently to determine Zr^{95} and/or Nb^{95} in samples that contain other gamma emitters; the necessity of complete purification of the sample is thereby eliminated.

LABORATORY AND SEMI-WORKS CONTROL GROUP

L. T. Corbin G. R. Wilson

The Chemical Technology Division requested 97% of the analyses done by the Laboratory and Semi-Works Control group in the past six months; the Chemistry, Metallurgy, Operations, and Physics Divisions and the HRP requested the other 3%. The interference of iron in the sodium tungstate method for vanadium was shown to be eliminated by ether extraction of the iron.[3] Also, it was shown that the addition of aluminum nitrate will eliminate the interference of phosphate in the Thoron colorimetric procedure for thorium.[4]

PILOT PLANT CONTROL LABORATORY

L. T. Corbin C. E. Lamb

The training of Pilot Plant Control Laboratory personnel in the analysis of samples from the Thorex pilot plant has been completed. Major determinations required are thorium,[5] protactinium,[6] uranium-233,[7] and gross gamma.[8] Additional methods have been employed for the routine determination of mercury,[9] thorium in tributyl phosphate (TBP)–Amsco solutions,[10] and fluoride in thorium nitrate solutions.[11] Also, a modification of the hexone extraction method[7,12] has been

[3] J. E. Morton, Secret Notebook No. 4047, p 21–22, Oct. 26, 1954.

[4] *Ibid.*, p 34–36, Nov. 21, 1954.

[5] G. R. Wilson, "Thorium, Spectrophotometric Thoron Method," Method Nos. 1 218710 and 9 00718710 (3-26-54), *ORNL Master Analytical Manual.*

[6] S. A. Reynolds and F. L. Moore, "Protactinium-233 in Thorex Process Solutions, Diisobutylcarbinol Extraction Method," Method No. 9 0123670 (9-30-54), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and III.

[7] G. R. Wilson, "Uranium-233 in Thorex Process Solutions, Hexone Extraction Method," Method No. 9 0123920 (6-25-53), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and III.

[8] E. I. Wyatt, "Gross Gamma," Method No. 9 0733002 (8-14-53), *ORNL Master Analytical Manual.*

[9] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2d ed., p 444–446, Interscience, New York, 1950.

[10] P. F. Thomason, "Determination of Microgram Amounts of Thorium in Tributyl Phosphate–Amsco Solutions," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 2.

[11] J. G. Surak and P. F. Thomason, "Semimicrodetermination of Fluorides in Metal Dissolver Samples of the Thorex Process by Pyrohydrolysis," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 6.

[12] J. E. Morton, *Study of Hexone Extraction of Uranium-233 Using Aluminum Nitrate as a Salting Agent*, tentative method, available from J. E. Morton, Special Analyses Laboratory.

used for the determination of trace quantities ($<10^3$ counts/min/ml) of U^{233} in solutions that contained as much as 300 mg of thorium per milliliter. New equipment (cf. "Remotely Controlled Falling-Drop Densimeter," this report) for measuring remotely the specific gravity of Thorex feed solutions by the falling-drop method has greatly reduced the radiation exposure, the time required for the determination, and the physical fatigue of the operator.

Decontamination tests were made on highly contaminated equipment with the use of alternate washes of 20% sodium hydroxide–2% sodium tartrate (citrate and/or oxalate) solution and of 30% nitric acid. The wash solutions from these tests were analyzed for thorium,[5] protactinium,[6] and uranium-233.[7] Interfering ions were destroyed by fuming the samples with nitric acid–potassium perchlorate.

The majority of the remaining analyses were for the Metal Recovery Unit of the Chemical Technology Division relative to their programs shown in Table 7.

The metal recovery process is now in operation to recover uranium and plutonium from Brookhaven reactor fuels. Major determinations required are uranium by colorimetric[13] and fluorometric[14] methods and plutonium.[15]

Fluoride in uranium tetrafluoride samples from the Excer process is being determined by pyrohydrolysis for the Unit Operations Group of the Chemical Technology Division.

[13]U. Koskela and C. E. Lamb, "Uranium, Spectrophotometric Ammonium Thiocyanate Method," Method Nos. 1 219210 and 9 00719210 (11-12-53), *ORNL Master Analytical Manual.*

[14]R. L. Walker, "Uranium, Fluorometric Method," Method Nos. 1 219240 and 9 00719240 (7-10-53), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and III.

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

TABLE 7. CHEMICAL TECHNOLOGY DIVISION PROGRAMS THAT ESPECIALLY REQUIRE SERVICES OF PILOT PLANT CONTROL LABORATORY

Program	Material Processed	Purpose	Major Analyses Required
Clementine	Plutonium reactor fuel	To decontaminate and recover plutonium	Plutonium,[a] Am^{241}[b]
Interim-23	Irradiated thorium	To isolate U^{233} from thorium	Thorium,[c] U^{233},[d] gross gamma,[e] protactinium[f]
HRE fuel recovery	HR fuel	To decontaminate U^{235}	Gross beta,[g] uranium,[b,i] gross gamma[e]

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

[b]G. W. Smith, "Americium-241," Method No. 2 31030 (5-18-54), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and II.

[c]G. R. Wilson, "Thorium, Spectrophotometric Thoron Method," Method Nos. 1 218710 and 9 00718710 (3-26-54), *ORNL Master Analytical Manual.*

[d]G. R. Wilson, "Uranium-233 in Thorex Process Solutions, Hexone Extraction Method," Method No. 9 0123920 (6-25-53), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and III.

