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ANNUAL PROGRESS REPORT

FOR PERIOD ENDING DECEMBER 31, 1957

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FOR PERIOD ENDING DECEMBER 31, 1957

Page	Column	Line	Errata
18	1	3	<i>for 1 mμa read 1 μa</i>
18	1	10	<i>for 500 mμa read 500 μa</i>
18	1	30	<i>for 10-mμf read 10-μf</i>
18	2	8	<i>for 4, and 10 times read 4 and 10, or 1, 2, 4, and 10 times</i>
23	1	4	<i>for micro- read macro-</i>
34		Fig. 7	<i>for Cs⁵¹ read Cr⁵¹</i>

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Chemistry-General
TID-4500 (13th ed. Rev)

Contract No. W-7405-eng-26

ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

For Period Ending December 31, 1957

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

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CONTENTS

SUMMARY	xi
PRESENTATIONS OF RESEARCH RESULTS	xvii
ANALYTICAL CHEMISTRY DIVISION – X-10 SITE	
RESEARCH AND DEVELOPMENT	1
Ionic Analyses	1
Spectrum of PuO_2^{++} in Sulfate Media – Resolution of the 8350-Å Absorption Peak of PuO_2^{++} into a Doublet	1
Autoreduction of PuO_2^{++} by Products of the Alpha-Particle Radiolysis of Water – Kinetics and Mechanisms	4
Determination of Plutonium(III) and (IV) in PuF_3 - PuF_4 Mixtures Contained in Fused NaF - BeF_2	5
Polymerization and Disproportionation of Plutonium(IV) in Sulfate Media	6
Coulometric Titration of Potassium Pertechnate in a Solution of Potassium Phosphate	7
Determination of Nickel and Chromium in Mixtures of Fluoride Salts	7
Distillation of Amsco 125-82 and Identification of Its Major Constituents	8
Determination of Niobium	9
Analysis of Yttrium Alloys	9
Study of Chemical Changes in UO_2 -Al Reactor Fuel Elements During Fabrication	10
Enthalpymetric Determination of Free Acid in the Presence of Certain Hydrolyzable Ions	11
Polarographic Behavior of Niobium in Citric Acid Medium	11
Identification and Determination of Chloride in Metallex Amalgams	11
Determination of Oxides of Nitrogen	12
Analytical Instrumentation	12
In-Line Instrumentation Program at ORNL	12
Service Instructions for the ORNL Model Q-1728, Velocity-Servo, Automatic, Potentiometric Titrators	14
ORNL Model Q-1887, Recording and Scanning, High-Sensitivity, Flame Spectrophotometer	14
Simplified Controlled-Potential Coulometric Titrators	14
Gamma Absorptometer	14
Specialized Modifications of Commercial Apparatus Used for Analyses Performed Remotely in the High-Radiation-Level Analytical Facility (HRLAF)	15
Modification of the Jarrell-Ash Arc and Spark Stand	15
Electromatic Buret for Use in the High-Radiation-Level Analytical Facility (HRLAF)	16
Cam Switching Attachment for Argonne Model 8 Master-Slave Manipulators	16
Automatic, Derivative, Spectrophotometric Titrator	16
Conversion of a Gilmont Micropipet-Buret to a Constant-Delivery-Rate Buret	16
Electronic Coulometric Stripper for the Determination of Submicrogram-to-Microgram Amounts of Halides	16
Controlled-Potential and Derivative Polarograph	17
Radiochemical Analyses	19
Nuclear Properties	19
Electromagnetic Radiation from Pu^{239} , Pu^{240} , and Pu^{241}	19

Experimental L-Shell Fluorescence Yields	19
Measurement of Radioactivity	19
Effects of Low-Energy Beta Activity on Alpha Counting	19
Instrumental Analyses	21
Analysis of Radioactive Materials by Gamma Scintillation Spectrometry	21
Beta Scintillation Spectrometry	21
Radioisotope Analysis	21
Isotopic Analysis	21
Fission-Product Methods	22
Analysis of Mixtures of Fission-Product Noble Gases	22
Heavy Elements	22
Radiochemical Determination of Iodine	22
Reactor Analyses	22
Testing for Leaks in the HRT Equipment	22
Electronuclear Research Program	22
Solvent-Extraction Methods	22
Amine Extractions	22
Activation Analyses	23
Quantitative Applications of Activation Analysis	23
Nondestructive Methods of Assay in Activation Analysis	23
Determination of Sulfur by Activation Analysis with Fast Neutrons	23
Use of Activation Analysis in the Isotopic Analysis of Uranium	29
Determination of Oxygen by Activation Analysis	30
Quantitative Determination of Trace Elements in Animal Tissue	30
Activation Analysis as a Qualitative or Semiquantitative Method	30
Use of Activation Analysis in Reactor Technology	31
Identification and Determination of Radionuclides in Reactor Cooling Water	31
Determination of Trace Amounts of Argon in Water	32
Measurement of Induced Radioactivities	32
Particle-Size-Distribution Analysis by the Activation Analysis-Sedimentation Method	32
Determination of Particle-Size Distributions in Multiple-Component Systems by Activation Analysis	35
Particle-Size-Distribution Analysis in the Submicron Range by Activation Analysis-Centrifugation Method	37
New Applications of Activation Analysis	40
Mass Spectrometry	40
Mass Spectrometry Research and Development	40
New Mass Spectrometer	40
Potassium Analysis Program	40
Thermal Diffusion	41
Separation of Isotopes of Krypton	41
Separation of Mass-36 Isotope of Argon	41
Spectrochemical and X-Ray Analyses	42
Determination of Rare-Earth Elements	42
Porous-Cup Excitation with Air-Interrupted Spark Source	42
High-Radiation-Level Analytical Facility (HRLAF)	42
X-Ray Diffraction	42
X-Ray Fluorescence	44
Design of Solution Cell	44
Analysis of U-Nb-Zr Alloys	44
Flame Photometry	44

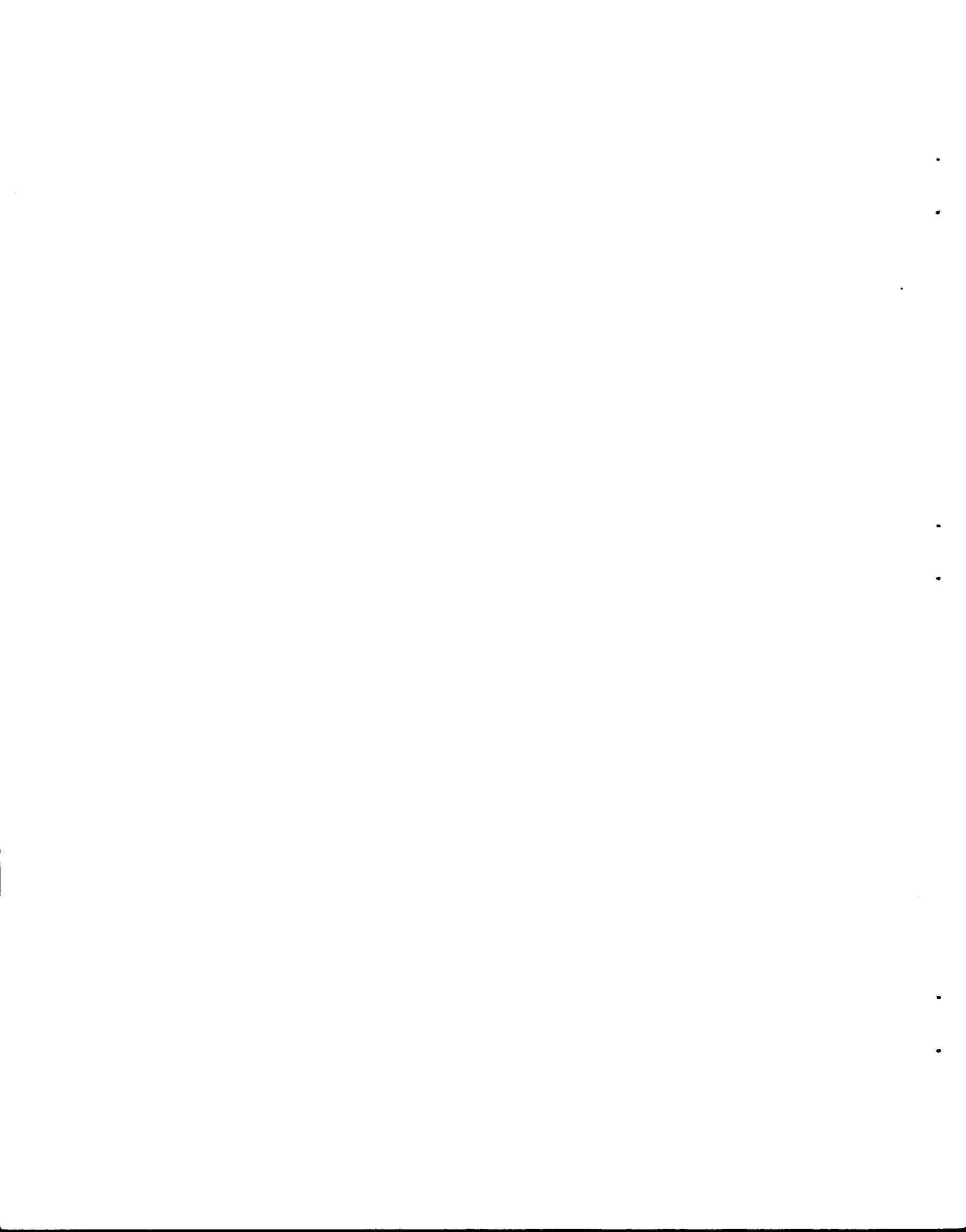
Inorganic Preparations	44
Optical and Electron Microscopy	45
Optical and Electron Microscopy of Thorium Oxide	45
Examination of Thin Films, Corrosion Products, and Surface Structures	48
Electron and Optical Microscopy of Crystallites, Metal Powders, and Exchange Resins	48
Methods and Techniques	48
ORNL Master Analytical Manual	48
SERVICE ANALYSES	50
Ionic Analyses	50
Radiochemical Analyses	50
Activation Analyses	50
Mass Spectrometric Analyses	50
Laboratory Control Group	50
Pilot-Plant Control Laboratory	52
Isolation Analyses	52
Special Analyses Laboratory	53
Radioisotope-Radiochemistry Laboratory	53
High-Radiation-Level Analytical Facility (HRLAF)	54
Reactor Analyses	54
Analysis of Mixtures of Fluoride Salts	55
Determination of Dissolved Oxygen in Water	55
Controlled-Potential Coulometric Titrator	55
Preparation of Samples for Isotopic Analysis	55
Automatic Potentiometric Titration of Free Acid in Uranyl Sulfate Solutions	56
Determination of Lithium in Beryllium Metal	56
Modified pH Electrode Assembly	56

ANALYTICAL CHEMISTRY DIVISION – Y-12 SITE

RESEARCH AND DEVELOPMENT	57
HRP Analytical Chemistry	57
Removal of Fluoride from Inorganic Material by Pyrolysis	57
Polarographic Determination of Zinc	58
Extraction and Spectrophotometric Determination of Molybdenum	58
Flame Photometric Determination of Lanthanum	59
Spectrophotometric Determination of Aluminum in Thorium Oxide	61
Flame Photometric Determination of Aluminum	61
Spectrophotometric Determination of Microgram Quantities of Titanium in Thorium Oxide	61
Distribution of Hydrazine in Thorium Oxide Slurries	62
Polarographic and Beta-Counting Determination of Technetium	62
Determination of Sulfate by Indirect, Potentiometric Titration	62
Determination of Lower Limit of Quantitative Measurement of Potassium by Flame Photometry	63
Determination of Cerium in Solutions of Uranyl Sulfate by Redox Titration	63
Spectrophotometric Determination of Arsenic in Solutions of Uranyl Sulfate	63

Spectrophotometric Determination of Cobalt in Slurries of Thorium Oxide	63
Pyrolytic Separation and Spectrophotometric Determination of Ruthenium	64
Flame Photometric Determination of Ruthenium	64
Methods Development Group	64
Extraction of Elements from Acidic Solutions with Tri- <i>n</i> -octylphosphine	
Oxide (TOPO) in Cyclohexane	64
Zirconium	64
Molybdenum	65
Uranium	65
Bismuth	66
Thorium	66
Niobium	66
Tantalum	66
Titanium	66
Formation of Colored Species with Tri- <i>n</i> -octylphosphine Oxide (TOPO) in	
Cyclohexane Solutions	66
Zirconium–Pyrocatechol Violet	67
Zirconium-Alizarin	67
Thorium-Alizarin	67
Titanium Thiocyanate	67
Extraction of Acids by Tri- <i>n</i> -octylphosphine Oxide (TOPO) in Cyclohexane Solution	68
Infrared Absorption Spectra of Trialkylphosphine Oxides	68
Spectrophotometric Determination of Iron in Hydrocarbon Solutions of Di(2-ethylhexyl)	
Phosphoric Acid with <i>o</i> -Phenanthroline	70
Oxidation of Chromium with Argentic Oxide	71
Determination of Uranium Metal in the Products of the Reaction Between Uranium	
Hexafluoride and Metallic Sodium	71
Spectrophotometric Determination of Microgram Quantities of Aluminum in	
Sulfuric Acid Solutions with Pyrocatechol Violet	72
Spectrophotometric Determination of Vanadium by the Benzohydroxamic	
Acid Method	72
Spectrophotometric Determination of Nickel with 4-Isopropyl-1,2-	
cyclohexanedionedioxime	72
Organic Preparations	73
Tris-2-octylphosphine Oxide	73
Tris-2-ethylhexylphosphine Oxide	73
Tri- <i>n</i> -octylphosphine Oxide	73
4-Isonitroso-1-phenyl-3-methyl-5-pyrazolone	73
4-Isopropyl-1,2-cyclohexanedionedioxime	73
Raw Materials Analytical Chemistry	74
Determination of Sulfur Dioxide Absorbed in <i>n</i> -Butyl Alcohol Solutions of Amines	74
Comparison of Two Methods for the Decomposition of Di-2-ethylhexyl Phosphoric	
Acid and the Conversion of the Phosphorus to Orthophosphate	74
Determination of Bismuth with Disodium Ethylenediaminetetraacetate	74
Spectrophotometric Determination of Phosphate in Vanadium Oxide	75
Quality Control	75
Analysis of UO ₃	76
Determination of Molybdenum by the Butyl Acetate–Thiocyanate Method	76
Determination of Nitrate by the Phenoldisulfonic Acid Method	76
Fluorometric Determination of Uranium	76
Determination of Uranium by the Stannous Chloride–Thiocyanate Method	76

SERVICE ANALYSES.....	77
HRP Analytical Chemistry	77
Raw Materials Analytical Chemistry	78
Miscellaneous Analyses	78
ORGANIZATION CHART.....	81



ANALYTICAL CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

SUMMARY - X-10 SITE

RESEARCH AND DEVELOPMENT

Ionic Analyses. - Spectrophotometric studies of plutonium in sulfate systems have been continued. A method for the determination of plutonium(III) and plutonium(IV) in PuF_3 - PuF_4 mixtures in fused melts of NaF - BeF_2 has been developed. Studies of the reduction of KTcO_4 by means of a constant-potential coulometric titrator have shown the existence of a pink solution of technetium(IV) and a green solution of technetium(III) in a potassium phosphate buffer (pH, 7.0) solution. Instrumental methods for the determination of nickel and chromium in mixtures of fluoride salts have been developed for use in the High-Radiation-Level Analytical Facility (HRLAF). The diluent Amsco 125-82, used for solvent extraction processes, has been fractionated by means of a 6-ft by 12-mm distillation column. The fractions have been studied by use of a gas chromatograph instrument. A spectrophotometric determination of niobium by use of hydroquinone is being studied; also, the polarographic behavior of niobium in 2 M citric acid is being evaluated. Yttrium alloys have been analyzed by conventional methods. The chemical changes that occur in UO_2 -Al fuel elements during fabrication have been studied.

An enthalpymetric determination of free acid in the presence of certain hydrolyzable ions has been developed. The analysis of gaseous oxides of nitrogen is being studied spectrophotometrically by use of the visible and the infrared regions of the spectrum. Chloride was shown to be present in washed amalgams from the Metallex process.

Analytical Instrumentation. - The In-Line Instrumentation Program has consisted in the development and testing of the following instruments. An interface-level controller system has been constructed for use with a conductivity-type digital probe that has been under test since April 1957. The level, at a pulsed interface in a contactor, is to be proportionally controlled to $\pm \frac{1}{4}$ in. Testing of the complete system is scheduled to begin January 1958. An a-c polarograph has been designed for monitoring uranium losses at a maximum level of 10 ppm in raffinate streams. Fabrication

of a prototype gamma activity monitor was completed. It has been tested in the IAP stream of the Thorex Pilot Plant. A falling-stream cell having low background has been developed for use with the monitor. A radio-frequency monitor for nitric acid concentration in process feed streams was designed and was demonstrated to be successful. Several flow-rate meters have been tested for proper operation: two turbine-type meters, a modified turbine-type meter, an electromagnetic flow-rate meter, and a bubble-velocity photoelectric meter. The bubble-velocity flow meter is being developed to measure accurately low rates of flow of a radioactive process stream; neither moving parts nor flow restrictions can be present. A potentiometric type of monitor for chloride ion is being developed for the Darex process. A continuous monitor of the alpha activity of waste streams is being developed on the basis of liquid scintillation detection; it is planned to extend the technique to the measurement of the gamma activity of aqueous process streams. Another type of alpha monitor under development depends on the nebulization of the process stream within a moving envelope of air. A densimeter that was designed to anticipate column losses and that uses organic-filled dip tubes is being fabricated for evaluation in a pulse column of the Metal Recovery Plant. A sonic, velocity densimeter is being investigated along with the dip-tube instrument. The testing of the Savannah River Laboratory model 1 flow colorimeter has been completed and a terminal report is in preparation. The colorimeter operated very satisfactorily.

The development work of the Analytical Instrumentation Group has included the extension of projects reported previously and the development of several new instruments. Instructions have been written for the adjustment, repair, and maintenance of the ORNL model Q-1728, velocity-servo, automatic, potentiometric titrators. An ORNL model Q-1887 flame spectrophotometer has been designed and fabricated. It has very high sensitivity, particularly in the red spectral region, it records, and it has a wavelength-scanning drive.

A manual has been written for the servicing of this instrument. A simplified controlled-potential coulometric titrator has been designed and fabricated and is giving satisfactory service. It is planned to redesign the titrator to make use of a recently marketed operational amplifier which should drastically reduce the cost of fabrication. A gamma absorption photometer has been designed, fabricated, and tested for the rapid determination of uranium and plutonium in relatively pure solutions. It includes an Am^{241} source and a scintillation detector. The recorded output of the instrument is directly proportional to the gamma absorbancy of the test solution. Good sensitivity, reproducibility, and stability have been obtained. A Jarrell-Ash Company arc and spark stand was converted for remote operation. An Electromatic, solenoid-operated buret has been substituted for the diaphragm-valve controlled buret of the Beckman model K titrator in order to improve the reliability of the titrator as a remotely operated device. A thumb-operated, cam switch attachment has been designed and fabricated for Argonne model 8 master-slave manipulators so that the operator need not use both hands to cam a manipulator. An automatic, spectrophotometric titrator has been designed and fabricated. It consists of derivative and spectrophotometric attachments that are used to adapt the Sargent-Malmstadt titrator for spectrophotometric titrations with automatic reagent cutoff at the end point. A constant-delivery-rate buret for enthalpy titrations has been designed and fabricated from a Gilmont micropipet-buret. Apparatus and procedures for the determination of microgram amounts of halides are being developed. The method involves the electrodeposition at controlled potential of a halide film on a mercury microelectrode followed by coulometric stripping of the accumulated deposit. An analog computer is used for integration. The chloride concentration of solutions containing as little as $0.1 \mu\text{g}$ of chloride per milliliter can be determined. A controlled-potential and derivative polarograph has been designed, a prototype has been fabricated, and its performance is being evaluated. A three-electrode electrolysis cell is used. A potential-control, stabilized amplifier supplies whatever voltage is required to the working electrode in order to force the potential of the dropping mercury electrode to be the controlled value with respect to a saturated calomel

reference electrode. The polarograph may therefore be used with media of extremely high resistance. Another unique design feature is a peak-follower, operational, amplifier circuit which filters out the current fluctuations that result from the growth and fall of the mercury drops but introduces very little distortion in the average current waveform. The polarograph also has a linear compensator, wide-range zero set, RC damping, amplifier overload indicators, parallel-T filters, and built-in test provisions. The feedback configuration of the stabilized current amplifier provides 22 current ranges, from 0–0.005 to 0–500 μa and eliminates the usual correction for "current measuring resistor" potential. An analog computer circuit may be switched into the signal bias to record the derivative of the averaged polarographic current with respect to the controlled applied potential as a function of the applied potential. In spite of the many unique and versatile features of this polarograph, it can be fabricated at relatively low cost.

Radiochemical Analyses. – Studies have been made of the electromagnetic radiations from plutonium isotopes and of *L*-shell fluorescence yields of several nuclides. Interference in alpha counting by low-energy beta radiation was studied. Several recent applications of gamma spectrometry and a preliminary study of beta scintillation spectrometry are reported. Analyses of noble-gas mixtures for four radionuclides are described. A radiochemical method for ionium (Th^{230}) and solvent-extraction separations of uranium and plutonium are discussed. Most of the analyses for the Reactor Experimental Engineering Division involved establishing gamma spectra of metal plates, from which the neutron flux to which they had been exposed could be deduced.

Activation Analyses. – Neutron activation analysis was applied to the determination of microgram and submicrogram amounts of many elements in a variety of samples; these applications are summarized. Nondestructive methods of analysis for a large number of elements are presented. The applications of neutron activation in particle-size-distribution analyses are discussed. In particular, an activation analysis–centrifugation method of particle-size-distribution analysis applicable to submicron particles and a method of analysis for multiple-component particle systems

are reviewed. Studies of interest in reactor technology were also made, for example, the identification and determination of the radionuclides present in reactor cooling water and the determination of the amount of radioactivity induced into certain selected materials by irradiation under controlled conditions.

Mass Spectrometry. — A 60-deg, 6-in.-radius mass spectrometer capable of the simultaneous collection of two neighboring isotopes of mass as small as 20 and capable of direct display of their ratio on a strip-chart recorder was designed, built, and applied to the precise measurement of a number of special potassium samples.

Argon-36 has been enriched to 30% concentration, Kr⁸⁶ to 80%, Kr⁸⁴ to 73%, Kr⁸⁰ to 17%, and Kr⁷⁸ to 3.4% by thermal-diffusion separation. The separation of C¹³ and O¹⁸ from CO is being investigated.

Spectrochemical and X-Ray Analyses. — Microgram quantities of the rare-earth elements in solution can be separated quantitatively from aluminum by treating the solution with excesses of carbonate and phosphate at pH 11.5. The Mitchell-Scott procedure, in which 8-quinolinol and tannin are used, was found effective for the collection of the rare-earth elements, tungsten, tantalum, niobium, and antimony. Optimum conditions were established for use of an air-interrupted, high-voltage spark source with the porous-cup electrode. A spectrographic installation was made at the High-Radiation-Level Analytical Facility; it is described briefly. An x-ray diffraction and fluorescence service laboratory was established during the year. A procedure was developed for analyzing U-Zr-Nb alloys by x-ray fluorescence. Through the use of alcohols as solvents, the spectrographic limit of detection of lithium and cesium was lowered considerably.

