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ANALYTICAL CHEMISTRY DIVISION

SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING OCTOBER 20, 1954

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ANALYTICAL CHEMISTRY DIVISION

SEMIANNUAL PROGRESS REPORT

for Period Ending October 20, 1954

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

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ABSTRACT

ANALYTICAL CHEMISTRY DIVISION – X-10 SITE

The coulometric method for the determination of iron has been successfully modified for application to the determination of plutonium in amounts ranging from 0.2 to 1 mg in the presence of uranium. Also, a coulometric method based on the electrolytic generation of silver ions was utilized for the determination of milligram quantities of chloride in uranyl sulfate solutions. A method for the determination of thorium in TBP-Amsco solutions from the BU and CW streams of the Thorex process is described. Selected portions of the absorption spectrum of neptunium in aqueous solutions of uranyl sulfate under certain conditions are presented. A method that was used for the determination of sulfur in a sample of molybdenite and methods that were used for the determination of iodine and iodate in Homogeneous Reactor fuel solutions are reported. The 2,2′-biquinoline (cuproine) reagent for the colorimetric estimation of copper was evaluated for use in the analysis of Homogeneous Reactor fuel solutions. Tests on modifications of the standard procedure for the determination of iron in Homogeneous Reactor fuel by remote operation in the High-Radiation-Level Analytical Facility reveal that the method can be simplified somewhat by the addition of a citrate buffer (pH 6.9), which eliminates the trial-and-error method previously used to control the alkalinity of the solution.

The method for the determination of nickel based on the formation of a nickel chelate with the disodium salt of ethylenediamenetetraacetic acid followed by titration of excess salt with a ferric chloride solution has been evaluated for use in the analysis of Homogeneous Reactor fuel solution. A procedure is given for the separation of rhenium and molybdenum in ores and in flue dusts that is based on the adsorption of both molybdenum and rhenium by the hydroxide form of Dowex 2 resin and the subsequent specific desorbability of molybdenum with 1 *N* sodium hydroxide followed by desorption of rhenium with 2 *N* perchloric acid. Some progress has been made in developing an adaptation of a carrier-precipitation method followed by pyrohydrolysis of the separated fluoride salts for possible utilization in the determination of the fluoride content of Thorex metal dissolver solutions.

An improved and simplified automatic titrator with velocity-servo control of titrant addition has been built and is being tested for pH and redox titrations. Aliquots that contained about 5 mg of uranium were titrated with a relative standard error of ±0.25% at the 95% probability level. An electronic-timing and turret-control section and a new turret that contains six thermostated fall tubes have been built for the falling-drop densimeter, model Q-1551. The fall-tube turret and the model Q-1551 falling-drop densimeter are being used for the determination of the density of synthetic Thorex MD and AF streams. Two "dropping" oil compositions have been found which permit the coverage of the entire anticipated density ranges of the two streams.

Two different types of apparatus for the pyrohydrolytic determination of fluorides have been built and are undergoing tests. The first apparatus has two separate heaters constructed from replacement heating elements, and a single unaltered commercial tube furnace for both superheating and pyrohydrolysis is used in the simplified apparatus. An automatic coulometric titrator for the current range of 2×10^{-6} to 8×10^{-3} amp has been designed and is being tested. The reagent-generating current is held constant to within 0.1% or better, and a timing clock is used. The instrument may be set to shut off automatically at a predetermined end-point potential or it may be used manually. For titrations involving slow chemical reactions, an optional time-delay circuit is available, and a dummy cell permits the initial value for the generating current to be selected without the necessity for a flow of current through the coulometric cell. A variable polarizing current of 0 to 20 μa is available.

A new high-sensitivity general-purpose and derivative polarograph is being developed. A novel filter section has been designed which completely eliminates from the strip-chart record the current fluctuations that result from the growth and fall of the mercury drops. There is less distortion of the polarographic wave form with this filtering action than with the quadruple parallel-T, R-C filter. This improvement should increase the applications of the derivative function. Modifications to the Brown amplifier in the recorder eliminate the preamplifier that is ordinarily

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required for high-sensitivity polarographs. The current-feedback amplifier which has an over-all voltage gain of 500 and several megohms input impedance also consists of a modified Brown amplifier.

A new dielectric constant meter, model Q-1549, has been built and has been used to perform satisfactory analyses. A commercial photomultiplier pickup head and indicator unit has been experimentally compared with the corresponding sections in the ORNL model Q-1165 fluorophotometer. A new sample cell has been built for the model Q-946 dielectric constant meter. Certain potentiometric microtitrations involving sample volumes of about 3 ml are more satisfactorily performed at a temperature of about 70°C; therefore a new heater, placed between the magnetic stirrer and the bottom of the titration vessel, has been designed. The shielded cubicle has been modified to permit the introduction of highly radioactive materials from heavily shielded transfer carriers.

Decay schemes of V^{49}, Rb^{86}, and certain rare earths have been investigated. The alpha and beta standards of the Analytical Chemistry Division have been recalibrated, and an improved scintillation spectrometer and coincidence counter will soon be in use. Preliminary results on the analysis of Thorex samples by gamma spectrometry are reported. Two new methods for fission-product determination have been evaluated. Studies of specific-activity determinations and of electrodeposition of plutonium have been made, and the development of a method for Pa^{233} has been completed. In the field of reactor analyses, scintillation spectrometry and radiochemical analyses have been applied to the measurement of gaseous activities, radioelements in cooling water, and uranium burnup. Analytical assistance in various phases of the program of the Electronuclear Research Division requires the full-time effort of two staff members and part of another's time.

The application of neutron-activation analyses to the determination of microgram or submicrogram quantities of chlorine in Graphitar bearings; europium in lithium iodide; arsenic, silicon and gold in crude oils and petroleum fractions; and nickel in blood is discussed. In addition, the determinations of macro and micro concentrations of lanthanum and americium in AMEX solutions and of sodium, potassium, and cesium in rubidium carbonate radioisotope target materials are discussed. Several examples of the use of a combined neutron-activation–gamma-ray spectrometer analysis are presented. This nondestructive method of analysis has included work on the determination of lanthanum and americium in AMEX process solutions, tungsten in crystals of pure iron, europium in solutions of lithium iodide, and arsenic and gold in petroleum. A method of determining particle-size distribution in thorium oxide–water slurries has been developed. The investigation of a qualitative analysis scheme has continued. A survey of the target materials used in radioisotope production has begun. The specific activity of the radioisotope of interest, contaminant radioactivities, activation cross sections, and half lives will be especially considered in the survey. Inquiries regarding new applications of activation analysis are summarized.

A nomograph has been prepared which permits the obtaining of spark-discharge temperatures directly from band-line-intensity data, without computation. The discharge temperature at a porous-cup electrode surface is 5500°K in a 0.25 *M* solution of silver perchlorate in 1% perchloric acid and 5450°K in a 0.25 *M* solution of cupric perchlorate in 1% perchloric acid. A set of tables has been computed to show the effect of undetected changes in emulsion contrast on observed spectral line intensity ratios when background is present. A d-c arc procedure has been developed that will determine boron in carbon and in graphite in concentrations as small as 0.50 ppm; a spark procedure has been devised that will make the same determination of concentrations as small as 0.25 ppm. Both procedures have standard deviations of approximately 2.5% of the amount of boron present. A sample of graphite from the ORNL Graphite Reactor showed a boron content of 0.45 ± 0.01 ppm. The extraction of thorium from aqueous solution by TTA was accelerated by the use of a warm water bath. Work was begun on a method of determining traces of silicon in thorium oxide without the use of fluorides. Electrodeposition of chromium onto a mercury cathode was made more reliable by destroying inner complex chloro-chromium compounds. New working curves were prepared for the determination of yttrium, ytterbium, cerium, lanthanum, neodymium, and europium by the porous-cup method, and of minor amounts of foreign alkalies in lithium,

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cesium, and rubidium salts by the flame photometric method. A list of available translations of spectrochemical papers was prepared for the American Society for Testing Materials.

In the study by the Physics Division of the first-period transition elements from vanadium to cobalt, new ternary oxides of the general formula $LaMO_3$ were prepared. The methods of preparation of uranium tri-iodide were investigated, and 125 g was prepared. For the Chemistry Division, the complex fluoride K_2NiF_6 was finally produced in quantity in pure form. Larger quantities of several materials were purified for the Physics Division, and some new phosphors were prepared.

Electron-diffraction results from examinations of oxide films and corrosion products of interest in reactor technology are discussed. Optical and electron microscopy were used to study thorium oxide before and after loop runs, various organic colloidal solutions and biological preparations, the glass and enamel coatings on steel, a large number of exchange resins, titanium, zirconium, Zircaloy, and steels containing pearlite. Particle-size determinations were made on a wide variety of samples, and autoradiographic studies were made of electroplated plutonium.

Ten new methods have been issued to the *ORNL Master Analytical Manual.*

Analytical service analyses are summarized in tabular form; special problems are discussed briefly. The extent of interest in activation-analysis services is summarized. The status of work on the new High-Radiation-Level Analytical Facility is indicated. Recently observed half-life values are reported for five radionuclides. Development work on the micro-pyrohydrolysis of fluoride has been augumented by adaptation of a spectrophotometric method of titration for fluoride. An improved apparatus has been fabricated for the xylene extraction of water from fluoride salts and subsequent use of the Karl Fischer titration method. Special analyses and separations of rare earths and other elements from various alloys are reported. An extensive investigation of vacuum-fusion analysis and techniques which give comparable results is discussed.

ANALYTICAL CHEMISTRY DIVISION – Y-12 SITE

The ANP Analytical Chemistry Laboratory has been concerned mainly with the analysis of mixtures of lithium, sodium, and potassium fluorides (Flinak), and $NaZrF_5$ materials which are currently under consideration for use as solvents for reactor fuels.

The analytical chemistry of the HRP was related to the problems of determining corrosion products and additives in thorium oxide, thorium compounds, and uranyl salt solutions. Procedures were developed and evaluated for the determination of titanium, zirconium, beryllium, palladium, aluminum, thorium, and phosphate in thorium oxide and for the determination of nickel, tetravalent uranium, dissolved oxygen, and mixed halides in uranyl sulfate solutions.

In addition to these methods, a physico-chemical method for determining the purity of a thorium oxide slurry was developed; the adsorptive property of a thorium oxide material was studied, and a physical method for estimating the thickness of oxide films on zirconium and on titanium was evaluated and used. Several methods were modified for the analysis of special samples. These procedures are related to the separation of rare earths and thorium, the determination of aluminum in the presence of iron, the spectrophotometric determination of chloride, the determination of uranium in the presence of thorium, the spectrophotometric determination of cerium, and the spectrophotometric determination of dissolved oxygen.

The Methods Development and Special Problems Group has been concerned with the problems of the dissolution and analysis of monazite sands, the determination of sodium, potassium, rubidium, and cesium by methods of flame photometry, the determination of carbamate and carbonate in mixtures, the spectrophotometric determination of microgram amounts of ammonia in solutions of sodium hydroxide and slurries of calcium hydroxide, and the oxidation of chromium by perchloric acid.

Relative to the work of the Raw Materials Group, methods have been modified and tested for the determination of water in uranyl salts, sulfate in the 0.5- to 5-mg range, and iron in the presence of phosphate.

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

A tabulation of the 78,246 determinations reported by the service groups, indicating the distribution of work by divisions, is included. 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
Cohen, B. L., R. A. Charpie, T. H. Handley,* E. L. Olson	"Manganese-57"	*Phys. Rev.* 94, 953 (1954)
Cohen, B. L., E. Newman, R. A. Charpie, T. H. Handley*	"(p,pn) and (p,an) Excition Functions"	*Phys. Rev.* 94, 620 (1954)
Ellenburg, J. Y., G. W. Leddicotte, F. L. Moore	"Separation of Niobium and Tantalum by Liquid-Liquid Extraction"	*Anal. Chem.* 26, 1045 (1954)
Frierson,[a] W. J., P. F. Thomason,* H. P. Raaen*	"Elution Chromatography with Thick Filter Paper"	*Anal. Chem.* 26, 1210 (1954)
Handley, T. H.	"Neutron-Deficient Activities of Holmium"	*Phys. Rev.* 94, 945 (1954)
Handley,* T. H., E. L. Olson	"Ytterbium-167"	*Phys. Rev.* 94, 945 (1954)
Raaen, H. P., P. F. Thomason	"Separation of Pa^{233} and U^{233}"	*Reactor Sci. Technol.* 4, No. 3 (1954), TID-2014, p 93

[a]Summer visitor.

ORAL PRESENTATIONS

Author(s)	Title	Presented At
Cohen,[a] B. L., G. H. McCormick, T. H. Handley,* E. Newman	"($p,2n$), ($p,2p$), (p,t), (p,He^3), and (p,f) Cross Sections and Excitation Functions"	American Physical Society Meeting, Washington, D.C., April 29–May 1, 1954
Feldman, C.	"The Spectrochemical Power Source – An Independent Variable"	Oklahoma A & M College, Stillwater, Okla., April 7, 1954 and at Louisiana State University, Baton Rouge, La., April 8, 1954
Handley,* T. H., B. L. Cohen[a]	"New Isotope Identification Program on the Oak Ridge 86-Inch Cyclotron"	American Physical Society Meeting, Washington, D.C., April 29–May 1, 1954
Leddicotte, G. W.	"Nucleonics in Analytical Chemistry"	Second Analytical Chemistry Conference, Detroit, Mich., May 3, 1954

[a]Speaker.

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TOPICAL REPORTS

Author(s)	Title	Report No.
Edgerton, J. H., 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)
Horton, A. D., P. F. Thomason, M. T. Kelley	*Determination of Corrosion Products and Additives in Homogeneous Reactor Fuel*	ORNL-1746 (Sept. 10, 1954)
Manning, D. L., J. C. White	*Differential Spectrophotometric Determination of Zr*	ORNL-1725 (May 11, 1954)
Menis, O.	*The Determination of Zr by the Chloranilic Acid Method*	ORNL-1626 (April 7, 1954)
Raaen, H. P., P. F. Thomason	*Separation of U(VI) from Other Metals by Filter Paper Partition Chromatography with 2-Methyltetrahydrofuran and Its Quantitative Determination*	ORNL-1690 (July 21, 1954)
Reynolds, S. A.	*"Soup" Analyses and Counting "Factors"*	ORNL CF-54-4-128 (April 19, 1954)
Reynolds, S. A.	*"Burn-Up" Determination*	ORNL CF-54-5-32 (May 7, 1954)
Reynolds, S. A.	*Cesium Standards for "Burn-Up"*	ORNL CF-54-8-170 (Aug. 26, 1954)
Susano, C. D., J. C. White, J. E. Lee, Jr.	*Apparatus for the Pyrohydrolytic Determination of Fluoride and Other Halides*	ORNL-1744 (June 10, 1954)
Susano, C. D.	*Graphite and Al-Block Solution Evaporators*	ORNL-1735 (June 4, 1954)

METHODS ISSUED TO *ORNL MASTER ANALYTICAL MANUAL*

Author(s)	Title	Number(s)	Date
Phillips, T. R., J. C. White	"Potassium, Gravimetric Perchlorate Method"	1 216450 9 00716450	1-21-54
Phillips, T. R.	"Zirconium, Gravimetric Mandelic Acid Method"	1 219850 9 00719850	1-20-54
Reynolds, S. A.	"Proportional Alpha Counter"	2 00351 9 00351	12-28-53
Rickard, R. R.	"Copper, Lead and Zinc in Phosphorus-32 Product Solutions"	9 073200	2-1-54
Rickard, R. R.	"Nickel-63"	9 0733542	1-21-54
Ross, W. J.	"Water in Fluoride Salts and Salt Mixtures, Karl Fischer Method"	9 0922004	1-19-54

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Author(s)	Title	Number(s)	Date
Smith, G. W.	"Americium-241"	2 31030	5-18-54
Walker, R. L.	"Tributyl Phosphote in Tributyl Phosphate-Amsco Solutions for Thorex Process, Dielectric Constant Method"	9 012101	1-25-54
Wyatt, E. I.	"Chloride, Turbidimetric Method" (Revision to old method)	9 0732200	Revised 1-18-54
Wyatt, E. I.	"Sulfate, Turbidimetric Method"	9 0732812	1-27-54

[redacted]

[redacted]

ANALYTICAL CHEMISTRY DIVISION - X-10 SITE

RESEARCH AND DEVELOPMENT

IONIC ANALYSES

P. F. Thomason

Coulometric Determination of Plutonium in the Presence of Uranium

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

The coulometric determination of iron by titration with electrolytically generated uranium(IV) under the conditions and with the automatic timing device (Autid) mentioned previously[1] was found to have a relative standard deviation of 0.8% in the 1-mg-quantity range. Therefore application of this method to the determination of milligram and submilligram quantities of plutonium in the presence of uranium was investigated. The results will be described in a topical report.

In this application, titration was carried out under the same conditions as those recommended for the titration of iron,[1] except for the necessity of working in a perchloric acid medium and of determining plutonium by difference – that is, titrating an iron standard, adding the plutonium sample to this solution, and then retitrating. The difference, in millicoulombs, between the two titrations is used as a measure of the plutonium present in the solution.

The results in Table 1 were obtained by the use of a group of batteries as the current source.

[1]W. D. Shults, II, P. F. Thomason, and M. T. Kelley, "Coulometric Determination of Iron in the Presence of Uranium," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 4.

[2]J. J. Lingane, "Automatic Coulometric Titration with Electrolytically Generated Silver Ion. Determination of Chloride, Bromide, and Iodide Ions," *Anal. Chem.* **26**, 622 (1954).

It is planned to use the automatic coulometric titrator developed by Stelzner (cf. "Automatic Coulometric Titrator," this report) in this titration.

Coulometric Titration of Microgram Quantities of Chloride Ion

W. D. Shults, II

Milligram quantities of chloride have been determined by titration with silver ions which are generated electrolytically by means of a constant current at a silver-wire anode immersed directly in the test solution.[2] The end point was detected potentiometrically by means of a silver wire–calomel electrode system. This method, with slight modification, has been found to be satisfactory for the determination of microgram quantities of chloride ion in solutions of uranyl sulfate and should also be applicable to the analysis of HRT fuel solutions.

A 15-ml weighing bottle serves as the titration cell and is fitted with a rubber stopper; the stopper supports both the generating and the indicating silver-wire electrodes and the two salt bridges, one of which leads to the separated generating electrode and the other to the calomel electrode. Three milliliters of a stock solution containing 80% CH_3OH, 5% HNO_3, and 15% H_2O is placed in the cell, which is jacketed with ice water. After being cooled for 5 min, the solution is titrated automatically with constant current to an end-point potential of 0.230 v vs S.C.E. A 1-ml sample is then added to this solution, which is again cooled 2 min and titrated automatically back to 0.230 v vs S.C.E. The amount of chloride present can be calculated from the constant current

TABLE 1. COULOMETRIC DETERMINATION OF PLUTONIUM IN THE PRESENCE OF URANIUM

Number of Determinations	Plutonium		Relative Standard Deviation (%)
	Amount Present (mg)	Average Amount Found (mg)	
8	0.206	0.206	2.5
8	0.515	0.506	1.0
8	1.030	1.021	0.7

[redacted]

used and the time required to complete the back titration. The same current is used for the titration of the stock solution, and it is chosen so that the titration time will be approximately 200 sec.

Successive samples can be added to and titrated in a given solution, the number of such additions being limited by the successively increasing solution volume. The procedure of making triplicate determinations on a given sample in one solution was found to be satisfactory and required approximately 20 min per sample (triplicate determinations) when the chloride concentration was 20 μg or more per milliliter. Somewhat longer analysis times are required with smaller concentrations of chloride because the solutions reach equilibrium slowly during the titrations.

Table 2 is a summary of the results which were obtained when various amounts of chloride were determined by this method with the automatic coulometric titrator described by Stelzner (cf. "Automatic Coulometric Titrator," this report).

Determination of Microgram Amounts of Thorium in Tributyl Phosphate–Amsco Solutions

P. F. Thomason

It will be necessary to determine the amount of thorium in samples from the BU and CW streams in the Thorex process in order to evaluate the efficiency of the solvent extraction. Wet oxidation of the samples is not feasible because the TBP is converted to orthophosphate, which causes interference in the colorimetric method for the estimation of thorium. Therefore, three methods of determining thorium were tried.

It was thought that an eluate for colorimetric analysis could be obtained that had a concentration of thorium in the 100 μg/ml range by passing a large volume of the TBP-Amsco sample through Dowex 50 cation-exchange resin, which would adsorb the thorium. It was found that the thorium was adsorbed but could not be desorbed from the resin easily, even with oxalic acid; the acid had to be destroyed by heating before the thorium could be estimated colorimetrically.

Secondly, an attempt to adsorb the thorium as a thorium-Thoron complex on Dowex A-1 anion-exchange resin failed because only about 20% of the red complex was adsorbed.

The third method seems to offer the most promise. It is known that the organic reagent Thoron is not very soluble in organic solvents[3] and that it forms a strong complex with thorium in an acid solution. It was suggested, therefore, that thorium could be extracted from the organic solution by the use of this reagent. Several synthetic samples were made by dissolving thorium nitrate (Code 103, Lindsay Light & Chemical Co.) in a sufficient volume of a mixture of 30% TBP–70% Amsco (vol/vol) to give a solution that contained 50 μg of thorium per milliliter. One-milliliter aliquots were pipeted into small separatory funnels to which 3 ml of dilute hydrochloric acid (2% vol/vol) and 1 ml of a 0.2% aqueous Thoron solution were added. The mixture was shaken for 5 min, and then it was set aside until the phases had separated. The aqueous phase was drained into a 10-ml volumetric flask. The organic phase was then rinsed twice with 2-ml aliquots of water, the rinsings being added to the solution in the volumetric flask. Four drops of concentrated hydrochloric acid were then added, and the volume was adjusted to the 10-ml mark with water. The

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

TABLE 2. COULOMETRIC DETERMINATION OF CHLORIDE

Number of Determinations	Chloride		Relative Standard Deviation	
	Amount Present (μg)	Average Amount Found (μg)	(μg)	(%)
15	82.2	82.8	0.74	0.9
15	20.6	20.6	0.50	2.4
15	4.1	4.2	0.16	3.7

spectral absorption of the solution was measured at 545 mμ vs a reference solution that was prepared by the extraction, with water, of a thorium-free TBP-Amsco mixture. A Beckman model DU spectrophotometer with 1-cm Corex cells was used in making these measurements. A series of samples that contained known amounts of thorium was analyzed by this method, by means of which a recovery of 95 to 98% was attained. At present the method is being evaluated by W. R. Laing.

Absorption Spectrum of Aqueous Ions of Neptunium

W. J. Wolkowitz

Members of the Chemical Technology Division requested spectrophotometric data on neptunium in solutions of uranyl sulfate. Measurements of the absorption spectrum were made with a Beckman model DU quartz spectrophotometer. The instrument was operated at a slit width of 0.0125 mm in the spectral region of 950 to 1020 mμ and of 0.015 mm in the region of 700 to 775 mμ. In the case of very sharp absorption bands, the peak maximum was located by slowly rotating the wavelength scale and finding the point of maximum deflection of the galvanometer.

A 0.003 *M* solution of neptunium(IV) in 1 *M* sulfuric acid was prepared by evaporation of a 7 *M* nitric acid solution of neptunium(VI) to copious fumes with concentrated sulfuric acid. The neptunium was then precipitated with ammonium hydroxide; the precipitate was filtered, washed, and redissolved in concentrated sulfuric acid. The solution was then diluted to the desired acid concentration and analyzed for total neptunium by gross beta counting.

The freshly prepared solution exhibited characteristic absorption peaks at 727 and 969 mμ.[4] After 2 hr a peak was observed at 983 mμ, thus indicating disproportionation between the oxidation states of neptunium(IV) and neptunium(V). The extinction coefficients for these peaks are shown in Table 3.