[e]E. I. Wyatt, "Gross Gamma," Method No. 9 0733002 (8-14-53), *ORNL Master Analytical Manual.*

[f]S. A. Reynolds and F. L. Moore, "Protactinium-233 in Thorex Process Solutions, Diisobutylcarbinol Extraction Method," Method No. 9 0123670 (9-30-54), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and III.

[g]R. L. Walker, "Gross Beta Activity in Aqueous or Organic Solutions," Method Nos. 9 012302 and 9 052302 (10-8-53), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and III.

[h]U. Koskela and C. E. Lamb, "Uranium, Spectrophotometric Ammonium Thiocyanate Method," Method Nos. 1 219210 and 9 00719210 (11-12-53), *ORNL Master Analytical Manual.*

[i]R. L. Walker, "Uranium, Fluorometric Method," Method Nos. 1 219240 and 9 00719240 (7-10-53), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and III.

ISOLATION ANALYSES

L. T. Corbin J. H. Cooper

Most of the work of the Isolation Laboratory was for the Chemical Technology Division relative to HR fuel reprocessing. The principal determinations were total plutonium by the lanthanum fluoride method[16] and plutonium valences by the Berkeley method.[17]

The Chemical Technology Division was assisted in the preparation of thorium samples for study of radioactive growth from Th^{228}. A thorium sample was decontaminated by solvent-extraction and ion-exchange methods. The thorium was extracted into a tributyl phosphate–Amsco solution and stripped into 0.2 *M* nitric acid. Protactinium contamination was removed from the nitric acid strip by extraction into hexone. The thorium solution was passed through an anion-exchange resin column, and thorium was extracted from the effluent into mesityl oxide. A water strip from the mesityl oxide phase was analyzed for total thorium and was saved for periodic scintillation counting in order to follow the growth of the daughters of Th^{228}.

The Isolation Laboratory participated in two "round-robin" analyses of plutonium. The first plutonium sample, in nitric acid solution, was analyzed at several AEC installations. The results from the Isolation Laboratory agreed favorably with those from the other sites. The second "round-robin" analysis was that of high-purity plutonium metal. A sample was weighed and then dissolved in hydrochloric acid, and the solution was analyzed for plutonium. The results of the second analysis have not been compiled. Anyone desiring high-purity plutonium (99.8%) should contact L. T. Corbin of the Analytical Chemistry Division.

The Isolation Laboratory separated thorium, U^{233}, and Pu^{239} from fission products and determined the background counts of the separated elements on the scintillation counter and on the ion chamber.

[16] R. L. Walker, "Plutonium, Lanthanum Fluoride Method," Method Nos. 2 31620 and 9 008620 (5-19-53), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I, II, and III.

SPECIAL ANALYSES LABORATORY

L. T. Corbin W. R. Laing

A variety of analyses were performed by the Special Analyses Laboratory. Thorium chloride samples were analyzed for thorium, chloride, thorium dioxide, and water, and their insolubility in methanol was determined. Nitrogen was determined in thorium amalgams and in thorium metal by a micro Kjeldahl distillation, followed by color development with Nessler reagent. The dithizone method has been employed for the determination of microgram quantities of mercury in thorium metal and for mercury in the presence of milligram quantities of uranium. Thorium in the quantity range of 60 μg to 6 mg was titrated photometrically with disodium dihydrogen ethylenediaminetetraacetate. Preliminary results indicated an error of 5% in the 0.6- to 6-mg range and an error of 10% for a quantity of 60 μg. Microgram amounts of chloride in thorium amalgams were determined by leaching with water, followed by a potentiometric titration. Silver, lead, and copper in thorium oxide samples have been determined with dithizone reagent. An automatic velocity-servo titrator was tested and used to determine uranium in the quantity range 25 to 35 mg, with a relative standard deviation of 0.11%.

HIGH-RADIATION-LEVEL ANALYTICAL FACILITY

E. J. Frederick

Construction of the High-Radiation-Level Analytical Facility was begun on October 25, 1954 by the Helrich Construction Co., Knoxville, Tennessee. The construction is approximately 40% completed.

Contracts have been let for the items listed in Table 8 that are to be purchased by Oak Ridge National Laboratory.

Equipment and Methods for High-Radiation-Level Analytical Facility

R. H. Powell

Work to establish the equipment and methods suitable for use in the High-Radiation-Level Ana-

[17] F. L. Moore, "Plutonium(III,IV) and Plutonium(V,VI), Lanthanum Fluoride Method," Method Nos. 2 31622 and 9 008622 (in press), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and II.

TABLE 8. ITEMS BEING PURCHASED FOR THE HIGH-RADIATION-LEVEL ANALYTICAL FACILITY

Item	Quantity	Supplier	Cost
Argonne model 8 master-slave manipulators*	15	American Machine & Foundry Co., Brooklyn, N. Y.	$52,700
Cerium glass (density = 3.27) package window for storage cells**	1	Corning Glass Works, Harrodsburg, Ky.	9,930
Zinc bromide solution	1045 gal	Michigan Chemical Corp., St. Louis, Mich.	13,432
Heavy plate commercial lime glass**	7 pieces (2 ft × 4 ft × 1 in.)	Pittsburgh Plate Glass Co., Pittsburgh, Pa.	343
Nonbrowning optical quality lime glass**	7 pieces (3 ft × 4 ft × 1 in.)	Bienenfeld Glass Works, Inc., Brooklyn, N. Y.	1,286
No. 116 Koroseal gasket material**	350 lin ft	B. F. Goodrich Co., Marietta, Ohio	110

*Anticipated delivery date, May 15, 1955.
**Delivered.

lytical Facility[18–20] has continued. Argonne model 8 master-slave manipulators ("through-the-wall" type) have been ordered. However, alterations will be required to the master grips, actuator switches, detonging devices, and boots. Specifications for an acceptable detonging device have been established, and a trial model is being constructed. A redesigned manipulator boot is being proposed. A model 8 manipulator, loaned by the Operations Division, has been installed in the hot-cell mockup in order to study further the alterations to it that will be required. High operator-fatigue is coincident with the use of the manipulators; this indicates the necessity for increasing the personnel allocation to the High-Radiation-Level Analytical Facility.