Inorganic Preparations. — The program in anhydrous transition metal halides for the Physics Division continued with emphasis on the preparation of large amounts of material for the growth of single crystals. A program in the preparation of fused salts to be used in solvent systems was carried on for the Metallurgy Division. Some further work was done in the preparation of hexahalorhenates for the Chemistry Division. A high-purity-materials program was undertaken for the Solid State Division.

Optical and Electron Microscopy. — The extensive study of thorium oxide in connection with

the slurry program was continued. A method for dispersing agglomerated, friable particles for observation under the electron microscope was developed. The oxides formed on stainless steel, titanium, and Zircaloy-2 were compared before and after exposure in the Van de Graaff generator. The reason for the nonconducting nature of indium coatings vaporized onto single crystals of germanium was determined. The critical nature of vacuum pressures in the vaporization of indium is mentioned. Other studies of corrosion products, oxide films, and surface structures were made. A number of compounds were studied by microscopy. Several changes which were made in the General Electric diffractograph in order to improve its performance are discussed. The possible use of automatic particle-sizing techniques in connection with the electron microscope was investigated and recommendations are made.

ORNL Master Analytical Manual. — Forty new and 30 revised methods were issued to the *ORNL Master Analytical Manual*; 33 new manuals were issued. Guide copies of the unclassified sections of the *Manual* were supplied to the AEC Technical Information Service Extension in Oak Ridge for reproduction purposes. Section 2, "Radiochemical Methods," of the *Manual* has been reproduced and made available for public sale; the other sections should be forthcoming soon.

SERVICE ANALYSES

The analytical service work is summarized in tabular form, and special problems are discussed briefly. Ionic analyses were related primarily to corrosion studies and to research in high-temperature solubilities, to ion exchange resins, and to fuel alloys. Radiochemical determinations were made for the identification and measurement of activities of the radionuclides in a variety of materials. Activation analysis was used to determine microgram and submicrogram amounts of many elements in many substances. The Analytical Mass Spectrometry Group has analyzed both gaseous and solid samples, including over 250 cylinders of argon for trace impurities, the product of the N¹⁵ plant for per cent N¹⁵, and separated stable isotopes for relative abundances.

The amount of work in the process analyses laboratories increased by a factor of approximately 2 during the past year; however, the number of personnel remained approximately the same. Analytical procedures were obtained or modified

for the determination of fluoride and acid in the presence of zirconium. Trioctylphosphine oxide was substituted for tributyl phosphate as an extractant for uranium in the fluorometric procedure for uranium when sulfuric acid is present. Uranium(IV) and uranium(VI) are being separated by water-leaching prior to analysis. Silver oxide was used successfully to oxidize chromium(III) to chromium(VI) in the determination of chromium in the presence of zirconium. A buret with electromagnetically activated valves was installed on a Beckman model K automatic titrator in the HRLAF and resulted in mechanical improvements in remotely controlled titrations. Samples of activity estimated to be 25,000 r/hr at contact were analyzed in the HRLAF cells. Several items of equipment that contributed a high level of background radioactivity in the cells were modified so that they could be eliminated inexpensively and rapidly. A total of 103 pellets of NpO_2 was prepared for the Health Physics Division for radiation dosimetry studies. A method was developed for the valence analysis of plutonium fluorides in mixtures of fused salt. A gamma scintillation spectrometer was obtained by the Isolation Analyses Group and was used extensively for qualitative analyses. Metals and alloys were analyzed for

boron, hydrogen, nitrogen, zirconium, and oxygen. Fluoride salts were analyzed for carbon, water, and boron. Surface-area determinations, gas analyses, and the plating of plutonium and neptunium were among the other service analyses made. Radioisotopes products were assayed prior to shipment. New procedures were developed for radioruthenium and for the carbonate capacity of resins. The half lives of several radionuclides were determined.

The HRLAF was operated successfully during the past year. Mechanical failures in the master-slave manipulators were normal and minor in nature. The following additional equipment was installed in the HRLAF: the Thorex overhead conveyor, a radiation monitoring system, two mobile air monitors, and one Exide Lightguard. As an additional preventive measure to control the spread of radioactive contamination, the north and south sides of the loading dock were enclosed.

The reactor analyses made during the past year were primarily for the HRP; however, some analyses were made for other groups. Modifications were made to some of the methods and equipment used in the HRLAF. Samples were prepared for isotopic analyses. Radioactive thorium slurries were prepared and analyzed.

SUMMARY - Y-12 SITE

RESEARCH AND DEVELOPMENT

The staff of the HRP Analytical Chemistry Laboratory continued to work on the improvement of methods for the determination of corrosion products both in solutions of uranyl sulfate and in slurries of thorium oxide. Among the methods developed or investigated for the determination of various constituents in solutions of uranyl sulfate were the following: a method for the estimation of zinc by means of an ORNL derivative polarograph, a redox method adapted for the titration of microgram quantities of cerium, a colorimetric method for the determination of small amounts of arsenic, a flame photometric method for the measurement of low concentrations of ruthenium, and a method for the separation of ruthenium from uranyl sulfate by pyrolysis and its subsequent colorimetric determination.

Procedures developed for the analysis of thorium oxide included a colorimetric method for the estimation of molybdenum as the quercetin complex, the colorimetric determination of cobalt as the 1-(2-pyridylazo)-2-naphthol (PAN) complex, the spectrophotometric determination of titanium with Tiron, the separation of aluminum by solvent extraction and its determination colorimetrically or by a flame photometric method, and a colorimetric method to establish the distribution of hydrazine in slurries of thorium oxide. In addition, work was continued on the flame photometric determination of lanthanum and the pyrolytic separation of fluoride from various inorganic materials. The methods of determining potassium by flame photometry were utilized in detecting and measuring the leakage of aqueous solutions from test loops during experimental runs. Other studies were made on a potentiometric method for the determination of

sulfate and on the estimation of technetium by polarographic and beta-counting methods.

The Methods Development Group evaluated further the applicability of tri-*n*-octylphosphine oxide (TOPO) in cyclohexane as an extractant for several elements, namely, zirconium, molybdenum, uranium, bismuth, thorium, niobium, tantalum, and titanium. Additional studies were made on the development of colorimetric methods for the determination of these elements in the organic extracts of TOPO, for example, zirconium as the pyrocatechol-violet complex or the alizarin complex, thorium as the alizarin complex, and titanium as the thiocyanate complex. The infrared absorption spectrum of TOPO, as well as the extractability of different acids with cyclohexane solutions of TOPO, was also established. Other methods were evaluated, such as the determination of iron in a solution of di(2-ethylhexyl) phosphoric acid, the determination of chromium after oxidation with argentic oxide, the colorimetric estimation of aluminum with pyrocatechol violet, the spectrophotometric determination of vanadium and nickel, and methods of synthesis of various organic reagents for specific use in further studies on solvent extraction.

The Raw Materials Group worked on the following problems: the determination of sulfur dioxide absorbed in solutions of amines in *n*-butanol, a comparison of two methods for the decomposition of di(2-ethylhexyl) phosphoric acid, the determination of bismuth, and the colorimetric estimation of phosphate in vanadium oxide.

A brief summary of the quality control program of the Division is given. Several studies were undertaken in connection with quality control, for example, evaluation of a cooperative analysis of a

standard sample of UO_3 , evaluation of the effect of temperature on the extraction of molybdenum thiocyanate, a review of the literature in connection with the determination of nitrate with phenol-disulfonic acid, and further studies on the fluorometric and colorimetric methods that are now being used for the determination of uranium.

SERVICE ANALYSES

The staff of the HRP Analytical Chemistry Laboratory continued to analyze samples of uranyl sulfate and thorium oxide from many sources for iron, nickel, chromium, chloride, and a host of other impurities and additives that are present in these solutions. Miscellaneous analyses and tests were made which included physical measurements (e.g., pH, conductance, and specific gravity) and the estimation of the concentration of various gases, such as oxygen, hydrogen, and carbon dioxide, in aqueous media of these materials.

The Raw Materials and Miscellaneous Analyses Group continued to make analyses of a wide variety of materials; among these were acid-leach solutions, organic solvents, and samples from the isotopic enrichment programs. The analyses included the fluorometric determination of uranium; the determination of molybdenum, vanadium, iron, aluminum, sulfate, phosphate, chloride, nitrate, and ammonia; the flame photometric determination of strontium and cesium; physical measurements, such as specific gravity, viscosity, surface tension, and interfacial tension; and the coulometric estimation of water.

A tabulation of the 138,166 analyses which were reported by the service groups is included in this report.

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PRESENTATIONS OF RESEARCH RESULTS

The Oak Ridge National Laboratory sponsored the First Annual Conference on Analytical Chemistry in Nuclear Reactor Technology at Gatlinburg, Tennessee, on November 4-6, 1957. C. D. Susano served as general chairman of the conference, and M. T. Kelley presided at the session "The Analysis of Reactor Materials." Several papers were presented by members of the Division. The proceedings of the meeting will be published by the AEC.

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

OPEN-LITERATURE PUBLICATIONS

Author(s)	Title	Publication
Feldman, C., J. Y. Ellenburg	"A Two-Piece Centrifuge Crucible for Handling Microchemical Precipitates"	<i>Anal. Chem.</i> 29, 1557 (1957)
Feldman, C., M. K. Wittels	"Sample Transport and Temperature Studies in Porous-Cup Discharges"	<i>Spectrochim. Acta</i> 9(1), 19 (1957)
Fisher, D. J., M. T. Kelley, R. W. Stelzner, E. B. Wagner, Jr.	"Radio-Frequency Analyzers for Laboratory and Plant"	<i>ISA Journal</i> 4, 474 (1957)
Gilbert, T. W., Jr., ¹ A. S. Meyer, Jr., J. C. White	"Spectrophotometric Determination of Lithium Carbide in Metallic Lithium as the Acetylene-Silver Perchlorate Complex"	<i>Anal. Chem.</i> 29, 1627 (1957)
Halbert, M. L., T. H. Handley,* J. J. Pinajian, W. H. Webb, A. Zucker	"Neutron-Transfer Reactions from the Nitrogen Bombardment of Be, C, O, Na and Mg ^{24,25,26} ."	<i>Phys. Rev.</i> 106, 251 (1957)
Horton, A. D., P. F. Thomason, M. T. Kelley	"Remote Controlled Determination of Corrosion Products and Additives in Homogeneous Reactor Fuel"	<i>Anal. Chem.</i> 29, 388 (1957)
Kahn, B., D. K. Smith,* C. P. Straub	"Determination of Low Concentrations of Radioactive Cesium in Water"	<i>Anal. Chem.</i> 29, 1210 (1957)
Kelley, M. T.	"The Analytical Chemist in Nuclear Technology"	<i>Anal. Chem.</i> 29, 21A (1957)
Kelley, M. T., D. J. Fisher, and Staff	"Special Equipment for Analytical Chemistry by Remote Control"	Fifth Hot Laboratories and Equipment Conference, March 14-15, 1957; The American Society of Mechanical Engineers, New York, <i>Proceedings of 1957 Nuclear Congress</i> , p 105-110 (Pergamon Press)
Kelley, M. T.,* D. J. Fisher,* R. W. Stelzner,* C. L. Burros,* E. B. Wagner, Jr., H. L. Hemphill	"Applications of Servo Systems to the Remotely Operated Chemical Analysis of Extremely Radioactive Solutions"	<i>ISA Proceedings, 1957 National Conference on Instrumental Methods of Analysis, Chicago, Ill., June 13-15, 1957</i> , Instrument Society of America, Pittsburgh, Pa., p A1 57-3-1-1

¹Now associated with Pennsylvania State University.

Author(s)	Title	Publication
Lazar, N. H., W. S. Lyon,* R. L. Macklin	"Neutron Activation Cross Sections with Sb-Be Neutrons"	<i>Bull. Am. Phys. Soc., Ser. 2, 2, 15</i> (1957)
Lyon, W. S.	"Determination of Neptunium-239 Counting Efficiency"	<i>Anal. Chem.</i> 29, 1048 (1957)
Lyon, W. S., J. S. Eldridge	"Radioactive Ge ⁷⁷ and Ge ^{77m} "	<i>Phys. Rev.</i> 107, 1056 (1957)
Lyon, W. S., S. A. Reynolds	"Assay of Electron-capture Nuclides with a Proportional Counter Spectrometer"	<i>J. Appl. Rad. Isotopes</i> 2, 80 (1957)
Macklin, R. L., N. H. Lazar, W. S. Lyon*	"Neutron Activation Cross Sections with Sb-Be Neutrons"	<i>Phys. Rev.</i> 107, 504 (1957)
Menis, O., D. L. Manning	"Spectrophotometric Determination of Silicon in Thorium Oxide"	<i>Anal. chim. Acta</i> 16, 67 (1957)
Menis, O., R. G. Ball, D. L. Manning	"Amperometric Titration of Mercury(II) with Tetraphenylarsonium Chloride"	<i>Anal. Chem.</i> 29, 245 (1957)
Menis, O., H. P. House, T. C. Rains	"Indirect Flame Photometric Method for Determination of Halides"	<i>Anal. Chem.</i> 29, 76 (1957)
Menis, O., D. L. Manning, G. Goldstein	"Color Reaction Between Thorium and Quercetin and Separation Scheme for Interfering Ions"	<i>Anal. Chem.</i> 29, 1426 (1957)
Mihelich, J. W., B. Harmatz, T. H. Handley*	"Nuclear Spectroscopy of Neutron-Deficient Rare Earths (Tb Through Hf)"	<i>Phys. Rev.</i> 108, 989 (1957)
Moore, F. L.	"Separation and Determination of Neptunium by Liquid-Liquid Extraction"	<i>Anal. Chem.</i> 29, 941 (1957)
Moore, F. L.	"Long-Chain Amines - Versatile Acid Extractants"	<i>Anal. Chem.</i> 29, 1660 (1957)
Moore, F. L.,* J. E. Hudgens, Jr.	"Separation and Determination of Plutonium by Liquid-Liquid Extraction"	<i>Anal. Chem.</i> 29, 1767 (1957)
Moore, F. L., S. A. Reynolds	"Determination of Protactinium-233"	<i>Anal. Chem.</i> 29, 1596 (1957)
Ross, W. J., A. S. Meyer, Jr., J. C. White	"Determination of Boron in Fluoride Salts"	<i>Anal. Chem.</i> 29, 810 (1957)
Schweitzer, G. K., ² J. S. Eldridge*	"Reproducibility of Radioactive Sample Preparation Techniques"	<i>Anal. chim. Acta</i> 16, 189 (1957)
Smith, G. W., ³ F. L. Moore	"Separation and Determination of Radiocerium by Liquid-Liquid Extraction"	<i>Anal. Chem.</i> 29, 448 (1957)
Wright, H. W., E. I. Wyatt, S. A. Reynolds, W. S. Lyon, T. H. Handley	"Half-Lives of Radionuclides, I"	<i>Nuclear Sci. and Eng.</i> 2, 427 (1957)

²University of Tennessee.

³Now associated with Curtiss-Wright Corp., Quehama, Pa.

ORAL PRESENTATIONS

Author(s)	Title	Presented at
Bate, L. C., G. W. Leddicotte ⁴	"The Determination of Oxygen and Other Trace Elements in Lithium"	Lithium Symposium, ORNL, Oak Ridge, Tenn., Aug. 7-8, 1957
Burns, J. F.	"Studies of Molecular Excitation and Dissociation Energies by Electron Impact"	University College, Dublin, Ireland, June 11, 1957
Cameron, A. E.	"Present Status of Electromagnetic Separation of Stable Isotopes at Oak Ridge National Laboratory"	International Symposium on Isotope Separation, Amsterdam, Holland, April 23-27, 1957
Feldman, C.	"A Thousand Ways to Use a Spectrograph - Applications in Atomic Energy"	Meeting of Society for Applied Spectroscopy, Philadelphia, Pa., April 16, 1957
Feldman, C.	"X-Ray Methods of Analysis"	1st Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Nov. 4-6, 1957
Fisher, D. J., M. T. Kelley ⁴	"Instrumental Methods of Derivative Polarography"	131st Meeting, American Chemical Society, Miami, Fla., April 7-12, 1957
Fisher, D. J., M. T. Kelley, R. W. Stelzner, ⁴ E. B. Wagner, Jr.	"Radio-Frequency Instruments"	1957 National Conference on Instrumental Methods of Analysis, Instrument Society of America, Chicago, Ill., June 13-15, 1957
Gilbert, T. W., Jr.	"Spectrophotometric Determination of Lithium Carbide in Metallic Lithium as the Acetylene-Silver Perchlorate Complex"	Lithium Symposium, ORNL, Oak Ridge, Tenn., Aug. 7-8, 1957
Goldstein, G., D. L. Manning, O. Menis ⁴	"Spectrophotometric Determination of Molybdenum as the Quercetin Complex in an α -Benzoin-oxime-Chloroform Medium"	132nd Meeting, American Chemical Society, New York, N. Y., Sept. 8-13, 1957
Horton, C. A.	"The Analysis and Chemistry of Fluorides"	Gordon Research Conference, New Hampton, N. H., Aug. 16, 1957
Kelley, M. T.	"The Analysis of Reactor Materials"	1st Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Nov. 4-6, 1957
Kelley, M. T., ⁴ D. J. Fisher, and Staff	"Special Equipment for Analytical Chemistry by Remote Control"	5th Hot Laboratories and Equipment Conference, 1957 Nuclear Congress, Philadelphia, Pa., March 14-15, 1957
Kelley, M. T.,* D. J. Fisher, ⁴ R. W. Stelzner,* C. L. Burros,* E. B. Wagner, H. L. Hemphill	"Applications of Servo Systems to the Remotely-Operated Chemical Analysis of Extremely Radioactive Solutions"	1957 National Conference on Instrumental Methods of Analysis, Instrument Society of America, Chicago, Ill., June 13-15, 1957

⁴Speaker.

Author(s)	Title	Presented at
Leddicotte, G. W.	"Radioactivation Analysis"	The Citadel, Charleston, S. C., March 7, 1957 1st Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Nov. 4-6, 1957
Leddicotte, G. W.	"Activation Analysis"	North Carolina State College, Raleigh, N. C., April 15, 1957 Symposium on Nuclear Reactors in Biomedical Research, Specula- tions and Facts, Massachusetts Institute of Technology, Cambridge, Mass., Dec. 3, 1957
Leddicotte, G. W.	"Nucleonics in Analytical Chemistry"	Annual Naval Reserve Nuclear Science Seminar, ORINS, Oak Ridge, Tenn., Dec. 9, 1957
Leddicotte, G. W., ⁴ W. A. Brooksbank, Jr.	"The Isotopic Analysis of Uranium by Neutron Activation Analysis"	USAEC Symposium on Modern Ap- proaches to Isotopic Analysis of Uranium, Chicago, Ill., Feb. 5-7, 1957
	"The Determination of U-235 Content of Uranium by Neutron Absorption"	
Lyon, W. S.	"Method for Determination of Neptunium-239 Counting Efficiency"	131st Meeting, American Chemical Society, Miami, Fla., April 7-12, 1957
Macklin, R. L., N. H., Lazar, ⁴ W. S. Lyon*	"Neutron Activation Cross Sections with Sb-Be Neutrons"	Winter Meeting, American Physical Society, New York, N. Y., Jan. 1957
Mann, C. K., ⁵ J. C. White ⁴	"Extraction of Chromium with Trioctylphosphine Oxide from Acidic Solutions of Alkali Metal Salts and Its Determination in Situ as the Chromium-Diphenylcarbazide Complex"	132nd Meeting, American Chemical Society, New York, N. Y., Sept. 8-13, 1957
Menis, O., D. L. Manning, G. Goldstein, ⁴ R. G. Ball	"The Spectrophotometric Determination of Thorium with Quercetin"	8th Pittsburgh Conference on Ana- lytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 4, 1957
Menis, O., T. C. Rains, ⁴ J. A. Dean ²	"Extraction and Flame Spectrophotometric De- termination of Lanthanum"	132nd Meeting, American Chemical Society, New York, N. Y., Sept. 8-13, 1957
Meyer, A. S., Jr.	"Determination of Oxygen in Metallic Lithium"	Lithium Symposium, ORNL, Oak Ridge, Tenn., Aug. 7-8, 1957
Moore, F. L.	"Radiochemical Determination of Neptunium-237"	Neptunium Information Meeting, Oak Ridge National Laboratory, March 7-8, 1957

⁵Research participant from the University of Texas, Austin.

Author(s)	Title	Presented at
Powell, R. H., O. Menis ⁴	"Separation of Fluoride from Inorganic Compounds by Pyrolysis"	132nd Meeting, American Chemical Society, New York, N. Y., Sept. 8-13, 1957
Reynolds, S. A.	"Promethium-147 Intercomparison"	National Research Council Conference on Radioactivity Standards and Measurements, Easton, Md., Oct. 9-11, 1957
Rush, R. M.	"Anion Exchange Studies of a Number of Elements of Groups III, IV, and V in Hydrochloric Acid and Hydrochloric-Hydrofluoric Acid Solutions"	131st Meeting, American Chemical Society, Miami, Fla., April 7-12, 1957
Ward, T. J., K. P. Jacob, J. W. Mihelich, T. H. Handley,* ⁴ B. Harmatz	"Electron Capture of Tb ¹⁵⁵ to Levels in Gd ¹⁵⁵ "	Meeting of the American Physical Society, Notre Dame University, Notre Dame, Ind., June 1957
Ward, T. J., J. W. Mihelich, B. Harmatz, T. H. Handley* ⁴	"Electron Capture of Hf ¹⁷³ to Levels in Lu ¹⁷³ "	Meeting of the American Physical Society, St. Louis, Mo., Nov. 1957
White, J. C.	"Trialkylphosphine Oxides - Versatile Solvent Extractants for Analytical Separation"	8th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 4, 1957
White, J. C.	"Solvent Extraction"	1st Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Nov. 4-6, 1957
White, J. C., W. J. Ross, ⁴ A. S. Meyer, Jr.	"Use of Trioctylphosphine Oxide and Tridecylphosphine Oxide in the Extraction and Determination of Uranium and Chromium"	8th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 4, 1957
Young, J. P.	"Why You Should Be an Analytical Chemist"	King's College, Wilkes-Barre, Pa., May 9, 1957 (Travel Lecture Program)
Young, J. P., ⁴ J. R. French, J. C. White	"Determination of Microgram Quantities of Zirconium in Sulfuric Acid Solutions with Pyrocatechol Violet"	132nd Meeting, American Chemical Society, New York, N. Y., Sept. 8-13, 1957
Zucker, A., M. L. Halbert, T. H. Handley,* ⁴ J. J. Pinajian, W. H. Webb	"Nitrogen-Induced Neutron Transfer Reactions in Be, C, O, Na, and Mg ^{24,25,26} "	Meeting of the American Physical Society, New York, N. Y., Jan. 1957

TOPICAL REPORTS

Author(s)	Title	Report No.
Bate, L. C., G. W. Leddicotte	"Determination of Submicron Particle Sizes by an Activation Analysis - Centrifugation Method"	ORNL CF-57-1-116 (Jan. 29, 1957)
Edgerton, J. H., ⁶ H. G. Davis	"Determination of Microgram Quantities of Carbon by Low-Pressure Combustion"	ORNL-2211 (Jan. 15, 1957)
Emery, J. F., G. W. Leddicotte	"Survey of Reactor Cooling Water from Bulk Shielding Facility"	ORNL CF-57-11-41 (Nov. 7, 1957)
Gilbert, T. W., Jr., ¹ J. C. White	"Determination of Trace Amounts of Sulfur in Fluoride Salts"	ORNL CF-57-6-89 (June 24, 1957)
Goldberg, G., A. S. Meyer, Jr., J. C. White	"A Practical Small-Volume, 5-cm Absorption Cell"	ORNL CF-57-5-88 (May 27, 1957)
Horton, C. A., J. C. White	"Separation of Uranium by Solvent Extraction with Tri- <i>n</i> -octylphosphine Oxide and Its Direct Colorimetric Determination with Dibenzoyl-methane"	ORNL CF-57-7-43 (July 15, 1957)
McDowell, B. L., A. S. Meyer, Jr., J. C. White	"Spectrophotometric Determination of Cerium with Tiron"	ORNL CF-57-6-64 (June 14, 1957)
Menis, O., C. M. Boyd	"A Preliminary Study of the Adsorption of Metal Cations and Negative Radicals of Inorganic Acids on Thorium Oxide"	ORNL CF-57-7-124 (July 15, 1957)
Menis, O., H. P. House, C. M. Boyd	"Particle-Size Distribution of Thorium Oxide by a Centrifugal Sedimentation Method"	ORNL-2345 (Aug. 5, 1957)
Menis, O., G. Goldstein, D. L. Manning	"Spectrophotometric Determination of Molybdenum as the Quercetin Complex in an α -Benzoinoxime-Chloroform Medium"	ORNL CF-57-5-102 (May 31, 1957)
Moeller, D. W. ⁷	"Radionuclides in Reactor Cooling Water - Identification, Source and Control"	ORNL-2311 (June 12, 1957)
Moeller, D. W., ⁷ G. W. Leddicotte	"Source of Fission Products in LITR Cooling Water"	ORNL CF-57-3-120 (March 23, 1957)
Reynolds, S. A.	"Radioactivity Associated with Uranium, Thorium, and Plutonium"	ORNL CF-57-6-82 (June 18, 1957)
Robinson, M. T., W. A. Brooksbank, Jr., S. A. Reynolds,* H. W. Wright,* T. H. Handley*	"Some Aspects of the Behavior of Fission Products in Molten Fluoride Reactor Fuels"	ORNL-2374 (Aug. 28, 1957)

⁶Now associated with Lockheed Aircraft Corp., Marietta, Ga.