An analysis of this solution by the Radiochemical Group indicated that it contained 84% neptunium(IV) and 16% neptunium(V). No change in the valence states was observed during the next 72 hr.

TABLE 3. ABSORPTION BANDS OF NEPTUNIUM IN 1 *M* H_2SO_4

Wavelength of Absorption Band (mμ)	Ion	Molar Extinction Coefficient, *E*
727	Np(IV)	70.3
969	Np(IV)	56.1
983	Np(V)	57.3

When a small crystal of $FeSO_4 \cdot 7H_2O$ was added to the solution, the 983-mμ peak disappeared immediately, with an accompanying rise in the molar extinction coefficients to 92.1 and 73.0 at the 727- and 969-mμ peaks, respectively. Even though exposed to air, this solution was stable for several days.

In order to determine the effect of high concentrations of uranyl sulfate on neptunium(IV), the following experiment was tried. The neptunium and iron were precipitated out of the solution by means of ammonium hydroxide; then the washed precipitate was redissolved in concentrated sulfuric acid. An amount of uranyl sulfate was then added to give a concentration of 300 mg of uranium per milliliter. The solution was adjusted to 1 *M* sulfuric acid. Measurements taken with the spectrophotometer revealed that all the neptunium was in the neptunium(IV) state. The solution was then heated to 250°C in an autoclave and again examined. The absorption peaks at 727 and 969 mμ, which are characteristic of the neptunium(IV) state, were completely absent. The neptunium(V) peak, which is normally at 983 mμ, was found to have shifted to 998 mμ.

In order to reduce the neptunium to the quadrivalent state, 35 mg of $FeSO_4 \cdot 7H_2O$ was added, and, in the presence of this excess of iron, the solution was again heated to 250°C. Upon reexamination, it was observed that all the neptunium was in the quadrivalent state. There was no evidence of precipitation or oxidation of any kind; thus it was indicated that subsequent reactions which occur at 250°C are inhibited by the addition of excess ferrous sulfate to the solution. The effect of excess acidity in this system is now being investigated.

[4] J. C. Hindman, L. B. Magnusson, and T. J. LaChapelle, "Chemistry of Neptunium," *Report for Month of March 1945. Chemical Research – Basic Chemistry of Plutonium*, CN-2767 (April 13, 1945).

Determination of Sulfur in Purified Molybdenite

W. J. Wolkowitz

Members of the Chemistry Division are making heat-capacity measurements of molybdenite and have requested analyses of their purified material. Sulfur was determined in the purified molybdenite by the following method. A 0.2- to 0.3-g sample of molybdenite was treated, in a covered 400-ml beaker, with 30 ml of a saturated solution of potassium chlorate in concentrated nitric acid. The solution was heated gently until it became white; then 0.5 g of $KClO_3$ was added, and heat was applied until the solution was almost completely evaporated. Following the addition of 15 ml of concentrated hydrochloric acid, the solution was heated until all the brown fumes had disappeared. The residue was treated with 50 ml of water and 10 ml of bromine water. After the solution was boiled for 5 min, the sulfur was precipitated as barium sulfate.

Volumetric Determination of Iodine and Iodate in Homogeneous Reactor Fuel Solutions

A. D. Horton C. L. Burros

Samples of Homogeneous Reactor fuels were submitted to the Analytical Chemistry Division for the determination of iodine and iodate. These fuels contained 40 mg of uranium per milliliter as uranyl sulfate, 1.7 mg of chromium(VI) per milliliter, 0.635 mg of copper(II) per milliliter, and 0.10 mg of iodide per milliliter as potassium iodide. Prior to its submission for analysis, the synthetic fuel had been subjected to high temperature and pressure.

Iodine was determined by extracting it from the fuel with two 3-ml portions of carbon tetrachloride. The iodine was then extracted, as iodide, from the carbon tetrachloride by 5 ml of a 0.05% solution of sulfurous acid; the iodide was determined volumetrically by potentiometric titration[5] with a solution of silver nitrate.

Total iodide in the sample was determined by reducing the iodine and iodate to iodide by the addition of hydrazine hydrate and nitric acid, then titrating potentiometrically with a solution of silver nitrate. The iodide equivalent to iodate was determined by subtracting the iodide equivalent to iodine from the total iodide. The results are given in Table 4.

TABLE 4. VOLUMETRIC DETERMINATION OF IODINE AND IODATE IN SYNTHETIC HRT FUEL

	Present (μg)	Found (μg)	Recovery (%)
I_2 as I^-	45.6	43.5	95.4
	45.6	43.2	94.7
	45.6	44.3	97.1
IO_3^- as I^-	50.0	49.9	99.8
	50.0	49.9	99.8
	50.0	46.4	92.8

Evaluation of 2,2′-Biquinoline as a Reagent for the Colorimetric Determination of Copper in Homogeneous Reactor Fuel

A. D. Horton C. L. Burros

According to Hoste,[6] 2,2′-biquinoline (cuproine) is a specific reagent for copper. This reagent is claimed to be 100 times more sensitive than ammonium hydroxide and 10 times more sensitive than diethyldithiocarbamate; but it is 4 times less sensitive than dithizone. The reagent was evaluated for application to the determination of copper in Homogeneous Reactor fuel. It was found that titanium and zirconium, when present in concentrations of 10 μg/ml, interfered seriously with the estimation of copper. This method does not offer any advantages over the existing colorimetric and polarographic methods for copper.

Simplification of the Spectrophotometric Determination of Iron in Homogeneous Reactor Fuel

A. D. Horton C. L. Burros

In order to determine iron in Homogeneous Reactor fuel by remote control in the High-Radiation-Level Analytical Facility, it is necessary to reduce the number of manipulations to a minimum.

[5] P. F. Thomason, "Automatic Potentiometric Titration of Halides," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1951*, ORNL-955, p 12.

[6] J. Hoste, "On a New Copper Specific Group," *Anal. Chim. Acta* 4, 23 (1950).

The standard procedure[7] provides for the adjustment of the pH of the sample to 9.0 after the addition of orthophenanthroline and ammonium citrate solutions. The adjustment must be made by trial and error by adding ammonium hydroxide and testing with pHydrion paper. In order to eliminate this step in the procedure, a buffer solution was sought that would produce the proper conditions for the development of the color of the ferrous orthophenanthroline complex and also maintain a stable color for a reasonable length of time.

Borate buffers were unsatisfactory because a precipitate was produced. A citrate buffer was sought which would prevent precipitation of the uranium and at the same time provide a stable condition for the development of the color. Sörenson's citrate buffer[8] (pH 6.9) was satisfactory in preventing precipitation of uranium, and the complex was stable for more than 24 hr when it was used. A standard calibration curve based on the use of Sörenson's buffer for pH adjustment obeyed Beer's law in the range of 10 to 60 μg of iron per 25 ml of total volume.

Indirect Volumetric Determination of Nickel in Homogeneous Reactor Fuel

A. D. Horton C. L. Burros

The method for determining nickel, as reported by Pribil *et al.*,[9] is an indirect determination that is based on the formation of a nickel chelate with the disodium salt of ethylenediamenetetraacetic acid, followed by titration of the excess salt with a ferric chloride solution. The conditions outlined by Pribil specify adding 1 ml of 50% (wt/vol) ammonium acetate solution per 100 ml of sample (nickel concentration not specified), adjusting the pH to 5 to 6, then adding excess disodium salt of ethylenediamenetetraacetic acid (0.1 *M*) and back-titrating with 0.1 *M* ferric chloride solution.

Initially, a study was made to determine the pH at which the desired potential break would occur in a system in which platinum and glass electrodes are used. The concentrations of nickel, disodium ethylenediaminetetraacetate, and ammonium acetate were held constant, and titrations were made in solutions that had pH values ranging from 2.5 to 6. The titration curve was smooth and had a potential break of approximately 150 mv at a pH of 3. It was noted that after several titrations the platinum electrode became passivated. Consequently, it became necessary to remove the electrode, flame it for several seconds, and then polish it with crocus cloth or fine emery paper.

Several analyses were made of solutions with amounts of nickel that ranged from 50 to 500 μg; the recovery was 97 to 100%. Additional work is to be done in the range of nickel quantities below 50 μg.

Ion-Exchange Separation and Polarographic Determination of Rhenium in Molybdenum Ores and in Flue Dusts

H. H. Miller

A procedure for the determination of rhenium in molybdenum ores and in flue dust has been developed. Preliminary experiments[10] on separations of rhenium from molybdenum by means of Dowex 1 resin columns were not successful because molybdenum could not be washed from the column, even with large volumes (3 liters) of 1 *N* sodium hydroxide. Because the molybdenum polarographic wave precedes the ReO_4^- wave, it is necessary to remove all the molybdenum; therefore Dowex 1 resin did not appear to be suitable for the separation. Possibly a larger wash volume would have removed the molybdenum; however, a different resin was used in order to save time.

Since ReO_4^- is held by the hydroxide form of Dowex 2 resin and molybdenum is passed through, Dowex 2 was investigated. It was found that when sample solutions containing 1- to 5-g of molybdenum ore (MoS) were passed through a 3 × $^3/_4$ in. column the molybdenum could be washed off completely with 2 liters of 1 *N* sodium hydroxide.

The final procedure was carried out as follows. A 1- to 5-g sample of ore was fused with 10 to 50 g of Na_2O_2 in a zirconium crucible. After the

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

[8] W. M. Clark, *The Determination of Hydrogen Ions*, p 211, Williams & Wilkins, Baltimore, 1928.

[9] R. Pribil, Z. Koudela, and B. Matyska, "Uses of Complexones in Chemical Analysis. XIII. Potentiometric Determination of Certain Cations by Means of 'Complexeone III' Solutions," *Collection Czechoslov. Chem. Communs.* 16, 80 (1951).

[10] H. H. Miller, "Ion-Exchange Separation and Polarographic Determination of Rhenium in Molybdenum Ores and Flue Dusts," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 3.

melt was cooled, it was dissolved in water and the solution made up to a volume that was approximately 1 *N* in sodium hydroxide. This solution was passed through the column of hydroxide-form Dowex 2 resin. The resin was washed with 2 liters of 1 *N* sodium hydroxide, sufficient water to remove the sodium hydroxide, and 20 ml of 0.1 *N* perchloric acid solution; the ReO_4^- was then eluted with 35 ml of 2 *N* perchloric acid. This eluate was made up to 50-ml volume with concentrated perchloric acid, which gave a final concentration of supporting electrolyte of 4 *N* perchloric acid. Results of the analysis showed rhenium to be present in various ores in concentrations of from 3 to 7000 ppm. A study of the precision of the method will be made.

Semimicrodetermination of Fluorides in Metal Dissolver Samples of the Thorex Process by Pyrohydrolysis

J. G. Surak P. F. Thomason

It will be necessary to know the concentration of fluorides in the Thorex metal dissolver samples, because the presence of large quantities of fluorides may affect the solvent process. Since the method of Warf *et al.*[11] for the determination of fluorides in solid samples seemed to offer a means of separating fluorides from large quantities of thorium and aluminum, its applicability to liquid samples was investigated.

It was found that fluoride could be carried to a large extent by the aluminum and thorium hydroxides precipitated by the addition of ammonium hydroxide to aluminum and thorium solutions. The residual fluoride in the ammoniacal solution can be adsorbed by the addition of a magnesium oxide slurry. All the solids were filtered onto a Whatman No. 41H filter paper and then thoroughly dried under a heat lamp. The paper and its contents were transferred to a nickel crucible and then ignited at 1000°C to drive off any nitrates that remained. After uranium oxide (U_3O_8) was added as a pyrohydrolytic accelerator, the crucible and its contents were placed in the all-nickel pyrohydrolytic apparatus of Susano *et al.*[12] The hydrofluoric acid evolved by the pyrohydrolytic method was absorbed in a known amount of standard sodium hydroxide solution. The fluoride was then estimated from the volume of standard acid used in the back-titration of the excess sodium hydroxide.

Samples that contained approximately 0.3 to 0.5 meq (6 to 10 mg) of fluoride, 1.0 *M* thorium nitrate, 0.37 *M* aluminum nitrate, and 6.5 *M* nitric acid were analyzed by this procedure, with a recovery of 90% of the fluoride.

Another method of separating the thorium from the fluoride – that of precipitating the thorium with oxalic acid – resulted in poor recovery and was abandoned.

ANALYTICAL INSTRUMENTATION

D. J. Fisher

Simplified Model of Automatic Titrator with Velocity-Servo Control of Titrant Addition

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

An automatic titrator in which a velocity-servo system is used to control the rate of titrant addition has been reported.[13] A redesigned, simplified version of this type of titrator has been built, and it should prove to be more reliable and less expensive to duplicate and service than the original model.

With the zero point set so that the voltage range of +1 to –2 v is covered, extensive reworking of the Brown recorder is not necessary. The need for a preamplifier has been eliminated by the use of a standard Brown amplifier, which is modified for a high-impedance input. By location of the chart-drive Brown amplifier, the two-phase motor, the tachometer, and the selsyn transmitter on the control-unit chassis, the number of cables between the Brown recorder and the chassis was greatly reduced; thus construction and service are simplified. The mechanical design of the servo subassembly has been greatly improved.

This simplification has not lowered the precision obtainable for redox-type titrations. Aliquots that contained approximately 5 mg of uranium were

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

[12] C. D. Susano, J. C. White, and J. E. Lee, Jr., *Apparatus for the Pyrohydrolytic Determination of Fluoride and Other Halides*, ORNL-1744 (July 14, 1954).

[13] M. T. Kelley, D. J. Fisher, N. D. Lee, H. L. Hemphill, and R. W. Stelzner, "Automatic Titrator with Velocity-Servo Control of Titrant Addition," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 10.

titrated with a relative standard error of ±0.25% at the 95% probability level. Preliminary tests indicate that the instrument will also work satisfactorily with pH electrodes.

Fall-Tube Turret for Electronically Timed Falling-Drop Instrument for the Determination of Densities of Aqueous Solutions

M. T. Kelley H. L. Hemphill
N. D. Lee

An instrument for the determination of densities of liquids by the falling-drop method has been described.[14,15] However, the determination of densities of radioactive solutions has required certain design changes in the previously reported instrument. The high radiation levels which are anticipated make it mandatory that the instrument be designed to operate entirely by remote control and, at the same time, have a versatile range of sensitivity.

In order to meet the two requirements of remote operation and versatility, the fall-tube assembly and the storage facility for unused fall tubes were combined into one vessel. The new unit is built as a turret and is constructed from two concentric cylinders. The phototubes are mounted inside the inner cylinder, and the light sources and focusing lenses are mounted on the outer cylinder, diametrically opposite the phototubes. The space between the two cylinders contains the six fall tubes and also serves as the constant-temperature bath. The top for the vessel is a turret that is driven by a Bodine motor and on which the six fall tubes are mounted. When the operator wishes to change to an oil of different density, he presses the switch controlling the Bodine motor, and the turret revolves, bringing another tube into alignment with the optics. The position of the turret is indexed so that a fall tube is always in the proper optical alignment.

Q-1551 Falling-Drop Densimeter

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

The Q-1551 falling-drop densimeter was constructed by the Instrument Department for use in the remote-control determination of the densities of radioactive solutions. The design of the instrument is based upon the externally triggered flip-flop timing circuit described in a previous report.[15] A 0.01-sec Standard electric clock is used for timing the fall of the drop in the viscous medium. Control circuits to operate the turret (see the preceding section) have been installed, and the Q-1551 is being calibrated and tested with synthetic solutions for routine operation. The greater sensitivity of the new timing circuit permits reliable operation of the unit with approximately 4.5 v (a-c) on the lamp filaments; thus the life of the lamps is appreciably extended.

An effort was made to use the light that is scattered in the backward direction by the drop as it passes through the beam; however, the effort was not successful with the present apparatus because of insufficient sensitivity of the phototubes. This arrangement would possess the advantage of decreasing the fatigue of the phototubes, but it would necessitate the use of either photomultiplier tubes or a light source of increased intensity. This scheme was abandoned when the fatigue problems of the type 925 phototubes were solved by the diffusion screens being mounted in front of the sensitive surfaces.

Dropping Oils for the Q-1551 Falling-Drop Densimeter

M. T. Kelley W. R. Laing
R. W. Stelzner D. J. Fisher
R. B. Quincy

When the Q-1551 falling-drop densimeter is used for the determination of the density of Thorex MD and AF process streams, the so-called "dropping" oil should meet the following specifications:

1. a density of approximately 1.5 g/ml at 30°C,
2. chemical inertness toward nitric acid,
3. a Reynolds number of less than 0.2 for the shortest time to be measured, in order to ensure streamline flow and adherence to Stokes' law,
4. constancy of physical properties (especially viscosity and density) with time,
5. stability toward radiation,
6. no leaching of the drop.

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[14] M. T. Kelley and N. D. Lee, "Electronically Timed Falling-Drop Instrument for the Determination of Densities of Aqueous Solutions," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1953*, ORNL-1639, p 5.

[15] M. T. Kelley, D. J. Fisher, and R. W. Stelzner, "Externally Triggered Flip-Flop Timing Circuit for the Falling-Drop Densimeter," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 7.

A ternary system of Nujol, phenylcyclohexane, and 1,1,2,2,-tetrabromoethane appears to meet these specifications except for the criterion of Reynolds number. The system permits coverage of the requested density range of 0.1 g/ml with one oil. This oil is the best compromise obtained thus far; therefore it is planned to use it in the apparatus and to continue a search for an oil with a lower Reynolds number. The silicone fluids appear to be promising because of their high viscosities and their flat viscosity-temperature characteristics.

Apparatus for the Pyrohydrolytic Determination of Fluorides

M. T. Kelley H. L. Hemphill

Apparatus for the determination of fluorides and other halides have been described.[16,17] A slightly modified version of the apparatus designed by Susano *et al.*,[16] in which pure nickel was used for the reactor tube, has been fabricated and put into service. The two heaters are constructed from replacement heating elements. A glass condenser is used. Testing of the apparatus has been completed, but no precision data have been compiled.

Simplified Apparatus for the Pyrohydrolytic Determination of Fluorides

M. T. Kelley J. G. Surak[18]
D. J. Fisher

An apparatus, of simplified construction and based upon several designs described above, for the pyrohydrolytic determination of fluorides has been built. The one-piece reaction tube is of nickel, and a single commercial Hevi-Duty tube-furnace is utilized without alteration for both superheating and pyrohydrolysis. The sample-port closure is less elaborate than that of the previous design, yet forms a tight seal. The condenser is of welded all-metal construction; no steam trap is needed. The apparatus is undergoing test.

Automatic Coulometric Titrator

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

An automatic coulometric titrator for the current range of 2×10^{-6} to 8×10^{-3} amp was designed for the Ionic Analyses Group and is being tested (cf. "Coulometric Determination of Plutonium in the Presence of Uranium," this report). The reagent-generating current is held constant to 0.1% or better over a cell resistance range of 0 to almost 10,000 ohms by means of a constant-current pentode in series with the cell. An adjustment of the control-grid bias of the pentode ("coarse" and "fine" controls) permits a selection of an operating current in the range of the instrument. The current stability of the instrument is increased by the use of an electronically regulated power supply and a 6.3-v Sola Electric Co. constant-voltage transformer for the filament of the constant-current pentode.

A Leeds & Northrup model 7664-A1 pH-millivolt meter is used to indicate the potential of an indicator electrode system and to furnish voltage for a type 2D21 a-c operated thyratron in a variable automatic-cutoff circuit. A ten-turn Helipot ("automatic cutoff adjust") selects an emf corresponding to the end point of the reaction for the cutoff of the generating current. An R-C time-delay circuit can be introduced into the cutoff circuit by means of a switch on the front panel. This time delay (proportional to the drop in the emf) prevents chattering near the end point of sluggish reactions. Provision is made for selection of the cutoff emf in either direction (0 to 1400 mv or 1400 to 0 mv). Calibration curves of the ten-turn Helipot cutoff-adjust permit selection of the desired end-point cutoff at the start of a titration.

The generating current is determined from a reading of a Weston Electrical Instrument Corp. model 741, 0- to 1-ma ammeter placed in the plate circuit of the constant-current pentode. Currents may be read from 0 to 1 ma or from 0 to 10 ma on the meter through selection of a current-range switch. The current-range switch automatically adjusts the bias range of the constant-current pentode to avoid inadvertent damage to the meter. A more accurate indication of the generating current flowing through the cell is obtained by measuring with a potentiometer the voltage across a precision 100-ohm resistor that is also located in the plate circuit of the constant-current pentode.

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[16] C. D. Susano, J. C. White, and J. E. Lee, Jr., *Apparatus for the Pyrohydrolytic Determination of Fluoride and Other Halides*, ORNL-1744 (July 14, 1954).

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

[18] Research participant from Marquette University.

Initial adjustment of the generating current, without current flowing through the coulometric cell, is made possible by the use of a dummy cell. A relay switch leads from the dummy cell to the coulometric cell and activates a timing clock at the start of a titration. At the end of the titration, the dummy cell is automatically switched back into the pentode circuit, and the timing clock is stopped. This arrangement permits a current flow through the pentode at all times, thereby avoiding changes in current that would be introduced by on-off transients. The timing clock operates only when current flows through the coulometric cell.

A variable polarizing current of 0 to 20 μa is available so that the instrument can be used with a polarized indicator electrode. If desired, the instrument can be operated manually by throwing a selector switch to the "manual" position.

New High-Sensitivity General-Purpose and Derivative Polarograph

M. T. Kelley D. J. Fisher

Development of a new high-sensitivity general-purpose and derivative polarograph is in progress. The polarizing unit of this instrument is essentially the same as the units used in the model Q-1160 high-sensitivity polarograph, the model Q-1338 derivative polarograph, and the dual dropping-mercury-electrode polarograph. It will include both linear and residual compensators and a switch for the reversal of the direction of polarity. The filter section, which differs from filter sections found elsewhere, completely eliminates from the strip-chart record the fluctuations in current due to the growth and fall of the mercury drops, as does the quadruple parallel-T, R-C network. Preliminary tests show that this performance of the new filter is achieved with less distortion of the form of the polarographic wave than was formerly possible, which should increase the field of application of the derivative function. The use of the new filter requires a great amplification of the cell current. A chopper current-feedback amplifier having an input impedance of several megohms has been built for this purpose. It has an over-all voltage gain of 500 and consists of a slightly modified standard Brown amplifier. This amplifier, like the special amplifier of the model Q-1338 polarograph, cancels the voltage drop across the current-measuring resistor and thereby permits the use of high-value resistors to give a high signal-to-noise ratio without the introduction of a voltage drop in series with the cell and the polarizing source. No preamplifier is required for the recorder. The standard Brown amplifier in the recorder is slightly modified for high input impedance.

Model Q-1549 Dielectric-Constant Meter

M. T. Kelley G. A. Holt[19]
R. D. Sidnam[19] D. J. Fisher

A new dielectric-constant meter has been fabricated by the Instrument Department. The design is based on that of the model Q-1282 TBP-Varsol meter and the model Q-1462 relative composition indicator. It has been found that analyses performed by means of the model Q-1282 TBP-Varsol meter can be done equally well with the new instrument and that identical calibration curves are obtained. In addition, the Q-1549 instrument is more stable after warmup. This feature would permit chart recording of the meter readings, if required.

Evaluation of the Aminco Photomultiplier Pickup Unit for the ORNL Fluorophotometer

M. T. Kelley D. J. Fisher

The optical head and the photomultiplier voltage-supply and current-reading circuits of the ORNL model Q-1165 fluorophotometer have been designed for reliability, stability, sensitivity, and linearity over a wide range of uranium concentrations. Economic considerations led to the evaluation of the Aminco photomultiplier pickup and indicator unit as a substitute for the units of corresponding function in the ORNL fluorophotometer. It was found that the Aminco unit is less stable and is linear over a narrower range of uranium content.