Certain other equipment has been tested directly for use in the High-Radiation-Level Analytical Facility. A Dietzgen model 6385 20X transit, which is a 12-in. internal-focusing monocular telescope, has been found suitable for detecting a volume change as small as 0.002 ml in a 2-ml microburet when the buret is viewed from outside the hot cell through the transit. The stability of the Bausch & Lomb Spectronic 20 spectrometer was determined over a 24-hr period; however, other considerations favored the Densichron-type instrument. A Voland model 75OD Speedigram balance was altered for use within the hot cell. A mechanical shaker, designed by N. D. Lee, was compared with a magnetic stirrer; the magnetic stirrer is preferred because of lower initial cost and fewer maintenance problems. A light-weight basket has been designed that will permit more effective use of the "blind recess" of the access drawers of the hot cell.

Re-examination of certain analytical operations for possible ways of simplification was recommended, for example, the substitution of a solvent-extraction method for the ion-exchange method of isolation of U^{235}, which can then be determined outside the cell. A similar re-examination of the spectrophotometric method for the determination of iron in HR fuel[21] resulted in the simplification

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

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

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

[21] A. D. Horton, "Spectrophotometric Determination of Iron in HRP Materials," Method No. 9 08204 (in press), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and III.

reported earlier.[22]

Work space for specific analytical operations has been allocated tentatively; consideration was given to the nature of the operations and to the anticipated work load.

REACTOR ANALYSES

U. Koskela

The analysis of in-pile loop and bomb samples for the HRP constituted the majority of the work of the Reactor Analyses Group. Preparatory to relocation of the Reactor Analyses Group in the High-Radiation-Level Analytical Facility, new personnel are being trained.

Determination of Lithium in In-Pile Loop Samples

W. R. Warren H. L. Webb
J. Slessinger, Jr.

In the LITR in-pile loop experiments, sampling techniques require flushing of the sample lines with water between sampling operations. In order to determine whether the samples are being diluted, the Radiation Corrosion Group of the HRP intends to add lithium sulfate solution to the wash water as a tracer. The lithium is to be determined by means of a flame photometer that is now ready for use. There was no interference in the flame photometric determination of lithium in "cold" synthetic HR samples that contained uranium, copper, and nickel, as well as lithium.

[22]A. D. Horton and C. L. Burros, "Simplification of Spectrophotometric Determination of Iron in Homogeneous Reactor Fuel," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 4.

[23]M. T. Kelley, R. M. Farnham, and H. L. Hemphill, "Shielded Filter Photometer," *Anal. Chem. Semiann. Prog. Rep. Apr. 20, 1953*, ORNL-1547, p 2.

Precision of Uranium Determination

C. P. Baker

The relative standard deviation of the results of the colorimetric determination of uranium by the thiocyanate method when the ORNL model Q-1201 shielded filter photometer[23] was used has been found to be 1.8%; 41 aliquots from the same standard solution of uranium were analyzed during two weeks.

Evaluation of the use of macroburets with the ORNL model Q-945 automatic titrator was mentioned previously.[24] The results of analyses of "cold" samples indicated that approximately 5 mg of uranium was titrated with a relative standard deviation of 0.25%. When the High-Radiation-Level Analytical Facility is completed, an evaluation of the automatic titrimetric determination of uranium by remote control will be made.

Determination of Cobalt in In-Pile Loop Samples

W. R. Warren J. Slessinger, Jr.

Cobalt in HR fuels is usually determined polarographically.[25] However, since an independent check method was needed, the potentiometric method of Thomason[26] was used; results by the two methods checked satisfactorily.

[24]C. P. Baker, "Precision of Uranium Determination by Means of the ORNL Model Q-945 Automatic Titrator," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 37.

[25]U. Koskela, "Determination of Nickel and Cobalt in Homogeneous Reactor Solutions," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 37.

[26]P. F. Thomason, "Automatic Potentiometric Titration of Microgram Quantities of Cobalt," *Anal. Chem. Quar. Prog. Rep. Oct. 10, 1950*, ORNL-867, p 11.

ANALYTICAL CHEMISTRY DIVISION - Y-12 SITE

RESEARCH AND DEVELOPMENT

ANP ANALYTICAL CHEMISTRY

J. C. White

The status of work in progress in the ANP Analytical Chemistry Laboratory is reported elsewhere.[1,2]

HRP ANALYTICAL CHEMISTRY

O. Menis

Spectrophotometric Determination of Nickel

O. Menis

Variables in the spectrophotometric method for the determination of nickel, in which the nickel-dimethylglyoxime complex is formed in a solution of potassium persulfate and sodium carbonate, were studied. The variables included ammonium ion concentration, pH, and excess dimethylglyoxime. Optimum conditions for maximum absorbancy of the complex were established. It was found that, at pH 11 or greater and in a solution of 0.3 *M* ammonium hydroxide, maximum absorbancy was attained within the first 5 min of color development, whereas, at the same pH and in the absence of ammonium ions, the absorbancy does not become constant even after 24 hr. As a result of these tests, the optimum conditions for maximum absorbancy were established to be pH 11 or greater and an ammonium hydroxide concentration of 0.3 *M*. This optimum pH was confirmed by tests with 0.3 *M* ammonium hydroxide solutions of pH that was varied from 10 to 11.5 by adjustment with sodium hydroxide solution.