⁷Now associated with U. S. Public Health Service, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

Author(s)	Title	Report No.
Ross, W. J., J. C. White	"The Solvent Extraction of Iron with Tri- <i>n</i> -octylphosphine Oxide"	ORNL-2382 (Sept. 26, 1957)
Susano, C. D., R. L. McCutchen	"Evaluation of Data for Standard Samples with Both Moisture-Content and Methods of Analysis as Determinable Factors"	ORNL CF-57-10-108 (Oct. 21, 1957)
White, J. C., G. Goldberg	"Formation of Carbides by the Reaction of Pump Lubricants and NaK at Elevated Temperatures"	ORNL CF-57-10-22 (Oct. 4, 1957)
White, J. C. (W. J. Ross)	"Extraction of the Elements with Tris-2-ethylhexyl- and Trihexylphosphine Oxides from Acidic Solutions"	ORNL CF-57-1-5 (Jan. 2, 1957)
White, J. C. (W. J. Ross)	"Extraction of Metal Ions with Di-2-ethylhexyl Phosphoric Acid"	ORNL CF-57-2-37 (Feb. 8, 1957)
White, J. C., W. J. Ross	"Extraction of Chromium with Trioctylphosphine Oxide"	ORNL-2326 (July 9, 1957)

METHODS ISSUED TO THE ORNL MASTER ANALYTICAL MANUAL

Author(s)	Title	Number(s)	Date
New Methods			
Ball, R. G.	"Mercury, Amperometric Tetraphenylarsonium Chloride Method"	1 214921	10-12-56
		9 00714921	
	"Copper, Electrogravimetric Internal Electrolysis Method"	1 212321	11-1-56
		9 00712321	
Biggers, R. E.	"Phosphorus (Phosphate), Gravimetric Magnesium Ammonium Phosphate Method"	1 216050	5-14-57
		9 00716050	
Brady, L. J.	"Density (Specific Gravity) of a Liquid, Pycnometer Method"	1 100041	8-5-57
	"Specific Gravity (Density) of a Liquid, Hydrometer Method"	1 100042	8-5-57
Corbin, L. T., G. W. Leddicotte, S. A. Reynolds, P. F. Thomason	"Safety"	1 0020	5-2-57
		2 0050	
		5 0050	
		9 0055	
Edgerton, J. H. ⁶	"Fluoride in Mixtures of Fluoride Salts, Micro Pyrohydrolysis Method"	1 212890	9-20-56
		9 00712890	
Emery, J. F.	"Magnesium, Spectrophotometric Titan Yellow Method"	1 214710	5-24-57
		9 00714710	
	"Silicon, Gravimetric Acid Dehydration-Hydrofluorination Method"	1 217750	5-24-57
		9 00717750	
	"Zinc, Spectrophotometric Dithizone Method"	1 219710	5-24-57
		9 00719710	

Author(s)	Title	Number(s)	Date
Fisher, D. J.	"Polarograph, ORNL Model Q-1338, High-Sensitivity, Derivative, Recording"	1 003041 9 003041	2-14-57
	"Polarograph, ORNL Model Q-1673, High-Sensitivity, Diode Filter, Derivative, Recording"	1 003042 9 003042	2-13-57
	"Densimeter, Falling-Drop, Remotely Controlled"	1 003100 9 003100	2-7-57
French, J. R.	"Titanium in Mixtures of Fluoride Salts, Spectrophotometric Tiron Method"	9 0922900	5-21-57
Hill, F. M.	"Ion-Exchange Separation of Boron from Other Elements"	1 00701	5-24-57
	"Boron (Borate), Potentiometric Mannitol-Sodium Hydroxide Titration Method"	1 211220 9 00711220	7-2-57
Horton, A. D.	"Copper, Polarographic Versenate Method"	1 212320 9 00712320	5-7-57
	"Fluorine in Mixtures of Gases, Iodometric Method"	1 212871 9 00712871	5-9-57
Lynn, E. C.	"Niobium, Gravimetric Acid Hydrolysis Method"	1 215550 9 00715550	5-13-57
Manning, D. L.	"Silicon, Spectrophotometric Molybdenum Blue Method"	1 217710 9 00717710	5-27-57
	"Silicon in Thorium Oxide, Spectrophotometric Molybdenum Blue Method"	1 217711 9 00717711	11-5-56
McDowell, B. L.	"Niobium in Mixtures of Fluoride Salts, Spectrophotometric Thiocyanate Method"	9 0922550	6-20-57
Roins, T. C.	"Spectrophotometer, Bausch & Lomb Spectronic 20"	1 003031 9 003031	5-3-57
	"Cerium, Spectrophotometric Peroxide Method"	1 211810 9 00711810	5-6-57
Rains, T. C., L. J. Brady	"Molybdenum, Spectrophotometric Thiocyanate-Stannous Chloride Method"	1 215010 9 00715010	5-10-57
Rains, T. C.	"Sulfate (Sulfur), Turbidimetric Barium Chloride Method"	1 218160 9 00718160	5-14-57
	"Titanium in Solutions of Uranyl Sulfate, Spectrophotometric Thymol Method"	1 219011 9 00719011	5-15-57
Rickard, R. R.	"Cobalt-60 Activity in Iron-55, 59 Product Solutions, Isopropyl Ether Extraction Method"	9 0733222	5-1-57
Roemer, A. F., Jr.	"Uranium, Spectrophotometric L-Ascorbic Acid Method"	1 219211 9 00719211	11-6-56
	"Uranium, Spectrophotometric Ethyl Acetate-Ammonium Thiocyanate-Ethanol Method"	1 219212 9 00719212	5-23-57

Author(s)	Title	Number(s)	Date
Ross, W. J.	"Boron in Mixtures of Fluoride Salts, Spectrophotometric Carminic Acid Method"	9 0922120	5-17-57
Rush, R. M.	"Tributyl Phosphate in Aqueous Solutions of Uranyl Nitrate, Infrared Spectrophotometric Method"	1 221001 9 00721001	5-16-57
Vaughan, W. F.	"Chromium, Spectrophotometric 1,5-Diphenylcarbohydrazide Method"	1 212110 9 00712110	5-6-57
	"Uranium, Automatic Potentiometric Potassium Dichromate Method"	1 219223 9 00719223	5-15-57
Walker, R. L.	"Specific Gravity of a Liquid, Westphal Balance Method"	1 101 9 00601	8-6-57
White, J. C.	"Carbonate in Alkali Hydroxides, Gasometric Method"	1 230001	6-13-57
Wyatt, E. I.	"Proportional Beta Counter, Windowless"	2 00352 5 00352 9 00352	5-1-57
	"Alpha Energy Analyzer, ORNL Model Q-970"	2 00353 9 00353	7-2-57
Young, J. P.	"Boron (Borate), Volumetric Mannitol-Sodium Hydroxide Method"	1 211270 9 00711270	5-3-57
	"Tantalum in Mixtures of Fluoride Salts, Spectrophotometric Pyrogallol Method"	9 0922820	5-20-57
Revised Methods			
Druschel, R. E.	"Thorium-234 (UX) in Aqueous or Organic Solutions"	2 31871	R. 5-1-57
Raagen, H. P.	"Writing Methods for the <i>ORNL Master Analytical Manual</i> "	01	R. 4-24-57
Rickard, R. R.	"Nickel-63"	9 0733542	R. 10-22-57
Wyatt, E. I., R. R. Rickard	"Iodine Activity in Aqueous or Organic Solutions"	2 21391	R. 5-1-56
Wyatt, E. I.	"Gross Gamma"	9 0733002	R. 10-25-56
	"Chromium-51, Product Analysis Guide"	9 0733211	R. 10-19-56
	"Iodine-131, Gamma Scintillation Counting Method"	9 0733393	R. 9-20-56
	"Iridium-192, Product Analysis Guide"	9 0733401	R. 10-23-56
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	"Mercury-203, Product Analysis Guide"	9 0733491	R. 9-20-56
	"Neodymium-147-Promethium-147, Product Analysis Guide"	9 0733511	R. 9-20-56

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	"Phosphorus-32, Product Analysis Guide"	9 0733601	R. 10-22-56
	"Potassium-42, Product Analysis Guide"	9 0733641	R. 10-22-56
	"Praseodymium-143, Product Analysis Guide"	9 0733651	R. 10-22-56
	"Rubidium-86, Product Analysis Guide"	9 0733721	R. 10-23-56
	"Ruthenium-103,106, Product Analysis Guide"	9 0733731	R. 10-22-56
	"Scandium-46, Product Analysis Guide"	9 0733751	R. 10-22-56
	"Selenium-75, Product Analysis Guide"	9 0733761	R. 10-22-56
	"Silver-110, Product Analysis Guide"	9 0733781	R. 10-22-56
	"Sodium-24, Product Analysis Guide"	9 0733792	R. 10-22-56
	"Strontium-85, Product Analysis Guide"	9 0733803	R. 10-22-56
	"Sulfur-35, Product Analysis Guide"	9 0733811	R. 10-22-56
	"Tantalum-182, Product Analysis Guide"	9 0733821	R. 10-22-56
	"Thallium-204, Product Analysis Guide"	9 0733861	R. 10-22-56
	"Tin-113, Product Analysis Guide"	9 0733891	R. 10-22-56
	"Tungsten-185, Product Analysis Guide"	9 0733911	R. 10-22-56
	"Yttrium-91, Product Analysis Guide"	9 0733961	R. 10-22-56
"Zinc-65 HSA, Product Analysis Guide"	9 0733971	R. 10-22-56	
"Zirconium-95-Niobium-95, Product Analysis Guide"	9 0733981	R. 10-22-56	

ANALYTICAL CHEMISTRY DIVISION — X-10 SITE

RESEARCH AND DEVELOPMENT

IONIC ANALYSES

P. F. Thomason

Spectrum of PuO_2^{++} in Sulfate Media — Resolution of the 8350-Å Absorption Peak of PuO_2^{++} into a Doublet^{1,2}

R. E. Biggers

All previous attempts to make quantitative spectrophotometric measurements of plutonium(VI) have met with difficulty. The spectrum of PuO_2^{++} has been thought to consist of a needle-sharp (~ 80 Å wide at half-peak height), major peak at 8350 Å, together with two very much less intense peaks at 9600 and 9850 Å. The 8350-Å peak is the only peak suitable for the spectrophotometric determination of plutonium(VI). In no previous work did the absorbancies at 8350 Å obey Bouguer's law and Beer's law. This anomaly has long been recognized and much discussed. The lack of obedience to these laws has been attributed primarily to instrumental variances, such as spherical aberration, resolving power, and slit width, and to combinations of these variances. These factors, together with the narrowness of the 8350-Å peak, are believed to have resulted in incomplete resolution of that peak.^{3,4}

Reasonably satisfactory spectrophotometric determinations of plutonium(VI) can be made if calibration curves are prepared in such a way as to compensate for changes in molar absorbancy indexes that are apparently caused by the inter-related effects of slit width, concentration, and cell length. An alternative procedure suitable for

solutions of plutonium(VI) concentration greater than several hundred parts per million consists in the absorbancy being measured in successively thinner cells until an absorbancy is obtained below which there are no deviations from Bouguer's law and Beer's law. However, such a procedure is very inconvenient and involves the great possibility of spillage and resulting alpha contamination.

As far as can be determined, previous measurements of plutonium(VI) were made with a Beckman model DU spectrophotometer. At this Laboratory a Cary model 14 spectrophotometer was used to examine a solution containing a small amount of PuO_2^{++} . The results indicated that the 8350-Å peak might actually be a closely spaced doublet. Therefore it was decided to extend the preliminary study; a Cary model 14PM (serial No. 136) spectrophotometer, which has an incident spectral slit width of 4 Å at 8350 Å, was used in this study. The narrowest slit width obtainable under optimum conditions with the Beckman model DU spectrophotometer (and a modified Warren Spectracord) at 8350 Å ranges from approximately 17 to 25 Å; aberration in the collimating mirror probably increases this range to approximately 45 to 50 Å. The dispersions of the two instruments at 8350 Å are as follows: Cary model 14PM, 37 Å/1.0-mm slit; Beckman model DU, 695 Å/1.0-mm slit. At 0.9 peak height the peak width of the 8350-Å peak is only 13 Å; a spectral band width greater than this would therefore result in a decrease in the observed peak intensity. At a spectral slit width greater than about 8 to 10 Å, the doublet structure of this peak would not have been seen.

The spectrum of PuO_2^{++} (no other forms of plutonium were present) recorded by means of the Cary model 14PM spectrophotometer revealed that what has heretofore been considered to be a single peak at 8350 Å is actually two peaks of different intensity and symmetry, the more intense one occurring at 8350 Å and the less intense one occurring at 8305 Å. Figure 1 shows the spectrum obtained with the Cary model 14PM spectrophotometer, an expansion of the doublet, and, for

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

²Abstracted in part from a paper submitted for presentation at the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 8-13, 1958.

³J. M. Chilton and R. E. Biggers, ORNL CF-57-9-103 (June 25, 1957) (classified).

⁴R. E. Biggers, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 1 (classified).

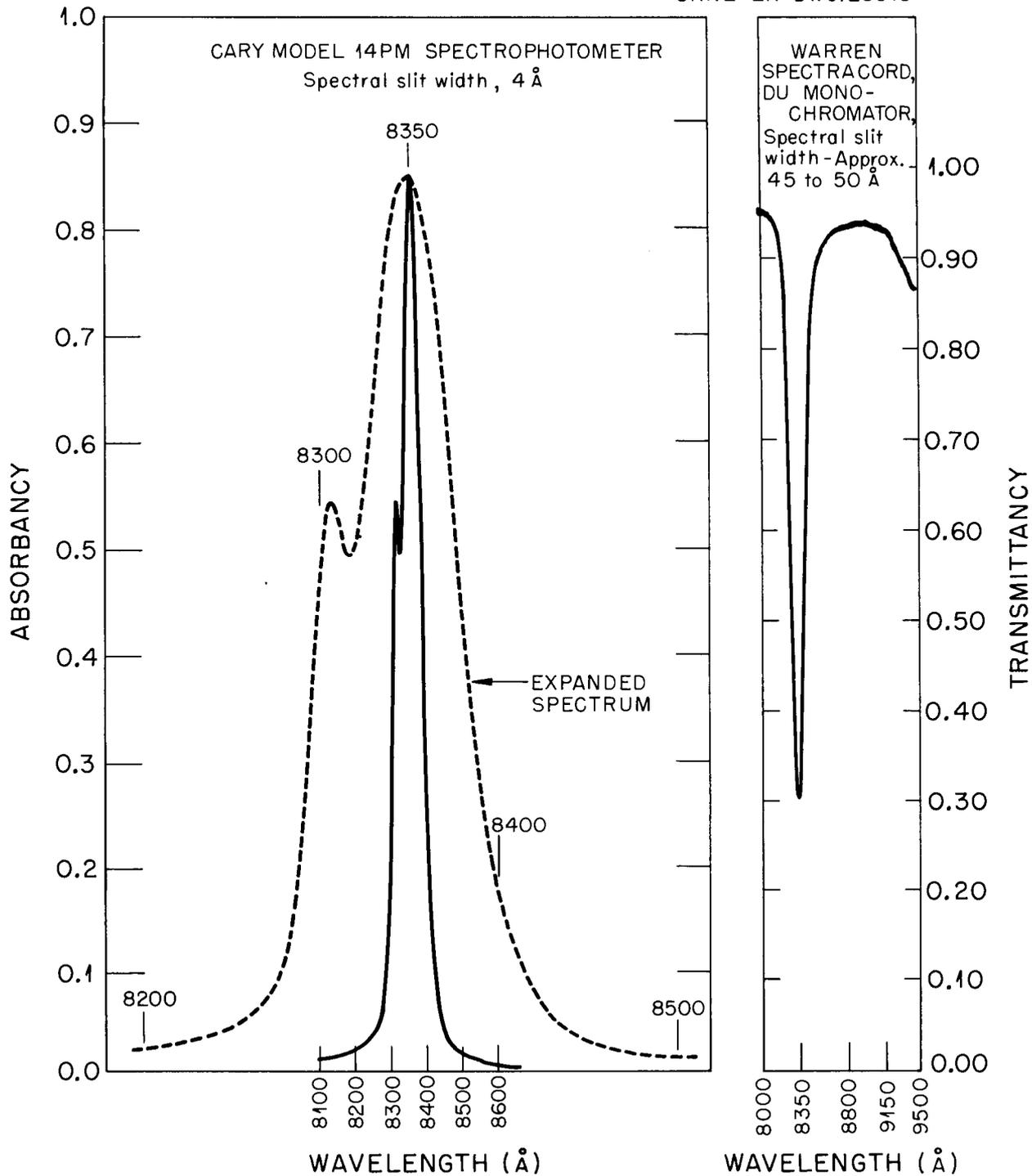
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Fig. 1. Comparison of the Absorption Spectrum of PuO_2^{++} in the Region from 8200 to 8500 Å Obtained by Means of a Cary Model 14PM Spectrophotometer with That Obtained by Means of a Beckman Model DU Monochromator (Warren Spectracord).

comparison, a spectrum obtained by means of a Beckman model DU instrument. A spectrum obtained manually by use of the Beckman instrument was identical with that obtained automatically with a Warren Spectracord; and in neither case did an expanded spectrum show any trace of the doublet. Analysis of the data obtained by means of the Cary instrument shows that both peaks of the doublet follow Bouguer's law and Beer's law at long cell lengths and even at moderately high concentrations of plutonium(VI). The spectrum is being investigated more carefully since it is of great importance in the determination of PuO_2^{++} and in following the course of reactions in which PuO_2^{++} is involved.

The resolution of the 8350-Å peak into a doublet has implications regarding the structure of PuO_2^{++} . It is fairly certain that the sharp spectra exhibited by the transuranic elements are caused by "forbidden" electronic transitions of the 5f-subshell electrons and that few or no primary perturbations are caused by the solvent and ionic background (cf. the 4f electronic transitions which result in the similarly sharp spectra of the rare earths). Either the energy level represented by the major transition is degenerate or there are two separate transitions, perhaps one from another shell, but this latter possibility is somewhat unlikely.

Additional studies of the PuO_2^{++} doublet are in progress. Although there are little or no primary perturbations caused by the ionic environment, the ratio of the heights of the 8350- and 8305-Å peaks does appear to be somewhat sensitive to the ionic environment. Preliminary studies have been carried out in sulfate media ranging from 0.3 M sulfuric acid to 1.4 M uranyl sulfate (at a concentration of 310 g of uranium per liter). At a given total PuO_2^{++} concentration, the molar absorbancy index of plutonium(VI) at 8305 Å increases as the sulfate concentration increases but at 8350 Å seems to be independent of the media or environment and is proportional to the PuO_2^{++} concentration; this is shown in Fig. 2. For PuO_2^{++} in 1.4 M uranyl sulfate, the height of the 8305-Å peak is ~90% of the height of the 8350-Å peak, whereas in 0.3 M sulfuric acid it is only 66.4% of the height of the 8350-Å peak. However, in any given medium the ratio of the heights of the 8305- and 8350-Å peaks is constant with increasing plutonium concentration, and the system obeys both Bouguer's law and Beer's law at each wavelength. At the present time it is

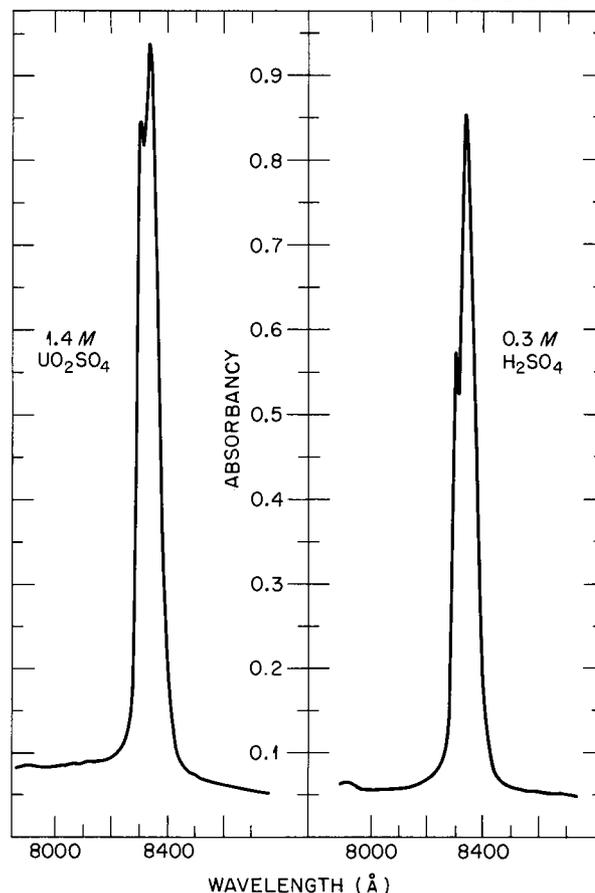
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Fig. 2. Relative Heights of the PuO_2^{++} Doublet in the Absorption Spectra of Two Different Sulfate Media of Similar PuO_2^{++} Concentrations.

impossible to make definite conclusions regarding the relationship between the formation of PuO_2^{++} sulfate complexes and the height of the 8305-Å peak. More work should help to clarify whether this relationship causes secondary perturbations or is related to them. There are no significant changes in the wavelengths of the maxima when the medium is changed from sulfuric acid solution through intermediate solutions to 1.4 M uranyl sulfate.