New Cell for the Model Q-946 Dielectric-Constant Meter

D. J. Fisher

A new sample cell has been fabricated for the model Q-946 dielectric-constant meter. The design is very similar to that of the cells previously used but incorporates changes necessitated by the obsolescence of components of the former cells. Testing of the new design is in progress.

[19] Instrumentation and Controls Division.

Heater for Microtitrations

M. T. Kelley D. J. Fisher

Certain potentiometric microtitrations involve chemical reactions that take place slowly at room temperature. The small liquid volume used, about 3 ml, is reduced rapidly by macroheating methods. A miniature heater has been designed that is small enough to be placed between a magnetic stirrer and the bottom of the microtitration vessel. The heater is constructed from the replacement element supplied for the Fisher Hot Spotter and is operated from a Variac. By use of this heater, 3 ml of liquid may be heated to a steady temperature of 70°C, which can be maintained with the Variac set at about 40, with low loss of liquid during a titration, and so improved titration results are obtained. The life of the heater element should be much longer than its full-voltage life because it is operated at 35% of its voltage rating.

Modifications to Shielded Cubicle for Chemical Analysis of Radioactive Materials

M. T. Kelley J. H. Edgerton
H. L. Hemphill

The shielded cubicle for use in handling radioactive materials[20] has been modified by the addition of a sample entrance at the face of the lead barricade. A counterweighed lead door has been installed to allow a portable lead sample carrier (designed by C. C. Webster, Solid State Division) to be wheeled into the cubicle on a small carriage from a special, track-equipped, 1-ton-capacity transfer table. This arrangement allows the transfer carrier, containing four 30-ml solution bottles held in place by spring clamps, to be positioned directly under the remotely controlled pipetor within the cubicle. As a result, the samples remain shielded from the time the bottles are loaded in the master-slave hot cells until the analytical operations are completed in the shielded cubicle. The transfer carriers and the cubicle door modifications are shown in Fig. 1.

[20] M. T. Kelley, J. H. Edgerton, and H. L. Hemphill, "Shielded Cubicle for Use in Handling Radioactive Materials," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 9.

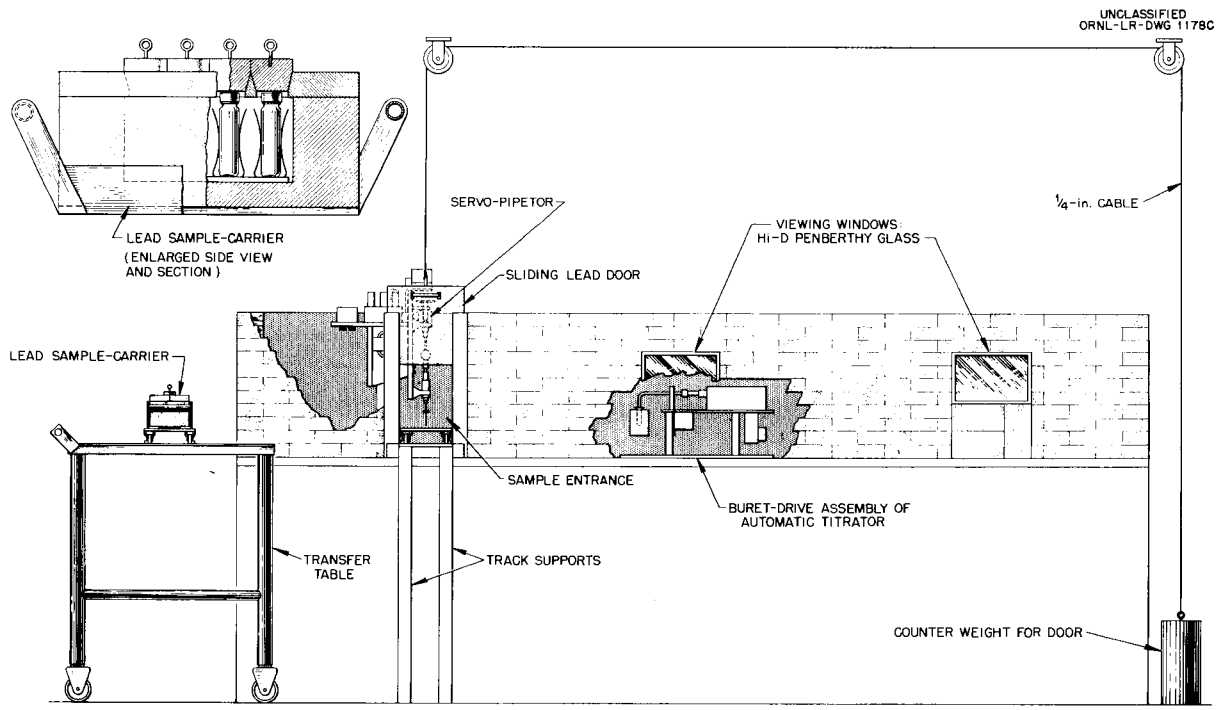

Fig. 1. Sample Carrier and Entrance Modification of Shielded Cubicle.

RADIOCHEMICAL ANALYSES

S. A. Reynolds

Nuclear Properties

W. S. Lyon T. H. Handley

The decay schemes of various activities of gadolinium, holmium, terbium, and dysprosium are being studied, and the results will be reported in the open literature.

The nuclide V^{49} has been identified, and the radioactive characteristics have been studied. The decay scheme of Rb^{86} has been studied. These results will also be published.

Measurement of Radioactivity

Recalibration of Alpha and Beta Standards (S. A. Reynolds). The standards which are used in the Analytical Chemistry Division for checking the performance of proportional alpha counters and Geiger-Mueller beta counters have been recalibrated. The procedure was simply to count each standard on all available counters in the Division laboratories and average the results. The values of the alpha standards were not appreciably different from the values obtained in the original calibration,[21] but the counting rates of the beta standards had increased approximately 7.7% because of the substitution of commercial G-M tubes for the locally constructed tubes in use at the time of the earlier calibration.

Instrumental Methods

Improved Scintillation Spectrometer and Coincidence Counter (W. S. Lyon, S. A. Reynolds). A new scintillation head for the gamma spectrometer has been obtained. It contains a 3 × 3 in. sodium iodide (thallium-activated) crystal. Improvements in sensitivity, resolution, and photopeak-to-Compton ratio have been noted. The spectrometer is being incorporated into a greatly improved coincidence counter, which has a variable delay of the pulses from the beta detector. The latter feature allows the study of coincidences between beta and delayed gammas. It is believed that the new instrument will facilitate the study of decay schemes, the absolute assay of certain radioisotopes, and the identification of radioelements.

[21] W. A. Brooksbank, "Alpha Standards," *Chem. Quar. Prog. Rep. Sept. 30, 1949*, ORNL-499, p 165.

Analysis of Thorex Solutions by Gamma Spectrometry (H. W. Wright). Preliminary research has been completed on the application of the gamma spectrometer to the analysis of Thorex samples. Further development will be done when actual samples are received. Synthetic samples contained approximately 10^8 gamma counts per minute per milliliter; 98% was Pa^{233} and 2% was radioisotopes of zirconium, niobium, ruthenium, and cerium. It was necessary to extract the protactinium to avoid overloading the spectrometer. This extraction apparently caused a bias of −5% in the zirconium-niobium results, presumably because of niobium losses. The observed precision of a limited number of experiments is given below; the "Single" column refers to a technique involving only one recording of each peak, and "Triple" refers to average values of three measurements.

	Estimated Standard Deviation (%)	
	Single	Triple
Protactinium	5.2	2.2
Zirconium-niobium	8.6	8.2
Ruthenium	5.4	5.1
Cerium	~4	3.5

The time required for various operations is as follows (the time given for the second item will be approximately 0.5 hr if single peak recordings are made):

	Time (hr)
Dilution and extraction	0.5
Instrument operation	1.25
Measurement and interpretation	0.75
Total	2.5

Fission Products

Evaluation of Radiochemical Procedures (H. W. Wright). A new procedure for cerium developed by L. E. Glendenin and E. Steinberg, of the Argonne National Laboratory, and based on the extraction of tetravalent cerium with hexone has been evaluated. The procedure offers the advantages of speed (separation in duplicate, approximately 45 min) and excellent decontamination from

the usual fission products (cerium, 99+% pure); neptunium interferes markedly. A serious disadvantage is the potential hazard caused by the use of the easily oxidized solvent in the extraction step.

Heavy Elements

Routine Determination of Plutonium Specific Activity (G. W. Smith). On the basis of a report[22] from the Los Alamos Scientific Laboratory that a good correlation exists between the per cent of Pu^{238} determined by alpha-pulse analysis and the plutonium specific activity, it seemed probable that specific activity could be routinely determined. Thus, by means of a relatively rapid alpha count and a pulse analysis, the time-consuming potentiometric titration of plutonium might be avoided. However, a preliminary investigation of the pulse analysis requirements with E. Fairstein (Chemistry Division) showed that it would be necessary to develop an instrument of higher sensitivity in order to carry out the pulse analysis with the accuracy required (±0.5%). It was learned later from C. F. Metz[23] of the Los Alamos Scientific Laboratory that the original information was premature and that the Pu^{238} specific activity relationship varied widely, depending upon the reactor in which the plutonium was produced. It was therefore concluded that since the Pu^{238} content could not be used to measure specific activity the local work should not be continued.

Electrodeposition of Plutonium for Fission Counting (G. W. Smith F. L. Moore). A request was made for the development of a plutonium electrodeposition method for preparing plates for fission counting in connection with cross-section studies in the Chemistry Division. Such a procedure was developed, based on the method of McAuliffe[24] for uranium deposition, in which plutonium is deposited from its tetravalent solution in an ammonium oxalate medium. Films of satisfactory uniformity having surface densities of plutonium as high as 0.14 mg per square centimeter were deposited on 2- and 5-in.-dia stainless steel and platinum plates. This method will be included in the *ORNL Master Analytical Manual* and in a paper to be submitted for publication in *Nucleonics*.

Determination of Pa^{233} in Organic Thorex Process Solutions (F. L. Moore). A method was developed for the determination of Pa^{233} in organic Thorex process solutions. The procedure involves stripping the Pa^{233} into 1 *N* sulfuric acid and subsequently extracting it into diisobutylcarbinol. Details will be published in a topical report.

Reactor Analyses

Xenon Experiment – ANP (W. A. Brooksbank, S. A. Reynolds). Previous work[25] has shown that even though xenon may be sparged readily from fused-salt fuels by helium it apparently diffuses out of such a fuel very slowly. The Analytical Chemistry Division has been requested to repeat and extend these experiments.[26]

In previous experiments, $Xe^{133,135}$ was adsorbed on charcoal and measured in the high-pressure ionization chamber. The present experiments will require a gamma scintillation spectrometer to measure the xenon* in the helium stream. (Xenon* refers to all active isotopes of xenon with half-lives longer than 1 min.) This method has the advantage of the flow being monitored continuously, which permits rapid changes in xenon* concentration, as a function of helium flow rate, to be evaluated.

The spectrometer (see Fig. 2) consists of a sodium iodide (thallium-activated) crystal assembly and a conventional electronic system. It differs from the conventional model in that four discriminator circuits are connected to the linear amplifier. This modification will permit simultaneous measurement of three energies, that is, the photopeak of any particular isotope of xenon under study and the Compton distribution on both sides of this peak. Data are recorded by linear rate circuits feeding into a multipoint Brown recorder. The fourth channel records, four times each hour,

[22] *Excerpts from the Progress Reports, Los Alamos Scientific Laboratory, Dec. 20, 1953*, WASH-141 (April, 1954).

[23] Letter to G. W. Smith from C. F. Metz, CMR-1-163 (July 6, 1954).

[24] C. McAuliffe, *Quantitative Electroplating of Uranium for Isotopic Analysis*, Monthly Progress Report No. A-3626 (Feb. 27, 1946).

[25] M. T. Robinson and D. D. Davies, "Xenon-135 in Fluoride Fuels," *Solid State Quar. Prog. Rep. Aug. 10, 1952*, ORNL-1359, p 19.

[26] M. T. Robinson, *Release on Xenon from Fluoride Fuels: Proposal for an Experimental Program*, ORNL CF-54-6-4 (June 2, 1954).

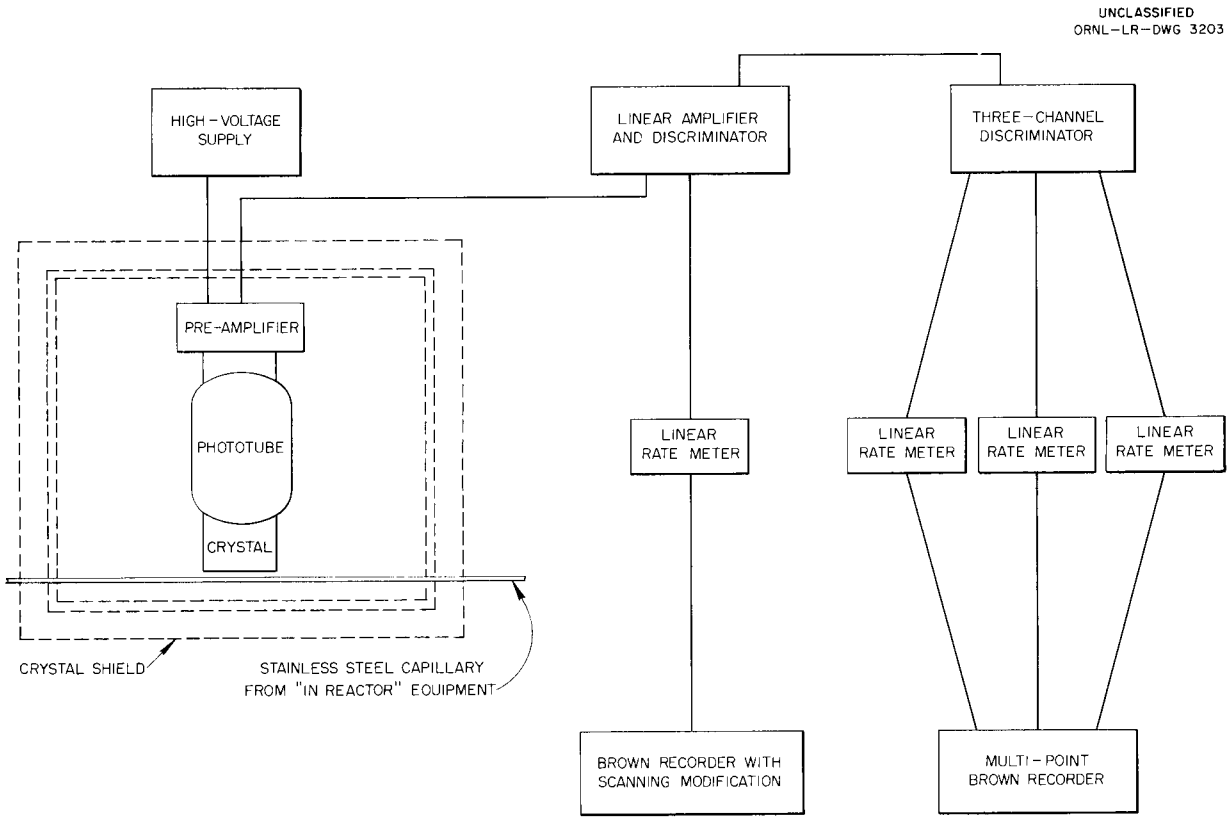

Fig. 2. Block Diagram of Xenon Spectrometer.

the over-all gamma spectrum from 0 to 1 Mev. This part of the circuit will show how decay products from noble-gas parents build up in the sample cell. The helium stream will pass the face of the crystal in a stainless steel capillary (0.017-in. ID). Crystal shielding will consist of 0.25 in. of aluminum, 4 in. of steel, and sufficient lead to reduce reactor background. The experiment is scheduled for in-pile tests by October 15, 1954.

Activities in LITR Water (W. S. Lyon, S. A. Reynolds). The radioactive constituents of LITR cooling water have been studied. An ORNL memorandum containing the results is being prepared, and publication in *Nucleonics* is contemplated.

Activities Volatilized from Reactor Elements (S. A. Reynolds). At the request of the Ceramics Laboratory of the Metallurgy Division, analyses have been made of the activities volatilized from neutron-bombarded reactor fuel elements which were heated in a furnace. The volatile radioelements were condensed in a liquid-nitrogen trap. The activities were allowed to decay for at least two days before samples were received. The methods used have included gamma-spectrometry and gamma-decay measurements by means of an ionization chamber and scintillation counters. Chemical methods have also been used to confirm the findings obtained by the above techniques. The gamma spectrometry technique has been described by Kahn and Lyon.[27] The nuclides listed in Table 5 have been found in the samples. A typical gamma spectrum is shown in Fig. 3. Results will be reported more fully by the Metallurgy Division.

In connection with the above program, a new gamma ray was found in 2.4-h I^{132}. The energy of the ray is approximately 0.77 Mev, and its intensity is approximately 60% as great as that of the 0.69-Mev gamma previously reported.[28]

[27] B. Kahn and W. S. Lyon, "Use of a Scintillation Spectrometer in Radiochemical Analysis," *Nucleonics* 11, No. 11, 61 (1953).

[28] F. C. Maienschein, J. K. Bair, and W. B. Baker, "Gamma-Radiation from I^{132}," *Phys. Rev.* 83, 477 (1951).

TABLE 5. ACTIVITIES VOLATILIZED FROM REACTOR ELEMENTS

Nuclide	Half Life	Gamma Energy[a] (Mev)
Xenon-133	5.3 d	0.08
Tellurium-132	77 h	0.22
Iodine-131	8 d	0.36
Iodine-132	2.4 h	0.67, 0.77
Iodine-133	20 h	0.53
Molybdenum-99[b]	67 h	0.14
Tungsten-187[b]	24 h	0.06, 0.14
Gold-198[c]	2.7 d	0.41
Neptunium-239[c]	2.3 d	0.10, 0.23, 0.28

[a]As measured in the current program.
[b]Occasionally found.
[c]Found in only one sample.

Burnup Determinations of Uranium (W. S. Lyon, S. A. Reynolds). The determination of uranium burnup in reactor fuel elements[29] has continued. The method has been adapted for routine handling; it has been described in two memoranda.[30,31]

Cyclotron Research

Neutron-Deficient Rare-Earth Radionuclides (T. H. Handley). Further progress has been made in the study of neutron-deficient radionuclides of the rare earths. Upon completion of the research, the results will be published in the open literature.

(p,α) Cross Sections (D. J. Coombe). Work has been continued on (p,α) cross-section determinations. The 86-in. cyclotron is being used as a source of protons. Cross-section data for the following (p,α) reactions have been taken: $Fe^{54}(p,\alpha)Mn^{51}$; $Ni^{58}(p,\alpha)Co^{55}$; $Cd^{116}(p,\alpha)Ag^{113}$(?); $Te^{130}(p,\alpha)Sb^{127}$; $Hg^{204}(p,\alpha)Au^{201}$(?). Since it was desired to utilize the limited time available, before the cyclotron is shut down, for making as many bombardments as possible, final calculations were not made. The determinations followed by question marks have not yet been verified.

As soon as the final calculations have been completed, a report will be submitted for publication.

[29]W. S. Lyon and S. A. Reynolds, "Reactor Analyses," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 12.

[30]S. A. Reynolds, *Burn-Up Determination*, ORNL CF-54-5-32 (May 7, 1954).

[31]S. A. Reynolds, *Cesium Standards for Burn-Up*, ORNL CF-54-8-170 (Aug. 26, 1954).

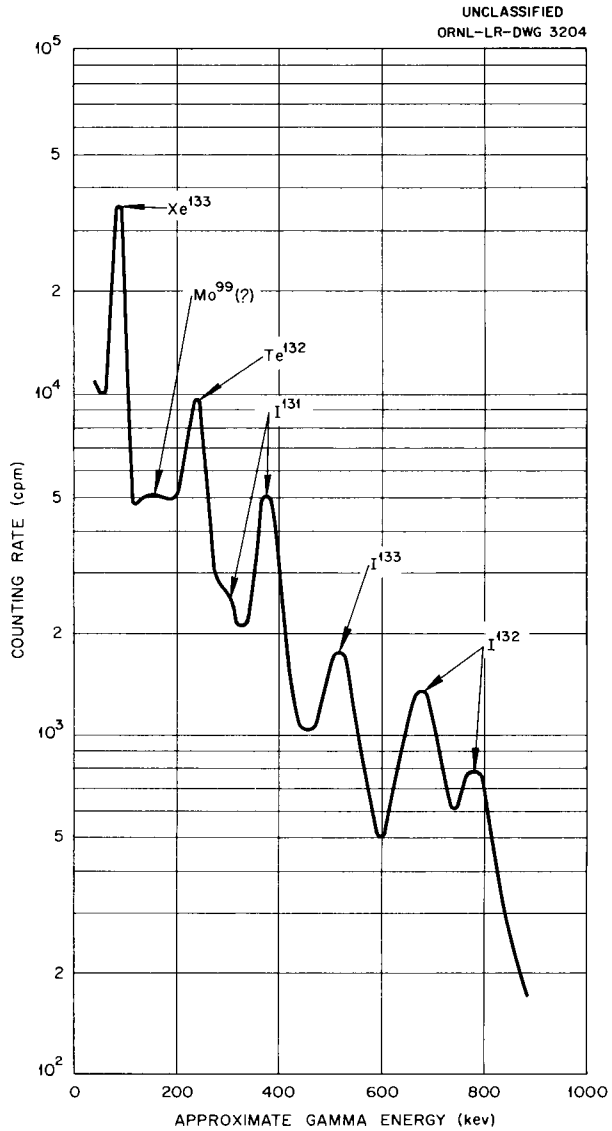

Fig. 3. Typical Spectrum of Volatile Fission Products (Adapted from Recorder Trace).

Cross Sections of Nickel, Copper, and Rubidium (W. S. Lyon). In collaboration with F. Green of the Electronuclear Research Division, a program has been initiated for the determination of the ratios of the cross sections for various proton-induced reactions. Included were cross-section measurements for (p,n), $(p,2n)$, (p,α), and $(p,2p)$ reactions on nickel and copper. The results will appear in the open literature. In addition, the reaction cross section of $Rb^{85}(p,n)Sr^{85}$ has been studied, and the cross-section ratio for the production of Sr^{85m} (70 m) and Sr^{85} (65 d) has been found to be $\sigma_{65\,d}/\sigma_{70\,m} = 58$.

Ion Exchange and Chromatography

Protactinium Decontamination in Thorex Solutions (G. W. Smith). The suggestion was made that anion exchange be used as a method for decontaminating Thorex solutions from protactinum so that fission-product activities could be determined with the scintillation spectrometer. According to the work of Kraus and Moore,[32] it may be possible to separate rare earths, zirconium, and protactinium and leave niobium and ruthenium on the column. Preliminary work on the preparation of tracers has begun.

ACTIVATION ANALYSES

G. W. Leddicotte

Determination of Lanthanum in AMEX Solutions

W. A. Brooksbank G. W. Leddicotte

Neutron-activation analysis and gamma-ray spectrometry have been applied to the quantitative determination of lanthanum in solutions from the AMEX process. The nuclear reaction $La^{139}(n,\gamma)La^{140}$ ($t_{1/2}$ = 40.0 h) is the basic nuclear reaction used in this determination. As it decays, La^{140} emits both beta and gamma radiations. After the irradiation, the basis for the analysis is the characteristic 1.596-Mev gamma[33] of La^{140}. A gamma spectrometer is employed in the radiation measurements. The lanthanum concentration of a sample can be calculated by comparing the gamma spectrum area of the 1.596-Mev gamma in the unknown sample with the same area in a comparative sample containing a known amount of lanthanum. The comparative sample and the unknown sample were irradiated and processed under the same conditions.