The absorption characteristics are shown in Fig. 6, curve A, for the nickel-dimethylglyoxime complex formed in the presence of a 1:4 mole ratio of nickel to dimethylglyoxime at pH 11 and in a 0.4 *M* sodium carbonate–0.3 *M* ammonium hydroxide medium. The maximum absorbancy occurs in the region of 465 mμ. However, if the ratio of nickel to dimethylglyoxime is 1:2 and the other conditions are the same, the absorption characteristics (Fig. 6, curve B) are similar to those observed when the concentration of ammonium ion is high, no sodium carbonate is present, and the pH is less than 11. The complex formed at the 1:2 ratio is very unstable; its absorbancy decreases rapidly within 3 to 5 min. These observations would indicate that the stable complex is formed at pH 11 or greater in 0.4 *M* sodium carbonate–0.3 *M* ammonium hydroxide when the ratio of nickel to dimethylglyoxime is 1:4 but that at lower pH and higher concentrations of ammonium ion the unstable complex is formed even in the presence of a 4-mole excess of dimethylglyoxime.

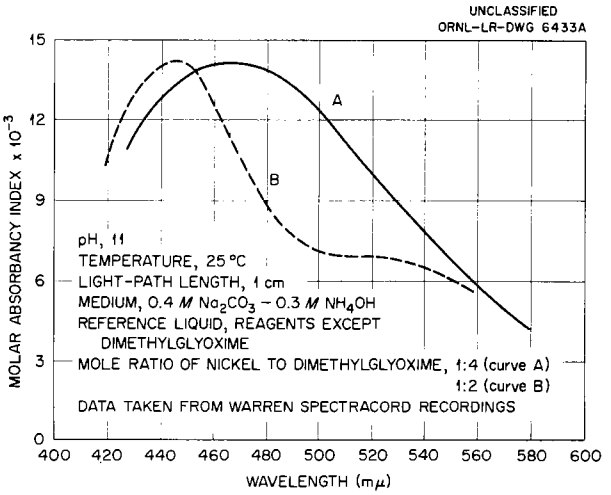

Fig. 6. Molar Absorbancy Index–Wavelength Curves for Nickel Dimethylglyoxime Complexes.

Electrodeposition of Copper from Uranyl Sulfate Solutions at a Controlled-Cathode Potential

R. G. Ball

The electrodeposition of copper from uranyl sulfate solutions by means of a controlled-cathode potential was investigated. The cathode potential

[1] J. C. White, "Analytical Chemistry of Reactor Materials," *ANP Quar. Prog. Rep. Dec. 10, 1954*, ORNL-1816, p 129–33.

[2] J. C. White, "Analytical Chemistry of Reactor Materials," *ANP Quar. Prog. Rep. March 10, 1955*, ORNL-1864, p 157–163.

was controlled[3] at −0.2 v vs the S.C.E., which was the optimum potential for obtaining maximum rate of deposition and adherent deposits of copper.[4] In uranyl sulfate solutions (40 mg/ml), copper in the range of from 12 to 61 mg was determined with a relative standard deviation of 0.3%. The constant for the rate of deposition, K, of copper was estimated to be 0.04 min^{-1}.

Electrodeposition of Nickel from Uranyl Sulfate Solutions at a Controlled-Cathode Potential

R. G. Ball

A study of the electrodeposition of nickel from uranyl sulfate solutions was initiated. About 7% of the nickel in a uranyl sulfate solution that contained copper and a known amount of nickel was deposited by means of a controlled-cathode potential after copper had been removed and the uranyl ions had been precipitated with pyridine. This quantity of nickel will be sufficient for the determination of nickel by a method that is a combination of a proposed isotopic dilution method and a mass spectrometric method.

Spectrophotometric Determination of Mixtures of Chromium(III) and (VI) in Aluminum Nitrate and Nitric Acid Solutions

C. M. Boyd

A spectrophotometric method for measuring the absorbancies of chromium(III) and chromium(VI) was applied to the analysis of solutions of chromium(III) and (VI) that were either 2 *M* in aluminum nitrate and 1 *M* in nitric acid or 7 *M* in nitric acid. In this method the absolute amount of both chromium(III) and (VI) can be determined by measurement of the total absorbancy at two wavelengths, for each of which the molar absorbancy indexes of both chromium(III) and (VI) are known. In establishing the molar absorbancy index of chromium(VI) in the two solutions, it was found that traces of oxides of nitrogen cause interference by reducing chromium(VI) to chromium(III).

Polarographic Determination of Oxygen in Uranyl Sulfate Solutions

C. M. Boyd

The determination of oxygen in uranyl sulfate solutions by the procedure reported previously,[5] in which a mixed ion-exchange resin was used to separate the interfering ions, resulted in low values for oxygen. For this reason, a polarographic method for the determination of oxygen in these solutions was investigated. Ammonium carbonate and the trisodium salt of *N*-hydroxyethylenediaminetriacetic acid (Versen-ol) were used to form complexes with the other components of the uranyl sulfate solution and thus to shift their reduction waves to potentials more negative than those of the uncomplexed components. It was found that the magnitude of the diffusion currents could not be related directly to the oxygen concentration of the solutions because the passage of oxygen, air, and nitrogen through the solutions produced secondary reactions which affected the magnitude of the diffusion currents.

Conductivity and pH Measurements of Aqueous Slurries of Thorium Compounds

R. E. Corcoran

The evaluation of conductivity measurements for the estimation of impurities in thorium oxide slurries and for the characterization of thorium oxide from various sources was continued.[6] Experiments are being made in order to estimate the effect of small amounts of thorium sulfate [5 to 50 mg of $Th(SO_4)_2$ per g of ThO_2] on the conductivity of aqueous slurries of thorium oxide. The conductivity and pH values under equilibrium conditions are being determined for slurries of high-purity thorium oxide, of thorium sulfate, and of thorium oxide that contains approximately 0.7% thorium sulfate.