Work is also in progress on the effect of temperature (up to 90°C) on the spectrum of PuO_2^{++} . It is expected that implications regarding ionic complexation can be deduced therefrom. As temperature increases, there is a nonlinear decrease in the height of the absorption peaks and

a shift of the wavelengths of the maxima toward longer wavelengths.

Autoreduction of PuO_2^{++} by Products of the Alpha-Particle Radiolysis of Water – Kinetics and Mechanisms^{2,5}

R. E. Biggers

J. M. Chilton⁶

Since the early days of the Plutonium Project, it has been known that when solutions of pure plutonium(VI) stand for some time, the plutonium ions become reduced to lower valence states. The reduction reaction is slow, but for reactions and experiments carried out for extended times, the reduction becomes of great importance. Even for solutions that are only a few days old, the extent of the reduction can be of considerable importance. The reduction is attributed to the presence of reducing agents that are formed by the action of the alpha radiation of plutonium on water. Results have been obtained which offer the first experimental evidence that very probably two different radiolysis products are responsible for the autoreduction of plutonium(V) and (VI).

Although study of the autoreduction of plutonium ions has not been extensive, the autoreduction has often been attributed to the reaction of PuO_2^{++} with hydrogen peroxide and other species produced by the impact of alpha particles on water. It appears desirable to interpret the "self-reduction" of PuO_2^{++} by alpha particles in the light of knowledge concerning the radiolysis of water by high-energy particles that has been obtained in the past ten years. The PuO_2^{++} concentration of a solution has been reported to decrease as a linear function of time, that is, the reaction is of pseudo zero order, the PuO_2^{++} reacting with reducing species as fast as they are produced by the alpha-particle radiolysis.

Most of the previous work has been carried out at concentrations of plutonium in the range from 5×10^{-3} to 1.5×10^{-1} M. The work reported herein was carried out with 9.28×10^{-4} M plutonium solutions having PuO_2^{++} concentrations of 7.68×10^{-4} M. The most interesting fact to come from the present work is that the reduction reaction did not proceed at the same rate over the

1500-hr period during which the reaction was studied; two distinct rate behaviors were observed (Fig. 3). It is probable that in prior work the concentration effect prevented the observation of the two rate behaviors, which apparently result from different reaction mechanisms. Since the

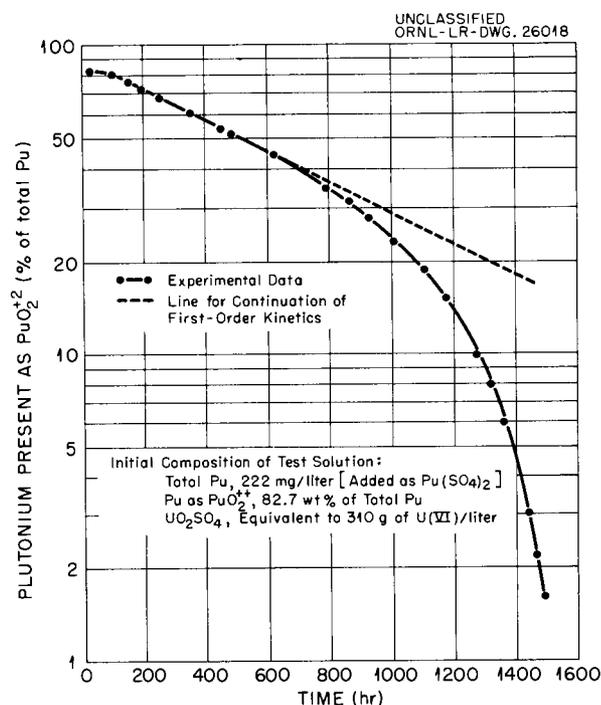


Fig. 3. Plot of Data Showing the Decrease in PuO_2^{++} Concentration of a Concentrated Uranyl Sulfate Solution of Plutonium with Time.

reaction is very slow, the definite curvature observed in the linear plots (not shown) of the data taken during one time period could easily be overlooked at higher concentrations of plutonium, especially if only a few experimental points were obtained. Also, there is no indication from most of the previous work as to whether the solutions of plutonium used contained plutonium initially in forms other than PuO_2^{++} , or if in the form of PuO_2^{++} , the per cent used. In order to obtain maximum information regarding the autoreduction reaction, it is essential to study the reaction over periods of time sufficiently long to allow the reduction of PuO_2^{++} to Pu^{4+} to be about 99% complete.

Calculations show that not enough hydrogen peroxide is produced from alpha-particle radiolysis

⁵J. M. Chilton and R. E. Biggers, ORNL CF-57-9-104 (July 8, 1957) (classified).

⁶Chemical Technology Division.

of water to account for the extent of the observed reduction of PuO_2^{++} . The remainder of the reduction is probably a free-radical process. The experimental results have been thoroughly analyzed from several points of view and interpreted in the light of what is known concerning the radiation chemistry of water. As a result, it is possible to discuss the mechanisms and kinetics of the reaction. Since the self-reduction phenomenon for plutonium has never been studied in detail, it is hoped that this investigation will serve as an impetus for future work on the many additional parameters that need to be investigated.

The concentration of plutonium in its various valence states, especially PuO_2^{++} , must be determined with the greatest possible precision and accuracy. Any appreciable error in the PuO_2^{++} determination would mask the true course of the reduction process and lead to an erroneous interpretation of the data. In most of the previous work, the methods used for the determination of the valence states of plutonium have not been indicated. It is therefore impossible by evaluation of any of the data to obtain information regarding mechanisms or kinetics. In addition, most of the work was not carried out for a sufficiently long time to permit the PuO_2^{++} concentration to change from a high to a very low value. Previous work on this type of reaction has been reviewed,⁵ as was recent work on the action of ionizing radiations, particularly alpha particles, on water.

Some data obtained from the autoreduction of a solution of PuO_2^{++} in 1.4 M uranyl sulfate are shown in Fig. 3. First-order kinetics are obeyed for approximately the first 37% of the autoreduction; then a zero-order process follows. These experimental results, interpreted on the basis of what is known concerning the alpha-particle radiolysis of water, show that there is not enough hydrogen peroxide produced to account for the extent of the reduction of PuO_2^{++} observed. A thorough analysis of these data indicates that the two radiolysis products, that is, $\text{H}\cdot$ and H_2O_2 , are responsible for the autoreductions of plutonium(V) and (VI). The half-time ($t_{1/2}$) value, calculated from the slope of the linear section of the curve given in Fig. 3 in accord with first-order kinetics, is 609.3 hr, which is equivalent to a reaction rate of 2.69% per day for this half time. However, during the subsequent part of the reaction, the rate of reduction of PuO_2^{++} is 1.26% of the total plutonium per day.

Hydrogen peroxide reduces part of the PuO_2^{++} throughout the course of the reduction. Hydrogen radicals reduce the remainder of the PuO_2^{++} to PuO_2^+ . The first stage of the reaction involves the regeneration of PuO_2^{++} via the disproportionation of PuO_2^+ . In the second stage, PuO_2^+ is reduced to Pu^{4+} by $\text{H}\cdot$, probably via the transient PuO_2 .

Kinetic treatment of the data has been used to obtain information regarding the reduction via both $\text{H}\cdot$ and H_2O_2 . Approximately 32 ev was required for the reduction of one PuO_2^{++} ion to Pu^{4+} , or ~ 16 ev/equivalent. Treatment of the data from the point of view of energetics indicated that one ion pair reduced one PuO_2^{++} to Pu^{4+} . Comparisons were made for radiolytic reactions involving neptunium, plutonium, and americium.

The rates of reduction of PuO_2^{++} to Pu^{4+} by products of the alpha-particle radiolysis of water are also being studied in 0.3 M sulfuric acid and in concentrated solutions of uranyl sulfate (310 g of uranium per liter) having plutonium(VI) concentrations ranging from 50 to 1000 mg/liter. Additional experiments are being performed at fixed concentrations of total plutonium in the approximate range from 50 to 200 mg/liter, all the plutonium being present initially as PuO_2^{++} , in which Am^{241} or Po^{210} is used to increase the alpha-particle emission by factors ranging up to 20. The experiments are expected to show why there is a change in the rate and in the mechanism of the autoreduction of PuO_2^{++} during the course of the reaction. As long a time as four months is sometimes required for the complete transformation of PuO_2^{++} into Pu^{4+} . The two sets of experiments should show conclusively whether or not the plutonium concentration affects the rate behavior. Because these experiments are very slow, they are being carried out concurrently with other work. These autoreduction reactions are of importance in the computation of PuO_2^{++} concentrations and must be considered when experiments involving even as short a time as several days are carried out.

Determination of Plutonium(III) and (IV) in PuF_3 - PuF_4 Mixtures Contained in Fused NaF - BeF_2

R. E. Biggers J. H. Cooper

The absorption spectra of separate solutions of PuF_3 and of PuF_4 in 1.0 M sulfuric acid-0.1 M aluminum sulfate have been determined; all the

plutonium in each solution was in one valence state only. Since fluoride ion is much more strongly complexed by aluminum(III) than by plutonium(III) or (IV), the spectra are those of either the uncomplexed plutonium(III) and (IV) ions or the sulfate complex of plutonium(IV) if it exists in this medium. It has been found that PuF_3 can be readily dissolved in this medium under an atmosphere of nitrogen that is completely free of oxygen without any of the plutonium(III) oxidizing, whereas the dissolution of PuF_4 requires 2 hr or more.

The absorption spectra of mixtures of PuF_3 and PuF_4 have also been obtained in 1.0 M sulfuric acid-0.1 M aluminum sulfate solution. Each of these plutonium fluorides can be dissolved in this medium in the presence of the other without a change taking place in the ratio of the two valence states of the plutonium. This background solution has been found to be suitable for the spectrophotometric determination of the Pu(III)/Pu(IV) ratio in samples of fused NaF- BeF_2 which contains 57 mole % NaF and 43 mole % BeF_2 . Simultaneous equations have been set up for the determination of the Pu(III)/Pu(IV) ratio at several combinations of wavelengths. It appears that the system obeys Beer's law and that the absorbancies are additive. The presence of beryllium does not result in interfering absorption bands but does appear to cause a general increase in the background absorbancy; its presence is therefore compensated by the use of a reference solution that contains the same concentration of fused-salt mixture (but not plutonium) as is contained in the solution of the sample.

The suitability of background solutions that are more concentrated in both sulfuric acid and aluminum sulfate than 1.0 M and 0.1 M, respectively, is being studied. The higher concentrations are necessary in order to complex all the fluoride that is present if the plutonium content of the sample of fused NaF- BeF_2 is small and the test portion that is taken must therefore be large. Accurate values for Pu(III)/Pu(IV) ratios have been obtained on melts that contain less than 1 wt % plutonium.

Polymerization and Disproportionation of Plutonium(IV) in Sulfate Media^{1,2}

R. E. Biggers

Several experiments have been made in order to reinvestigate the disproportionation of plutonium(IV)

in concentrated solutions of uranyl sulfate and in dilute sulfuric acid. The solutions of plutonium(IV) are being prepared by the dissolution of pure $\text{Pu}(\text{SO}_4)_2 \cdot \frac{1}{2} \text{H}_2\text{O}$ in the desired solvent and are free, initially at least, of polymeric plutonium. Spectra of plutonium(IV) in the absence of other valence states of plutonium have been determined in both concentrated solutions of uranyl sulfate and in dilute solutions of sulfuric acid. The extent of the disproportionation of plutonium(IV) (200 mg of plutonium per liter) into plutonium(III) and plutonium(VI) (i.e., PuO_2^{++}) determined by means of the Cary model 14PM spectrophotometer is less than that which was determined previously by means of the Beckman model DU spectrophotometer.^{7,8} This difference is a result of numerous factors too detailed to be discussed herein. At a much higher concentration (770 mg of plutonium per liter), plutonium(IV) disproportionates extensively into plutonium(III) and plutonium(V) (i.e., PuO_2^+) as the temperature is increased to 90°C. The rate of the disproportionation appears to be very fast, and the disproportionation equilibrium is reached immediately following the temperature change. The temperature coefficient of the spectrum of plutonium(IV) has also been obtained in these two media.

It has been found that PuO_2^+ is apparently stable at 90°C as long as the solution is kept at 90°C. The first step of the disproportionation reaction is: $\text{Pu(IV)} + \text{Pu(IV)} = \text{Pu(III)} + \text{Pu(V)}$. The second step in the disproportionation reaction, that is, $\text{Pu(V)} + \text{Pu(IV)} = \text{Pu(III)} + \text{Pu(VI)}$, apparently does not occur at high concentrations of plutonium in concentrated solutions of uranyl sulfate, even though this step is known to be a rapid reaction at low concentrations of plutonium, because it consists only of an electron transfer and does not involve any oxygenation steps. The analysis of the voluminous amount of data from these experiments is still in progress but should be completed soon.

Experiments are being carried out at plutonium(IV) concentrations in the range from 770 mg/liter to as low as it is possible to go by means of the spectrophotometric technique (i.e., ~50 mg/liter); 10-cm cells are used. Fortunately, the lowest concentrations of PuO_2^{++} at which an adequate

⁷J. M. Chilton and R. E. Biggers, ORNL CF-57-9-105 (July 9, 1957) (classified).

⁸R. E. Biggers and J. M. Chilton, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 1 (classified).

spectrum can be obtained is about 10 mg/liter/10-cm cell.

Coulometric Titration of Potassium Pertechnetate in a Solution of Potassium Phosphate

P. F. Thomason

An integrating, coulometric titrator that is a modified version of the instrument built by Booman⁹ was used to titrate the pertechnetate ion (TcO_4^-) in a potassium phosphate buffer solution of pH 7.0. This instrument was built by H. C. Jones and M. T. Kelley (see "Simplified Controlled-Potential Coulometric Titrators," this report). Some crystals of KTcO_4 of high purity were obtained from R. H. Busey of the Chemistry Division. They were carefully weighed on a microbalance and were dissolved in a potassium phosphate buffer solution of pH 7.0 to give a solution that contained 1.971 mg of KTcO_4 per milliliter. One-milliliter aliquots of this solution were electrolyzed at a potential of -0.80 v vs an Ag-AgCl reference electrode. The colorless solution of KTcO_4 became pink after a few minutes of electrolysis. When the electrolysis was complete, as was shown by the return of the current to 0.05 ma (i.e., the same current as the background current for the same buffer solution that contained no KTcO_4), the color of the solution was green. The number of faradays of electricity obtained from the integrating circuitry showed that a 4-electron process (value calculated from the faradays of electricity = 3.80) had occurred and that the technetium in the green phosphate solution was present as Tc^{3+} . An absorption spectrum of the green solution, obtained by means of a Warren Spectracord, did not show any fine structure but rather a single, broad absorption band that extended over the wavelength range from 350 to 760 $m\mu$.

The green solution was allowed to come into contact with air, whereupon its color immediately became pink. The solution was stirred in contact with air for 1 hr; then it was again electrolyzed until the green color returned and the background current was 0.05 ma. The number of faradays of electricity was found to be equivalent to a 1-electron change (value calculated from the faradays of electricity = 0.94). Evidently the form of technetium that is present in the pink phosphate

solution is Tc^{4+} . The absorption spectrum of the pink solution showed a broad absorption band from 500 to 540 $m\mu$; no fine structure was present.

This work was done in order to clarify the polarographic results obtained by Miller.¹⁰ His calculations indicated that the reduction of the TcO_4^- ion in a phosphate buffer solution at the dropping mercury electrode and at $E_{1/2}$ of -0.68 v vs the saturated calomel electrode is a 3-electron process. The electrolysis of the KTcO_4 solutions by means of a large mercury-pool cathode shows that it is possible to reduce the TcO_4^- ion to Tc^{3+} (green solution); however, the polarographic reduction at the dropping mercury electrode may nevertheless be a 3-electron reduction, as calculated from the slope of the polarogram, because the solution of Tc^{3+} is very unstable and Tc^{3+} is formed only in the complete absence of air and after a long electrolysis time.

Determination of Nickel and Chromium in Mixtures of Fluoride Salts

A. D. Horton P. F. Thomason

Instrumental methods suitable for use in the High-Radiation-Level Analytical Facility were developed for the determination of nickel and chromium in solid mixtures of fluoride salts.

For the determination of nickel a portion of a sample reported to contain 55 ppm nickel and 60 ppm chromium was dissolved in a silica dish in a 1:4 v/v mixture of concentrated nitric and sulfuric acids. The solution was evaporated to dryness, and the residue was dissolved in 0.1 M sulfuric acid. The nickel was separated from interfering constituents by ion exchange on a sulfate-form, Dowex 1, anion exchange resin. Nickel as the pyridine complex was determined polarographically by the standard-addition method. The results obtained for the determination of nickel by this method are given in Table 1.

For the chromium determination a portion of the sample was dissolved and the solution was evaporated in the same manner as that used for the nickel determination. The residue from the evaporation was dissolved in 5 drops of concentrated sulfuric acid, the resulting solution was

⁹G. L. Booman, "Instrument for Controlled Potential Electrolysis and Precision Coulometric Integration," *Anal. Chem.* 29, 213 (1957).

¹⁰H. H. Miller, *Polarography of Technetium. Reduction of Pertechnetate in Various Supporting Electrolytes*, unpublished report in the files of P. F. Thomason (Sept. 1955).

Table 1. Results of Determination of Nickel in Mixtures of Fluoride Salts

Final volume: 10 ml
Nickel blank: 0.317 $\mu\text{g/ml}$

Sample Weight (mg)	Total Nickel Found ($\mu\text{g/ml}$)	Net Total Nickel		
		Micrograms per Milliliter	Micrograms	Parts per Million
54.2	0.621	0.304	3.04	56.1
58.4	0.644	0.327	3.27	56.0
62.6	0.660	0.343	3.43	55.0
62.8	0.677	0.360	3.60	57.3

diluted with water to give a 1 M sulfuric acid solution, and the chromium was determined potentiometrically by the following method, which was adapted from that of Lingane and Davis.¹¹ A measured amount (~ 30 mg) of Divisil (AgO) was added to oxidize chromium to chromium(VI), and the sample was then heated to incipient boiling to reduce the excess AgO . The sample was cooled, and chromium(VI) was titrated with a standard solution of ferrous sulfate, approximately 0.01 M. It was necessary to obtain a blank on all reagents for both the nickel and the chromium determinations. The results obtained by use of this method are shown in Table 2.

Unusual care must be taken in all phases of the determinations in order to prevent contamination from metals. Silica ware was used whenever possible because it contains very few metallic

contaminants. Volumes of reagents were kept to a minimum. More washing of glassware than is usual was required in order to maintain a low blank. Double-distilled or distilled-demineralized water was used for all reagents and dilutions.

Distillation of Amsco 125-82 and Identification of Its Major Constituents

A. D. Horton W. H. Baldwin¹²

Work is being continued on the identification of the major constituents of Amsco 125-82.¹³ A 2-ft by 20-mm distillation column, packed with glass helices, was used for the rough distillation of Amsco 125-82. A 6-ft by 12-mm distillation column was constructed and packed with an evacuated 6-mm glass tube that was wound

¹²Chemistry Division.

¹³A. D. Horton, J. G. Surak, and P. F. Thomason, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 4-5 (classified).

Table 2. Results of Determination of Chromium in Mixtures of Fluoride Salts

Chromium blank: 0.03 μg

Sample Weight (mg)	Total Chromium Found (μg)	Net Chromium Found	
		Micrograms	Parts per Million
52.2	2.69	2.66	51.0
51.2	2.69	2.66	52.0
56.8	3.05	3.02	49.9
50.0	2.57	2.54	50.8
75.2	3.92	3.89	51.8

spirally on $\frac{1}{2}$ -in. centers with No. 16 aluminum wire. The second column was used to separate the major fractions from the desired cuts obtained from the first distillation.

The purity of the fractions from both distillations was determined by gas-liquid chromatography on a 4-ft dinonylphthalate column, which has been described previously.¹⁴ The components corresponding to 5 of the 12 peaks on the chromatogram of untreated Amsco 125-82 have been separated and have been shown to be pure or nearly pure fractions. The five compounds have not been identified completely; however, the data given in Table 3 can be reported.

Determination of Niobium

H. Kubota

Process control analyses for niobium, uranium, zirconium, and phosphate were requested by the Chemical Technology Division. Whereas methods are available for the last three constituents mentioned, it was necessary to adapt or to develop a method for niobium. The peroxide method¹⁵ does not have the degree of sensitivity desired (down to

¹⁴*Ibid.*, p 5.

¹⁵F. C. Palilla, N. Adler, and C. F. Hiskey, "Analytical Chemistry of Niobium and Tantalum. Simultaneous Spectrophotometric Determination of Tantalum and Niobium," *Anal. Chem.* 25, 926 (1953).

10 ppm). The thiocyanate method^{16,17} is very sensitive but requires very careful control of both reagent purity and of procedure. A recent paper¹⁸ that describes the use of hydroquinone for the determination of tantalum mentions niobium as the most serious interference. The spectrum of niobium-hydroquinone in concentrated sulfuric acid was found to give good absorbancy, the wavelength of maximum absorbancy being 419 m μ . Zirconium and phosphate do not seem to interfere. The spectra of niobium-hydroquinone in the presence of large amounts of uranium indicate that it may be possible to determine niobium without the prior separation of uranium. Work is in progress to establish the validity of and the optimum conditions for this particular determination.

Analysis of Yttrium Alloys

H. Kubota

Yttrium metal that had been prepared by the reduction of yttrium chloride with calcium, magnesium, and lithium was analyzed for the total

¹⁶C. E. Crouthamel, B. E. Hjelte, and C. E. Johnson, "Thiocyanate Spectrophotometric Analysis of Titanium, Vanadium, and Niobium," *Anal. Chem.* 27, 507 (1955).

¹⁷B. L. McDowell, "Niobium in Mixtures of Fluoride Salts, Spectrophotometric Thiocyanate Method," Method No. 9 0922550 (6-20-57), *ORNL Master Analytical Manual*.

¹⁸G. R. Waterbury and C. E. Bricker, "Separation and Determination of Tantalum," *Anal. Chem.* 29, 1474 (1957).

Table 3. Preliminary Physical Data on the Identification of the Major Fractions of Amsco 125-82

Fraction Number ^a	Mass ^b	Boiling Point ^c (°C)	Density, <i>d</i> (g/ml)	Index of Refraction, η
2	142	166 ⁷⁴⁰ mm	0.7397 ²¹	1.4141 ²⁴
5	156	176 ⁷⁴⁵ mm	0.7525 ²²	1.4189 ²⁵
7	170	183 ⁷⁵² mm	0.7592 ²⁴	1.4224 ²⁴
9	184	194 ⁷⁵² mm	0.7597 ²⁴	1.4219 ²⁴
11		201 ⁷³⁶ mm	0.7651 ²⁴	1.4251 ²⁴

^aDetermined by the order of emergence of the peaks, from right to left, of the vapor chromatogram of Amsco 125-82 (see ref 13).

^bData furnished by J. L. Sites of the Mass Spectrometry Group.