This method of analysis is unique in that it is usually not necessary to separate the radioactive lanthanum in the irradiated sample. The analysis is specific for radiolanthanum because no other radioelement of comparable half life gives the same gamma spectrum as La^{140}. The presence of gross amounts of chlorine or sodium in the sample material will cause some interference in the analysis. Radiochlorine, Cl^{38}, induced by the reaction $Cl^{37}(n,\gamma)Cl^{38}$, has a half life of 38.5 m, but this interference can be eliminated by allowing the irradiated sample materials to decay for several hours. The interference from the 15.0-h Na^{24}, produced in the reaction $Na^{23}(n,\gamma)Na^{24}$, can be eliminated by a simple precipitation of the lanthanum with hydrofluoric acid. The precipitate of lanthanum fluoride is washed and then transferred by slurrying to a mount (a watch glass or pyrex culture tube) for the gamma-spectrometer measurements.

Inherent difficulties have been experienced in the determination of very small quantities (10^{-3} mg or less) of lanthanum because of the presence of fissionable material, such as plutonium, in the solution. Lanthanum-140 is also produced in fission as the daughter activity of the 12.8-d fission Ba^{140}. The usual technique in eliminating this interference is to make a Ba^{140} radiochemical analysis on the sample and to correct the gross amount of La^{140} in the sample for the presence of this added fission La^{140}.

In samples in which the interferences from fission products have been slight, it has been possible to establish a lower limit of detection by this direct analysis method. The practical limit of detection is 0.001 mg. A forthcoming report will more fully describe the method and will establish its precision.

Determination of Microgram and Submicrogram Quantities of Europium in Lithium Iodide by Neutron-Activation Analysis

J. E. Strain G. W. Leddicotte

In lithium iodide crystals in which the weight ratio of europium to lithium iodide is 1:100 or greater, the europium concentration can be estimated by neutron-activation analysis. The basic nuclear reaction used is $Eu^{151}(n,\gamma)Eu^{152}$. Europium-152 decays with a half life of 9.2 h, and in its decay emits both beta and gamma radiations. The characteristic gamma spectrum,[33] particularly that portion due to the 0.122-Mev gamma, can be surveyed by means of a gamma spectrometer. The europium concentration can be calculated by comparing the integrated area of the 0.122-Mev gamma spectrum in the unknown to the same area in the gamma spectrum of a sample of known europium content; the two samples are processed and irradiated in the same manner. Interferences from the radioactivities induced in lithium and

[32] K. A. Kraus and G. E. Moore, "Anion Exchange Studies. III. Protactinium in Some HCl–HF Mixtures: Separation of Niobium, Tantalum and Protactinium," *J. Am. Chem. Soc.* 73, 2900 (1951).

[33] J. M. Hollander, I. Perlman, and G. T. Seaborg, "Table of Isotopes," *Revs. Mod. Phys.* 25, 469 (1953).

iodine will be absent, because the radioelements of these elements, which are produced, do not have comparable gamma spectra. Also, a short decay period after the irradiation can be used to eliminate these interferences, since the induced radioisotopes decay with half lives of 0.825 s (Li^8) and 25.0 m (I^{128}).

It was presumed that a portion of the irradiated sample could be analyzed directly. However, the high absorption cross section (67.0 barns) of natural lithium for thermal neutrons and the high lithium content (0.37 *M*) of the material produced a flux depression which caused the results to be low. The introduction of a *preirradiation* separation of the europium on a ferric hydroxide precipitate with a subsequent ignition to ferric oxide removed the lithium interference. The time of irradiation was sufficiently short (1.0 hr) so that the amount of radioiron produced (Fe^{59}, $t_{1/2}$ = 45.1 d) did not interfere in the assay. Concentrations as small as 0.16 μg per milliliter of solution were determined by this method. The results obtained compared favorably with the results of ordinary chemical analyses of the same material.

Determination of Microgram and Submicrogram Quantities of Elements by a Combined Neutron-Activation–Gamma-Spectrometer Technique

J. E. Strain G. W. Leddicotte
W. A. Brooksbank

The direct method of analysis described above for the determination of lanthanum in AMEX solutions and for the determination of europium in crystals of lithium iodide has also been extended to the determination of tungsten in an iron crystal, of arsenic and gold in petroleum products, and of americium in AMEX process solutions. The assay, in each instance, was made by taking a portion of the irradiated material and surveying the gamma radiation spectrum by means of a gamma spectrometer. A summary of the characteristic gamma radiations of the radioelements of interest is given in Table 6. The area of the gamma peak used in the analysis was integrated and was compared with the same area found in a comparative sample containing a known amount of the element of interest, which had been irradiated and processed in a similar manner to that of the unknown sample.

This method of analysis was used in the assay of several samples from each category mentioned above. A preliminary survey would indicate that it is possible to determine at least 10 ppb of arsenic and at least 1 ppb of gold in oils by this method. Also, about 1 ppm of americium could be determined in solutions from the AMEX process. Several hundred parts per million of tungsten were determined in the iron crystals, and the assay indicated that these particular elements could be determined without loss of precision or accuracy when in the order of several parts per million.

It is believed that the technique can be extended to routine analyses of other gamma-emitting radioelements in a variety of materials. This study will be continued and the results will be compiled in a topical report.

Determination of Microgram and Submicrogram Amounts of Chlorine in Graphitar Bearings

W. A. Brooksbank J. E. Strain

Microgram and submicrogram amounts of chlorine in Graphitar bearings that are used in certain experiments of the HRE were determined by means of neutron-activation analysis. Portions of each bearing were irradiated in the ORNL Graphite Reactor for 45 min. The induced Cl^{38} ($t_{1/2}$ = 38.5 m) produced by the nuclear reaction $Cl^{37}(n,\gamma)Cl^{38}$ was then separated by an isotopic-carrier method. The inactive chlorine carrier and the radiochlorine were distilled from a finely divided suspension of the irradiated sample in concentrated sulfuric acid. The volatile carrier and the radioelement were absorbed in sodium hydroxide solution. The chloride was precipitated as AgCl and weighed for a chemical-yield determination. After the weighing, the AgCl precipitate was transferred to a pyrex culture tube for a determination of the Cl^{38} radioactivity by means of a gamma scintillation counter. The concentration of chlorine in the bearing materials was calculated by comparing the Cl^{38} radioactivity of the unknown sample with the Cl^{38} radioactivity found in a comparative sample which contained a known weight of chlorine and which had been irradiated and processed under the same conditions used for the unknown sample. The results obtained in the assay of a number of samples indicated that chlorine in concentrations as small as a few parts per million could be determined with a relative standard deviation of ±5%.

TABLE 6. GAMMA RADIATION CHARACTERISTICS OF CERTAIN ELEMENTS ANALYZED BY GAMMA-SPECTROMETER–NEUTRON-ACTIVATION TECHNIQUE

Stable Isotope	Radioelement	Half Life	Gamma Radiations (Mev)*	Gamma Used in Analysis (Mev)
La^{139}	La^{140}	40.0 h	0.093, 0.335, 0.490, 0.820, 1.596, 2.50	1.596,**0.490
Eu^{151}	Eu^{152}	9.2 h	0.122, 0.244, 0.344	0.122
As^{75}	As^{76}	26.8 h	0.55, 1.20, 1.70	0.55
W^{186}	W^{187}	24.1 h	0.072, 0.134, 0.480, 0.552, 0.618, 0.690, 0.775	0.134
Au^{197}	Au^{198}	2.69 d	0.412, 0.676, 1.088	0.412
Am^{241}	Am^{242m}	16.01 h	0.035, 0.038, 0.053	0.053

*Data from J. M. Hollander, I. Perlman, and G. T. Seaborg, "Table of Isotopes," *Revs. Mod. Phys.* 25, 469 (1953).
**Used most often.

Determination of Microgram Amounts of Nickel in Blood

W. A. Brooksbank

A preliminary investigation of the feasibility of using neutron-activation analysis to determine microgram amounts of nickel in blood (and other biological materials) is being made. The basic nuclear reaction is $Ni^{64}(n,\gamma)Ni^{65}$ ($t_{1/2}$ = 2.56 h). The beta radiations emitted in the decay of the Ni^{65} will be counted by a Geiger-Mueller counter. Sample preparation for irradiation and sample processing after irradiation are being studied. Preliminary results indicate that 1.0 ± 0.2 μg of nickel can be determined by the method being considered.

Determination of Sodium, Potassium, and Cesium in Rubidium Carbonate

J. E. Strain

Neutron-activation analysis is now being applied to the determination of submicrogram amounts of sodium, potassium, and cesium in rubidium carbonate, which is being used as a target material for the production of the Rb^{86} ($t_{1/2}$ = 19.5 d) radioisotope distributed by the Radioisotope Sales Department. A modification of the ion-exchange technique described previously[34] is being used for separating the induced activities of the elements of interest. In the present separation technique, a column 44 cm long × 1 cm in diameter packed with larger than 120 mesh IR-100 resin is used. The eluting solvent is 0.15 *M* hydrochloric acid, and the flow rate is 0.5 ml/min. Approximately 0.10 g of rubidium carbonate was dissolved in 0.15 *M* hydrochloric acid and loaded onto the column. Excellent separations of the alkali radioactivities are achieved. The time required for total elution of the column is approximately 40.0 hr. The combined cuts for each radioactivity peak are evaporated to a known volume and aliquoted to pyrex culture tubes for a measurement of the gamma radioactivity on a gamma scintillation counter. The amount of the contaminant alkali element is calculated by a comparative-sample method in which a sample containing a known weight of the element of interest is irradiated and processed in the same manner as that employed for the unknown material.

It has been possible, by this method of analysis, to determine a few parts per million of other alkali elements as contaminants of the rubidium carbonate with a relative standard deviation of ±5%.

[34] G. W. Leddicotte and J. Y. Ellenburg, "Determination of Cesium in Rubidium Carbonate," *Anal. Chem. Quar. Prog. Rep. June 26, 1952*, ORNL-1361, p 22.

Determination of Microgram and Submicrogram Amounts of Silicon in Petroleum

W. T. Mullins G. W. Leddicotte

An investigation of the feasibility of determining microgram and submicrogram amounts of silicon in petroleum by neutron-activation analysis is being made. Preparation of samples and the method of processing the sample material after irradiation are being studied.

Radioisotope-Target-Materials Survey

G. W. Leddicotte

At the request of the Radioisotopes Sales Department, a survey of the specific activity to be obtained in the irradiation of radioisotope target materials in the ORNL Graphite Reactor is being made. In addition, contaminant radioelements are being considered, as well as other factors such as activation cross-section studies and half-life determinations. So far, target materials for the production of the radioisotopes of barium, arsenic, sodium, potassium, cesium, and tungsten have been included in the survey. A topical report will be issued at the end of the investigation.

Use of Radioactivation Analysis as a Qualitative or Semiquantitative Analytical Method

M. M. Vick[35] H. A. Mahlman[36]
G. W. Leddicotte

A previous report[37] describes the progress of the investigation of radioactivation analysis as an analytical method and briefly describes the technique as applied to the acid-sulfide and basic-sulfide group separations in the Freserrius scheme of qualitative analysis. The scope of the investigation has been enlarged to include analysis of the ammonium hydroxide group [$Fe(OH)_3$ precipitate].

The members of the hydroxide group which can be determined by activation analysis are: cobalt, chromium, iron, gallium, zinc, tantalum, zirconium, tungsten, yttrium, lanthanum, thorium (as protactinium), and the rare earths. Radioactive traces of these elements were used in the work described here. When an unknown mixture is analyzed, any of these metals may be carried down with the carrier precipitate. Individual elements may be separated on an ion-exchange column of Dowex 1 resin by use of the chloride complexes of the metallic ions. The radioactive material was dissolved in 12 *M* HCl and put onto the ion-exchange resin column, which had been previously treated with 12 *M* HCl. Those ions which did not form complex chlorides (chromium and the rare earths) were rapidly eluted. Elution with other solutions having different concentrations of hydrochloric acid followed. The order of elution is shown in Fig. 4.

Suitable conditions for the adsorption and desorption of those ions that are not retained on the chloride column were considered. The use of oxalate complexes appeared to be satisfactory. The chloride resin was converted to the oxalate form by mechanical shaking for 16.0 hr with 0.5 *M* potassium oxalate solution followed by centrifugation. An oxalate solution of the radioactive material was placed on a column 0.8 cm in diameter by 11 cm in length, having 100- to 200-mesh resin, and the elution followed. It was found that adsorption was less in high concentrations of oxalate ion than in low concentrations of the oxalate ion. Figure 5 shows these separations.

When the initial solution was 0.01 *M* oxalic acid, chromium was not retained any longer than the time required for the passage of a column volume. Changing the eluting solvent to 0.10 *M* oxalic acid effected the elution of lanthanum and cerium. The slow rate of elution caused a tailing of the lanthanum into the cerium fraction and precluded quantitative separation. Changing to a 0.4 *M* oxalic acid wash solution caused europium and yttrium to be eluted in twin peaks like those of lanthanum and cerium. Protactinium could not be eluted under these conditions but could be removed by washing the column with 1.0 *M* sulfuric acid. Protactinium-233 (27.4 d) is the daughter activity of Th^{233} (23.5 m) and is used in the determination of thorium by activation analysis.

Additional work was directed toward effecting a more rapid elution and thus improving separations. Figures 6 through 9 indicate some of the results with eluting solvents of (1) various concentrations of hydrochloric acid, (2) ammonium nitrate solutions, (3) mixtures of oxalic acid and sulfuric

[35] Research participant from Louisiana State University.

[36] Chemistry Division.

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

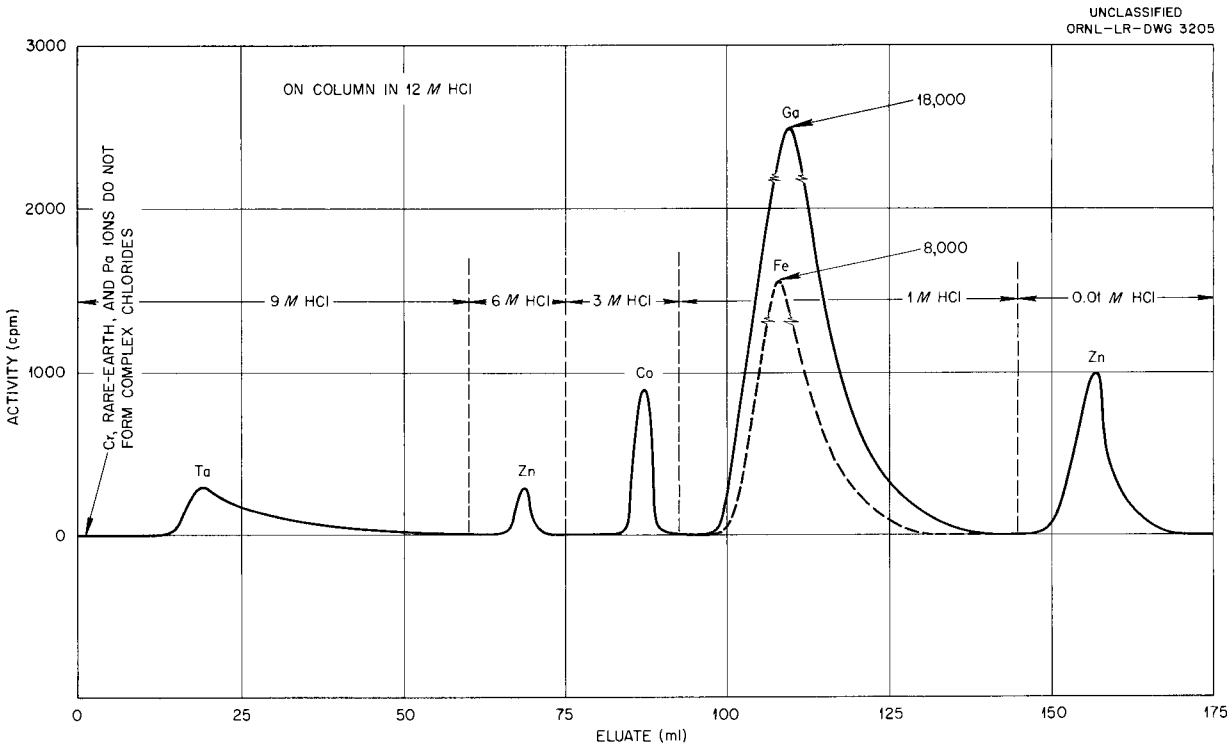

Fig. 4. Separation of Chloride Complexes on Dowex 1 Chloride Resin Bed.

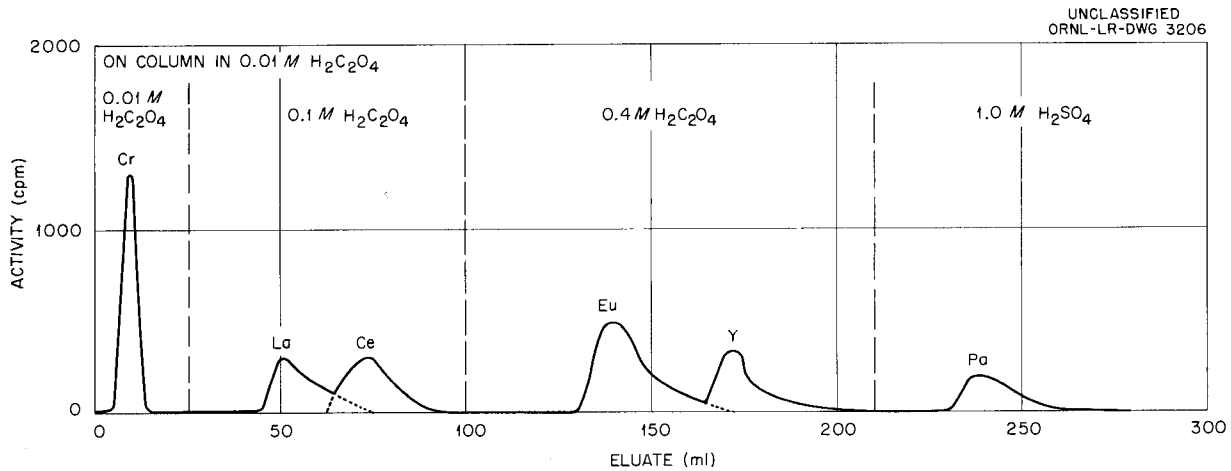

Fig. 5. Separation of Oxalate Complexes on Dowex 1 Oxalate Resin Bed.

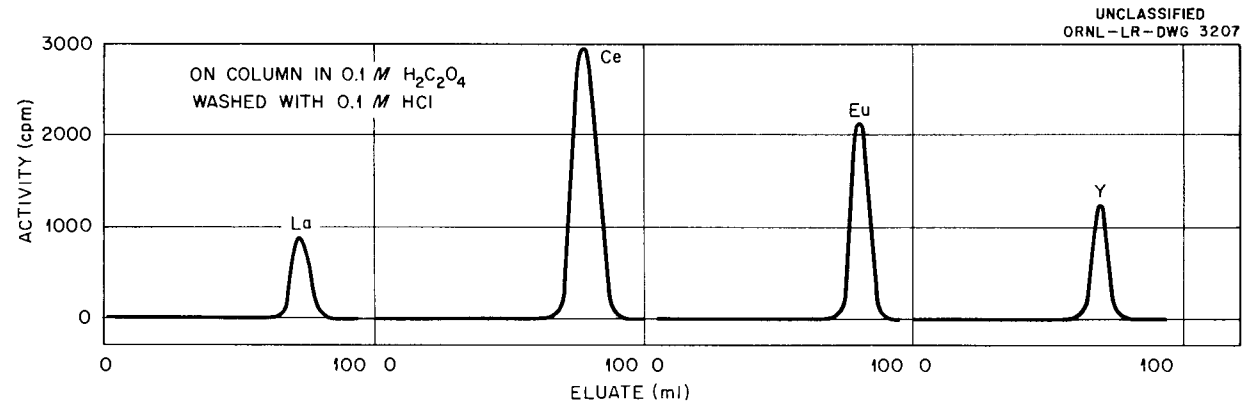

Fig. 6. Eluting Patterns for Some Oxalate Complexes on Dowex 1 Oxalate Resin Bed.

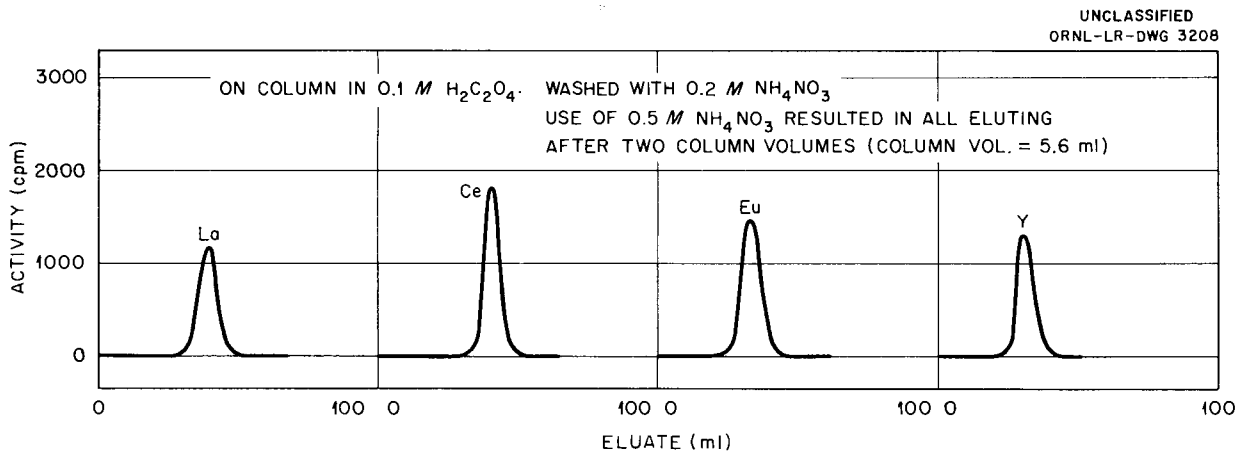

Fig. 7. Eluting Patterns for Some Oxalate Complexes on Dowex 1 Oxalate Resin Bed.

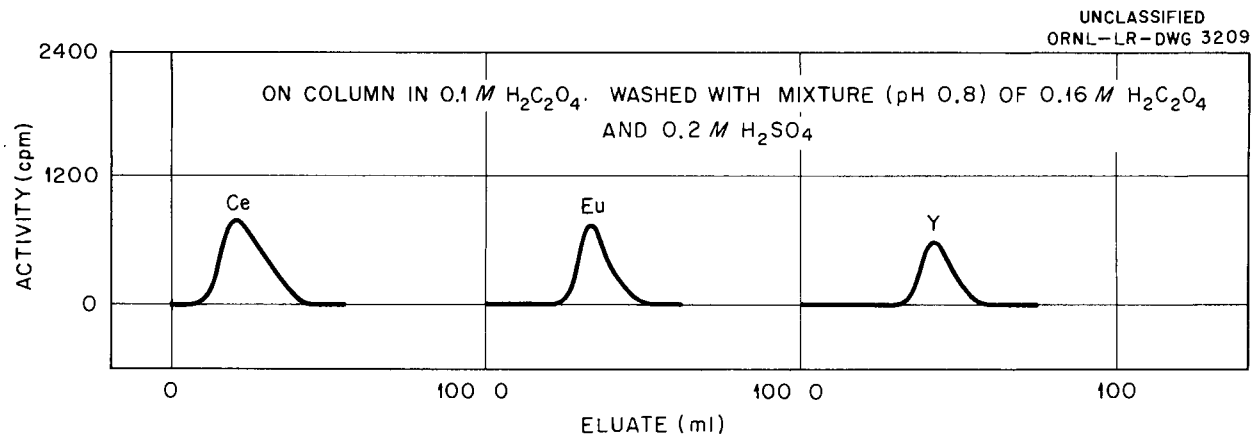

Fig. 8. Eluting Patterns for Some Oxalate Complexes on Dowex 1 Oxalate Resin Bed.