Loss of Water from Thorium Oxide Slurries as a Function of Temperature and Time

R. E. Corcoran

The loss of water from an aqueous slurry of thorium oxide, which slurry had undergone tests at a high temperature and pressure, was studied

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[3] R. W. Lamphere and L. B. Rogers, "Instrument for Controlled-Potential Electrolysis," *Anal. Chem.* **22**, 463 (1950).

[4] J. J. Lingane, *Electroanalytical Chemistry*, p 272, Interscience, New York, 1953.

[5] C. M. Boyd, "Determination of Dissolved Oxygen in Solutions of Uranyl Sulfate," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 43.

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

as a function of time and temperature. It was found that, at 41°C, water is lost from the slurry at the rate of about 8% of the original slurry weight per hour for the first 5 hr. An additional loss of only 0.5% of the original slurry weight occurred when the temperature was increased to 260°C.

Polarographic Determination of Barium

R. E. Corcoran

A polarographic method was investigated for the determination of microgram quantities of barium[7] in solutions of thorium oxide. A linear relation between the diffusion current and the concentration of barium was established at $E_{1/2} = -1.94$ v vs the mercury pool electrode. The relative standard deviation was 1% for barium in barium chloride solutions of concentrations in the range 0.5×10^{-3} to 1.5×10^{-3} *M*. When 2-thenoyltrifluoroacetone was used for the extraction of thorium from solutions of thorium oxide that contained barium, a diffusion current for barium in the raffinate was not obtained.

Dissolution of Refractory Mixtures of Thorium Oxide and Titanium Oxide

M. L. Hubbard

The methods used to dissolve thorium oxide slurries[8] were not suitable for slurries of thorium oxide that contained a relatively high percentage of titanium oxide. Of the other methods tried, that is, prolonged boiling with a mixture of hydrofluoric and perchloric acids, fusion with sodium hydroxide in gold crucibles, and heating with hydrochloric acid in a sealed tube in an autoclave at 250°C, the last method was the most effective. The reaction of the oxide mixture with hydrochloric acid in a sealed tube at 250°C resulted in complete dissolution of the oxide.

Dissolution of Aluminum Oxide and Determination of Platinum

M. L. Hubbard

Methods were investigated for dissolving pellets of aluminum oxide, which are very refractory, prior to the estimation of their platinum content. Treatment with aqua regia and fusion with sodium hydroxide, in nickel or gold crucibles, either failed to dissolve the sample completely or resulted in a loss of platinum. The aluminum oxide was dissolved successfully by treatment with hydrochloric acid at 250°C in a sealed quartz tube. The platinum residue was dissolved in aqua regia; then the platinum was estimated as the platinum–stannous chloride complex according to the procedure of Ayres and Meyer.[9] The precision for the estimation of platinum was better than 1%.

Flame Photometry of Silver

W. R. Musick

The flame photometry of silver was studied in order to develop a rapid and sensitive method for the estimation of silver in thorium oxide slurries and in uranyl sulfate solutions. The optimum conditions of gas pressure, slit width, voltage of the photomultiplier tube, instrument sensitivity, and solvent medium that would give maximum sensitivity were established. For concentrations of silver in the range 0 to 40 ppm, the slope of the calibration curve was 1.00 relative emissivity unit per ppm of silver. The standard deviation of the calibration data in this range was 1%.

Spectrophotometric Determination of Palladium with α-Furildioxime

T. C. Rains

The spectrophotometric procedure by which palladium is determined as the palladium–α-furildioxime complex[10] was investigated further. The effects of a large number of ions and of the addition of ethanol as a stabilizing agent on the estimation of palladium were determined. The method was found to be highly specific for palladium because a large number of elements, including those of the transition and of the platinum groups, do not interfere. Optimum precision is obtained in the range of palladium concentration of from 1.2 to 3.0 ppm in a 10% ethanol solution.

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[7] I. M. Kolthoff and H. P. Gregor, "Polarographic and Amperometric Determination of Barium," *Anal. Chem.* 20, 541 (1948).

[8] C. K. Talbott, "Analysis of Thorium Oxide Slurries – Dissolution of the Oxide," *Anal. Chem. Semiann. Prog. Rep. April 20, 1953*, ORNL-1547, p 19.

[9] G. H. Ayres and A. S. Meyer, Jr., "Spectrophotometric Study of the Platinum(IV)–Tin(II) Chloride System," *Anal. Chem.* 23, 299 (1951).

[10] T. C. Rains, "Spectrophotometric Determination of Palladium with α-Furildioxime," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 41.

Spectrophotometric Determination of Ethylenediaminetetraacetic Acid as the Copper Complex

I. B. Rubin

A method for the determination of ethylenediaminetetraacetic acid as the copper complex, which is described in an industrial bulletin,[11] was investigated. The following conditions were studied: wavelength of maximum absorbancy, effect of buffer, selection of reference solution, sensitivity, and color stability. Maximum absorbancy was found to occur at 262 mμ. At this wavelength and in 0.2 *M* buffer, the molar absorbancy index is 9700. The sensitivity increased as the concentration of the buffer was increased, whereas the precision decreased under these conditions. For concentrations of ethylenediaminetetraacetic acid in the range of 20 to 60 μg per milliliter of final volume, the relative standard deviation of the data was about 5%. The relative standard deviation was improved by a factor of 5 when a calibration curve was used instead of a calibration factor.