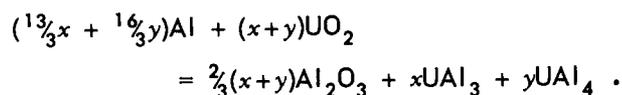
^cDetermined by the Percolator method (R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 2d ed., p 92-93, Wiley, New York, 1940).

yttrium content, as well as for the residual calcium, magnesium, or lithium incorporated by the reduction process. The sample was dissolved in a little more than the minimum amount of hydrochloric acid necessary to effect dissolution. The solution was diluted with water to give a solution having about 5% total salt concentration; the resulting solution was then filtered in order to remove the small amount of insoluble refractory material. The yttrium was precipitated with oxalic acid, the mixture filtered, and the residue ignited to Y_2O_3 . The filtrate was analyzed for magnesium by the precipitation of the magnesium as magnesium ammonium phosphate; the magnesium was weighed as $Mg_2P_2O_7$. Large amounts of calcium were separated as calcium oxalate and weighed as CaO . Small amounts of calcium and magnesium and any lithium that was present were determined by flame photometry of the filtrates from the precipitations. The results of a typical analysis are: yttrium, 79.16%; magnesium, 17.19%; and lithium, 3.01%.

Study of Chemical Changes in UO_2 -Al Reactor Fuel Elements During Fabrication

H. Kubota

A reactor fuel element of UO_2 -Al made by a powder metallurgical method has many desirable properties. In the course of heat treatment, however, deformations often occur which are responsible for a high percentage of rejects. One of the many approaches to solving the problem of decreasing the number of deformations is to determine the nature and extent of any reaction between the constituents. The following reaction has been proposed:¹⁹



It has been established¹⁹ by x-ray diffraction that the intermetallics UAl_3 and UAl_4 are formed and that the amount of UAl_4 increases as the duration of the heat treatment is extended. It was also proposed in the same work that amorphous U_3O_8 is present as an intermediate compound.

The reaction was studied experimentally in the following way. Sets of four representative cores,

¹⁹M. L. Picklesimer, *The Reaction of UO_2 with Aluminum*, ORNL CF-56-8-135 (Aug. 7, 1956).

each weighing 0.8 g, were made that contained 50 wt % each of high-density UO_2 and high-purity aluminum powder. Each core was sealed individually in an evacuated quartz capsule. The capsules were placed in a furnace at $600^\circ C$, and one was removed for analysis after each of the following periods of heat treatment: 8, 12, 16, and 24 hr. The analyses were conducted in the following manner. The core was dissolved in 1 M sodium hydroxide, and the volume of evolved hydrogen was measured as an indication of the unreacted aluminum. The solution of sodium hydroxide was analyzed for aluminum by the gravimetric oxine method. The intermetallics were dissolved in 1 N sulfuric acid; the uranium in solution was determined by a volumetric method, and the aluminum by the gravimetric oxine method. The residue from the treatment with 1 N sulfuric acid was dissolved in concentrated phosphoric acid by heating to $160^\circ C$ under an argon atmosphere in order to dissolve the uranium oxide without changing the valence of the uranium. Any residue from the phosphoric acid dissolution was collected and ignited, and the residue from the ignition was weighed as Al_2O_3 .

It was found that the amount of aluminum recovered gravimetrically from the solution of sodium hydroxide was always greater than the aluminum equivalent to the volume of hydrogen evolved. This occurrence has been attributed to the partial solubility of the Al_2O_3 in sodium hydroxide solution. The treatment at $600^\circ C$ apparently is not sufficient to bring about the complete calcination of Al_2O_3 . Some Al_2O_3 was also dissolved by the phosphoric acid.

Another complication is the apparent slow reaction between UAl_4 and NaOH. The extent of this reaction is difficult to determine because the UAl_4 prepared directly and that resulting from the reaction may not have identical characteristics.

The following conclusions have been established: (1) A reaction between UO_2 and aluminum takes place at $600^\circ C$ which proceeds slowly to completion with time. (2) There is no stage at which any U_3O_8 is formed. (3) The compound Al_2O_3 is a final product of the reaction.

It is difficult at this time to make many other specific conclusions, because cores made in different lots have not behaved very similarly even though the treatment was nearly identical.

The results of the chemical analyses do not indicate the role of the intermetallics. The assumption that UO_2 is reduced to metallic uranium seems to give a better fit of the analytical results to the assumed reaction in some cases. On the other hand, x-ray diffraction has failed to detect any uranium metal. It is planned to continue the study by investigating possible improvements in the methods of preparation and analysis of the cores.

Enthalpymetric Determination of Free Acid in the Presence of Certain Hydrolyzable Ions

F. J. Miller

In some favorable cases it has been found possible to determine free acid in the presence of hydrolyzable ions by enthalpymetric (thermometric) titration.^{20,21} Solutions of uranyl sulfate in excess sulfuric acid and of zirconyl fluoride in excess hydrofluoric acid have been studied to date. A solution of thorium nitrate in nitric acid is presently being investigated. Test samples that contain quantities of free acid of the order of 0.02 meq can be titrated. The apparatus consists of a Thermistor that is incorporated as a leg in a simple d-c bridge, a recording potentiometer that records the potential across the bridge, a constant-delivery-rate buret, a Dewar flask, and a 300-rpm stirrer. The determination depends upon the heat of hydrolysis of the cation being much less than the heat of neutralization of the free acid. The titration plot of temperature vs volume of titrant results in a double-branched curve. The end point is obtained by extrapolation of the straight-line portions of the curve to their intersection. This work is being described in a forthcoming topical report and in a method for issue to the *ORNL Master Analytical Manual*.

Polarographic Behavior of Niobium in Citric Acid Medium

P. F. Thomason H. P. Raen

The polarographic behavior of niobium in 2 M citric acid solution of pH 1, a medium recommended by Ferrett and Milner,²² was studied by means of a

²⁰H. W. Linde, L. B. Rogers, and D. N. Hume, "Automatic Thermometric Titrations," *Anal. Chem.* 25, 404 (1953).

²¹J. Jordan and T. G. Alleman, "Thermochemical Titrations. Enthalpy Titrations," *Anal. Chem.* 29, 9 (1957).

²²D. J. Ferrett and G. W. C. Milner, "The Polarography of Niobium," *J. Chem. Soc.* 1956, 1186.

high-sensitivity, derivative, recording polarograph (ORNL model Q-1673) in the concentration range from 0 to 250 $\mu\text{g}/\text{ml}$. Difficulties were encountered with the procedure recommended by Ferrett and Milner, as well as with modifications of their procedure. The difficulties included precipitation of the niobium during the steps preliminary to obtaining the solution of it in 2 M citric acid; irreproducibility of the derivative polarograms with respect to numbers, heights, shapes and half-wave potentials of the derivative peaks; instability of solutions of niobium in 2 M citric acid of pH 1; and, with the exception of one set of results, lack of achievement of the sensitivity reported.²² However, the great sensitivity and the linearity of the diffusion current-concentration relationship displayed by the one set of results lend hope that if the elusive and critical variables can be determined and controlled a highly sensitive polarographic method for niobium may result. The study will be continued.

Identification and Determination of Chloride in Metallex Amalgams

P. F. Thomason H. P. Raen

Because of the deleterious effect of chloride on the product thorium from the Metallex process, it must be known whether the intermediate-stage, washed amalgam, which is presumed to be chloride-free, is actually chloride-free. The quality of thorium billets obtained from washed amalgams that were shown by usual analytical methods to be chloride-free belied the analytical results. The analytical procedures were therefore re-evaluated in terms of the possible forms and concentration of chloride in the amalgams. Extractions of large volumes of the amalgam samples were made with water, concentrated ammonium hydroxide, pyridine, and ethyl amine. Other extractants, for example, propylenediamine and hydrazine, were considered because they were solvents for certain possible forms of the chloride but were not used because of inherent difficulties in working with them. The extracts were analyzed by various methods, among which were the Volhard and Mohr methods (and modifications thereof), x-ray diffraction, and electron microscopy. The results indicated qualitatively that chloride was present in Metallex amalgams that were presumed to be chloride-free and that the chloride was present in a form more soluble in ammonium hydroxide than in water.

No satisfactory quantitative results were obtained either because the extracts contained interferences or because the concentration of chloride present was below the limit of quantitative measurement for the methods used.

The use of the electronic coulometric stripper (see "Electronic Coulometric Stripper for the Determination of Submicrogram-to-Microgram Amounts of Halides," this report) for the analysis of the amalgam and/or extracts from them was suggested by R. L. Walker. By means of standard-addition techniques, a limit of quantitative measurement of chloride concentration of $0.1 \mu\text{g/ml}$ has been realized with the instrument. A series of extracts in water and in ammonium hydroxide were obtained systematically, and the extracts were analyzed by H. E. Zittel²³ by means of the electronic coulometric stripper. The results confirmed that chloride was present in the "chloride-free" amalgams and that it was present in a form only very slowly extractable by water but rapidly extractable into concentrated ammonium hydroxide. On the basis of these results, a program was planned to evaluate the electronic coulometric stripping technique for the analysis of the amalgams directly and of extracts of the amalgams. The program included the establishment of the accuracy, and also the precision, of the method by means of laboratory-prepared amalgams of composition simulating the washed Metallex amalgams and containing known amounts of ThCl_4 and Hg_2Cl_2 . The program is being carried out by the Analytical Instrumentation Group.

Determination of Oxides of Nitrogen

W. D. Shults, II

The concentrations of the oxides of nitrogen (i.e., NO , N_2O , and NO_2) in off-gas samples from aqua regia dissolver systems have been determined spectrophotometrically by use of the visible and the infrared wavelength regions of the spectrum. A fourth component of the off-gas, that is, NOCl , may also be determinable by this method. The method is presently being evaluated for these four determinations.

²³Summer research participant from Fisk University, Nashville, Tenn.

ANALYTICAL INSTRUMENTATION

D. J. Fisher

In-Line Instrumentation Program at ORNL

M. J. Kelly²⁴ T. S. Mackey²⁵
J. W. Landry²⁵ R. W. Stelzner

Development of the following instruments comprises the work that was done in furtherance of the In-Line Instrumentation Program:

1. conductivity-type, interface-level controller for contactors,
2. a-c polarograph for monitoring uranium losses in raffinate streams,
3. gamma-radiation monitor having a falling-stream cell,
4. radio-frequency monitor for nitric acid in feed streams,
5. flow-rate meters,
6. chloride-ion monitor for Darex processing,
7. alpha-radiation monitor for aqueous process streams,
8. densimeters for pulse columns.

An interface-level controller system has been constructed for use with a conductivity-type, digital probe that has been under test in the IA column of the Metal Recovery Plant since April 1957. The controller is designed to give proportional control, at a pulsed interface, with an accuracy of $\pm \frac{1}{4}$ in. of interface level. A pressure-resistant probe, formed from a molded assembly of stainless steel electrodes and fluorothene insulators, has been designed to control the interface level in the bottom in the IS column of the Metal Recovery Plant. The controller associated with this unit is designed to give on-off control at a quiescent interface, with an accuracy of $\pm \frac{1}{4}$ in. This controller is scheduled for testing alongside a conventional, hydraulic, dip-tube controller in the IS column beginning January 1958.

Construction of an a-c polarograph for the measurement of uranium losses in raffinate streams (IIAW and possibly IAW) has been approximately 90% completed. The polarograph is designed to monitor losses of uranium at a maximum concentration level of 10 ppm. Electrical phase discrimination and automatic elimination of the

²⁴Instrumentation and Controls Division.

²⁵Chemical Technology Division.

voltage drop across a high-valued measuring resistor are employed to gain high sensitivity.

The fabrication of a prototype gamma-activity monitor was completed. The instrument was tested in the IAP stream of the Thorex Pilot Plant that had a gamma activity of 10^5 counts/min/ml. It measured specific gamma emissions from the gamma emitters present in the stream. Shielding of the unit is effective in permitting a count of as low as 5 counts/min in the presence of an ambient field of 100,000 counts/min. A liquid-level alarm system has been added to the instrument to shut off the sampler in the case of operational failure of the IAP stream. This shutoff eliminates splashing in the cell. In addition, the stream has been refrigerated to minimize contamination arising from condensate on cell surfaces. Recorder response has been optimized to give a sufficiently fast response to transient conditions with a minimal amount of "hunting."

The radio-frequency monitor for nitric acid concentration in process feed was operated for a period of several months on an air-lifted, recirculating feed stream. The instrument demonstrated good sensitivity and good stability in the range for which it was designed (~ 0.5 M HNO_3); it maintained good precision ($\sim \pm 0.05$ M HNO_3) even at higher concentrations (4 M HNO_3). The air lift is being replaced with a pumped system to eliminate concentration changes caused by air-lifting. The instrument is being used on a feed stream of 0.5 M HNO_3 , 1.8 M $\text{Al}(\text{NO}_3)_3$, and 3 g of uranium per liter.

Two turbine-type flowmeters were installed in ORNL pilot plants for operational testing. The one in the Thorex Pilot Plant has been installed on the interfacial purge system, and the one in the Metal Recovery Plant, on the acid-addition line. Both flowmeters, which measure flow rate as well as total flow, have operated in satisfactory fashion on these streams since their installation.

A flow-rate meter of the turbine type has been modified for installation in the Volatility Plant. The sleeve bearings were replaced with carburized Hastelloy B cone bearings; sleeve bearings and ball-point-to-flat-plate bearings were found unsatisfactory for this service.

An electromagnetic flow-rate meter, which was purchased for use on the IAF stream of the Metal Recovery Plant, has been rebuilt. Adjustments that had been located on the flow-head are now located at the operating panel in the plant.

A glass model of a photoelectric bubble-velocity meter for measuring liquid flow rate in the range of 0 to 60 gph was tested and was found to be accurate within $\pm 1\%$ over this range. The accuracy increased with a decrease in flow rate. A stainless steel model for plant evaluation is being assembled. A sonic pickup will be used to detect the bubble passage inside the stainless steel tubing. The sonic components were designed by the Non-destructive Testing Group of the Metallurgy Division. Timing of the bubble passage is accurate to within ± 0.01 sec. The objective of this development was to produce an instrument that will measure accurately low rates of flow of a radioactive process stream and that will have no moving parts and no flow restrictions.

A chloride-ion monitor for the Darex process is being developed. The instrument is based upon the potentiometric measurement of the electrical potential of an Ag-AgCl electrode vs the S.C.E. A side stream that is diluted by a factor of 100 is used for the measurement. Calibration by means of known standards is required.

Two new designs for the continuous monitoring of the alpha activity of a raffinate stream are being investigated. The design features are described in another report.²⁶

A densimeter is being constructed for evaluation in a pulse column of the Metal Recovery Plant. It will be installed at a position ten plates below the column feed point and will measure the density of the aqueous phase for the purpose of anticipation of column losses. The densimeter consists of a sampling pot, organic-filled dip tubes, and a pressure recorder. Column pulse energy is used to obtain the sample, the spent sample being returned to the column at the inlet. Since sonic velocity is directly proportional to the density of the solution tested, a sonic type of instrument is being investigated along with the dip tubes.

The testing of the Savannah River Laboratory model 1 flow colorimeter, which was developed at the Savannah River Laboratory, on the ICU stream of the Metal Recovery Plant has been completed, and a terminal report is in preparation. The colorimeter demonstrated very satisfactory operation in the continuous measurement of uranium in the concentration range of 25 to 35 g/liter.

²⁶*Chem. Tech. Monthly Prog. Rep. June 1957, ORNL-2362, p 69 (classified).*

Service Instructions for the ORNL Model Q-1728, Velocity-Servo, Automatic, Potentiometric Titrators

D. J. Fisher

Instructions have been written for the repair and maintenance of the ORNL model Q-1728, velocity-servo, automatic, potentiometric titrators.²⁷ These instructions consist in a trouble-shooting guide and in detailed procedures for service adjustments. The titrator has been described previously.²⁸

ORNL Model Q-1887, Recording and Scanning, High-Sensitivity, Flame SpectrophotometerM. T. Kelley D. J. Fisher
H. C. Jones

An ORNL model Q-1887 flame spectrophotometer has been fabricated by the Instrument Department of the Instrumentation and Controls Division. It is similar to the model Q-1457A flame spectrophotometer that has been described.²⁹ The new instrument was designed to have high sensitivity, particularly in the red spectral region. The lithium concentration of aqueous solutions that contain less than 0.5 ppb of lithium can be easily determined³⁰ by use of this flame spectrophotometer. The instrument is also very stable. A set of drawings that give constructional details for the instrument has been prepared (Instrumentation and Controls Division Dwg. Nos. Q-1887-1 through -12). Performance specifications, check-out and field maintenance procedures, and a trouble-shooting guide have been written.³¹ A paper that describes the design and performance of this instrument is being prepared.

²⁷D. J. Fisher, *Instrument Service Instructions ORNL Model Q-1728 Velocity-Servo Automatic Potentiometric Titrator*, Instrument Department, ORNL Instrumentation and Controls Division, RS-1728 (Sept. 12, 1957).

²⁸E. B. Wagner, "Automatic Potentiometric Titrator, Velocity-Servo, ORNL Model Q-1728," Methods Nos. 1 003028 and 9 003028 (6-21-56), *ORNL Master Analytical Manual*.

²⁹H. C. Jones, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 9-10 (classified).

³⁰R. L. Walker, private communication to D. J. Fisher, Oct. 23, 1957.

³¹D. J. Fisher, *Performance Specifications Check-Out and Field Maintenance Procedures Trouble-Shooting Guide References for ORNL High-Sensitivity Recording, Scanning, Single-Beam Flame Spectrophotometer Models Q-1457A and Q-1887*, Specification No. SI-162, Instrument Department, ORNL Instrumentation and Controls Division (Aug. 12, 1957).

Simplified Controlled-Potential Coulometric Titrators

M. T. Kelley H. C. Jones

A simplified model of the controlled-potential coulometric titrator³² has been built and is now in operation. This model has proved to be satisfactory, as did the first model. Modifications incorporated in the simplified model include the following. The power supply contains two 200-ma, selenium rectifiers in place of the 5U4 power rectifier tube and also contains a single 6080 twin triode to replace the two 6080 triodes used in the first model. Also, the choke input to the power-supply filter has been removed. The source of the potential applied to the potential-control amplifier is a single RM-12-R mercury battery instead of the two 1½-v dry cells. The voltmeter has been removed from the panel and replaced by two test jacks that are connected across a 10-turn Helipot, which has a precision dial and whose potential is adjusted to 1.00 v by means of a 3-turn Helipot in series with the 10-turn Helipot; this adjustment is made by means of a Rubicon 1-v potentiometer. The control potential is read directly from the precision dial. Two other simplifications that have reduced the cost and space requirements of the instrument are the elimination of the bias batteries on two of the operational amplifiers and the reduction of the size of the integrating capacitor.

It is intended to redesign the instrument again in order to use as the potential-control amplifier a Philbrick USA-3 amplifier, which is a printed-circuit unit that should be a satisfactory replacement for two conventional amplifier modules. Because the USA-3 amplifier has higher output than the two modules now used, it should also make possible the elimination of the cathode-potential control amplifier. It is planned to build several of the redesigned instruments.

Gamma Absorptometer

M. T. Kelley W. L. Maddox

The gamma absorptometer³³ for the determination of plutonium in solution has been built and tested.

³²H. C. Jones and M. T. Kelley, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 12 (classified).

³³M. T. Kelley and W. L. Maddox, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 12 (classified).

Americium-241 is used as a source of low-energy (60-kev) gamma photons. The source is encapsulated in plastic, and the capsule is then sealed in a thin-windowed aluminum container.³⁴ The container is surrounded by a brass fitting which serves as a radiation shield and gamma-ray collimator. A solution to be analyzed is inserted into the beam as an absorber. The detector is a 0.1×1.5 in. crystal of thallium-activated sodium iodide. A thin crystal is used in order to minimize interference from radiations of higher energy which may be present in the samples.

The basic circuit employed in this instrument was described by Malmstadt and Roberts³⁵ (see also, "Automatic Derivative Spectrophotometric Titrator," this report). The current output of the multiplier phototube (detector) is passed into a feedback system in such a way that any change in this current results in a change of the voltage applied to the dynodes. This voltage change is of such sign and magnitude as to hold the current essentially constant, with the result that the dynode voltage is proportional to the absorbancy of the solution. The operating range is chosen by means of a switch that takes an arbitrary portion of the dynode voltage and presents it to a Brown recorder.

Data for testing and evaluating the instrument have been obtained from standard solutions of uranium. Samples of constant depth are obtained by delivering precisely measured amounts of solutions into open-topped, plastic absorption cells. In order to compensate for both long-term drift and short-term fluctuations of the dynode voltage, a "background" is obtained by placing a metal absorber or a standard solution in the cell position between the measurement of samples and averaging the measurements for each material over a period of approximately 3 min. Absorption curves are then plotted that show the difference between the values for the background and those for the sample as a function of concentration. The curves are linear. As an illustration, a series of test solutions were prepared in 3 M and in 6 M nitric acid. These solutions were used in the construction of calibration curves from which the

uranium concentrations of samples intermediate in nitric acid concentration were obtained by interpolation. The results of the analysis of a sample by this method have been checked within 0.1% by potentiometric titration.

All elements present in the sample interfere with the determination to some extent by contributing to the absorption of the radiation. Interference from lighter elements, such as iron, is minimized as a result of the strong dependence of the absorption of the low-energy gamma photons on the atomic number of the absorber. Materials present in the sample in large and varying amounts, nitric acid, for example, will have a significant effect on the apparent concentration of uranium or plutonium. In the specific application for which this instrument was developed, such constituents of the sample are determined quantitatively and corrections are applied.

Concentration measurements may be made with this instrument over the range from 0.5 to 100 g/liter, although it was designed primarily for operation in the 25 to 50 mg/ml range. The precision of measurement is approximately ± 0.1 mg/ml in this range.

Specialized Modifications of Commercial Apparatus Used for Analyses Performed Remotely in the High-Radiation-Level Analytical Facility (HRLAF)

In order that certain commercial apparatus might be used efficiently for remote analyses in the HRLAF, specialized modifications of them were designed and fabricated. The Jarrell-Ash Co. arc and spark stand was converted for remote use. An Electromatic solenoid-operated buret was adapted to the Beckman model K titrator. Also, a cam switching attachment was designed for the Argonne model 8 master-slave manipulators so that the operator need not detach his hand from the manipulator in order to cam it.

Modification of the Jarrell-Ash Arc and Spark Stand (H. C. Jones). – The Jarrell-Ash Co. arc and spark stand was modified so that it could be operated by remote control. The two knobs used to raise and lower the individual electrode holders were replaced by crank handles that can be operated by means of a master-slave manipulator. The knob used for opening and closing the electrode holders was replaced by a 2-rpm Bodine motor. The control switch for this motor will be located outside the

³⁴R. C. Milham, *The Preparation of an Americium Gamma Source*, DP-173, p 10 (Aug. 1956).

³⁵H. V. Malmstadt and C. B. Roberts, "Automatic Derivative Spectrophotometric Titrations," *Anal. Chem.* 28, 1408 (1956).

hot cell. The arc stand was also fitted with legs that can be adjusted in length from 0 to ~5 in.

Electromatic Buret for Use in the High-Radiation-Level Analytical Facility (HRLAF) (W. L. Maddox). — An Electromatic buret obtained from the Houston Glass Fabricating Co. has been adapted to the Beckman model K titrator for use in the HRLAF (see "Pilot-Plant Control Laboratory," this report). The delivery solenoid of the buret was substituted for the diaphragm-valve control in the titrant delivery unit of the model K titrator. Both the delivering and the filling solenoids supplied with the buret have been replaced with Guardian Manufacturing Co. series No. 200, interchangeable, relay coil assemblies (115-v, a-c). These assemblies have given satisfactory service for several months.