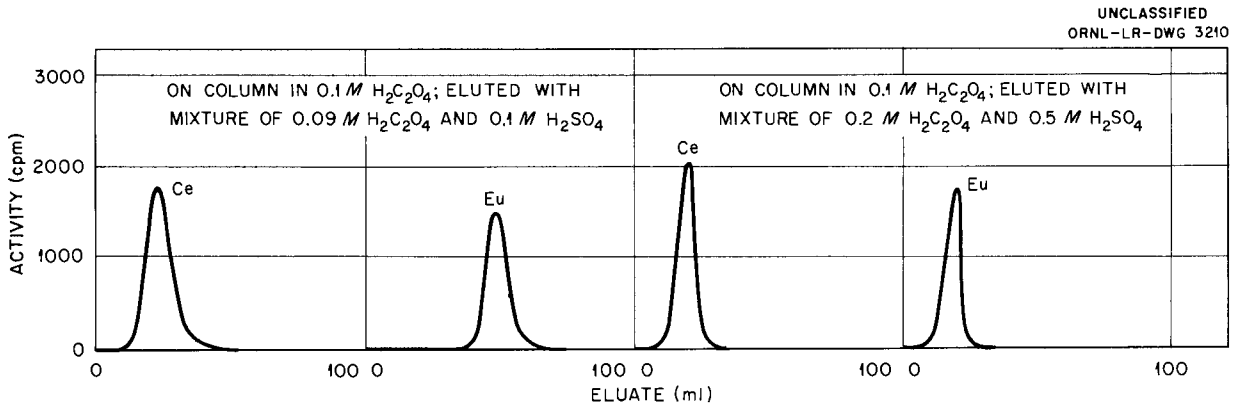

Fig. 9. Eluting Patterns for Some Oxalate Complexes on Dowex 1 Oxalate Resin Bed.

acid, and (4) oxalate solutions of equal oxalate strength but having different pH values (obtained by incremental additions of ammonium hydroxide to oxalic acid solutions).

The use of 0.2 *M* ammonium acetate effected a more nearly complete separation of europium from lanthanum and yttrium than was effected by any of the solutions mentioned above. Lanthanum and yttrium were not separated, but a subsequent wash with 0.1 *M* hydrochloric acid eluted lanthanum first and then yttrium with a minimum of contamination of yttrium by lanthanum. These separations are shown in Fig. 10.

It is believed that the results of these experiments will assist in establishing a reasonable separation procedure for the hydroxide-group elements; the procedure will be included in the present scheme of qualitative and semiquantitative analysis by activation analysis.

Particle-Size Distribution

G. W. Leddicotte H. H. Miller[38]

The feasibility of determining the apparent particle-size distribution in thorium oxide–water slurries by means of a method that utilizes both neutron-activation analysis and sedimentation analysis has been demonstrated. The method is a refinement of the ordinary pipet technique for determining subsieve particle sizes[39] and involves, essentially, measuring the decrease in concentration of particles at or above a particular level in a suspension as sedimentation proceeds.

The principle of the sedimentation method is based on the fact that a sample withdrawn after

[38] Ionic Analyses Group.

[39] E. H. Arnstein and B. A. Scott, "The Measurement of Particle-Size Distribution by Sedimentation Methods," *J. Appl. Chem. (London)* 1, Suppl. No. 1, S10 (1951).

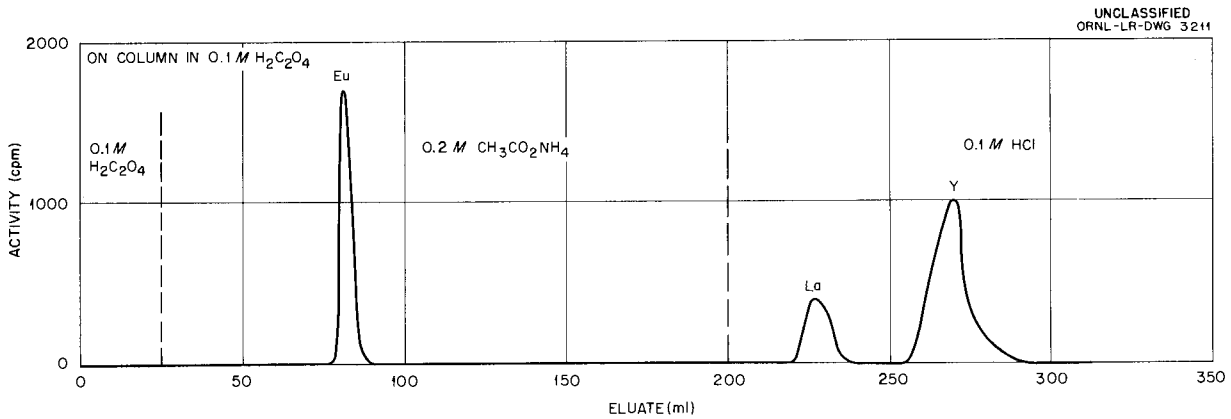

Fig. 10. Separation of Oxalate Complexes on Dowex 1 Oxalate Resin Bed.

a time t by means of a pipet whose tip is at a depth h below the surface of a dilute suspension of the material under test, in a suitable liquid, will contain particles smaller than those which have just fallen through a distance h in time t under the influence of gravity. After collection, the samples are evaporated to dryness, and the percentages (by weight) of the original sample are determined. The values obtained represent the total number of particles whose size is smaller than d_s, where d_s from Stokes' law is

$$d_s = \sqrt{\frac{9hn}{2(D_1 - D_2)gt}} ,$$

where

d_s = Stokes' diameter of particle, μ,

n = viscosity of suspending medium, cp,

h = distance between liquid surface and pipet tip when sample is withdrawn, cm,

D_1 = specific gravity of suspended particles,

D_2 = specific gravity of suspending medium,

g = acceleration due to gravity, cm/sec^2,

t = time from start of analysis, sec.

By the method described here, the thorium oxide-water slurry can be made radioactive by irradiation in the ORNL Graphite Reactor so that the induced radioactivity can be used for determining the particle-size distribution in a suspension. Thorium-232 can be made radioactive by the nuclear reaction $Th^{232}(n,\gamma)Th^{233}$. Thorium-233 decays with a 23.3-m half life to Pa^{233}, which decays with a half life of 27.4 d. As it decays, Pa^{233} emits both beta and gamma radiations. The gamma radiations are of diverse energies,[40] with a large portion attributed to the 0.310-Mev gamma, all of which can be detected by means of a gamma-scintillation counter. The counter is made up of a suitable scintillator optically coupled to a photomultiplier tube, a highly regulated high-voltage power supply, a linear amplifier, and a scaling circuit.

The present apparatus is shown in Fig. 11. It consists of a glass cylinder 1.5 in. in diameter and at least 30 in. in length; one end of the

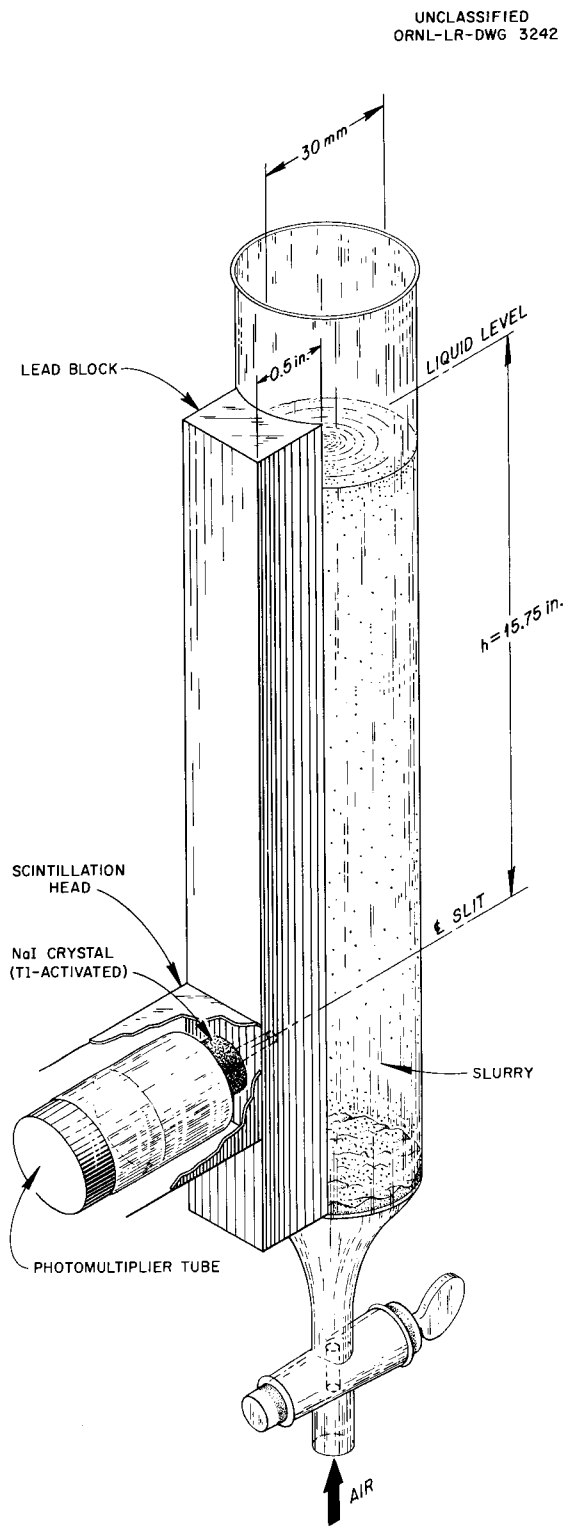

Fig. 11. Apparatus Used in Studies of Particle-Size Distribution in Thorium Oxide–Water Slurries.

[40] J. M. Hollander, I. Perlman, and G. T. Seaborg, "Table of Isotopes," *Revs. Mod. Phys.* 25, 469 (1953).

cylinder contains a medium-porosity glass frit and an air inlet. The cylinder has an approximate capacity of 700 ml; only 500 ml of solution is used, however, in an analysis. The scintillation head of the counter is placed against the outer wall of the cylinder and is surrounded by a lead shield which contains an open slit located in line with the scintillator of the counter (sodium iodide crystal, thallium-activated). This arrangement eliminates the need for the pipet used in conventional sedimentation apparatus and the need for withdrawing samples for evaporation and weighing in order to obtain the apparent concentrations, since the amount of Pa^{233} radioactivity will be proportional to the concentration of thorium in that part of the solution being observed by the counting apparatus. Because the particle size is related to Stokes' law, the sedimentation of the radioactive particles after some time interval will give the concentration of a particular particle size in relation to the total observed radioactivity at zero time, the start of the analysis. The observed radioactivity at any time is automatically recorded on a Brown recorder.

The usual technique in analysis is to place the irradiated sample in the apparatus. A dispersion agent for the particles, such as sodium pyrophosphate, is added and the column filled to a known volume (usually 500 ml) with water. The suspended particles are distributed by bubbling air through the solution. This agitation period is at least 5 min; then the air flow is turned off and the sedimentation of the radioactive particles is measured by means of the counting apparatus. Figure 12 is a typical curve of the per cent of radioactivity plotted against particle size d_s.

Potentially, this method of determining particle-size distribution offers a number of advantages over other methods. It is considered to be significantly faster than pipet techniques and can be adapted to the simultaneous assay of several samples. It also eliminates the necessity of withdrawing samples for evaporation and weighing in order to obtain per cent concentration; thus, it overcomes the possibility of disturbing the suspension, as is sometimes the case in the pipet method. Also, preliminary studies indicate that the method will afford a more representative picture of particle-size distribution than will such methods as microscopic analysis. The method requires that the concentration of thorium oxide

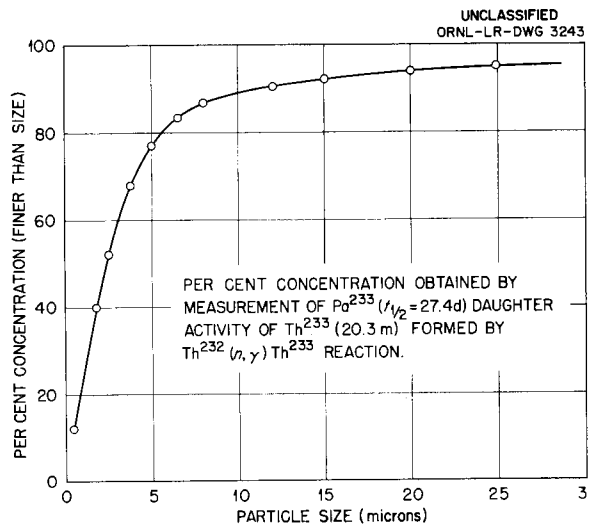

Fig. 12. Typical Curve of Particle-Size Distribution in Thorium Oxide–Water Slurries Obtained by Neutron-Activation–Sedimentation Analysis.

in the slurry be above a certain minimum and that particle agglomeration be absent. These limitations are now being 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: arsenic in skin specimens; antimony, tellurium, and tin in Hastelloy; phosphorus in iron; silicon in petroleum; contaminant elements in copper crystals; rhenium in ion-exchange resins; tantalum in metal alloys; and sulfur in crude oil.

SPECTROCHEMICAL ANALYSES

C. Feldman

Nomograph for Temperature Calculations by the Hydroxyl-Band (R_2 Branch) Rotational-Velocity Method

C. Feldman

Reduction of experimental data by the hydroxyl-band rotational-velocity method usually involves plotting log (I_k/A_k) against E_k, where I_k is the intensity of the kth line of the R_2 branch of the

$^2\Sigma$-$^2\Pi$ (0,0) band of hydroxyl. This line represents a transition in which the final rotational quantum number is k; A_k is the corresponding transition probability, and E_k is the energy of the initial state. The slope of this line equals $-(\log_{10} e/kT)$. The use of logarithms has been circumvented by development of the special graph paper shown in Fig. 13. The ordinate scales are logarithmic and are spaced at abscissas corresponding to the E_k value (in cm^{-1}) for the upper energy state of the transition-producing line R_2K. Each logarithmic scale is displaced vertically, with respect to the one to the left, by a distance corresponding to $\log A_k - \log A_{k+1}$. The experimental intensity value for each line, corrected for background, is plotted on the appropriate log scale. The relative vertical displacement of these scales automatically subtracts $\log A_k$ from each reading. The series of points thus obtained defines a line whose slope, measured with a specially prepared protractor, gives the temperature corresponding to the band-line-intensity distribution in question.

Temperatures of Porous-Cup Discharges

D. E. Fornwalt

Temperatures and temperature gradients of porous-cup discharges in 0.25 *M* cupric perchlorate and silver perchlorate solutions were measured by the technique described previously;[41] the results are given in Table 7.

Effect of Undetected Changes in Contrast Factor of Photographic Emulsions on Accuracy of Observed Spectral Line-Intensity Ratios When Background Is Present

C. Feldman

The following equation has been derived for expressing a line-to-line intensity ratio obtained from an emulsion calibration curve of photometric data, and may be used even though the contrast factor of the emulsion becomes changed (e.g., during storage) after the calibration is performed:

$$\frac{L_2'}{L_1'} = (1 + e_b)\frac{(1 + e_1)L_1 + e_1B_1}{(1 + e_2)L_2 + e_2B_2},$$

where L_1, L_2, B_1, and B_2 represent the true intensities of the two lines and their respective backgrounds and where the primed quantities represent the apparent intensities obtained from the altered emulsion by using the original calibration curve,

$$e_1 = \frac{(L_1' + B_1')/B_1'}{(L_1 + B_1)/B_1},$$

$$e_2 = \frac{(L_2' + B_2')/B_2'}{(L_2 + B_2)/B_2},$$

$$e_b = \frac{(B_2'/B_1')}{(B_2/B_1)}.$$

For any intensity ratio I_2/I_1,

$$1 + e = \left(\frac{I_2}{I_1}\right)^{(\tan\theta'/\tan\theta)-1},$$

where $\tan\theta$ and $\tan\theta'$ are the original and altered slopes, respectively, of the straight-line portion of the Seidel function calibration curve. Tables have been computed for measurement of the distortion factor $\phi = (L_2'/L_1')/(L_2L_1)$ caused by

[41] C. Feldman *et al.*, "Spectrochemical Analyses," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 18.

TABLE 7. POROUS-CUP ELECTRODE SURFACE TEMPERATURES AND NEAR-BRANCH TEMPERATURE GRADIENTS IN POROUS-CUP DISCHARGES*

Solution	Temperature at Surface of Porous-Cup Electrode (°K)	Temperature Gradient of Near Branch (°K/mm)
0.25 *M* $AgClO_4$ in 1% $HClO_4$	5500	−850
0.25 *M* $Cu(ClO_4)_2$ in 1% $HClO_4$	5450	−900

*Gap width, 2 mm.

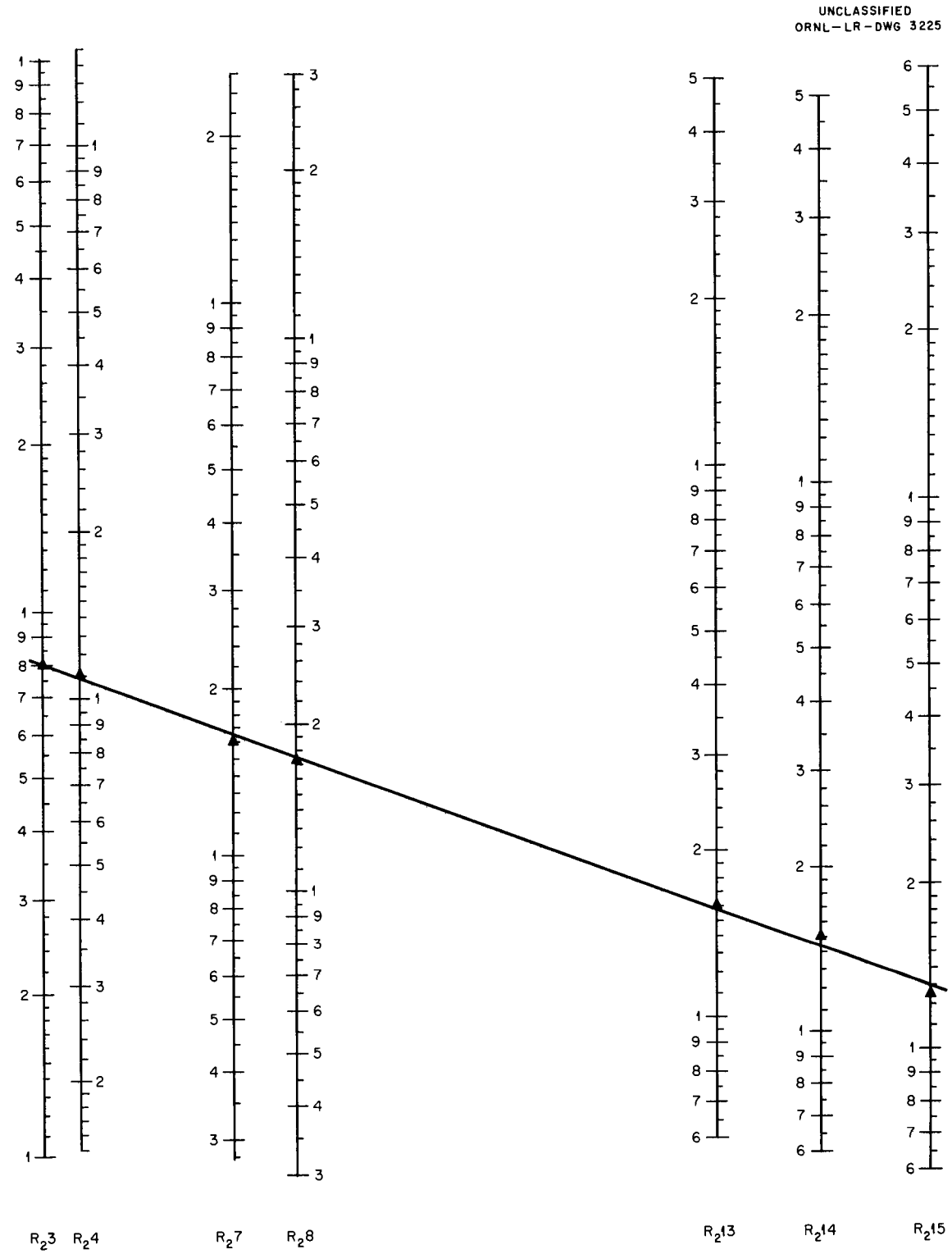

Fig. 13. Nomograph for The Determination of Temperature from Hydroxyl-Band-Line Intensities. Data plotted correspond to a temperature of 4250°K.

changes in emulsion characteristics of the magnitude reported.[42] Values of ϕ are reported for $\tan \theta'/\tan \theta = 0.950$ to 1.150, with $L_2/L_1 = 0.0625$ to 16.000, L_1/B_1 and $L_2/B_2 = 0.500$ to 8.000, and $B_2/B_1 = 0.5$ to 1.

Determination of Boron in Carbon and Graphite

J. Y. Ellenburg C. Feldman

Both d-c arc and a-c spark procedures for the determination of boron in carbon and graphite have been successfully developed.

Direct-Current Arc Procedure. Difficulties previously encountered in obtaining long-range reproducibility on the determination of boron in carbon and graphite have been overcome by operating the discharge in an 80:20 mixture of argon and oxygen in an Owen gas chamber[43] with removable front and rear windows. The samples are mixed with 35 ppm of iridium, loaded into Strock-type electrodes, and burned in a 250-v, d-c arc at 9.0 amp. The center 20% of the discharge is photographed on a Jaco Wadsworth mounting spectrograph at 5 Å/mm. The best sensitivity achieved so far is 0.50 ppm, with a standard deviation of 2.5%. Sensitivity now appears to be limited by an interference from a minor band line produced by some molecular fragment that contains carbon. Sensitivity could probably be improved by using the same exposure technique with a spectrograph having a grating blazed in higher orders.

Spark Technique. The operating range of the sifter-electrode technique has been extended down to 0.25 ppm of boron by conducting the discharge in commercially pure argon.[41] The Baird multisource has been found to be suitable for excitation with this electrode. The copper oxide used as an internal standard must be ignited at 800°C for 1 hr in order to prevent it from becoming hygroscopic, which in turn causes the electrode to become clogged. Otherwise, the procedure and precision obtained are as described previously.[44] A sample of graphite from the ORNL Graphite Reactor was found to contain 0.45 ± 0.01 ppm of boron.

Determination of Traces (ppm Range) of Rare Earths in Thorium

J. Y. Ellenburg C. Feldman

It was found that solutions from which most of the thorium had been removed by the cellulose-column method still contained sufficient thorium to interfere with spectrographic determination of the rare earths. However, by agitation of the solution for 5 min at 60°C with one volume of 0.5 *M* TTA (thenoyltrifluoroacetone), 20 mg of thorium as the nitrate could be extracted from aqueous solution at pH 0.75. Rare earths are not extracted under these conditions.

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

J. Y. Ellenburg C. Feldman

In solution methods for performing the determination of traces of silicon in thorium dioxide, whether chemically or spectrographically, all known methods for dissolving thorium metal or oxide necessitate the use of at least a trace of fluoride ion. It is thus difficult to be sure that the quantity of silicon present at the final measurement is neither more, because of contamination, nor less, because of volatilization, than was originally present. It was therefore decided to seek a spectrographic method in which thorium oxide is used directly and to prepare the sample by ignition (if originally thorium) or by evaporation and calcination (if a compound or solution of thorium).