Determination of Titanium in the Presence of Thorium After Separation from Corrosion Products

I. B. Rubin

Investigation of the chloroform–8-quinolinol method for the determination of titanium in the presence of thorium[12] was extended to the study of methods for the removal of interfering cations. The use of 1,10-phenanthroline and cyanide, as suggested by Margerum *et al.*,[13] failed to eliminate the interferences of iron, chromium, nickel, and manganese. However, the interferences of these metals were eliminated by mercury-cathode electrolysis[14] in a perchloric acid medium after prereduction of chromium in higher valence states to chromium(III) with hydrogen peroxide.[15]

[11] "The Versenes," Sec. III, p 2–4, *Technical Bulletin No. 2*, Bersworth Chemical Co., Framingham, Mass., 1954.

[12] H. R. Hunt, Jr., "Separation and Spectrophotometric Determination of Titanium in the Presence of Thorium by the Chloroform–8-Quinolinol Method," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 40.

[13] D. W. Margerum, W. Sprain, and C. V. Banks, "Spectrophotometric Determination of Aluminum in Thorium," *Anal. Chem.* 25, 249 (1953).

[14] C. J. Rodden (Editor-in-Chief), *Analytical Chemistry of the Manhattan Project*, p 511–22, McGraw-Hill, New York, 1950.

[15] T. D. Parks, H. O. Johnson, and L. Lykken, "Removal of Metals at the Mercury Cathode," *Anal. Chem.* 20, 148 (1948).

RAW MATERIALS

L. J. Brady

Spectrophotometric Determination of Uranium in the Presence of Phosphate by the Alkaline Peroxide Method

L. J. Brady

The alkaline peroxide spectrophotometric method for the determination of uranium[16] was adapted for use with materials that contain relatively high concentrations of phosphate. Sufficient 5 *M* phosphoric acid is added to both standards and samples to adjust the phosphate concentration to 0.4 *M*. The relative standard deviation of the data for uranium in the concentration range 0.01 to 0.05 mg/ml is 2%.

Determination of Uranium by the Ethyl Acetate–Ammonium Thiocyanate Method

A. F. Roemer, Jr. L. J. Brady

The ethyl acetate–ammonium thiocyanate spectrophotometric method of DeSesa and Nietzel[17] for the determination of uranium in the colorimetric range has been modified. The modifications were substitution of a less concentrated solution of aluminum nitrate for a saturated solution, addition of tartaric acid to prevent the interferences of iron and vanadium, and the use of mechanical shakers, other special equipment, and techniques for the extraction of uranium. The modified procedure, together with illustrations and a detailed description of the equipment used for the extraction, is given in a special report.[18]

Effect of Uranium on the Determination of Vanadium by the Spectrophotometric Peroxide Method

A. F. Roemer, Jr. L. J. Brady
C. D. Susano

The effect of uranium in the concentration range 2.2 to 4.4 mg/ml on the determination of vanadium

[16] C. J. Rodden (Editor-in-Chief), *Analytical Chemistry of the Manhattan Project*, p 91, McGraw-Hill, New York, 1950.

[17] M. A. DeSesa and O. A. Nietzel, *Spectrophotometric Determination of Uranium with Thiocyanate*, ACCO-54 (July 1954).

[18] C. D. Susano and L. J. Brady, *Some Selected Methods for Determining Uranium and Vanadium in the Presence of Each Other*, ORNL CF-55-1-77 (Jan. 12, 1955).

by the spectrophotometric peroxide method[19] was determined from absorbancy curves obtained in the wavelength range 400 to 500 mμ by means of a Warren Spectracord. It was noted that the absorbancy at 455 mμ was increased about 6%, whereas at 480 mμ the increase was less than 3%. These results indicate that the amount of uranium which can be present without causing significant interference in the determination of the vanadium in this concentration range is increased more than twofold when measurements are made at 480 mμ instead of at 455 mμ.

MISCELLANEOUS ANALYSES

H. P. House

Determination of Vanadium(IV) in Solutions That Contain Both Vanadium(IV) and (V)

J. R. Lund J. L. Mottern

A colorimetric method for the direct determination of vanadium(IV) in solutions that contain both vanadium(IV) and (V) was investigated. A study of the absorption spectra of the two species of vanadium revealed a region of maximum absorbancy for both at a wavelength of 320 mμ and an additional region of maximum absorbancy at 790 mμ for vanadium(IV). The absorbancy at 790 mμ is increased appreciably by the addition of oxalic acid, but, with or without oxalic acid, the relation between the absorbancy and the concentration of vanadium(IV) is linear over the concentration range 0.2 to 1 mg/ml. This method for vanadium(IV) is not affected by the presence of vanadium(V). The effects of cations of the following elements were determined: sodium, potassium, tin, magnesium, titanium, chromium, iron, manganese, calcium, barium, nickel, copper, cerium, lead, zinc, cobalt, bismuth, silver, cadmium, and mercury; also, the effects of the following anions were determined: vanadate, chloride, bromide, iodide, nitrate, perchlorate, phosphate, acetate, arsenate, molybdate, and fluoride. The maximum concentrations of these constituents that can be present without causing interferences were established. The precision of the method is of the order of 2%.

Spectrophotometric Determination of Microgram Quantities of Boran

J. R. Lund J. L. Mottern

A spectrophotometric method for the determination of microgram quantities of boron,[20] which depends on the color developed with carminic acid in concentrated sulfuric acid, has been applied successfully to aqueous extracts from organic solutions of boron trifluoride. At a fluoride-to-boron weight ratio of 5, the color is reduced by no more than 5%. Copper does not interfere at a copper-to-boron weight ratio of 5. Boron in the range 8 to 10 μg can be determined with a relative standard deviation of 5% or better. Boron-free glassware was needed only when it was necessary to concentrate the sample prior to the boron determination.