Cam Switching Attachment for Argonne Model 8 Master-Slave Manipulators (H. C. Jones, M. T. Kelley). — A cam switching attachment has been devised to replace the original cam switch that controls the reach of the Argonne model 8 master-slave manipulators fabricated by the American Machine and Foundry Co. With this attachment the operator no longer has to use both hands to control all movements of the manipulator. The attachment consists of a thumb-operated, leaf-type actuator which can easily be moved forward or backward to actuate one or the other of two miniature microswitches. Each of the microswitches in turn operates one of two relays. One of the relays connects the d-c power source to the cam motor in such a direction as to increase the reach of the slave hand. In a similar manner, the other relay decreases the reach of the slave hand.

Automatic, Derivative, Spectrophotometric Titrator

M. T. Kelley H. C. Jones

An automatic, derivative, spectrophotometric titrator has been constructed and is now in use. The photometric circuitry of the instrument was adapted from that originally described by Gilford *et al.*³⁶ and also used by Malmstadt and Roberts.³⁵ The 60- to 120-cycle filter and the measuring circuit were eliminated from the original circuit, and a phase-splitter was connected to the output of the first-derivative network. The output of the

phase-splitter was connected to the input of a Sargent-Malmstadt, automatic-titrator control unit. In order to stabilize the triggering circuit, it was necessary to install a grid-leak resistor on the input to the control unit. This, in effect, changed the triggering pulse from the third to the fourth derivative of the dynode voltage change, which is produced at the end point of the titration. A housing has been constructed for a 1P28 multiplier phototube which is being used to replace the 931A multiplier phototube. This housing is attached to a Bausch & Lomb Spectronic 20 colorimeter, which is being used as a source of monochromatic light and has been modified to furnish a suitable titration cell compartment.

Conversion of a Gilmont Micropipet-Buret to a Constant-Delivery-Rate Buret

H. C. Jones

A 1-ml-capacity Gilmont micropipet-buret has been converted to a constant-delivery-rate buret. The buret is driven through a 1:1 ratio gear train by a 1-rpm Bodine electric motor. This drive mechanism gives a titrant flow rate of approximately 30 $\mu\text{l}/\text{min}$. A mechanism for the quick release of the drive motor makes possible the rapid refilling of the buret by means of a hand-operated crank. The constant-delivery-rate buret is being used at present in enthalpy titrations²¹ (see "Enthalpymetric Determination of Free Acid in the Presence of Certain Hydrolyzable Ions," this report) as a substitute for the automatic syringe-buret described by Lingane.³⁷

Electronic Coulometric Stripper for the Determination of Submicrogram-to-Microgram Amounts of Halides

H. E. Zittel W. L. Maddox
M. T. Kelley H. C. Jones
W. R. Warren³⁸

Microgram amounts of chloride in HRP samples are now determined by means of the constant-current, coulometric titrator.³⁹ The sensitivity of this method is not great enough to meet the anticipated requirements; therefore an instrument that

³⁷J. J. Lingane, "Automatic Potentiometric Titrations," *Anal. Chem.* **20**, 285 (1948).

³⁸Reactor Analyses Group.

³⁹R. W. Stelzner and W. L. Maddox, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 11 (classified).

³⁶S. R. Gilford *et al.*, "An Improved Cuvette Densitometer for Cardiac Output Determination by the Dye-Dilution Method," *Rev. Sci. Instr.* **24**, 696 (1953).

is based on the principle of coulometric stripping, which is described by Nikelly and Cooke,⁴⁰ has been designed and fabricated.

The instrument, whose circuitry is described in ORNL-LR-Dwg. No. 24166, provides a means of applying a constant potential to a mercury micro-electrode for a measured period of time. When the mercury electrode is made the anode, halides in solution will be deposited on it as mercurous halides. The potential applied to the mercury is then changed to a value at which the halide is discharged into solution. The current that flows through the cell during the stripping (i.e., discharge) process is integrated electronically over a measured length of time. This integral appears as a voltage at the instrument output and is proportional to the halide concentration.

The instrument and technique have been evaluated for the determination of chloride, bromide, and iodide. The effects of pH, supporting electrolyte, deposition time, stripping time, extraneous ions, and other variables have been studied. It has been shown that the limit of quantitative measurement of chloride concentration is 0.1 $\mu\text{g}/\text{ml}$.

In addition to its use in the analysis of HRP samples, the method is being evaluated for the determination of chloride in washed amalgams from the Metallex process.

Controlled-Potential and Derivative Polarograph

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

A prototype controlled-potential and derivative polarograph has been built that is designed for both regular and derivative polarography at full-scale sensitivities from 0.005 to 500 μa . Its unique design features made possible the analysis of solutions having very high electrical resistance, and in spite of its unusual versatility, the fabrication cost is relatively low. It is planned to evaluate the performance of this polarograph relative to that of other polarographs. Test solutions will include solutions having high resistance, high concentration, extremely low concentration, several reducing species, and species giving polarographic waves with maxima. A brief description of the components of the polarograph follows.

⁴⁰J. G. Nikelly and W. D. Cooke, "Anodic Stripping Polarography," *Anal. Chem.* 29, 933 (1957).

A three-electrode electrolysis cell is used. The current between the dropping mercury electrode (D.M.E.) and the working electrode is recorded. The potential of the D.M.E. with respect to a reference S.C.E. is forced electronically by the potential-control amplifier to equal the algebraic sum of the initial and span potentials regardless of the internal resistance of the cell and independently of the value of the current-measuring resistor. Essentially no current flows through the potential-measuring circuit.

The potential-control amplifier is a stabilized amplifier fabricated from GAP/R electronic analog computer modules, available from George A. Philbrick Researches, Inc., a model K2-X operational amplifier, and a model K2-P stabilizing chopper amplifier.⁴¹ The use of these plug-in units substantially reduces the cost of fabrication. Booman has used GAP/R modules in an instrument designed for controlled-potential electrolysis and precision coulometric integration.⁴² When the polarograph is in operation, the potential-control amplifier supplies to the working electrode whatever voltage, up to the limiting value of 100 v, is required to force the voltage of the D.M.E. to be the proper value with respect to the S.C.E. An indicator located on the instrument panel lights up if the potential-control amplifier limits. For example, a current of 5 $\text{m}\mu\text{a}$ could be forced by a potential difference of 100 v through a resistance of 20,000 megohms.

An initial potential of 0 to ± 3 v may be applied. The value applied is indicated on a panel meter.

The value of span potential to be applied by the polarizing unit is indicated on a panel meter. A 10-turn "per cent span potential" dial indicates the portion of the span potential that is applied to the D.M.E. vs the S.C.E. The selected span potential is applied from a 10-turn potentiometer driven by a reversible, synchronous motor through a Hycor magnetic clutch. The clutch is energized only while the motor is energized; it is therefore easy to manually return the "per cent span potential" dial to zero.

A linear compensator is included. It can be used to cancel residual current that increases at a

⁴¹GAP/R Electronic Analog Computers (catalog data sheet), George A. Philbrick Researches, Inc., Boston 10, Mass.

⁴²G. L. Booman, "Instrument for Controlled Potential Electrolysis and Precision Coulometric Integration," *Anal. Chem.* 29, 213 (1957).

linear rate with applied potential. Generally, this compensator is useful with full-scale current ranges of less than 1 μa .

The current amplifier is fabricated from a GAP/R model K2-X operational amplifier and a GAP/R model K2-P stabilizing amplifier. The feedback configuration is designed to give full-scale current ranges from 0 to 0.005, 0.05, 0.1, 0.2, 0.3, 0.5, 0.75, 1, 1.5, 2, 3, 5, 7.5, 10, 15, 20, 30, 50, 100, 200, 300, and 500 μa . The iR potential drop across the current-measuring resistor does not appear at the cell because the feedback of the current amplifier cancels it. A "current amplifier overload" indicator, which is mounted on the front panel, becomes illuminated whenever the output of the current amplifier exceeds 100 v. The output of the current amplifier that corresponds to full scale on the recorder is 25 v.

A zero-set circuit provides for the cancellation of certain currents, such as those due to residual currents or diffusion currents of ions having lesser half-wave potentials, of magnitude as great as three times the full-scale value of the current range in use. The zero-set control is used to instantaneously set the recorder pen near the right end of the recorder chart paper prior to the start of a polarogram.

A relatively small amount of conventional RC damping is available. A 10-turn, 25,000-ohm potentiometer and a 10- μf capacitor are used.

A peak-follower, functional-operator circuit has been designed that uses nonlinear circuit elements. The output voltages of this circuit consist of the peak values of signals applied to it. A capacitor is charged by the input signal through a thermionic diode so that the capacitor cannot readily discharge below peak values of the input signal. A GAP/R model K2-X operational amplifier, which is wired to function as a voltage follower, isolates the capacitor from the signal bus. The amplifier has an input impedance greater than 100 megohms and an output impedance of less than 1 ohm. A toggle switch mounted on the front panel can be used to switch the peak-follower in or out of the signal bus. This circuit filters out current fluctuations that correspond to the growth and fall of drops from the D.M.E. but introduces very little distortion to the waveform of the polarographic-cell current as averaged through a history of successive drops.

The capacitor memory can be erased by the use of a "diode discharge" switch.

A parallel-T filter network can also be switched into the signal bus by means of a toggle switch.⁴³ In this polarograph a "filter sections" switch permits the choice of any of three combinations of parallel-T networks that correspond to 1 and 2, 4, and 10, times the null frequency of the network of lowest null frequency. The input terminal of the parallel-T filter network is driven by a low-impedance source. The output terminal is connected to a GAP/R model K2-X operational amplifier that is used as a voltage follower so that the parallel-T filter network looks into a very high impedance and so that the signal bus is fed by a source of very low impedance.

By use of a "derivative network" switch, an analog computer circuit can be switched into the signal bus so that the derivative of the polarographic current with respect to the applied potential is recorded as a function of applied potential. The computer consists of a GAP/R model K2-X operational amplifier, wired as an inverting differentiator, followed by another K2-X wired as an inverting, proportioning element.

Two of the four positions of the "function" switch provide for test conditions. The "cell open" position is used to identify on the chart recorder the point corresponding to zero polarographic cell current. In the "test 1 $\mu\text{a}/\text{v}$ " position of the "function" switch a precision resistor is substituted for the polarographic cell so that the operation of the instrument can be checked. This position also makes possible precise and accurate adjustment of the initial and span potentials.

The power supply for the eight electronic analog computer modules consists of a GAP/R model R-100 compound, regulated power supply and of a filament transformer. The d-c power supply for the Hycor magnetic clutch consists of an isolation transformer and a solid-state rectifier.

The recorder consists of an unmodified, low-impedance Brown Electronik strip-chart recorder having a 10-mv span, a 180-rpm pen-drive motor, and a chart speed of 1 in./min.

⁴³M. T. Kelley and D. J. Fisher, "Unique Polarographic Damping Circuit for Selective Elimination of Current Fluctuations Due to Dropping Mercury Electrodes," *Anal. Chem.* 28, 1130 (1956).

RADIOCHEMICAL ANALYSES

S. A. Reynolds

Nuclear Properties

Electromagnetic Radiation from Pu²³⁹, Pu²⁴⁰, and Pu²⁴¹ (W. S. Lyon, F. L. Moore). — The amount of *K* and *L* x rays, together with the amount of gamma radiation associated with the decay of Pu²³⁹, Pu²⁴⁰, and Pu²⁴¹, has been measured. These data will be presented in an open-literature report at a future date.

Experimental *L*-Shell Fluorescence Yields (W. S. Lyon, N. H. Lazar⁴⁴). — The *L* fluorescence yield (w_L) has been measured for a number of elements by means of a coincidence technique in which coincidences between *K* and *L* x rays, $P(L)$, are obtained. The *K* x rays are observed by the use of a 3 in. × 3 in. crystal of sodium iodide, and the *L* x rays are observed by the use of a 1.5 in. × 0.13 in. crystal of sodium iodide in a beryllium can. By means of the expression

$$P(L) = C(K) \epsilon_p \Omega A \frac{K_a}{K} w_L$$

the fluorescence yield can be obtained. The term $C(K)$ represents the counting rate in the window which is due to *K* x rays; ϵ_p is the peak efficiency of the counter for *L* x rays; Ω is the solid angle subtended by the small crystal; A is the absorption correction (transmission of *L* x rays through beryllium and other matter); and K_a/K is the

⁴⁴Physics Division.

measured number of K_a x rays per *K* x-ray transition.⁴⁵

The values obtained thus far are listed in Table 4. The agreement of results with those obtained by Lay,⁴⁶ who used a photographic technique, is excellent.

Measurement of Radioactivity

Effects of Low-Energy Beta Activity on Alpha Counting (S. A. Reynolds). — It has been known for many years that the conventional type of proportional alpha counter responds to high levels of beta activity ($\sim 10^9$ d/min) and that the settings of the voltage and gain controls are critical; for example, the instrument will function as a beta counter at sufficiently high voltage. In order to test the alpha counters in the Analytical Chemistry Division for "beta sensitivity," a number of sources of Sr⁹⁰-Y⁹⁰ were prepared several years ago. These sources have a surface radiation intensity of ~ 4 r/hr. All counters are routinely tested by the use of these sources, and their proper operation is indicated by the observation of a very low counting rate. It has been assumed that any sample emitting beta radiation of less intensity than that of the Sr⁹⁰-Y⁹⁰ source will suffer no beta interference in alpha counting.

C. E. Lamb and L. T. Corbin have observed interference, that is, high and erratic counting

⁴⁵A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment*, 2d ed., p 640, Van Nostrand, New York, 1935.⁴⁶H. Lay, "Die Fluoreszenzausbeute des *L*-Gebiets," *Z. Physik* 91, 533 (1934).Table 4. Measured *L* Fluorescence Yields

Radionuclide	Atomic Number of Daughter	w_L	Remarks
Bi ²⁰⁷	82	0.40	<i>K</i> x rays arise mostly from <i>K</i> capture; no coincidences of <i>K</i> x rays with gamma rays observed
Tl ²⁰⁴	80	0.36	X rays from $\sim 3\%$ electron-capture branch
Hg ²⁰³	81	0.39	<i>K</i> x rays from internal conversion (i.c.) of 0.279-Mev gamma ray
Lu ¹⁷⁶	72	0.26	X rays from i.c. of 0.089-Mev gamma ray
Tm ¹⁷⁰	70	0.22	X rays from i.c. of 0.084-Mev gamma ray
Gd ¹⁵⁹	65	0.18	X rays from noncoincident gamma rays of various energies

rates, in the counting of samples that contained Pa^{233} of much lower activity than the $\text{Sr}^{90}\text{-Y}^{90}$ sources. Recently, in the analysis of certain in-pile loop samples for plutonium, the same effect was observed. Gamma spectrometric studies showed that the principal activities on the plates were Np^{239} and Zr^{95} . The samples had been prepared by extracting the plutonium and evaporating the extract on stainless steel disks, which were then "flamed" (i.e., heated to dull redness in a burner flame). These disks were counted in proportional alpha counters of the standard type in the Pilot Plant Control Laboratory. The counting rates were impossibly high, and they increased with time in the counter.

The studies reported herein were made by means of an alpha counter to which an oscilloscope was attached in order to observe the appearance of the pulses being counted. Beta radiation from the sample plates was measured by means of an end-window proportional beta counter and also by means of a windowless ionization chamber loaned by E. Kuna of the Health Physics Division. Sources of Np^{239} and Pa^{233} were prepared by F. L. Moore.

Several plates were obtained from C. E. Lamb for detailed study. The radiation readings at their surfaces were ~ 4 to 20 mr/hr, and their beta activities were $\sim 1.5 \times 10^5$ to 1×10^6 d/min, principally Np^{239} and Zr^{95} . The counting rates of these plates were observed as a function of voltage. Figure 4 shows a typical curve for one of the samples; curves for a 4-r/hr $\text{Sr}^{90}\text{-Y}^{90}$ source and a plutonium standard are also shown. Similar curves for sources of Np^{239} and Pa^{233} are shown in Fig. 5. One of the neptunium sources contained ~ 2 counts/min of its plutonium daughter. When beta activity from any of the sources was being detected, the oscilloscope showed many small pulses ("hash" or "grass"); however, when only alpha activity was being counted, the pulses were large and had characteristics identical with those from a pure alpha source.

The apparent growth of counting rate as a function of time in the counter was studied for some of the sample plates and for an Np^{239} source. This effect occurred, of course, only at voltages within the beta-sensitive range. The increase in counting rate was apparently independent of the rate of flow of gas through the counter. If the sample was removed from the counter and then

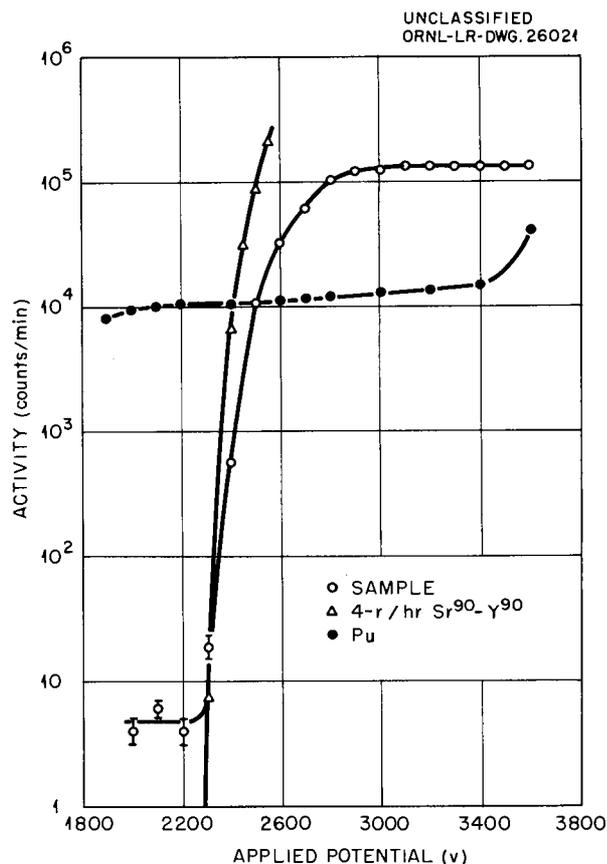


Fig. 4. Voltage vs Count Rate Curves for a Sample, $\text{Sr}^{90}\text{-Y}^{90}$, and Plutonium.

reinserted, the counting rate was low at first and increased as before.

It is apparent that the "plateau" for counting alpha radiation in the presence of moderate levels of low-energy beta radiation is very short. Careful setting of the voltage is required in order to secure proper counting of alpha activity (i.e., to be on the alpha plateau) without detecting beta activity. It appears from the data reported herein and from similar data taken on counters in the Pilot Plant Control Laboratory that a Pa^{233} source of $\sim 10^7$ d/min will serve as a test source for establishing the proper operating voltage. Further, a voltage setting that is about 50 v below the point where no counts are observed from the 4-r/hr $\text{Sr}^{90}\text{-Y}^{90}$ source should be adequate. If the correctness of results on a sample seems doubtful, the sample should be re-counted at a voltage that is 25 v below the normal value in

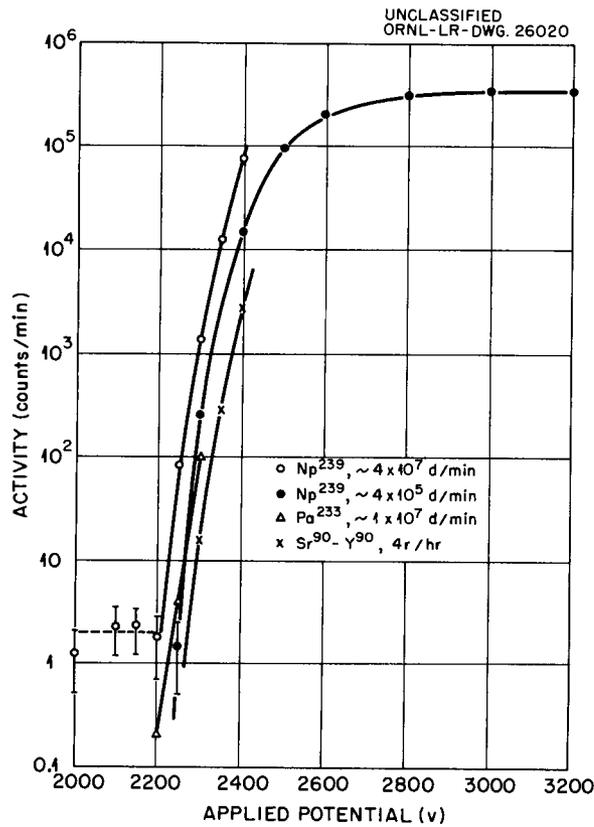


Fig. 5. Voltage vs Count Rate Curves for Np^{239} , Po^{233} , and $\text{Sr}^{90}\text{-Y}^{90}$.

order to confirm that the counts are due to alpha activity. At the conclusion of these studies, two of the counters in the Pilot Plant Control Laboratory were set at the proper voltage.

Instrumental Analyses

Analysis of Radioactive Materials by Gamma Scintillation Spectrometry (J. S. Eldridge,⁴⁷ T. H. Handley, W. S. Lyon, S. A. Reynolds). — A wide variety of samples was analyzed by gamma scintillation spectrometry. They included soil, plant materials, insects, gases, material filtered from air, ground seepage, and metal parts from in-pile loops. The method of gamma scintillation spectrometry is based on the measurement of the gamma photons emitted by the radioactive material. The photopeak energy of the gamma-emitting radio-nuclide provides qualitative identification of the nuclide; quantitative estimation is made by the

measurement of the area under the photopeak, which is then compared with the area under the photopeak obtained from a standard sample of known disintegration rate. The method is rapid and selective. It is limited to mixtures of radio-nuclides that differ sufficiently in energy to permit the photopeaks to be clearly resolved.

In a few cases when standards are not available, the total intrinsic efficiency of the thallium-activated crystal of sodium iodide is used to calculate the disintegration rate. A correction for geometry must also be made. This procedure is not so accurate as that of standards of known disintegration rate; also, other factors, such as branching ratio and conversion coefficient, must be taken into account. For this procedure, agreement between samples is excellent; however, the over-all accuracy suffers markedly.

Beta Scintillation Spectrometry (J. R. Wilkinson,⁴⁸ S. A. Reynolds). — Preliminary studies have been made of the determination of beta spectra by the use of an anthracene crystal (1.5-in. dia, 1-in. height) coupled with a multiplier phototube and a single-channel analyzer. It has been shown that end points are obtained in the spectra which are proportional to maximum beta energies and that conversion electrons (e.g., from $\text{Cs}^{137}\text{-Ba}^{137}$) appear as peaks in the pulse-height distributions. Further study in which a 20-channel analyzer will be used is contemplated.

Radioisotope Analysis

Isotopic Analysis (W. S. Lyon). — A method has been developed for the quantitative determination of each isotope in mixtures of two or more radioactive isotopes of the same element. These have included Re^{186} (90 hr) and Re^{188} (17 hr), Hf^{181} (43 days) and Hf^{175} (70 days), and Cd^{115m} (43 days) and Cd^{115} (54 hr). The method involves the measurement of one gamma ray from each of the isotopes and the determination of the absolute amount of activity by means of the gamma-ray spectrometer that uses a 3-in. by 3-in. crystal of sodium iodide. The method has been used for the assay of numerous isotopic mixtures that have been shipped from the Isotopes Division.