It has been found that the sifter electrode can be used to detect approximately 10 ppm of silicon in thorium oxide when an intermittent d-c arc is used for excitation. Precision is at present limited by the lack of resolving power. Work is being continued on this approach to the development of a quantitative method.

Improvement of Mercury-Cathode Procedure for Electrodeposition

C. Feldman

In the removal of chromium, iron, and nickel from solutions of stainless steel, Inconel, and similar alloys, the deposition of chromium has sometimes

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[42] J. Y. Ellenburg and C. Feldman, "Effect of Freezing on Photographic Emulsion Contrast Factors," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 20.

[43] L. E. Owen, "Chamber for Controlled Atmosphere Spectral Excitation," *J. Opt. Soc. Amer.* 41, 139 (1951).

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

been found to lag several hours behind the deposition of iron and nickel. Preparation of samples for electrolysis had included evaporation almost to dryness in the presence of excess hydrochloric acid. It was thought that this might have aided in the formation of chromium–chloride inner complexes, which might be more difficult to deposit than the hydrated chromium(III) ion. The drying step was therefore followed by boiling with 10 ml of concentrated perchloric acid; this oxidized the chromium from the trivalent to the hexavalent state and thus destroyed any trivalent complex that might have been present. The solution was then evaporated (until fumes of perchloric acid barely ceased), cooled, treated with 2 ml of concentrated perchloric acid, then diluted to 200 ml with water. Fifteen milliliters of 6% sulfur dioxide solution was added, and the solution was boiled vigorously for 10 to 15 min. Iron, chromium, and nickel were then removed by a 1- to 2-hr electrolysis at 5 amp with a mercury cathode.

New Working Curves

Porous-Cup Method (A. Estepp, M. Murray). Working curves were developed for 0.5 to 30 ppm of yttrium, 0.4 to 6.0 ppm of ytterbium, 6 to 100 ppm of cerium, 1 to 200 ppm of lanthanum, and 25 to 200 ppm of neodymium by using the Sc 3368 Å and the Sc 3372 Å lines as internal standards. Curves were also developed for 10 to 100 ppm of europium and 0.5 to 240 ppm of magnesium in citrate solution.

Flame Photometric Method (D. E. Fornwalt, C. Feldman). Working curves were developed for the following determinations: (1) 0 to 0.10% of lithium, 0 to 0.030% of sodium, 0 to 0.050% of potassium, and 0 to 0.20% of rubidium in cesium fluoride and cesium iodide; (2) 0 to 0.50% of lithium, 0 to 0.50% of sodium, 0 to 1.00% of potassium, and 0 to 10.0% of cesium in rubidium fluoride; (3) 0 to 1.20% of sodium and 0 to 1.20% of potassium; (4) 0 to 90 ppm of silver in dilute nitric acid solution.

List of Translations of Spectrochemical Papers

C. Feldman

A list of translations of approximately 200 German, Russian, French, and other foreign papers on spectrochemical analysis was compiled for Committee E-2 of the American Society for Testing Materials. The list is arranged alphabetically by authors and it notes where each translation can be borrowed or purchased.

INORGANIC PREPARATIONS

D. E. LaValle

Special Preparations

D. E. LaValle

The preparation of ternary oxides of the general formula $LaMO_3$ for the Nuclear Physics and Neutron Diffraction Group of the Physics Division was continued. Included were 50-g quantities of $LaFeO_3$ and $LaCrO_3$ alone and in various admixtures with the corresponding strontium compound. Preparation of the calcium-lanthanum manganite series was repeated in 100-g quantities, starting with pure lanthanum manganite and proceeding through admixtures with calcium manganite to pure calcium manganite. A 30-g quantity of $CuCl_2 \cdot 2D_2O$ was also made for this group.

For the Nuclear Polarization Group of the Physics Division, a 1-g quantity of samarium ethyl sulfate, $Sm(C_2H_5SO_4)_3$, enriched to 73% in Sm^{149} was prepared.

Chromium methylamine sulfate, $Cr(CH_3NH_3)(SO_4)_2 \cdot 12H_2O$, and the analogous aluminum compound were prepared in 50-g quantities for the Nuclear Physics and Low Temperature Group of the Physics Division. For the same group, a 40-g quantity of anhydrous manganese chloride was made and 5 g of $U^{235}O_3$ was converted to the compound $NaCu(U^{235}O_2)_3(C_2H_3O_2)_9 \cdot 9H_2O$.

To prepare a large quantity (125 g) of uranium tri-iodide for the Nuclear Physics and Low Temperature Group, several methods were investigated. It was found that the sublimation method of Gregory[45] was largely empirical and would therefore have to be repeated exactly to ensure successful preparation of the compound. In the methyl iodide method of Ayres,[46] some uranium hydride was found to remain unconverted. Therefore the previous[47,48] method of direct combination of the elements was used for preparing the material.

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

[46] J. A. Ayres, "The Preparation and Volatility of Uranium and Plutonium Iodides," *Report for Month Ending January 8, 1944, Metallurgical Laboratory, Chemical Research — Chemistry of Plutonium*, CN-1243 (Jan. 8, 1944), p 5-6.

[47] D. E. LaValle, "Special Preparations," *Anal. Chem. Semiann. Prog. Rep. April 20, 1953*, ORNL-1547, p 11.

[48] R. A. Webster, *Electrolytic Production of Uranium from Solutions of its Tribromide in Fused Salts*, CC-2105 (Aug. 15, 1944).

In the work for the Fused Salts Group of the Chemistry Division, the conditions necessary for the formation of K_2NiF_6 were finally determined, and a 30-g quantity of this material was prepared. After first being chlorinated at 400°C, $K_2Ni(CN)_4 \cdot H_2O$ is treated with fluorine at atmospheric pressure and room temperature. The resulting impure product is removed, ground to pass through a 200-mesh sieve, then treated again with fluorine at 20-lb pressure and 200°C for 1 hr. The final product is a homogeneous, reddish powder. No evidence of extraneous lines was observed in x-ray diffraction tests of the material.

Phosphors and Miscellaneous High-Purity Compounds

R. H. Sampley

The following compounds were purified for the Physics Division: xylene (65 gal), dioxane (500 g), lithium chloride and ammonium carbonate (pound quantities), hydriodic acid (liter amounts), europium trichloride (mg quantities), and sodium iodide and lithium iodide (100-g amounts). The following high-purity compounds were also prepared: lithium carbonate, hydriodic acid, and hydrated and anhydrous lithium iodide. The activated phosphors listed below were prepared for use in scintillation counter investigations:

	Activator
Xylene	*p*-Terphenyl + α-naphthyl phenyloxazol
LiF	$EuCl_3$, ThI_2, $CeCl_2$, SnI_2, $RuCl_2$, Re(potassium perrhenate), CsCl, Ga_2O_3, Ge_2O_3, $Y(NO_3)_3$, $YbCl_3$, $PdCl_2$
PbF_2	Same as for LiF
LiI	$EuCl_3$, $YbCl_3$
LiI + Li_2S	$EuCl_3$, $YbCl_3$
LiF	$EuCl_3$, $YbCl_3$
LiF + Li_2S	$EuCl_3$, $YbCl_3$

OPTICAL AND ELECTRON MICROSCOPY

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

Corrosion Studies

Examination and study of the oxide layers or films that are formed on stainless steel when it is exposed to aqueous solutions or slurries prepared for reactor use has been continued. Of chief interest have been those films found on stainless steel which has been exposed to solutions of uranyl sulfate containing chromate ion as an inhibitor.

Electron-diffraction studies indicate that the presence of chromate ion in the solution apparently changes the basic structure of the substrate oxide film from the α-Fe_2O_3 or Cr_2O_3 with a hexagonal lattice to a layer with a cubic spinel structure, which seemingly provides more protection. Transmission electron-diffraction patterns of these films are composed of broad lines, which make accurate measurement impossible. Within the limits of experimental error, however, it has been determined that the lines are those of a cubic structure and that the three strongest lines have approximate spacings of 2.51 to 2.53 Å, 2.08 to 2.11 Å, and 1.47 to 1.49 Å. This would suggest that the substrate oxide layer could be a cubic spinel structure containing combinations of the oxides of iron-chromium, iron-nickel, or chromium-nickel. Spectrographic analysis reveals that iron, chromium, and nickel are all strong components of these films. Further studies on the growth mechanism of this layer and its relationship to inhibitor concentration and time of exposure are being considered.

Of interest also are the results of the examination of the film layers formed on a type 347 stainless steel venturi rod and on an orifice plate in a thorium slurry loop operating at 250°C. Here, a substrate having an apparent cubic spinel-type structure was found by electron diffraction. Again the diffraction patterns were of a nature that made measurement extremely difficult. The lattice-spacing values achieved were approximately the same as those found with type 347 stainless steel exposed to a solution of uranyl sulfate to which a chromium inhibitor had been added. A layer of thorium oxide was found superimposed on the thin oxide substrate, and the thickness of this layer was apparently dependent on the position of the collecting metal surface in the slurry stream. Thus, the lightest deposit of thorium oxide was found at the center of the venturi rod and the heaviest was around the aperture in the orifice plate.

Other studies were also made of oxide films from type 347 stainless steel and titanium exposed to solutions of uranyl sulfate at various concentrations and temperatures.

Qualitative Analysis by Electron Diffraction and Microscopy

Electron-diffraction studies were made of the following materials to determine structural features or to identify components: the yellow precipitate that was found on the metal of the gas pressurizer in a uranyl sulfate loop, oxide films from stainless steel that had been cut from the Homogeneous Reactor system, thorium oxide, and the deposit that had formed on stainless steel fuel elements after they were subjected to radiation.

The electron microscope was used to study pearlite colonies in steel, the structure of types 347 and 308L stainless steel as welded and annealed, the colloidal nature of didecylamine sulfate in benzene with and without water, and the presence of particulate material other than phage ghosts in bacteriophage (P) fractions and in bacteriophage T-2 fractions.

Particle-Size Studies

Microscopic methods were used to make particle-size determinations of the following: thorium oxalate, Ames thorium oxide calcined at 900°C, various aluminum oxides, uranium-aluminum alloys, numerous samples of thorium oxide from thorium loop runs, plutonium oxide precipitates, clays that contained uranium, precipitates from solutions of uranyl sulfate (300 g/liter) saturated with thorium sulfate, and Ames thorium oxide calcined at 650 and 1100°C.

Photomicrographic, Metallographic, and Autoradiographic Studies

The following studies utilizing microscopic observations and photographs were made and the results were interpreted: ceramic bodies composed of aluminum oxide were studied before and after radiation; the thickness, uniformity, and nature of sputtered lithium sulfate films on a metal substrate were determined; plutonium-colonized plates were photographed; bubble uniformity in glass coatings and in porcelain enamels was studied and photographed; the structures of drawn and annealed stainless steel, titanium bar stock and welding rods, and various samples of Zircaloy were determined; and numerous samples of ion-exchange resins were photomicrographed. Also, electroplated plutonium was autoradiographed.

ORNL MASTER ANALYTICAL MANUAL

Authors of Methods	H. P. House
H. P. Raaen	J. E. McLaughlin

Ten new methods have been issued to the *ORNL Master Analytical Manual.* The authors, titles, numbers, and dates of these methods are given in the section of this report entitled "Presentations of Research Results." Ten new manuals were issued.

SERVICE ANALYSES

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

IONIC ANALYSES

P. F. Thomason

The major portion of the service work done by the Ionic Analyses Group was for the HRP. The analyses requested by members of the Chemistry Division were for their phase and corrosion studies of the Homogeneous Reactor fuel solutions. Conventional methods, which have been discussed previously,[1] were used for these analyses.

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

RADIOCHEMICAL ANALYSES

S. A. Reynolds

About 77% of the service work of the Radiochemical Analyses Group was done for the Electronuclear Research, Metallurgy, and Operations Divisions. The types of analyses included analyses of cyclotron-produced activities, studies of fission products volatilized from fuel elements, and assay and purity tests on unusual radioisotope products. Details of the first two types of analyses are reported elsewhere (cf. Secs. "Cyclotron Research" and "Activities Volatilized from Reactor Elements" of this report). The techniques employed in service work included gamma- and x-ray spectrometry, chemical separations, and electrodeposition.

TABLE 8. SUMMARY OF ANALYTICAL SERVICE WORK AT X-10 SITE FOR THE PERIOD ENDING OCTOBER 1954

	Number of Personnel		ORNL Divisions Requesting Analyses															Others Requesting Analyses		
	Technical	Nontechnical	Analytical Chemistry	ANP	Biology	Chemical Technology	Chemistry	Electronuclear Research	Engineering and Maintenance	Health Physics	HRP	Laboratory Protection	Materials Chemistry	Metallurgy	Operations	Physics	REED	Solid State	Others	Total Determinations
Group Making Analyses			Number of Determinations																	
Activation Analyses*	2	5	377	32		591	216	42		21	54		6	169	470	8		4		1,990
General Analyses	6	7				1,377	641		44	323	23	4		1673	221	146		1242	36	5,730
Ionic Analyses*	6	1	12			92	877			2					2	80	35			1,100
Laboratory and Semi-Works Control	3	8				16,710	170				40			224	29					17,173
Optical and Electron Microscopy	3	1	529	6	43	316	300				18		38	130	10		313			1,703
Pilot Plant Control	9	16				13,311	24				2									13,337
Plutonium Isolation Laboratory	2	4				3,561	40	26			46			6					48	3,727
Radiochemical Analyses*	6	2				65	17	160		17	5			121	144				26	555
Radioisotope Production Control	3	16		12		2,452	853			297				135	7851	146		14	28	11,788
Reactor Analyses	1	1	2			30	119				229						323			703
Special Analyses	4	4				30,690	118									17				30,825
Spectrochemical Analyses	5	0	20	19		145	155		1	18	2			277	54	11	30	6		738
Total	50	65	940	69	43	69,340	3530	228	45	678	419	4	44	2735	8781	408	701	1266	138	89,369

*These groups also do research and development work.

ACTIVATION ANALYSES

G. W. Leddicotte

The extent of interest that has been shown by the Oak Ridge plants and by outside organizations in activation-analysis service is summarized in Table 9. The difference in number between the inquiries and the requests 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 routinely in a variety of materials: copper, cobalt, zinc, iron, hafnium, zirconium, gold, barium, strontium, arsenic, uranium, thorium, sodium, potassium, rubidium, cesium, aluminum, tungsten, and chlorine.

GENERAL ANALYSIS LABORATORY

J. H. Edgerton

Micro-Pyrohydrolysis of Fluoride

J. H. Edgerton J. E. Lee, Jr.

Analytical procedures for use with the new microscale fluoride pyrohydrolysis apparatus[2] (see Fig. 14) have been improved to such an extent that a relative standard deviation of 0.8% has been obtained on uranium tetrafluoride standards in the range of 1 to 10 mg of fluoride. Test results equal to the theoretical value have also been achieved on eutectic salts and on liquid samples, such as Thorex feed. These results were obtained by acid-base titration or thorium nitrate titration of fluoride; visual end points were used.

It is believed that a fluoride titration having a more sensitive end point will permit more critical evaluation of the apparatus. For this reason, the titration of fluoride with thorium nitrate[3] has been adapted to a spectrophotometrically observed end point in which an alizarin red S indicator is used. The solution being titrated is circulated through a flow-type cell in a Beckman model B spectrophotometer. The calculation of the end point, in this case from the changes in optical density for each incremental addition of titrant, is similar to that used in a potentiometric titration. The titration of solutions that contained 0.5 to 5.0 mg of fluoride (prepared from Baker & Adamson reagent-grade NaF) gave an average recovery of 99%. The possibility of extension of the lower limit is being determined. The titration assembly is shown in Fig. 15.

Determination of Water in Fluoride Salts

J. H. Edgerton J. E. Lee, Jr.

An apparatus for the determination of water in fluoride salts, based on a modification of the method and equipment of Ross and White,[4] was

[2] J. H. Edgerton and J. E. Lee, Jr., "Micro-Pyrohydrolysis of Fluoride," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 29.

[3] J. H. Edgerton, "Fluoride in ANP Fuel Eutectics and Other Salts, Micro Pyrohydrolysis Method," Method No. 9 0922280 (May 20, 1953), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and III.

[4] W. J. Ross and J. C. White, *A Method for the Determination of Water in Fluoride Salts*, ORNL-1618 (Sept. 8, 1953).

TABLE 9. SUMMARY OF ACTIVATION ANALYSIS SERVICES

Period	Inquiries from Outside Organizations	Requests for Analyses	
		From Oak Ridge* Plants	From Outside Organizations
Prior to April 1954	255	192	85
April	14	10	4
May	14	15	5
June	14	12	3
July	12	15	9
August	24	20	4
Total	333	264	110

*Same as number of inquiries.

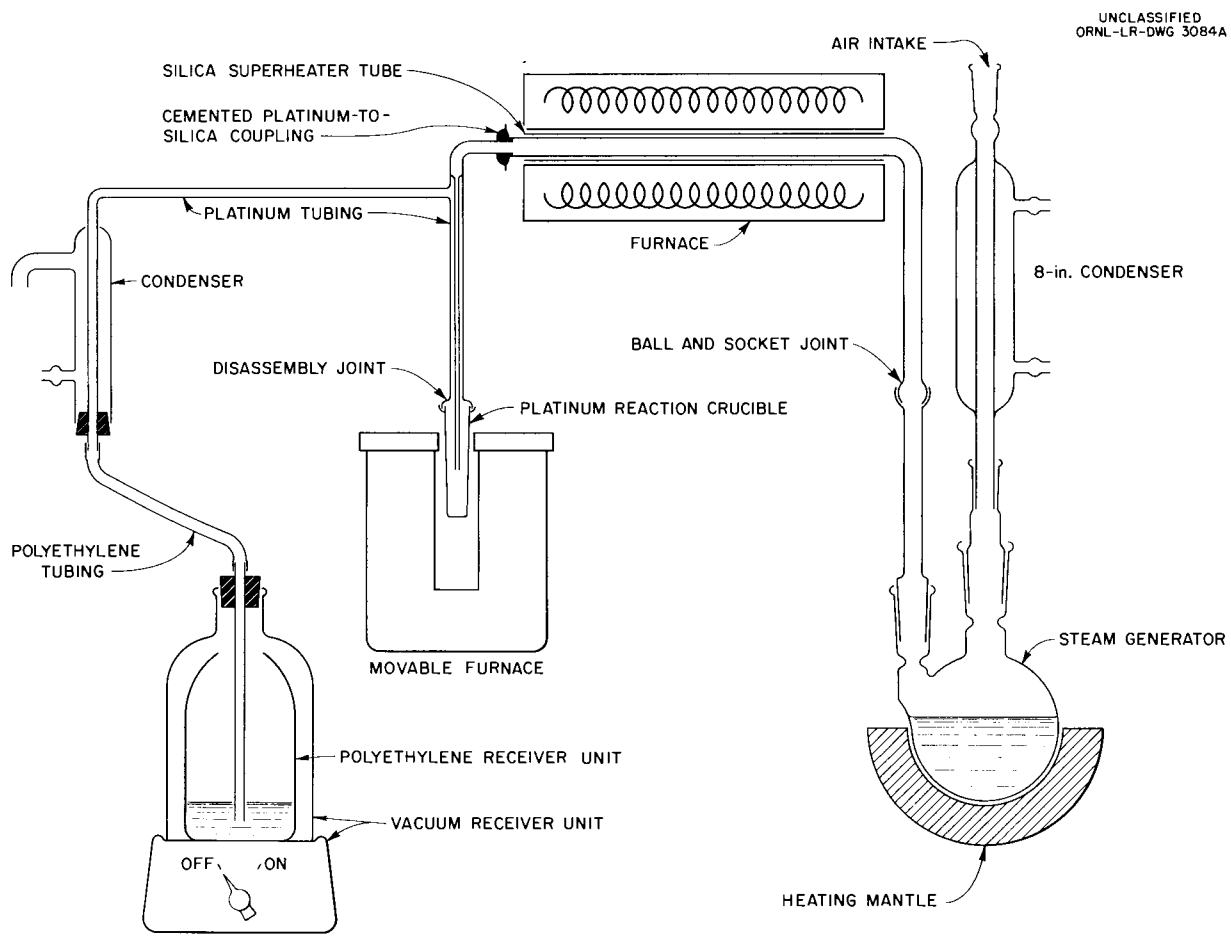

Fig. 14. Apparatus for Micro-Pyrohydrolysis of Fluorides.

designed and fabricated. A unique condenser arrangement is featured which greatly facilitates transition from xylene-reflux extraction to azeotropic distillation without exposure of the material in the apparatus to possible contamination by moisture.

The preliminary test results appear to be satisfactory. The capacity of this apparatus will be further investigated before electrodes are installed; the use of electrodes will permit instrumental detection of the Karl Fischer end point.

Special Analyses

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

A series of aluminum alloys submitted by the Metallurgy Division was analyzed[5] for aluminum, barium, cerium, cesium, molybdenum, niobium, palladium, rhenium, strontium, uranium, zirconium, and the rare earths. Samples of metallic beryllium were analyzed for aluminum, iron, and silicon. Concentrations of cadmium, chromium, iron, and silicon were determined in vanadium metal.

Determinations for the Chemical Technology Division included those for ammonia, chloride, formate, nitrate, nitrogen, oxalate, sulfate, and thorium in thorium slurries.

An increasingly large number of spot-test analyses are being made on various steels and alloys for several divisions. Barium, calcium, cesium, lithium, magnesium, potassium, sodium, and rubidium were determined by flame spectrophotometry. Polarography was utilized for a group of

[5] H. H. Willard, consultant, private communication to J. H. Edgerton, June 1954.

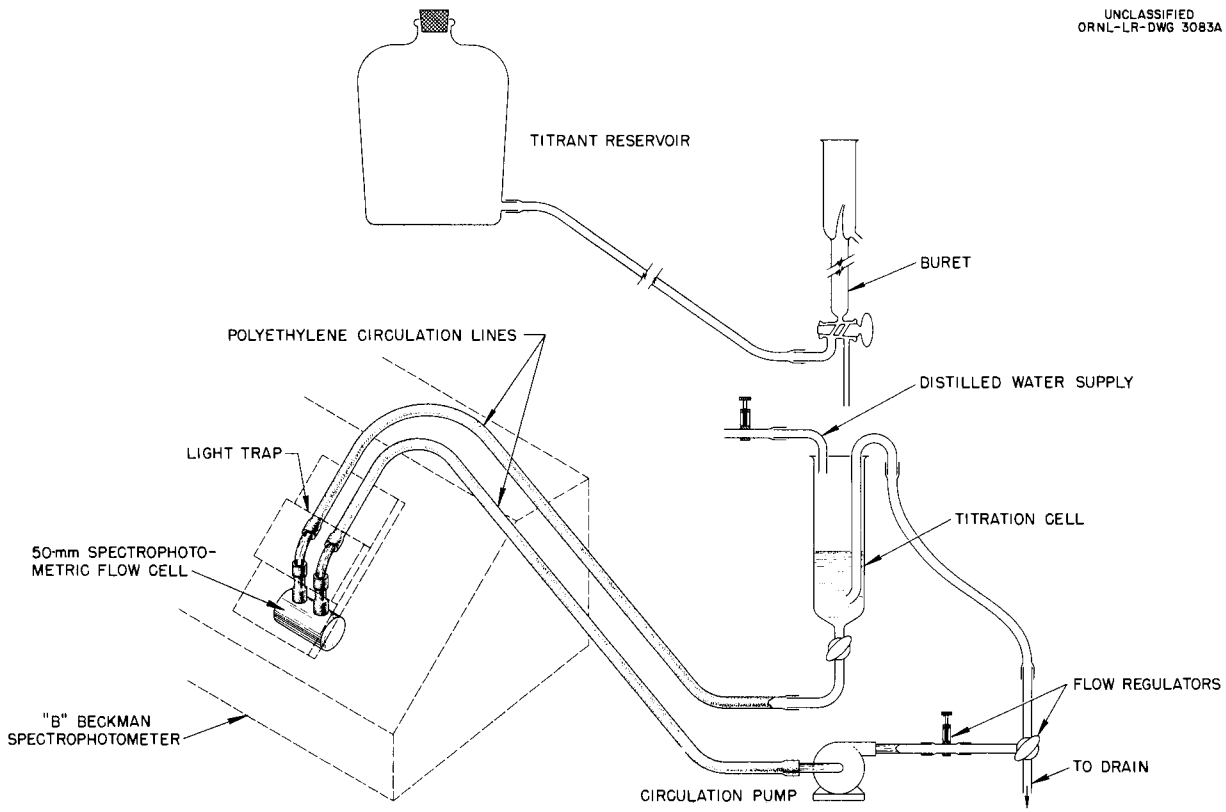

Fig. 15. Assembly for Spectrophotometric Titration of Fluorides.

cadmium, sulfate, tin, uranium, and zinc analyses, as well as for the determination of the uranium distribution in a series of experimental extractions made with TBP in Amsco solvent.