Determination of Cerium by a Modification of a Spectrophotometric Method

J. R. Lund J. L. Mottern

In the peroxide spectrophotometric method for the determination of cerium,[21] a concentrated solution of potassium carbonate is partially neutralized by the addition of hydrochloric acid. It was found that this time-consuming step of the cerium procedure could be avoided with no loss of precision by the addition, prior to the development of color, of the required amount of a potassium chloride–potassium carbonate solution that is adjusted to a pH of 10.5.

Separation of Thorium from Uranium

J. R. Lund J. L. Mottern

Solutions of thorium and uranium in 9 *M* hydrochloric acid that contained 200 μg of uranium and 50 mg of thorium per milliliter were passed through a small Dowex 1 resin column. Uranium was adsorbed onto the column and removed subsequently by elution of 0.015 *M* hydrochloric acid. The thorium content of the eluate that contained the uranium was 30 to 40 μg, and the ratio of thorium to uranium was less than 0.2. At this ratio of thorium to uranium, the thorium does not interfere in the fluorometric determination of uranium. This method can therefore be used to reduce the concentration of thorium to a level at which it does not interfere in the fluorometric determination of uranium.

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[19] C. J. Rodden (Editor-in-Chief), *Analytical Chemistry of the Manhattan Project*, p 463, McGraw-Hill, New York, 1950.

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

[21] G. Telep and D. F. Boltz, "Ultraviolet Spectrophotometric Determination of Cerium," *Anal. Chem.* 25, 971 (1953).

Flame Photometry of Alkali Metals and Alkaline-Earth Elements

J. M. Rogers

Studies have continued on the flame photometric determination of alkali metals and alkaline-earth elements. The interference of one element on the determination of the others and the operating conditions for specific elements in various concentration ranges have been included in the study.

Quantitative determinations have been made of the interferences, under specific operating conditions, of the elements shown in the vertical column of Table 9, on the flame photometric determination of the elements in the horizontal column. In this table, selected data that indicate the magnitude and direction of the interferences are presented.

The following limits of detection of the alkali metals by flame photometry were established:

Alkali Metal	Limit of Detection (ppm)
Sodium	0.0002
Potassium	0.004
Rubidium	0.04
Cesium	0.2
Barium	5.0

Flame Photometry of Barium

J. M. Rogers

In the flame photometric determination of barium, maximum sensitivity with a minimum of interferences occurs at a wavelength of 554 mμ. Optimum

TABLE 9. FLAME PHOTOMETRY OF THE ALKALI METALS AND ALKALINE-EARTH ELEMENTS: MUTUAL INTERFERENCES

Element Determined		Li	Na	K	Rb	Cs	Mg	Ca
Wavelength, mμ		672	559	767	795	852	383	622
Concentration, μg/ml		25	10	10	25	25	25	25
Interference Element	Interference Ratio[a]	Interference Factors[b]						
Li	100 400		0.38	0.15 0.38	0.21 0.49	0.21 0.48	c	1.55
Na	100 400				−0.06 −0.21	−0.14	c	c
K	100 400				c	−0.23	c	0.76 1.31
Rb	100			−0.12		−0.25	c	c
Cs	100 400				−0.20		c	c
Mg	100 400	0.09 0.11	0.01 0.06	0.09 0.16	0.13 0.36	0.17 0.43		c
Ca	100 400	0.03 0.09	0.13 0.13	0.13	0.05 0.13	0.07 0.19	c	

Region of No Interference

[a]Weight ratio, interfering element/element determined.

[b]Interference factor (F) indicates the amount of enhancement or of decrease of the relative emissivity caused by the interfering element. The observed emissivity x $(1 + F)$ equals the emission to be referred to a calibration curve in order to ascertain the concentration of the element being determined.

[c]Study not completed.

operating conditions for the Beckman flame photometer were: photomultiplier-tube (RCA 1P28) voltage, 630 v; slit width, 0.035 mm; oxygen pressure, 20 psi; and hydrogen pressure, 6 psi. The estimated standard deviation of the data is of the order of 25% for 5 μg of barium per milliliter.

Flame Photometry of Boron

J. M. Rogers

Test results for the determination of boron indicate that the carminic acid method[20] is more sensitive than the flame photometric method.

Determination of Ammonia and Carbonate in Ammonium Hydroxide–Ammonium Carbonate Solutions

J. M. Rogers H. P. House

Ammonia and carbonate are determined in ammonium hydroxide–ammonium carbonate solutions by measurement of total alkalinity, precipitation of carbonate at room temperature as barium carbonate, and subsequent volumetric determination of the carbonate. The method is unsatisfactory, apparently because of the presence of carbamate in the sample. When the solution was heated to 80 to 90°C for 5 min, carbamate was completely converted to carbonate prior to determination of carbonate. The modified procedure gave satisfactory results for solutions of carbonate in the concentration range 0.1 to 6 *M*.

QUALITY CONTROL

R. L. McCutchen C. D. Susano

Only minor changes have occurred in the types of materials being tested in the Analytical Chemistry Division Laboratories at the Y-12 site. These changes did not necessitate any changes in the types of solutions that are tested for control purposes. The frequency with which standards were tested for control purposes was decreased, as much as possible, commensurate with the maintenance of high precision of the test results.

As a consequence of the Thorex project, the control work at the X-10 site increased rapidly. Preliminary tests have been made in the General Analyses Laboratory for the purpose of implementing a control program for various elements in the colorimetric range. This increases the number of laboratories participating in the control program at the X-10 site to six, an increase of three over the previous six months.