⁴⁷Inorganic Preparations Group.

⁴⁸Summer research participant from The Citadel, Charleston, S. C.

Fission-Product Methods

Analysis of Mixtures of Fission-Product Noble Gases (T. H. Handley, J. S. Eldridge,⁴⁷ W. S. Lyon, S. A. Reynolds, H. A. Parker⁴⁹). – Samples of mixtures of fission-product noble gases were submitted by members of the Solid State Division. These samples, which contained approximately 0.1 to 1 mc of gamma activity, were analyzed by gamma spectrometry and by gamma decay studies in which an ionization chamber was used. The following nuclides were determined in each sample: Kr^{85m}, Kr⁸⁸, Xe¹³³, and Xe¹³⁵. The accuracies of the measurements are unknown; however, it is estimated that the following ranges of errors are reasonable: Kr⁸⁸, ±5%; Xe¹³⁵, ±15%; Kr^{85m}, ±25%; and Xe¹³³, factor of 2. The latter three values are uncertain because of low gamma energies (Xe¹³³, 0.08 Mev; Kr^{85m}, 0.15 Mev; Xe¹³⁵, 0.25 Mev). The decay schemes reported by Thulin⁵⁰ were assumed to be correct.

Heavy Elements

Radiochemical Determination of Ionium (F. L. Moore). – A carrier-free method for the determination of ionium (Th²³⁰) in process solutions of uranium-fluorination "ash" has been developed. Ionium is carried first on lanthanum hydroxide and then on lanthanum fluoride and is then extracted into a 0.5 M solution of 2-thenoyltrifluoroacetone (TTA) in xylene in order to effect high selectivity. The technique gives satisfactory results when applied to process solutions; yields average 97 ± 3%. The method can be used for the determination of ionium or other thorium isotopes in the presence of all other alpha emitters. Details of the method are given in a paper which has been submitted for publication in *Analytical Chemistry*.

Reactor Analyses

Testing for Leaks in the HRT Equipment (W. S. Lyon, G. E. Creek,⁵¹ G. W. Parker⁵¹). – A program is under way to test the HRT equipment for leaks. The vessels and piping to be tested have been pumped to 20 atm of pressure with a volume of air that contained 40 curies of Kr⁸⁵. Samples of the

⁴⁹Radioisotope-Radiochemistry Group.

⁵⁰S. Thulin, *Studies in Nuclear Spectroscopy with Electromagnetically Separated Gaseous Isotopes*, Almqvist and Wiksells, Uppsala, Sweden, 1954.

air that surrounds suspected points of leakage are taken by drawing the samples through charcoal traps; the traps are brought to the laboratory for Kr⁸⁵ determinations. The method consists in the excess gas being pumped off at the temperature of liquid nitrogen, then passed through a lithium furnace in which most of the oxygen is removed and thence to a small charcoal trap cooled in liquid nitrogen. After being passed through a second smaller furnace containing barium metal to remove the last traces of oxygen and gases other than the inert gases and krypton, the gas is swept into a counter tube by means of P-10 gas (90% A-10% CH₄). Krypton-85 is counted in the counter tube at ~2100 v and 1 atm pressure. Throughout the procedure, helium is used as a carrier gas for the Kr⁸⁵. Although considerable difficulty is experienced because of the quenching of the counter by traces of gaseous impurities, work is continuing in order to perfect the method.

Electronuclear Research Program

T. H. Handley

Work is continuing, in cooperation with members of the Electronuclear Research Division, on the investigation of neutron-deficient, rare-earth activities. Two oral presentations^{52,53} of the work were given, and a paper has been published in *The Physical Review*.⁵⁴

Solvent-Extraction Methods

Amine Extractions (F. L. Moore). – A new method has been developed for the liquid-liquid extraction of uranium and plutonium from hydrochloric acid solution. Triisooctylamine dissolved in either xylene or hexone separates uranium and/or plutonium from thorium, alkali metals, alkaline-earth elements, rare-earth elements, zirconium,

⁵¹Chemistry Division.

⁵²T. J. Ward *et al.*, *Electron Capture of Hf¹⁷³ to Levels in Lu¹⁷³*, a paper presented at the meeting of the American Physical Society, St. Louis, Mo., Nov. 29–30, 1957.

⁵³T. J. Ward *et al.*, *Electron Capture of Tb¹⁵⁵ to Levels in Gd¹⁵⁵*, a paper presented at the meeting of the American Physical Society, University of Notre Dame, Notre Dame, Ind., June 21–22, 1957.

⁵⁴J. W. Mihelich, B. Harmatz, and T. H. Handley, "Nuclear Spectroscopy of Neutron-Deficient Rare Earths (Tb Through Hf)," *Phys. Rev.* 108, 989 (1957).

niobium, ruthenium, and other elements that do not form anionic species under the conditions prescribed. The technique is applicable to either macro- or tracer quantities of uranium or plutonium. Details of the method will be published soon in *Analytical Chemistry*.

ACTIVATION ANALYSES

G. W. Leddicotte

Quantitative Applications of Activation Analysis

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

Neutron activation analysis has been used to determine microgram and submicrogram amounts of many elements in a variety of materials. These recent applications are summarized in Table 5. Neutron reactions of the (n, γ) type were used to induce most of the radionuclides that were measured in the determination of the concentrations of the elements; the exceptions are noted in Table 5. Information regarding these reactions has been reported elsewhere.⁵⁵ The neutron irradiations for the analyses were made in either the ORNL Graphite Reactor or the Low-Intensity Test Reactor. Both nondestructive and radiochemical separation techniques were used. All determinations were completed by the comparator-sample technique. Specific determinations believed to be of particular interest are discussed separately in this report; descriptions of the radiochemical separations, if any, and the radioactivity measurements used are included in these discussions.

Nondestructive Methods of Assay in Activation Analysis

G. W. Leddicotte	L. C. Bate
W. T. Mullins	J. F. Emery
W. A. Brooksbank, Jr. ⁵⁶	

Activation analysis has potential as a non-destructive assay method because each nuclear-reaction-induced radionuclide decays with its own characteristic ionizing radiations and half life.

⁵⁵G. W. Leddicotte, "Types of Neutron Reactions," Method No. 5 10102 (2-2-56), ORNL Master Analytical Manual.

⁵⁶Solid State Division.

An early example of direct assay methods involving decay measurements only has been reported⁵⁷ for the determination of microgram amounts of vanadium in oil. An example of a nondestructive method in which beta absorption was used has been reported by Boyd⁵⁸ for the determination of potassium in the presence of sodium. More recently, with the advent of gamma scintillation spectrometry, it has been possible to extend the usefulness of nondestructive activation analysis to the determination of many elements in many materials. Although, in some instances, the major elements present in the sample could give rise to numerous radionuclides that tend to complicate the gamma spectrum, it has been possible to complete quantitative analyses for microgram concentrations of a number of elements by choosing a specific gamma radiation from the spectrum and following its decay by means of repeated measurements of the radioactivity made under the same conditions. In all of these analyses, a comparator-sample method was used to determine the trace-element concentration.

An earlier example of the use of a multichannel gamma spectrometer has been reported elsewhere.⁵⁹ More recent uses of the 20-channel gamma scintillation spectrometer in activation analysis are given in Table 6, which summarizes briefly the nuclear reactions, the radionuclides, and the experimental conditions used, as well as the concentration range of the elements determined. The use of a beta absorption method of analysis for sulfur in plastics is also mentioned in Table 6. Many determinations of trace elements will be made in the future by similar nondestructive techniques.

Determination of Sulfur by Activation Analysis with Fast Neutrons

G. W. Leddicotte	J. F. Emery
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Thermal neutron (n, γ) reactions upon S^{34} and S^{36} produce S^{35} (87.1-day) and S^{37} (5-min), respectively, that can be used in certain analyses. However, in the instance of S^{35} the beta radiations

⁵⁷W. A. Brooksbank, Jr., G. W. Leddicotte, and H. A. Mahlman, "Analysis for Trace Impurities by Neutron Activation," *J. Phys. Chem.* 57, 815 (1953).

⁵⁸G. E. Boyd, "Method of Activation Analysis," *Anal. Chem.* 21, 335 (1949).

⁵⁹G. W. Leddicotte and W. A. Brooksbank, Jr., *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 23 (classified).

ANALYTICAL CHEMISTRY PROGRESS REPORT

Table 5. Summary of Recent Quantitative Applications of Neutron Activation Analysis

Element Determined	Induced Radionuclide	Technique ^a	Sample	Observed Concentration of Element Determined ($\mu\text{g/g}$) ^b	Estimated Limit of Measurement for Element Determined (μg) ^c
Al	Al ²⁸ (2.3 m) or Na ²⁴ (15 h) ^d	RC	Silicon	1.0	0.1
		ND	Soils	10 ³ to 10 ⁴	
Sb	Sb ¹²² (2.8 d) or Sb ¹²⁴ (60 d)	RC	Animal tissue	0.05 to 10.0	0.005
			Silicon	2 to 100	
As	As ⁷⁶ (26.8 h)	RC	Animal tissue	0.005 to 1.0	0.001
			Copper	1 to 2	
			Silicon	0.01 to 2.0	
		ND	Lubricants	0.005 to 0.05	
			Naphtha	0.005 to 4.0	
Br	Br ⁸² (35.87 h)	RC	Animal tissue	1 to 10	0.001
		ND	Naphtha	0.05 to 1.0	
Cd	Cd ¹¹⁵ (53 h) or Cd ^{115m} (43 d)	RC	Zirconium-cadmium alloys	10 ³ to 10 ⁴	0.01
Cs	Cs ^{134m} (3.2 h) or Cs ¹³⁴ (2.3 y)	RC	Animal tissue	1 to 10	0.05
Cl	Cl ³⁸ (38.5 m)	RC	Asbestos packing	10 ³	0.05
			Cadmium sulfide	2 to 20	
			Process solutions	1 to 30	
			Thorium oxide	10 to 225	
		ND	Polythene	10 to 300	
	RC or ND	Santocel	3 to 25		
Cr	Cr ⁵¹ (26.8 d)	RC	Aluminum	1 to 10	0.10
			Electrolytic iron	10 to 100	
			NaK	0.5 to 7.5	
			Process solutions	1 to 10	
			Zirconium	10 ³	
Co	Co ⁶⁰ (5.3 y)	RC	Animal tissue	0.1 to 1.0	0.05
			Nickel	3 to 25	
		ND	Aluminum alloys	10 ³	
			Glass	20 to 30	
			Inconel	10 ³	

Table 5 (continued)

Element Determined	Induced Radionuclide	Technique ^a	Sample	Observed Concentration of Element Determined ($\mu\text{g}/\text{g}$) ^b	Estimated Limit of Measurement for Element Determined (μg) ^c
Cu	Cu^{64} (12.8 h)	RC	Aluminum	20 to 30	0.001
			Beryllium	1 to 15	
			Lithium hydroxide	1 to 10	
			Silicon	1 to 10	
			Zirconium	1 to 330	
		ND	Aluminum alloys	20 to 30	
		RC or ND	Lithium	20 to 120	
Ga	Ga^{72} (14.3 h)	RC	Aluminum	1 to 5	0.01
Au	Au^{198} (2.69 d)	ND	Palladium	80 to 100	0.001
Hf	Hf^{181} (45 d)	RC	Nickel alloys	8 to 220	0.05
			Potassium fluoride-- zirconium fluoride	0.002 to 0.20	
In	In^{116m} (54 m)	RC	Zirconium alloys	10^3	0.0001
I	I^{128} (25 m)	RC	Blood protein	1 to 10	0.05
Ir	Ir^{194} (19.0 h) or Ir^{192} (74.4 d)	ND	Palladium	4 to 5	0.0001
Fe	Fe^{59} (45.1 d)	RC	Lead	0.8 to 30	0.2
			NaK	1 to 10	
			Silicon	1 to 10	
			Zirconium	1 to 200	
Mn	Mn^{56} (2.6 h)	RC	Lithium hydroxide	0.5 to 1.5	0.0001
			Lubricants	0.001 to 10.0	
		ND	Beryllium	0.001 to 1.0	
		Soils	10^1 to 10^3		
		RC or ND	Lithium	0.1 to 8.0	
Hg	Hg^{197m_2} (23 h)	RC	Organic solutions	0.01 to 100	0.1
Mo	Mo^{99} (67 h)	RC	Zirconium	1.0	0.2
			Zirconium alloys	1.0	

ANALYTICAL CHEMISTRY PROGRESS REPORT

Table 5 (continued)

Element Determined	Induced Radionuclide	Technique ^a	Sample	Observed Concentration of Element Determined ($\mu\text{g/g}$) ^b	Estimated Limit of Measurement for Element Determined (μg) ^c
Ni	Ni ⁶⁵ (2.56 h) or Co ⁵⁸ (72 d) ^e	RC	Aluminum	1 to 5	0.1
			Aluminum alloys	1 to 5	
			Animal tissue	0.5 to 2.0	
			Lubricants	1 to 20	
			NaK	1 to 5	
			Silicon	1 to 20	
			Zirconium	3 to 20	
Os	Os ^{191m} (14 h) or Os ¹⁹¹ (16.0 d) or Os ¹⁹³ (30.6 h)	RC	Palladium	10 to 100	0.02
O	F ¹⁸ (112 m) ^f	RC or ND	Lithium	10 ² to 10 ⁴	20.0
			Zirconium	10 ²	
P	P ³² (14.3 d)	RC	Lithium metal	0.5 to 1.0	0.04
			Silicon	2.0 to 5.0	
K	K ⁴² (12.4 h)	RC	Tissue	10 ² to 10 ³	0.02
		ND	Soils	10 ³	
Rb	Rb ⁸⁸ (17.8 m) or Rb ⁸⁶ (19.5 d)	RC	Animal tissue	1 to 10	0.1
			Water	0.5 to 8.0	
Sc	Sc ⁴⁶ (85 d)	ND	Beryllium	10 to 15	0.005
Se	Se ^{81m} (56.5 m) or Se ⁷⁵ (127 d)	RC	Animal tissue	2	0.02
			Arsenic	2 to 20	
			Steroids	10 to 20	
		ND	Quartz	1	
Si	Si ³¹ (2.6 h)	RC	Zirconium	4 to 100	1.0
			Zirconium alloys	4 to 100	
Ag	Ag ^{110m} (270 d)	RC	Palladium	1	0.1
Na	Na ²⁴ (15.0 h)	RC	Aluminum	1 to 10	0.007
			Animal tissue	10 ³	
			Magnesium	1 to 10	
		ND	Lithium	10 to 30	
		Soil	10 ¹ to 10 ⁴		

Table 5 (continued)

Element Determined	Induced Radionuclide	Technique ^a	Sample	Observed Concentration of Element Determined ($\mu\text{g/g}$) ^b	Estimated Limit of Measurement for Element Determined (μg) ^c
Sr	Sr^{87m} (2.8 h)	RC	Animal tissue	6 to 30	0.5
S	S^{35} (87.1 d) or P^{32} (14.3 d) ^g	RC	Aluminum alloys	1 to 100	1.0
			Arsenic	40 to 150	
			Benzene	1 to 7	
			Lithium	80 to 250	
			Lithium iodide	20 to 600	
			Nickel	6 to 1000	
			Nitrobenzene	1 to 7	
			Silicon	100	
			Sodium fluoride— zirconium fluoride	20 to 760	
				ND	
Ta	Ta^{182} (111 d)	ND	Lithium fluoride	0.1 to 10	0.002
			Niobium oxide	10^3 to 10^4	
			Yttrium	0.1 to 10	
			Cerium	0.1 to 10	
		RC or ND			
Te	Te^{131m} (30 h)	RC	Animal tissue	10 to 100	0.2
			Arsenic	10 to 330	
Th	Pa^{233} (27.4 d) ^b	RC	Flue dusts	10 to 100	0.01
			Soils	10^3 to 10^4	
			Water	0.07 to 1.0	
Sn	Sn^{125} (9.4 d)	RC	Aluminum	1.0	0.5
Ti	Sc^{46} (85 d) ⁱ or Sc^{47} (3.43 d) ⁱ	ND	Beryllium	10 to 15	5.0
W	W^{188} (24.0 h) or W^{185} (73.2 d)	RC	Iron	3 to 160	0.001
			Nickel	3 to 160	
U	Np^{239} (2.33 d) ^j or Ba^{140} (12.8 d) ^k	RC	Aluminum-uranium fuel elements	0.005 to 260	0.0001
			Beryllium	5 to 10	
			Flue dusts	10 to 100	
			Soils	10^2	

ANALYTICAL CHEMISTRY PROGRESS REPORT

Table 5 (continued)

Element Determined	Induced Radionuclide	Technique ^a	Sample	Observed Concentration of Element Determined ($\mu\text{g/g}$) ^b	Estimated Limit of Measurement for Element Determined (μg) ^c
U	Np ²³⁹ (2.33 d) ^j or Ba ¹⁴⁰ (12.8 d) ^k	RC	Water	0.0001 to 15.0	
		RC or ND	Zirconium phosphide	10 ³	
Zn	Zn ^{69m} (13.8 h) or Zn ⁶⁵ (250 d)	RC	Animal tissue	10 ¹ to 10 ³	0.02
		RC or ND	Silicon	10 to 20	
			Aluminum	1 to 25	
Zr	Zr ⁹⁷ (17.0 h) or Zr ⁹⁵ (65 d)	RC	Animal tissue	10	0.2
		RC or ND	Hafnium oxide	10 to 100	
			Indium alloys	10 ⁴ to 10 ⁵	

^aND = nondestructive assay; RC = radiochemical separation.

^bThe number of determinations varied; therefore a range is given for the element concentration.

^cBased on the conditions of irradiation and analysis employed. This value will vary with the duration of the irradiation, neutron flux, length of period required for separation or assay after discharge of sample from the reactor, and efficiency of counter used in the measurements of radioactivity.

^dProduced by the reaction $\text{Al}^{27}(n,\alpha)\text{Na}^{24}$.

^eProduced by the reaction $\text{Ni}^{58}(n,p)\text{Co}^{58}$.

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

^gProduced by the reaction $\text{S}^{32}(n,p)\text{P}^{32}$.

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

ⁱProduced by the reactions (1) $\text{Ti}^{46}(n,p)\text{Sc}^{46}$ and (2) $\text{Ti}^{47}(n,p)\text{Sc}^{47}$.

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

^kProduced by the reaction $\text{U}^{235}(n,f)$ fission products, i.e., Ba¹⁴⁰, etc.

are weak and are not easily measured. Sulfur-37 is too short-lived to permit a radiochemical analysis. Thus, the reaction $\text{S}^{32}(n,p)\text{P}^{32}$ has been used most frequently in activation analyses to determine microgram amounts of sulfur in materials resulting from corrosion studies. These samples include nickel metal, lithium metal, and fluoride salts. In this work, P³² (14.3-day) is separated radiochemically after the irradiated sample has been dissolved, and its radioactivity is measured in a Geiger-Mueller counter. Typical results obtained in analyses of this type are shown below (the

results obtained for lithium hydroxide indicate that the sample was not homogeneous):

Sample	Sulfur Concentration ($\mu\text{g/g}$)
Nickel	85.8 ± 2.2
	74.7 ± 3.5
Lithium	88 ± 1
Lithium hydroxide	100, 88
Metal fluorides	48.5 ± 2.5
	5.0 ± 0.8
	18.4 ± 0.2

Table 6. Typical Examples of Nondestructive, Activation Analysis Techniques

Element Determined	Sample	Nuclear Reaction	Half Life of Induced Nuclide	Activity Observed	Instrument Used	Potential Interferences Avoided
Al	Soil	$Al^{27}(n,\gamma)Al^{28}$	2.3 m	1.80-Mev gamma	Gamma scintillation spectrometer	**
A	Water	$A^{40}(n,\gamma)A^{41}$	1.82 h	1.30-Mev gamma	Gamma scintillation spectrometer	**
Co	Inconel	$Co^{59}(n,\gamma)Co^{60}$	5.3 y	2.55-Mev gamma*	Gamma scintillation spectrometer	Cr ⁵¹ , Co ⁵⁸ , Fe ⁵⁹
Mn	Beryllium, lithium	$Mn^{55}(n,\gamma)Mn^{56}$	2.58 h	0.85-Mev gamma	Gamma scintillation spectrometer	**
Na	Lithium	$Na^{23}(n,\gamma)Na^{24}$	15 h	2.75-Mev gamma	Gamma scintillation spectrometer	K ⁴² , Cl ³⁸
S	Plastics	$S^{32}(n,p)P^{32}$	14.3 d	1.75-Mev β^-	G-M counter	**
Cl	Polythene	$Cl^{37}(n,\gamma)Cl^{38}$	37.3 m	2.1-Mev gamma	Gamma scintillation spectrometer	Na ²⁴
V	Petroleum	$V^{51}(n,\gamma)V^{52}$	3.76 m	1.41-Mev gamma	Gamma scintillation spectrometer	**

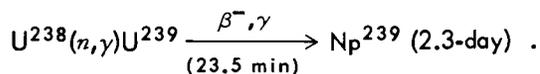
***Sum-peak** resulting from the coincidence of 1.17- and 1.38-Mev gamma radiations.

**There was no apparent interference in the type of material analyzed.

Use of Activation Analysis in the Isotopic Analysis of Uranium

G. W. Leddicotte

A special study was completed of the practical application of neutron activation analysis to the determination of U²³⁵/U²³⁸ isotope ratios. Uranium-235 was determined by the reaction U²³⁵(n, fission)Ba¹⁴⁰. The Ba¹⁴⁰ (12.8-day) was separated by an adaptation of the radiochemical procedure used in the determination of Ba¹⁴⁰ as a fission product.⁶⁰ Uranium-238 was determined by the neutron reaction



The radiochemical procedure used to separate Np²³⁹ is described elsewhere.⁶¹ Typical results

obtained in these analyses are shown below, where columns 1 and 2 give the average of results obtained in analysis of triplicate portions of each sample and the calculated relative standard deviation is <5%:

Weight of U ²³⁵ (mg)	Weight of U ²³⁸ (mg)	U ²³⁵ Enrichment (%)
0.00459	0.090	4.8
0.0192	0.077	20.0
0.000617	0.090	0.7
0.0685	0.023	74.9
0.0842	0.0028	97.0

In a further study, similar activation analysis techniques were used to determine the U²³⁵/U²³⁸ isotopic ratio in samples resulting from investigations in the fabrication process of aluminum-clad fuel plates. To some extent, it is significant that an isotopic ratio can be established by the activation analysis method for concentrations of

⁶⁰D. N. Hume, N. E. Ballou, and L. E. Glendenin, CN-2815, p 19-22 (June 30, 1945) (classified).

⁶¹H. A. Mahlman and G. W. Leddicotte, *Anal. Chem. Semiann. Prog. Rep. April 20, 1954*, ORNL-1717, p 15 (classified).

ANALYTICAL CHEMISTRY PROGRESS REPORT

total uranium as low as a few parts per billion. Typical results are given below (the theoretical enrichment of fuel plates was 93% U^{235}):

Uranium in Fuel Plate ($\mu\text{g/g}$)		U^{235} Enrichment (%)
U^{235}	U^{238}	
4.13, 4.35	0.23, 0.29	94.2
5.36, 5.03	0.31, 0.30	94.3
0.083, 0.077	0.0058, 0.0054	93.2
3.62, 3.22	0.30, 0.30	92.0
5.3, 5.9	0.37, 0.41	93.3

Determination of Oxygen by Activation Analysis

L. C. Bate G. W. Leddicotte

The method of Osmond and Smales⁶² for the determination of microgram concentrations of oxygen in beryllium has been modified to provide a satisfactory analytical method for trace oxygen in lithium and in zirconium. The tritons, H^3 , produced by the reaction $Li^6(n,\alpha)H^3$ can be effectively used to bombard the O^{16} atoms in these materials in order to produce F^{18} by the reaction $O^{16}(H^3,\alpha)F^{18}$. Fluorine-18 decays with positron emission and has a half life of 1.87 hr.