Vacuum-fusion analyses were completed for the determination of hydrogen, nitrogen, and oxygen in alloys of titanium, of zirconium, and in Hastelloy B for the Metallurgy and Chemistry Divisions. Chemical methods are being developed for the determination of nitrogen in titanium, in zirconium, and in their alloys; the results are to be compared with those of vacuum-fusion analyses. A hydrochloric acid volatilization apparatus is being constructed for the estimation of oxygen in zirconium.

An investigation was made of vacuum-fusion equipment for measurement of carbon, hydrogen, nitrogen, and oxygen concentrations in nonferrous metals and alloys. The results have been reported elsewhere.[6]

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

RADIOISOTOPE PRODUCTION ANALYSES

E. I. Wyatt

Data from the half-life determinations that were made by the Radioisotope Production Analyses Group during the period are presented in Table 10. After the decay studies were made, the samples were scanned by means of the gamma spectrometer for gamma-emitting impurities; none were found.

LABORATORY AND SEMI-WORKS CONTROL GROUP

L. T. Corbin L. G. Farrar
G. R. Wilson J. E. Morton

The Chemical Technology Division submitted 97% of the analytical work done by the Laboratory and Semi-Works Control Group during the past six months. The Chemistry, Metallurgy, Operations, and HRP Divisions accounted for the remaining 3%.

The General Electric Co. submitted ribbon-type fuel elements of type 310 stainless steel for the

TABLE 10. OBSERVED HALF LIVES OF SOME GAMMA-EMITTING RADIONUCLIDES

Radionuclide	Period of Observation	Observed Half Life	Instrument Used	Remarks
Be^7	175 d	54 d	High-pressure gamma chamber	Produced by $Li^7(p,n)Be^7$
Na^{24}	76 h	15.1 h	High-pressure gamma chamber	Produced by $Na^{23}(n,\gamma)Na^{24}$
Sr^{85}	180 d	64 d	Scintillation counter (NaI)	Produced by $Sr^{84}(n,\gamma)Sr^{85}$
Nb^{95}	300 d	35 d	High-pressure gamma chamber	Purified by solvent extraction from Zr^{95}
Ru^{103}	100 d	40 d	High-pressure gamma chamber	Fission product, bombarded only a few seconds; purified by distillation

determination of uranium in order to measure uranium burnup. No difficulty is encountered in the polarographic determination of uranium in the stainless steel[7] if the stainless steel is dissolved in perchloric acid. However, if aqua regia is used, the uranium must be separated from the chromium, nickel, and iron before the uranium can be determined. The separation was accomplished both by TBP extraction and by use of Dowex A-1 resin. After the separation, the uranium can be determined polarographically or colorimetrically.

The Metallurgy Division submitted an alloy that consisted of approximately 10% uranium, 10% bismuth, and 80% aluminum for uranium determination. The determination was made by heating the weighed sample in hydrochloric acid until the reaction ceased, then adding nitric acid until dissolution was complete. The bismuth was removed from an aliquot of the solution by using hydrogen sulfide to precipitate it as the sulfide. After filtration, the uranium in the filtrate was determined colorimetrically.

PILOT PLANT CONTROL LABORATORY

L. T. Corbin C. E. Lamb

The majority of the analyses by the Pilot Plant Control Laboratory have been made for the plutonium- and americium-recovery unit of the Chemical Technology Division. The determination of americium of approximately 1×10^5 counts/min/ml concentration in the presence of approximately 3×10^7 counts/min/ml of plutonium was made after the plutonium was removed by extraction with 30 vol % tributyl phosphate–70 vol % Amsco. Plutonium in the undissolved solid material, present in the dissolver solutions which were previously analyzed, was determined by gross alpha counting after the solid was washed repeatedly with 6 *N* nitric acid solution until the plutonium was apparently all removed. The trace of plutonium remaining in the extracted residue was estimated by gross alpha counting after the residue had been decomposed by evaporation to dryness in the presence of hydrofluoric and sulfuric acids and had been redissolved in nitric acid. Before americium[8] and plutonium[9] determinations could be made, many of the samples from the americium cycle required pH adjustment in order to redissolve precipitated ions.

The size of the group has been increased and the members are being trained in methods which will be required at the startup of the Thorex process by the Chemical Technology Division. In addition, methods of determining Pa^{233}, fluoride

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

[8] G. W. Smith, "Americium-241," Method No. 2 31030 (May 18, 1954), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I and II.

[9] R. L. Walker, "Total Plutonium, Thenoyltrifluoracetone Extraction Method," Method Nos. 2 31621 and 9 008621 (May 18, 1953), *ORNL Master Analytical Manual*, ORNL CF-53-1-235, Vols. I, II, and III.

by pyrohydrolysis, total phosphate, iron, chromium, nickel, and mercury were tested.[10-16]

Statistical evaluations are also being made, where necessary, of all the methods which are to be used for the analytical work in connection with the Thorex process.

ISOLATION ANALYSES

L. T. Corbin J. H. Cooper

The major portion of the work done by the Isolation Laboratory was the assay of plutonium products submitted by the Metal Recovery Group of the Chemical Technology Division. A method, which is unique for this project, was devised for sampling the plutonium-product shipment containers, which are 6-ft-tall stainless steel cans. The sampling technique consisted in inserting a Tygon tube into the can and siphoning a small amount into a sample vial. A hypodermic syringe was used to start the flow and a hemostat was clamped on the tube to stop it. The liquid remaining in the tube after the sampling was allowed to flow by gravity back into the can.

An americium sample was prepared for the Physics Division. Americium was precipitated from a chloride solution with ammonium hydroxide; the precipitate was washed several times with 1 *M* ammonium hydroxide and dried on aluminum foil.

The Isolation Laboratory prepared a solution of Pu^{240} for the Physics Division by dissolving plutonium dioxide. The sample was dissolved by heating the oxide in 8 to 10 *N* nitric acid and 0.02 *N* hydrofluoric acid. The plutonium solution was put in special stainless steel cells for cross-section studies of the Pu^{240}.

[10] S. A. Reynolds and F. L. Moore, "Protactinium-233 in Thorex Process Solutions, Diisobutyl Carbinol Extraction Method," Method No. 9 0123670 (in press), *ORNL Master Analytical Manual,* ORNL CF-53-1-235.

[11] J. G. Surak, Secret Notebook No. 3622, June 21, 1954.

[12] M. J. Gaitanis, "Phosphate, Spectrophotometric Phosphomolybdate Method," Method Nos. 1 216010 and 9 00716010 (Sept. 23, 1953), *ORNL Master Analytical Manual,* ORNL CF-53-1-235.

[13] E. B. Sandell, *Colorimetric Determination of Traces of Metals,* p 271-3, Interscience, New York, 1944.

[14] *Ibid.*, p 192.

[15] *Ibid.*, p 334-43.

[16] R. L. Walker, "Colorimetric Determination of Mercury by Dithizone Reagent," tentative method, available from R. L. Walker, ORNL.

SPECIAL ANALYSES LABORATORY

L. T. Corbin W. R. Laing

Nitrate was determined in samples of thorium oxide by an adaptation of a method developed by Menis.[17] The nitrate was leached from the oxide by slurrying with phenoldisulfonic acid.

Small amounts of iodine and iodate were determined by the starch-indicator method. Iodide was determined by the *o*-tolidine method. Samples containing I^{131} as iodine, iodate, and iodide were analyzed by converting separately the iodide and iodate to iodine and extracting the resulting iodine with chloroform. The extracts were counted on a scintillation counter.

Carbon in the evolved gases from ThC_2–ThO_2–C mixtures was determined by use of a modified carbon-train apparatus.

Milligram quantities of carbonate were determined by evolution of the carbon dioxide and subsequent reaction of the gas with an excess of standard barium hydroxide.

Lanthanum was determined successfully by reaction with an excess of a standard ethylenediaminetetraacetic acid solution and back-titration of the excess acid with a standard magnesium solution.

Dissolved hydrogen sulfide was determined by reaction with a standard solution of iodine.

Lead, iron, chromium, nickel, silicon dioxide, phosphate, alkali metals, alkaline earth metals, and sulfate have been determined in samples of thorium nitrate, thorium oxalate, and thorium oxide.

HIGH-RADIATION-LEVEL ANALYTICAL FACILITY

E. J. Frederick

Design and specifications for the High-Radiation-Level Analytical Facility were completed on June 30. However, the programs requiring analytical services for radioactive materials had to be re-evaluated after the 25 Program was cancelled by the AEC early in July, and it was found that there was an immediate need for a seven-cell facility instead of the original five-cell facility. The design and specifications were revised accordingly, and the project was released for bid.

[17] O. Menis, "Nitrate in Uranium Compounds, Phenoldisulfonic Acid Spectrophotometric Method," Method Nos. 1 215610 and 9 00715610 (in press), *ORNL Master Analytical Manual.*

An amended construction request will be submitted to the AEC for inclusion of additional funds made necessary by expansion of the facility.

Equipment and Methods for Proposed Hot Cell

R. H. Powell

The use of master-slave manipulators, which were installed in an analytical hot-cell mockup, was explored, and their limitations were determined. The alterations of conventional laboratory equipment that would be required because of the operational limitations of the manipulators and the special remote-control conditions imposed by the hot-cell were studied. The suitability of conventional ORNL analytical methods and laboratory equipment[18] was reviewed with respect to the reliability of operation, economics, and efficiency of over-all remote analytical work in conjunction with interim 23, Thorex, 25, HRP, ANP, and general high-level hot-cell laboratory use.

The results of this investigation indicate that many pieces of standard laboratory equipment can be utilized with only minor alterations if adequate viewing is provided. The general viewing through the cell window is excellent (with the exception of the external access drawer) when two GE-H-400 JI mercury fluorescent lights are used. However, viewing of small details, such as lines on a microburet or lines on an absorbancy scale of a spectrophotometer requires external optical aid.

A combination of an RCA television receiver installed external to the mockup and an RCA "TV Eye" camera placed inside the mockup was found to be unsatisfactory for detailed viewing; it was useful but not entirely adequate for general viewing.

A 24X transit proved to be the most satisfactory aid for detailed observation. Although a transit cannot be readily used with the master-slave manipulators because the position of the telescope is fixed, it is useful in reading meniscus levels or in viewing other fixed detail. A minimum focusing distance of 4 to 5½ ft is recommended.

Detailed plans and methods are being formulated for the remote use of the equipment listed below.

Mirrors
Fume hoods
Perchloric acid hoods
Muffle furnace
Pyrofusion apparatus
Sample-bottle decappers
Burets, stopcock-free
Pipetors
Specific gravity apparatus, falling drop
Ion-exchange apparatus, Fisher filtrator
Stirrers, magnetic and mechanical
Spectrophotometer
Shields for spectrophotometer filters
Microtitration apparatus
Automatic titrator, Beckman model K revised
Polarographic cells
Desiccators
pH meters
pH electrodes:
- general-purpose electrode
- 1-drop electrode
- microelectrode

Balance, Voland Speedigram model 750 D
Protective case for balance, dust-proof or pressurized
Magnifying glasses
Solvent-extraction apparatus
Centrifuges
Shaking and mixing devices
Beaker elevators or laboratory jacks
Polyethylene wash bottles

The basic purpose of this investigation is to determine ways of utilizing the master-slave manipulators to the fullest extent. For reasons of operational ease, reliability, and maintenance, many instrument-control boxes, switches, and control devices will be located upon an instrument chase that will be external to and below the front hot-cell window and convenient to the operator.

REACTOR ANALYSES

U. Koskela

With the cessation of operations of the HRE, the HRE Analyses Group has been renamed Reactor Analyses Group and has moved to a new location in Building 3019. Most of the work during the period has consisted in completing the analysis of HRE samples and in preparing for the LITR in-pile loop tests.

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

Determination of Nickel and Cobalt in Homogeneous Reactor Solutions

U. Koskela

The polarographic methods for nickel[19-21] in Homogeneous Reactor fuels have been modified to include the estimation of cobalt. Following the suggestion of F. Nelson of the Chemistry Division, the Homogeneous Reactor solution is pipeted onto an ion-exchange column of Dowex A-1 resin that has been treated with 3.5 *M* hydrochloric acid. The eluate, containing nickel and cobalt, is evaporated to about 1-ml volume and is transferred to a 10-ml stoppered graduate. Three drops of pyridine, 1 drop of bromothymol blue indicator, and 1 drop of a 1.0% aqueous gelatin solution are added. Ammonium hydroxide is added to a pH of about 6, and the solution is diluted to volume with water. In this supporting electrolyte, nickel and cobalt give well-defined polarographic waves at $E_{1/2}$ of −0.78 v and −1.07 v, respectively, vs the S.C.E.

Cobalt and nickel must be separated if large amounts of nickel are present. In order to separate the two, the solution is passed through an ion-exchange column of Dowex A-1 resin that has been treated with 3.5 *M* hydrochloric acid. The eluate, containing the nickel and cobalt, is made 9 *M* in hydrochloric acid and passed through a second Dowex A-1 column that has been treated with 9 *M* hydrochloric acid. The nickel passes into the eluate, and the cobalt, which is retained by the column, is then eluted with 0.1 *M* hydrochloric acid. Separate polarograms are then obtained for cobalt and nickel.

[19] M. T. Kelley, P. F. Thomason, and A. D. Horton, "Polarographic Determination of Nickel in HRE Solution," *Anal. Chem. Semiann. Prog. Rep. April 20, 1953*, ORNL-1547, p 1.

[20] M. T. Kelley, P. F. Thomason, and A. D. Horton, "Simultaneous Determination of Nickel and Manganese in HRE Solutions," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1953*, ORNL-1639, p 1.

[21] J. C. Howard and U. Koskela, "Nickel in HRE Fuel," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1953*, ORNL-1639, p 22.

Removal of Copper Interference in the Analysis of Homogeneous Reactor Fuel

C. P. Baker U. Koskela

Corrosion studies of Homogeneous Reactor fuels and components in the presence of 0.031 *M* copper are being made. This amount of copper interferes in the determination of uranium, nickel, and cobalt. The cadmium-strip method developed by Shults[22] for removal of copper from solution prior to the determination of uranium has been successfully utilized in preparing solutions for the ion-exchange polarographic determinations of nickel and cobalt.

Precision of Uranium Determination by Means of the ORNL Model Q-945 Automatic Titrator

C. P. Baker

In anticipation of the HRT startup, S. E. Beall of the REED requested that a study be made of the precision and accuracy of the titrimetric determination of uranium. It is hoped that critical concentrations of HRT fuel can be calculated from the results of the uranium analyses. An evaluation of the use of macroburets with the ORNL model Q-945 automatic titrator is now in progress.

[22] W. D. Shults, II, and P. F. Thomason, "Elimination of Copper Interference in a Potentiometric Titration of Uranium," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 2.

ANALYTICAL CHEMISTRY DIVISION - Y-12 SITE

RESEARCH AND DEVELOPMENT

ANP ANALYTICAL CHEMISTRY

J. C. White

A. S. Meyer, Jr. W. J. Ross
D. L. Manning G. Goldberg
J. M. Peele B. L. McDowell

Relative to the ANP Project, methods are being developed for the analysis of Flinak and $NaZrF_5$ materials, with particular emphasis being given to the determination of uranium trifluoride. The progress of this work is reported elsewhere.[1,2]

HRP ANALYTICAL CHEMISTRY

O. Menis

The problems related to the determination of trace elements present as corrosion products or additives in ThO_2 slurries, thorium compounds, and uranyl salt solutions are still the major concern of those engaged in the analytical chemistry of the HRP. In addition, special problems such as the adsorption characteristics of a ThO_2 material and the estimation of the thickness of oxide films which are formed as a consequence of corrosion were investigated.

Polarographic Determination of Titanium

O. Menis

A previously described[3] polarographic method for the determination of titanium was further investigated in order to improve the precision. It was found that the pH, the concentration of citrate ion, the concentration of gelatin, the deaeration time, and the maximum quantity of thorium and of corrosion products are critical. The optimum fixed conditions which were established are: a pH of 5.7, a citrate concentration of 0.6 *M*, a gelatin concentration of 0.0036%, a deaeration time of 30 min, a temperature of 26 ±2°C, and a drop time of 6 sec. A perchloric acid solution and a final volume of 10 ml are recommended when the ORNL model Q-1160 polarograph is used.

An evaluation of the data indicates that the half-wave potential vs the S.C.E. is shifted to less negative values in the presence of thorium, whereas an increase in the nickel concentration results in a shift to more negative values. The agreement between the polarographic and the peroxide methods for the determination of titanium was found to be within 5% for slurry standards that contained all the corrosion products which are ordinarily found as a consequence of contact with stainless steel. Titanium in the range of 50 to 200 μg was determined by the polarographic method with a relative standard deviation of 5% in the presence of 100 mg of thorium and 300 μg of corrosion products.

Determination of Titanium in Thorium by the Ascorbic Acid Method

H. R. Hunt, Jr.

A spectrophotometric method for the determination of titanium in which ascorbic acid is used as the chromogenic reagent is given in the literature.[4] The method was investigated to ascertain whether it could be adapted to the determination of microgram quantities of titanium in the presence of thorium. Test results reveal that the absorbancy varies as a function both of the ascorbic acid and of the thorium concentrations (see Fig. 16) and that the thorium concentration must be known when the method is applied to the determination of titanium in the presence of thorium. If the thorium concentration is not known, prior removal of the thorium is required. In the absence of thorium, the method has been found to be suitable for use in the concentration range of 5 to 25 μg of titanium per milliliter.

An attempt was made to separate titanium from thorium by means of a modification of a method

[1] J. C. White *et al.*, "Analytical Chemistry of Reactor Materials," *ANP Quar. Prog. Rep. June 10, 1954*, ORNL-1729, p 109.

[2] J. C. White *et al.*, "Analytical Chemistry of Reactor Materials," *ANP Quar. Prog. Rep. Sept. 10, 1954*, ORNL-1771, p 148.

[3] T. C. Rains and M. L. Druschel, "Analysis of Slurries," *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 35.

[4] E. Hines and D. F. Boltz, "Spectrophotometric Determination of Titanium with Ascorbic Acid," *Anal. Chem.* 24, 947 (1952).

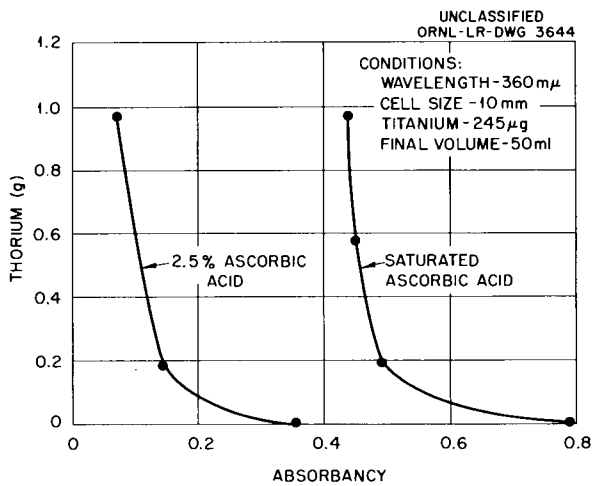

Fig. 16. Absorbancy of Titanium Ascorbate as a Function of Thorium and Ascorbic Acid Concentrations.

reported in the literature.[5,6] In the modified method, thorium is complexed with a solution of disodium ethylenediaminetetraacetate, and titanium hydroxide is precipitated with ammonium hydroxide in the presence of a magnesium carrier. It was found that titanium is not precipitated by the modified method because of the high concentration of disodium ethylenediaminetetraacetate required to complex the thorium. Another method for the separation and determination of titanium in thorium samples is presented in subsequent sections of this report.

Separation and Spectrophotometric Determination of Titanium in the Presence of Thorium by the Chloroform–8-Quinolinol Method

H. R. Hunt, Jr.

In order to develop a method for the determination of microgram quantities of titanium in the presence of large concentrations of thorium, variables in the chloroform–8-quinolinol extraction method for the separation and determination of titanium were studied. A concentrated acetate solution was used to prevent the extraction of thorium.[7] The optimum pH for the extraction was found to be 4.5 to 5.0, and the wave length of maximum absorption is 385 mμ. In the absence of thorium, 99% of the titanium is removed by two extractions with 20 ml of chloroform, but, when as much as 1 g of thorium is present, an additional extraction with 10 ml of chloroform is necessary for the complete recovery of titanium. In the presence of thorium, a relative standard deviation of about 2% is obtained for the determination of titanium in the range of 100 to 150 μg.

The use of an alkaline cyanide solution[7,8] for washing the chloroform extract of the titanium–8-quinolinol complex, thereby eliminating interference from copper, cobalt, and nickel, was studied. A slight decrease in sensitivity and a shift of the absorption maximum from 385 to 377 mμ were noted when the absorption spectrum of a standard sample, extracted at a pH of 4.8 and washed with the alkaline cyanide solution, was determined. Titanium in the range of 50 to 150 μg was determined with a relative standard deviation of 6% when a wash solution of alkaline cyanide was used. Experiments are being conducted in order to determine the effects of various corrosion products and to determine whether the range can be extended to lower concentrations of titanium when the absorbancy is measured at a different wave length.

Separation of Zirconium in Thorium Oxide Slurries by the Ion-Exchange Method

F. L. Layton

The separation of thorium and zirconium by means of an ion-exchange resin was investigated. Slurry samples which had been dissolved in 10 *N* hydrochloric acid were passed through a chloride-form, strong base (Dowex 1), resin column; then the thorium was eluted with 12 *N* hydrochloric acid. Complete elution of zirconium did not occur when the column was subsequently washed with 3 to 6 *N* hydrochloric acid solutions but did occur, as was shown by tracer activity, when 6 *N* sulfuric acid was used.

[5] W. F. Pickering, "The Rapid Separation and Estimation of Titanium by Means of Ethylenediaminetetraacetic Acid," *Anal. Chim. Acta* 9, 324-9 (1953).

[6] R. Pribil and P. Schneider, "The Use of Complexones in Chemical Analysis. XI. Gravimetric Determination of Titanium," *Collection Czech Chem. Communs.* 15, 886 (1950).

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

[8] C. H. R. Gentry and L. G. Sherrington, "The Direct Photometric Determination of Aluminum with 8-Hydroxyquenoline," *Analyst* 71, 432 (1946).

A spectrophotometric method previously developed in this laboratory[9] was used for the determination of zirconium. As a consequence of this work, it was shown that zirconium in the range of 20 to 70 μg can be determined with a relative standard deviation of 3% in solutions which contain thorium.