The distribution by laboratory of the 5691 determinations that were evaluated for control purposes is summarized in Table 10; the control data for the previous period are also shown for comparison.

TABLE 10. SUMMARY OF DETERMINATIONS EVALUATED FOR CONTROL PURPOSES

Laboratory	Determinations Evaluated for Control Purposes	
	April Through September 1954	October 1954 Through March 1955
Y-12 Site		
ANP	996	486
HRP	609	359
Raw Materials	202	200
Total	1807	1045
X-10 Site		
Building 3019		2601
Building 3508		350
Building 3550		493
Building 4500	812	972
General Analyses		230
Total	812	4646
GRAND TOTAL	2619	5691

SERVICE ANALYSES

A semiannual summary of the analytical service work at the Y-12 site is given in Table 11.

ANP ANALYTICAL CHEMISTRY

W. F. Vaughan

The service work of the ANP Analytical Chemistry Laboratory is reported elsewhere.[1,2]

HRP ANALYTICAL CHEMISTRY

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

The staff of the HRP Analytical Chemistry Laboratory made 22,950 determinations on 4,882 samples. This is an increase of 47% in the number of samples over the number for the previous six-month period. Solutions of uranyl sulfate were analyzed for uranium and for iron, nickel, and chromium, which were present as products of corrosion. Analyses were made occasionally for aluminum, cobalt, copper, sulfate, molybdenum, titanium, and chloride. Similar tests were made on thorium oxide and on other compounds of thorium. Solutions of 2 *M* aluminum nitrate in

[1] J. C. White, C. R. Williams, and W. F. Vaughan, "ANP Service Laboratory," *ANP Quar. Prog. Rep. Dec. 10, 1954*, ORNL-1816, p 133.

[2] J. C. White, W. F. Vaughan, and C. R. Williams, "ANP Service Laboratory," *ANP Quar. Prog. Rep. March 10, 1955*, ORNL-1864, p 163.

TABLE 11. SUMMARY OF ANALYTICAL SERVICE WORK AT Y-12 SITE

	Number of Personnel		ORNL Divisions Requesting Analyses						Others Requesting Analyses		Total Determinations
	Technical	Nontechnical	Materials Chemistry	ARE	Metallurgy	Stable Isotope Research and Production	Solid State	REED	Y-12	Miscellaneous	
Laboratory Making Analyses			Number of Determinations								
ANP Analytical	4	8	17,028	5,560	32		29	86			22,735
HRP Analytical	5	8						22,950			22,950
Miscellaneous Analyses	3	9	21,282		1,173			502	113	153	23,223
Raw Materials	2	7	16,855						432		17,287
Special Samples	2	0	1,610	75		13		51	6	198	1,953
Totals	16	32	56,775	5,635	1,205	13	29	23,589	551	351	88,148

1 *M* nitric acid, 2 *M* aluminum sulfate, and 7 *M* nitric acid were tested for iron, nickel, and chromium. Titanium was determined in a welding-rod flux. In addition to this work, turbidimetric methods and titrimetric methods, with tetrahydroquinone as the indicator, were applied to the determination of sulfate;[3] the polarographic method for the determination of lead in thorium oxide slurries was studied;[4] and zirconium was determined by the chloranilic acid method[5] after nitrate ions were removed by heating with hydrochloric acid and after ferric ions were removed by mercury-cathode electrolysis.

RAW MATERIALS ANALYTICAL CHEMISTRY

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

The number of samples analyzed by the staff of the Raw Materials Laboratory doubled during this period. Approximately 40% of the 6350 samples were derived from tests conducted by the Raw Materials Process Testing Group. Most of the samples were solutions derived from solvent-extraction studies; they consisted of acid-leach liquors, raffinates, organic extracts, and various acidic or alkaline solutions that had been used to extract uranium from organic materials. These samples were analyzed for uranium, vanadium, iron, and, less frequently, for aluminum, magnesium, calcium, molybdenum, titanium, phosphate, sulfate, nitrate, and chloride. Samples of uraniferous ores and of ore residues were analyzed for uranium, vanadium, iron, aluminum, magnesium, calcium, and chloride in order to evaluate the efficiency of separation processes based on the direct chlorination and sublimation of specific components of the ores.

MISCELLANEOUS ANALYSES

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

A total of 531 samples was analyzed in the Miscellaneous Analyses Laboratory during this period. This is a decrease of approximately 60% over the number of samples analyzed during the previous period. The decrease is largely the result of the transfer of the specification testing of lubricating oils for the Y-12 Stores Department from this laboratory to the Analytical Laboratory Department of the Y-12 Laboratory Division in November 1954.

Specification testing of steels, other alloys, and nonferrous metals continued. The number of samples of these types has increased in recent weeks.

Solutions derived from studies of chemical methods for the separation of isotopes were analyzed for carbonate, carbamate, and ammonia.

Illustrative of the wide variety of work of the laboratory is the following list: the identification of unknown solid residues and organic solvents, the determination of the ratio of nickel to ammonia in samples of Dowex 50 resin that was loaded with an adsorbed complex, the analysis of polyacrylic acid, the determination of carbon in thorium oxide, and the analysis of monoamino boron trifluoride.

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[3] W. H. Betz and L. D. Betz, *Betz Handbook of Industrial Water Conditioning*, 4th ed., p 218–20, Philadelphia, 1953.

[4] I. M. Kolthoff and J. J. Lingane, *Polarography*, 1st ed., p 267–69, Interscience, New York, 1941.

[5] O. Menis, *The Determination of Zirconium by the Chloranilic Acid Method*, ORNL-1626 (Sept. 23, 1953).