Determination of Beryllium in the Presence of Thorium

F. L. Layton

A procedure[10] for the separation of beryllium from aluminum was modified and investigated for use in the determination of beryllium in the presence of thorium. In this procedure, thorium is complexed by the addition of disodium ethylenediaminetetraacetate; the beryllium, which is not complexed, is precipitated as the hydroxide by the addition of ammonium hydroxide. In order to obtain accurate results, it was found necessary to carry out a double precipitation and to wash each precipitate with a solution of ammonium chloride. Satisfactory results were obtained for beryllium in the range of 20 to 35 mg in the presence of 200 to 400 mg of thorium when the precipitates of beryllium hydroxide were washed with a 2% solution of ammonium chloride. A complete separation of beryllium and thorium was accomplished by this method; the beryllium hydroxide was subsequently determined by ignition to the oxide. This procedure will be written for inclusion in the *ORNL Master Analytical Manual.*

Spectrophotometric Determination of Palladium with α-Furildioxime

T. C. Rains

The qualitative method reported by Reed and Banks[11] for detecting palladium, which is based on the formation of a yellow palladium–α-furildioxime complex, was modified for the quantitative estimation of palladium in the presence of thorium. The optimum conditions for a spectrophotometric method were established. Color is developed in a hydrochloric acid solution by means of a 1% solution of α-furildioxime, and the absorbancy is measured at 420 mμ. The method can be used for determining palladium in the range of 3 to 15 μg with a relative standard deviation of 5%.

Spectrophotometric Determination of Aluminum in the Presence of Thorium

H. R. Hunt, Jr.

A colorimetric method[7] for aluminum was adapted for the determination of microgram quantities of aluminum in the presence of thorium. Aluminum is determined spectrophotometrically after multiple extractions with a solution of 8-quinolinol in chloroform. Conditions were established in which a concentrated acetate solution is used to prevent the extraction of thorium. When great sensitivity is necessary, four extractions are required because the sensitivity has been found to vary with the extraction procedure. In the presence of as much as 1 g of thorium, 20 to 200 μg of aluminum can be determined with a relative standard deviation of about 5%. This procedure will be written for inclusion in the *ORNL Master Analytical Manual.*

Dissolution of Thorium Phosphate Samples and Determination of Thorium

F. L. Layton

A procedure for the dissolution and analysis of a thorium phosphate sample was studied. The dissolution was accomplished by fusion with sodium carbonate, followed by extraction with water. Two fusions were necessary in order to separate quantitatively thorium and phosphate. The fusion residues were subsequently dissolved in a mixture of nitric and perchloric acids to which several drops of hydrofluoric acid were added. Thorium was determined by precipitation as the oxalate, and phosphate was determined by precipitation as magnesium ammonium phosphate.

Analyses of pure thorium phosphate samples indicated that the ratios of Th to PO_4 agreed to within 0.5% of the theoretical ratio of 3 to 4.

Determination of Water-Soluble Impurities in Thorium Oxide by Conductance

C. M. Boyd

The specific conductance of aqueous slurries of thorium oxide has been utilized as a criterion

[9] O. Menis, *The Determination of Zirconium by Chloranilic Acid Method,* ORNL-1626 (April 7, 1954).

[10] P. I. Brewer, "The Determination of Beryllium in Beryl by Means of Ethylenediamine Tetra-Acetic Acid," *Analyst* 77, 539 (1952).

[11] S. A. Reed and C. V. Banks, "The Determination of Palladium and Nickel With Alpha-Furildioxime," *Proc. Iowa Acad. Sci.* 55, 267-75 (1948).

for estimating the amount of ionizable water-soluble impurities in the oxide and for determining the concentration of soluble corrosion products in experimental slurries. In a series of tests on samples of thorium oxide from different sources, it was observed that a sample of oxide from the Lindsay Light & Chemical Co. yielded aqueous extracts having the lowest conductance, and it was estimated from the conductance that the concentration of soluble impurities amounted to less than 50 $\mu g/g$. The highest conductance was observed in the water extracts of thorium oxides which had been prepared from thorium formate. In these cases, the conductance tests indicated that the amount of soluble material was of the order of 2000 $\mu g/g$. Spectrographic and photometric analyses of these extracts verified the estimated ionic concentrations.

Ionic Adsorption by Thorium Oxide

C. M. Boyd

The adsorption of various acids and of metal cations on thorium oxide was investigated. The adsorption was determined at 30°C (room temperature) and at 100°C. The maximum adsorption of the various ions on thorium oxide prepared from thorium formate ignited at 650°C is given below:

Ion	Compound	Amount Adsorbed (mg/g of ThO_2)	
		At 30°C	At 100°C
PO_4^{---}	H_3PO_4	14.3	30.8
SO_4^{--}	H_2SO_4	11.2	9.0
CrO_4^{--}	H_2CrO_4	10.7	8.4
NO_3^{-}	HNO_3	7.7	4.2
UO_2^{++}	$UO_2(NO_3)_2$	6.2	10.2
Ni^{++}	$Ni(NO_3)_2$	10.5	0.3
Fe^{+++}	$Fe(NO_3)_3$	12.5	24.8

Measurements of the conductance and of the pH of the acid solutions after adsorption indicated adsorption of the complete acid rather than the anions alone. The quantitative interpretation of the data can be expected to be related to the physical and chemical characteristics of a particular sample of thorium oxide under test.

Colorimetric Determination of Nickel in Uranyl Sulfate Solution

M. L. Druschel

Variables in the colorimetric method for the estimation of nickel, as described by Druschel *et al.*,[12] were re-evaluated in order to improve the precision and to allow for a higher tolerance in the concentration of uranium. It has been shown[13] that ammonium ions interfere in the determination of nickel by dimethylglyoxime. It is known, however, that precipitation occurs in a uranyl sulfate solution and thereby makes it impossible to determine nickel, particularly if the pH is high and if ammonium ions are absent. The method has been modified so that when 30% of ammonium citrate, 20 meq of ammonium hydroxide, and 0.5 meq of sulfuric acid are used and the final pH is adjusted with sodium hydroxide, as much as 100 mg of uranium can now be tolerated in the 50-ml final volume. Under these conditions, the nickel–dimethylglyoxime complex is stable and the uranium remains in solution over a pH range of 10.5 to 11.5. In the presence of higher concentrations of uranium (more than 100 mg/50 ml), however, erratic results were obtained or precipitation occurred. When 20% sodium carbonate was substituted for ammonium citrate, as much as 300 mg of hexavalent uranium did not affect the stability of the nickel complex at a pH of 11.5. The relative standard deviation for nickel in the range of 1.5 to 3.5 μg per milliliter of final volume is less than 1%, regardless of the uranium concentration, when sodium carbonate is present. Further work will involve the determination of nickel in the presence of copper.

Determination of Tetravalent Uranium by Chloranilic Acid

F. L. Layton

The determination of tetravalent uranium by the chloranilic acid method in the presence and absence of hexavalent uranium and at various ratios of perchloric and hydrochloric acids was

[12] M. L. Druschel, O. Menis, and R. Rowan, Jr., *Modifications of the Dimethylglyoxime Method for the Colorimetric Determination of Nickel Based on the Use of Potassium Persulfate as the Oxidant*, ORNL-1430 (Nov. 3, 1952).

[13] K. ter Haar and W. Westerveld, "The Colorimetric Determination of Nickel as $Ni_{(4)}$ Dimethylglyoxime," *Rec. trav. chim.* **67**, 71 (1948).

studied. The results compared favorably with those obtained in a previous investigation.[14]

Standards of tetravalent uranium were prepared in both the absence and the presence of hexavalent uranium. Results comparable to those previously reported were obtained when the hexavalent uranium was absent. In those instances where the tetravalent uranium was added to solid uranium trioxide and dissolution was effected in a mixture of perchloric and hydrochloric acids, there was no evidence of color development. The cause of the interference encountered in the presence of hexavalent uranium has not yet been determined.

Determination of Dissolved Oxygen in Solutions of Uranyl Sulfate

C. M. Boyd

A separation procedure for the removal of both cations and anions prior to the determination of dissolved oxygen in aqueous solutions was developed. A modification of the Winkler method was then applied in the determination of oxygen.[15] In the modified method, the dissolved oxygen reacts with potassium iodide to liberate iodine, and the absorbancy of the potassium iodate complex is measured at 353 mμ. As a consequence of the absorbancy of uranyl sulfate at this wave length and of the oxidizing power of certain corrosion products which may be present, both cations and anions are removed prior to the analysis. The removal is effected by means of a column of mixed ion-exchange resins of Dowex 50 in the hydrogen form and Dowex 1 in the chloride form in a closed system. The results obtained indicate a 90% recovery of oxygen, based on a standard prepared from an air-saturated water solution, with a relative standard deviation of 5%.

Amperometric Titration of Mixed Halides in Uranyl Sulfate Solutions

C. M. Boyd

The adaptation of the argentometric, amperometric titration method of Laitinen *et al.*[16] to the determination of traces of halides in solutions of uranyl sulfate has been investigated. This method is based on titrating the halides with a silver nitrate solution and determining the equivalence point by measuring the diffusion current that results from the excess silver ions added. A rotating platinum electrode is used as the indicating electrode. A potential of −0.23 v vs S.C.E. is used for the iodide titration in 0.1 *N* ammonium hydroxide, followed by the titration of the bromide in 0.1 *N* sulfuric acid at +0.15 v vs S.C.E. at which potential uranium does not interfere. Chloride is then titrated at 0.0 v vs S.C.E. in the presence of gelatin at 5°C. Uranyl sulfate at a concentration of 50 mg/ml does not interfere, but it must be complexed with ammonium citrate for the iodide titration in an ammonical medium.

An estimated relative standard deviation of 10% is indicated for the titration of the halides at a concentration of 10 μg/ml.

Determination of the Film Thickness of Zirconium Oxide and Titanium Oxide

C. M. Boyd

Consideration has been given to the measurement of the thickness of films of zirconium oxide and titanium oxide as a means of evaluating the corrosion of zirconium and titanium metals. Thin films of zirconium oxide are good insulators and show marked interference colors, the hues of which can be evaluated in terms of thickness of the film. These oxide films can be made to serve as the dielectric of a condenser in which the capacity per unit area is related to the thickness and dielectric constant of the film. A value of 27 has been reported for the dielectric constant of these films.[17] The thickness can also be estimated by comparison of the interference color given by the film with a series of standard films of zirconium oxide.

Oxide films which were produced by anodization of zirconium and Zircaloy-1 in borate, boric acid, and uranyl sulfate solutions were shown to be of the same insulating type and to give comparable capacitance and interference colors. In contrast, it was found that the oxide films formed on titanium have a capacitance which, although higher, is not

[14] M. L. Druschel, "Determination of Uranium(IV) in Uranyl Oxide," *Anal. Chem. Quar. Prog. Rep. Jan. 10, 1953*, ORNL-1474, p 46.

[15] T. C. J. Ovenston and J. H. E. Watson, "The Spectrophotometric Determination of Small Amounts of Oxygen in Waters," *Analyst* 79, 383 (1954).

[16] H. A. Laitinen, W. P. Jennings, and T. D. Parks, "Amperometric Titration of Mixtures of Halides Using the Rotating Platinum Electrode," *Ind. Eng. Chem. Anal. Ed.* 18, 358 (1946).

[17] J. J. Polling and A. Charlesby, *The Analysis of Formation Current in Electrolytic Oxidation of Zirconium*, AERE-M/R-1176 (April 29, 1953).

proportional to their thickness. Titanium oxide films do exhibit interference colors similar to those of zirconium oxide films, and their thickness has been estimated in the same manner.

RAW MATERIALS

H. P. House L. J. Brady

Analysis of Monazite Sand

J. R. Lund J. L. Mottern

A number of methods for the analysis of monazite sand and its variants were studied step-wise in some detail. Monazite sand was dissolved in a mixture of nitric and perchloric acids, and a double, homogeneous oxalate precipitation of thorium and rare earths[18,19] was made. The oxalate precipitate was dissolved in nitric acid or in a mixture of nitric and perchloric acids, and the thorium was extracted with mesityl oxide.[20,21] Thorium was removed from the organic phase with water and determined by the spectrophotometric Thoron method.[22]

It was found that a double oxalate precipitation, rather than a single precipitation, is necessary and that extraction with mesityl oxide can be made from a 1.2 *N* perchloric acid solution as well as from a nitric acid solution of equal acidity; however, the extraction cannot be made satisfactorily from a sulfate solution.

Tests also indicate that thorium and uranium are quantitatively extracted with mesityl oxide from 1.2 *N* nitric or perchloric acid solutions which are three-fourths saturated, rather than saturated, with aluminum nitrate, that the optimum shaking time for extraction and washing operations is 15 to 20 sec, and that the extraction effects quantitative separation of thorium from rare earths. Yttrium is extracted to a very small extent from a perchloric acid solution.

Determination of Water in Uranyl Sulfate by a Modified Karl Fischer Method

L. J. Brady

A modification of the method in which water is determined by direct titration with Karl Fischer reagent was used to determine water in an amine complex of uranyl sulfate. Laurene[23] reported that it is possible to determine water in the presence of ferric salts by direct titration with Karl Fischer reagent if the ferric iron is first reacted with a methanol solution of 8-quinolinol. The liberation of iodine by reaction of ferric iron with the Karl Fischer reagent is thus prevented. This same technique was applied to the determination of water in a complex salt of uranyl sulfate. The uranyl salt dissolved readily in the quinolinol–methanol solution, and the sharp endpoint obtained with the Karl Fischer reagent did not change significantly when the solution was stirred for an additional 3 min, the time required for the complete dissolution of the sample.

Volumetric Determination of Sulfate in the Micro Range

E. C. Lynn K. B. Roy

The volumetric method of Fritz and Freeland[24] for the determination of sulfate in the macro range of 20 to 400 mg was modified for the micro range of 0.5 to 5 mg. In order to effect this change, the volume of methanol in the titration medium was increased from the 40 to 50% recommended for the macro range of sulfate to 85%. When the volume of alcohol was so increased, a definite characteristic endpoint was obtained. The relative standard deviation for the determination of sulfate in the range of 0.5 to 5 mg is estimated to be of the order of 3%.

Determination of Iron in the Presence of Phosphate

E. C. Lynn J. J. McCown

In order to eliminate the interference due to phosphate, the orthophenanthroline method for the

[18] H. H. Willard and L. Gordon, "Thorium in Monazite Sand," *Anal. Chem.* **20**, 165 (1948).

[19] L. Gordon, C. H. Vaneslow, and H. H. Willard, "Precipitation of Thorium from Homogeneous Solution," *Anal. Chem.* **21**, 1323 (1949).

[20] H. Levine and F. S. Grimaldi, *Application of Mesityl Oxide to the Determination of Thorium*, AECD-3186 (Feb. 1950).

[21] C. H. Byrd and C. V. Banks, *Spectrophotometric Determination of Thorium with the Trisodium Salt of 2-(2-Hydroxy-3,6-Disulfo-1-Napthtylazo)-Benzenearsonic Acid and Some Properties of Complexes Involved*, ISC-456 (June 1953).

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

[23] A. H. Laurene, "Determination of Water by Karl Fischer Titration in the Presence of Ferric Salts," *Anal. Chem.* **24**, 1496 (1952).

[24] J. S. Fritz and M. Q. Freeland, *Direct Titrimetric Determination of Sulfate*, ISC-411 (Oct. 1, 1953).

determination of iron was modified by increasing the concentration of ammonium acetate. Samples in which as much as 0.25 *M* phosphoric acid was present were tested for iron without prior separation of phosphate.

MISCELLANEOUS ANALYSES

H. P. House

Flame Photometric Determination of Sodium, Potassium, Rubidium, and Cesium

J. M. Rogers

Optimum conditions for the flame photometric determination of sodium, potassium, rubidium, and cesium in mixtures thereof were experimentally determined, and a large number of samples derived from the operation of an ion-exchange column were tested. Detailed procedures for each of the four alkali metals were written.

The interference of one alkali metal with the determinations of the others was studied to a limited extent; lack of sufficiently pure rubidium and cesium hampered this study. Recently, relatively pure rubidium and cesium have become available through the column-extraction work; these materials are now being used in further interference studies. Both cerium and potassium in moderate to high concentrations interfere with the determination of rubidium because of background and enhancement. Sodium interferes only slightly in the rubidium determination.

Determination of Carbamate in the Presence of Carbonate

A. S. Meyer, Jr. J. M. Rogers

Carbonate and carbamate were determined in mixtures by a method[25] in which the carbonate is precipitated in a cold solution and removed by centrifugation as barium carbonate, after which the carbamate in an aliquot of the supernatant liquid is converted to carbonate by heating, removed as barium carbonate, and analyzed for carbonate by titration.

Determination of Ammonia in Microgram Amounts

A. S. Meyer, Jr. J. M. Rogers

Residual ammonia in very small amounts was determined in sodium hydroxide solutions and in slurries of calcium hydroxide by an adaptation of the spectrophotometric method of Kruse and Mellon.[26] In the range 1 to 5 μg of ammonia, the precision was 20% or less; for larger amounts, 10 to 25 μg of ammonia, the relative standard deviation was of the order of 5%.

Oxidation of Chromium by Perchloric Acid

H. P. House J. M. Rogers

In the spectrophotometric determination of chromium with diphenylcarbazide, boiling perchloric acid effects complete oxidation of the chromium so that subsequent addition of potassium permanganate, followed by hydrochloric acid to destroy excess permanganate, is unnecessary.

QUALITY CONTROL

R. L. McCutchen C. D. Susano

Little change has been made in the types of materials tested in the Analytical Chemistry Laboratories at the Y-12 Site.

The control work in the laboratories of the Division at the X-10 Site has decreased to the extent that only the laboratory in Building 4500 is reporting test results for control purposes. Preliminary work, however, is now being carried out for the purpose of installing a control program in connection with the Thorex project.

The distribution, by laboratory, of the 2619 determinations that were evaluated for control purposes is summarized in Table 11, and the control data for the previous period are also shown for purposes of comparison.

[25] G. H. Burrows and G. N. Lewis, "The Equilibrium Between Ammonium Carbonate and Ammonium Carbamate in Aqueous Solution at 25°," *J. Am. Chem. Soc.* **34**, 993-5 (1912).

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

TABLE 11. SUMMARY OF DETERMINATIONS EVALUATED FOR CONTROL PURPOSES

Laboratory	Determinations Evaluated for Control Purposes	
	September 1953 Through March 1954	April Through September 1954
Y-12 Site		
ANP	583	996
HRP	647	609
Raw Materials	254	202
Total	1484	1807
X-10 Site		
Building 3019	418	
Building 3508	164	
Building 4500	1003	812
Total	1585	
GRAND TOTAL	3069	2619

SERVICE ANALYSES

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

ANP ANALYTICAL CHEMISTRY

J. C. White W. F. Vaughan
C. R. Williams

The service work of the ANP Analytical Chemistry Laboratory has continued, for the most part, to be concerned with the analyses of those fluoride mixtures currently under consideration for use as reactor fuels. The determinations most often made during the period included lithium, sodium, potassium, rubidium, trivalent and tetravalent uranium, zirconium, nickel, iron, chromium, sulfur, and fluorine. Accounts of the work of this laboratory are given elsewhere.[1,2]

HRP ANALYTICAL CHEMISTRY

O. Menis C. K. Talbott
P. V. Hoffman T. C. Rains

The staff of the HRP Analytical Chemistry Laboratory made 20,675 determinations on 3306 samples. Solutions of uranyl sulfate and other uranyl salts were analyzed for uranium, sulfate, and the corrosion products iron, nickel, and chromium. Similar tests were made on thorium oxide and other thorium compounds. In addition to this work, methods were tested for the determination of aluminum in the presence of iron,[3] the spectrophotometric determination of chlorine,[4] the colorimetric thiocyanate determination of uranium in the presence of thorium, the spectrophotometric determination of cerium,[5] the spectrophotometric determination of dissolved oxygen,[6] and the separation of rare earths and thorium.[7,8]

[1] J. C. White, W. F. Vaughan, and C. R. Williams, "Summary of Service Analyses," *ANP Quar. Prog. Rep. June 10, 1954*, ORNL-1729, p 112.

[2] J. C. White, W. F. Vaughan, and C. R. Williams, "Summary of Service Analyses," *ANP Quar. Prog. Rep. Sept. 10, 1954*, ORNL-1771, p 154.

[3] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2d ed., p 152, Interscience, New York, 1950.

[4] I. Nusbaum and P. Skupeko, "Detection and Estimation of Free and Combined Chlorine Residuals," *Anal. Chem.* 23, 1881 (1951).

[5] R. E. Edwards, A. S. Ayers, and C. V. Banks, *Spectrophotometric Determination of Cerium*, ISC-165 (Aug. 31, 1951).

[6] T. C. J. Ovenston and J. H. E. Watson, "The Spectrophotometric Determination of Small Amounts of Oxygen in Waters," *Analyst* 79, 383 (1954).

[7] E. J. Center, W. M. Henry, and R. D. Householder, *The Determination of Rare Earths in Thorium*, BMI-260 (May 15, 1952).

[8] C. E. Feldman, private communication, May 1954.

TABLE 12. 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	ANP	Metallurgy	Isotope Research and Development	REED	ADP	Y-12 Steam Plant	Y-12 Stores	Miscellaneous	
Laboratory Making Analyses			Number of Determinations									
ANP Analytical	3	9	17,411	10,999			358					28,768
HRP Analytical	5*	8					20,675					20,675
Special Samples	1	0	27	674		4	382				4	1,091
Raw Materials	2	7	12,939		117		153			959	199	14,367
Miscellaneous Analyses	3	9	12,178	48	193	15	667	79	65	6	94	13,345
Total	14	33	42,555	11,721	310	19	22,235	79	65	965	297	78,246

*Two for four months only.

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RAW MATERIALS CHEMISTRY

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During this period 3270 samples were tested for the Raw Materials Group of the Materials Chemistry Division. This number represents an increase of about 18% as compared with the number of samples tested for this group during the previous six-month period. In addition to the determination of uranium in the colorimetric and fluorometric range, many samples were tested for aluminum, vanadium, iron, molybdenum, calcium, magnesium, sulfate, and perchlorate.

Samples derived from the study of the extraction of uranium by various high-molecular-weight amines in organic diluents were tested for uranium in the colorimetric and fluorometric range. When the iron and vanadium content of the samples is such as to cause interference in the stannous chloride–ammonium thiocyanate method for uranium, a diethyl ether extraction is used to separate uranium from these interfering components.

The tetraphenyl arsonium chloride method was substituted for the nitron method for the determination of perchlorate in order to eliminate the low results associated with the nitron method.

A number of samples were tested for thorium to determine the efficiency of certain amines as extracts for thorium. Thorium was separated from other constituents in the samples by a fluoride precipitation[9] and an extraction with mesityl oxide.[10] After this separation, thorium was determined by the colorimetric Thoron[11] method.

MISCELLANEOUS ANALYSES

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The number of samples tested during this period increased from 687 for the previous period to 1380. This increase, for the most part, is due to the large number of solutions of sodium hydroxide that were tested for ammonia and to ammonium carbonate solutions that were tested for pH, carbonate, carbamate, and total ammonia.

Tests were made of oils and of ferrous and nonferrous alloys for the purpose of determining conformance with specifications. Ordinarily, standard ASTM methods were used in these tests.

The chloride content of polyvinyl chloride plastics was determined by a peroxide fusion in a Parr bomb and precipitation as silver chloride. The hydrogen content of a series of Teflon samples was determined and was used to estimate the efficiency of various methods for the removal of lubricating oil from the surface of the plastic.

Such physical properties as specific gravity, boiling point, and refractive index and other tests, such as solubility and classification, were used to identify unknown organic solvents, stored in drums, for the Y-12 Stores Department. In addition, the water content of fluorocarbons and 2-ethylhexanol was determined by coulometric titration.

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

[10] H. Levine and F. S. Grimaldi, *Application of Mesityl Oxide to the Determination of Thorium*, AECD-3186 (Feb. 1950).

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

[redacted]