In the assay of lithium for oxygen the lithium in the sample matrix serves as the source of the tritons. After the irradiation the lithium is cleaned, weighed, and analyzed. The analysis can be completed either by nondestructive assay and the measurement by means of a gamma spectrometer of the 0.51-Mev annihilation gamma, which accompanies the positron emission, or by radiochemical separation in which contaminant radioelements are separated from a solution of the irradiated sample. Further characterization of the F^{18} can be made by a decay study.

In the analysis of zirconium, thin foils of the sample are immersed in a solution of LiF or packed in LiF powder for the neutron irradiation in the reactor. After the irradiation the foils are removed from the LiF and are assayed, usually by

a nondestructive method in which a gamma spectrometer is used. In the analyses the oxide coating of the foil was removed by use of an etch solution and was analyzed independently of the sample matrix. In all the analyses a comparator-sample method was used. Reports of these investigations will be made. Some typical results are given below:

Sample	Oxygen Concentration ($\mu\text{g/g}$)
Lithium	1200, 1240
Lithium	19,700, 22,700
Zirconium	20 to 100

A calculated limit of quantitative measurement for this method shows that it should be possible to determine as little as 20 ppm of oxygen. The sensitivity can be increased by the use of larger neutron sources, longer periods of irradiation, and more efficient methods of separation and measurement of the radioactivity. This method is now being used to determine oxygen in aluminum and beryllium, and in fluoride salts.

Quantitative Determination of Trace Elements in Animal Tissue

G. W. Leddicotte

In a special investigation for the Health Physics Division, activation analysis has been applied to the quantitative determination of trace amounts of arsenic, antimony, bromine, cesium, cobalt, potassium, rubidium, selenium, sodium, strontium, tellurium, zinc, and zirconium in animal tissues. The neutron reactions, conditions of irradiation, and methods of processing the irradiated samples will be reported soon for the analysis of such samples as bone, kidney, spleen, ovaries, testes, liver, and lung tissues. Typical results obtained in this work are included in Table 5.

Activation Analysis as a Qualitative or Semiquantitative Method

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

The use of activation analysis as a qualitative or semiquantitative analytical method has been

⁶²R. G. Osmond and A. A. Smales, *The Determination by Radioactivation of the Oxygen Content of Powdered Metals with Particular Reference to Beryllium*, AERE-C/R-1233 (Aug. 17, 1953).

reported.⁶³⁻⁶⁶ The results of the extended use of this method for the analysis of a number of materials are summarized in Table 7. In these applications, the analyses were completed either by a radiochemical separation procedure or by a nondestructive method; either a single-channel or a 20-channel gamma scintillation spectrometer was used. The radionuclides identified were also characterized by means of radioactive decay measurements.

Use of Activation Analysis in Reactor Technology

J. F. Emery R. L. Blanchard⁶⁷
 G. W. Leddicotte D. W. Moeller⁶⁸

Special studies involving the identification and determination of radionuclides in reactor cooling water, the determination of trace amounts of argon in water, and the determination of the amount of radioactivity induced into certain selected materials

⁶³H. A. Mahlman and G. W. Leddicotte, *Anal. Chem. Semiann. Prog. Rep. April 20, 1954, ORNL-1717, p 16-17 (classified).*

⁶⁴M. M. Vick, H. A. Mahlman, and G. W. Leddicotte, *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954, ORNL-1788, p 18 (classified).*

⁶⁵J. H. Oliver *et al.*, "Activation Analysis as a Qualitative or Semiquantitative Method," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955, ORNL-1973, p 14.*

⁶⁶J. H. Oliver, W. A. Brooksbank, and G. W. Leddicotte, *Anal. Chem. Semiann. Prog. Rep. April 20, 1956, ORNL-2070, p 14 (classified).*

by irradiation under controlled conditions have been completed. In these studies, techniques developed in activation analysis were employed. In most of the analyses the measurements of radioactivity were made by means of a gamma scintillation spectrometer. Information pertinent to these studies is given below.

Identification and Determination of Radionuclides in Reactor Cooling Water. - Moeller⁶⁹ showed that the nature and levels of activity of radionuclides in the cooling water of the ORNL Low-Intensity Test Reactor (LITR) readily indicate unusual conditions in the reactor system. These conditions could result from the rupture of fuel elements, failure of experiments, or excessive corrosion. Thus, the monitoring of the coolant system is essential to safe, as well as efficient, reactor operation. Radionuclides identified in the cooling system of the LITR included A⁴¹, Na²⁴, Np²³⁹, Cu⁶⁴, I¹³¹, I¹³², I¹³³, I¹³⁵, Mo⁹⁹, Tc^{99m}, Mn⁵⁶, Sr⁹¹, Y^{91m}, F¹⁸, Sb¹²², Pa²³³, Ba¹⁴⁰, La¹⁴⁰, Co⁶⁰, Ce¹⁴³, Ce¹⁴¹, and Te¹³¹. These were of two groups: fission products and neutron-induced radionuclides. Moeller⁶⁹ discusses the source of

⁶⁷U. S. Public Health Service trainee, assigned to ORNL Analytical Chemistry Division.

⁶⁸U. S. Public Health Service, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

⁶⁹D. W. Moeller, *Radionuclides in Reactor Cooling Water - Identification, Source and Control*, ORNL-2311 (June 12, 1957).

Table 7. Results of Qualitative Analysis of Certain Materials by Activation Analysis

Sample	Radionuclides*	
	Positively Identified	Probably Present
Alcohol	Na ²⁴ , Cl ³⁸	
Graphite	As ⁷⁶ , Sb ¹²² , Cu ⁶⁴ , Na ²⁴	
Thorium oxide	Pa ²³³	
Lithium	Mn ⁵⁶ , Cu ⁶⁴ , As ⁷⁶ , F ¹⁸ , Na ⁶⁴	Rb ⁸⁶ , K ⁴²
Lithium hydroxide	Cu ⁶⁴ , Na ²⁴ , F ¹⁸ , As ⁷⁶	Sb ¹²²
Animal tissue	Se ⁷⁵ , Te ¹³¹ , Cu ⁶⁴ , Na ²⁴ , As ⁷⁶ , Mn ⁵⁶ , K ⁴² , Rb ⁸⁶ , Cs ¹³⁴	Ag ¹¹⁰ , Br ⁸²
Beryllium	Mn ⁵⁶ , Sc ⁴⁶ , Np ²³⁹ , Cu ⁶⁴	Cr ⁵¹
Magnesium hydroxide	Cu ⁶⁴ , Na ²⁴ , As ⁷⁶ , Mn ⁵⁶	Sb ¹²²

*Products of (n,γ) reactions.

each radionuclide and gives information concerning its control.

In a less extensive investigation, Emery and Leddicotte⁷⁰ have studied the radionuclides found in the cooling water of the Bulk Shielding Reactor. The radionuclides A^{41} and Na^{24} and fission-product radioactivities were observed.

Determination of Trace Amounts of Argon in Water. — The results of Moeller's study⁶⁹ suggested the application of activation analysis techniques to the determination of the argon content of natural waters by use of the reaction $A^{40}(n,\gamma)A^{41}$ (1.82-hr). After a neutron irradiation the water samples were analyzed by means of a gamma scintillation counter. A typical gamma spectrum for A^{41} is shown in Fig. 6. The small gamma peak at approximately 0.23 Mev is believed to be associated with the decay of Xe^{135} (9.2-hr). On the basis of the observed radioactivity, it was estimated that at least 0.16 μg of argon per milliliter was present in the water analyzed. This work is now being extended to include the analysis of water from other sources.

Measurement of Induced Radioactivities. — Non-destructive activation analysis techniques, in which gamma scintillation spectrometry is utilized, have been used to determine the amount of radioactivity induced into the major and minor components of certain selected materials during an irradiation for a given time interval and at a definite neutron flux. Figure 7 shows the results of the application of such a technique to the assay of beryllium metal that was to be used in a reactor experiment. The observed radioactivity was used to establish an order of intensity of radioactivity, as well as to establish an order of magnitude for the concentration of the element producing the radionuclide. Other types of sample materials to be used in a reactor are being analyzed by similar techniques.

Particle-Size-Distribution Analysis by the Activation Analysis—Sedimentation Method

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

The previously described activation analysis—sedimentation method⁷¹ of particle-size-distribution analysis continues to be used in the analysis of thorium oxide. Studies concerned with convection effects caused by temperature differences and air currents (which can cause particle motion diverse

from the true motion of sedimentation) and with the analysis of the sample in an aqueous⁷¹ and in a high-viscosity⁷² medium have been made. Other studies were made in order to establish an analytical method based upon the use of acetone or methanol as a supporting medium. Also, the precision of the method was evaluated.

The results of the studies of the effects of convection showed that the insulation of the sedimentation tube would minimize small temperature changes and other effects within the sample environment. In the apparatus now used the sedimentation tube (30-mm OD) is placed inside a larger glass tube (50-mm ID), which forms an insulation jacket. The jacket is sealed to the sedimentation tube and is provided with attachments which permit it to be filled with water for additional insulation. Insulation of the sedimentation tube results in a better control of the sedimentation of particles having sizes greater than 5.0 μ (Fig. 8).

The second study resulted in a modification of the method to provide a means of analyzing samples of thorium oxide that contained particles of size greater than 7.0 μ without the sample having to be reanalyzed in a high-viscosity supporting medium.⁷² The method was modified to include a step for the conversion from water (0.917 centipoise) to a high-viscosity medium, in this instance, glycerol-water (19.53 centipoises). In this step the irradiated thorium oxide is allowed to settle in the aqueous medium for a certain time interval, after which the supernatant liquid is siphoned from the settled slurry and is replaced with the high-viscosity medium. The settled thorium oxide is reslurried and allowed to settle in the usual manner. Any loss of small-sized particles during the removal of the supernatant liquid and any dilution effects are compensated by means of an experimentally determined factor, K. Figure 9 shows typical results obtained by means of this method of analysis.

⁷⁰J. F. Emery and G. W. Leddicotte, *Survey of Reactor Cooling Water from Bulk Shielding Facility*, ORNL CF-57-11-41 (Nov. 7, 1957).

⁷¹G. W. Leddicotte and H. H. Miller, *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954*, ORNL-1788, p 21-23 (classified).

⁷²L. C. Bate, G. W. Leddicotte and R. E. Druschel, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 24 (classified).

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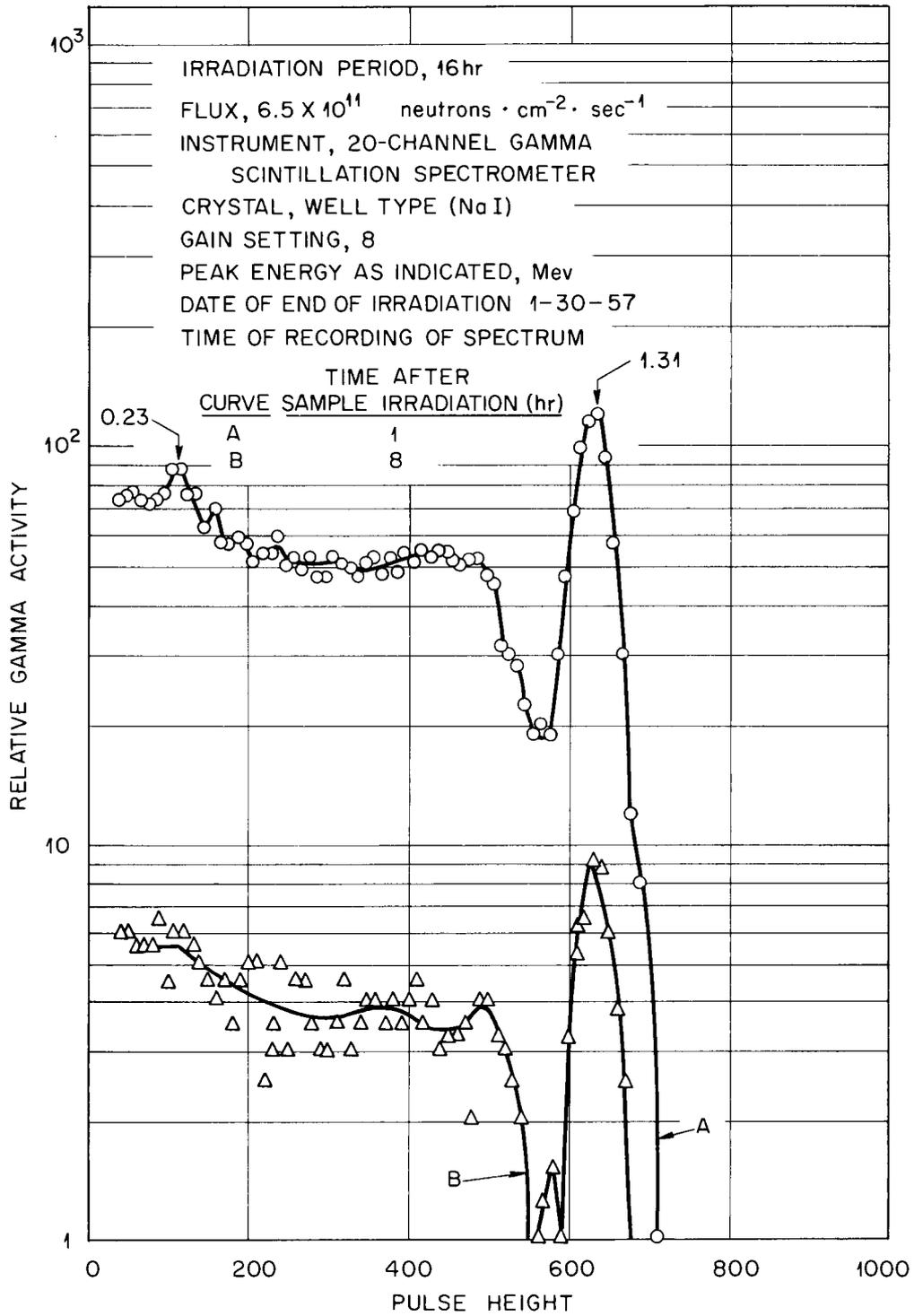


Fig. 6. Gamma Spectral Data for Neutron-Irradiated LITR Makeup Water: Radioactive Gas Nuclides.

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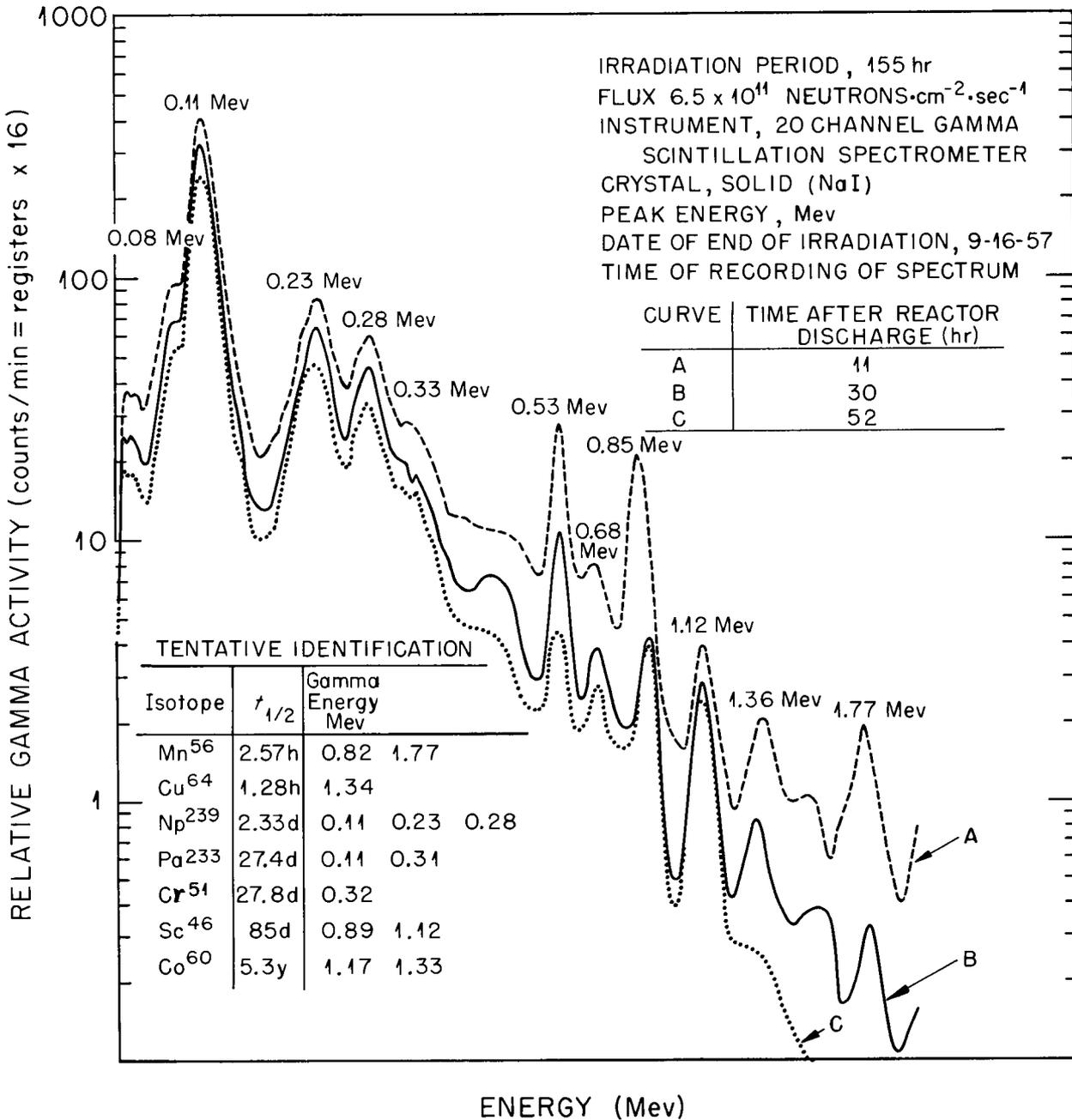


Fig. 7. Typical Gamma Spectrum of Irradiated Beryllium.

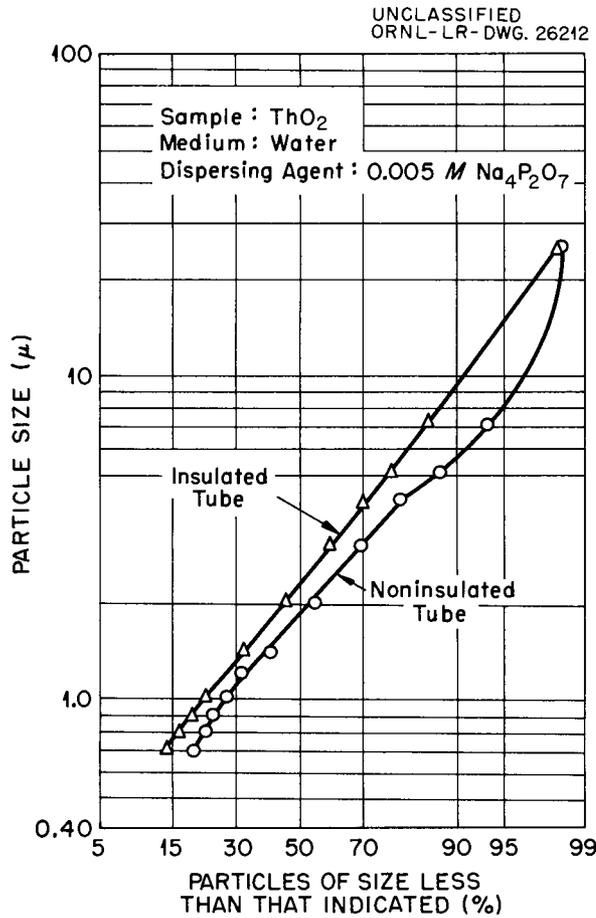


Fig. 8. Effect of Insulation of the Tube in Particle-Size-Distribution Analysis.

Studies of low-viscosity media have provided a rapid analytical method for samples that originated from a pilot-plant production operation. Techniques similar to those already described⁷¹ were used in the analysis. Sedimentation paths of 40 and 15 cm were used in establishing the conditions of analysis now being used. Figure 10 shows typical data obtained by this technique.

Data obtained from the repeated analysis of a sample of thorium oxide known as D-16 were compiled over a period of two and one-half years to show the precision of the activation analysis-sedimentation method. The precision was found to be excellent and will be discussed in a forthcoming report.

The activation analysis-sedimentation method has also been used satisfactorily for the particle-size-distribution analysis of thorium oxalate,

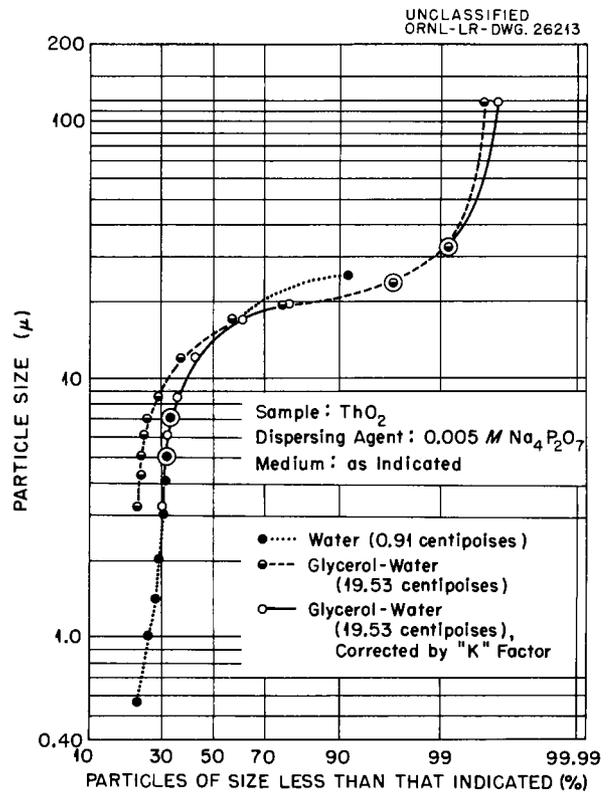


Fig. 9. Particle-Size Distribution of Thorium Oxide by a Modified Activation Analysis-Sedimentation Method.

thorium silicate, uranium dioxide, and zirconium oxide. The analysis of thorium oxalate was made in a variety of chemical dispersing agents.

Determination of Particle-Size Distributions in Multiple-Component Systems by Activation Analysis

G. W. Leddicotte L. C. Bate

The activation analysis-sedimentation⁷¹ method of particle-size-distribution analysis has been applied primarily to single-component systems, such as thorium oxide. Similar techniques were used to analyze samples that were mixtures of the oxides of thorium and uranium and mixtures of the oxides of chromium, iron, zirconium, and uranium (Fig. 11). However, these analyses indicated only the composite behavior of the mixed oxides and did not differentiate any of the individual components. Thus, on the assumption that each individual component of the mixture could behave in its own particular way, a method that makes use of gamma scintillation spectrometry was devised. The

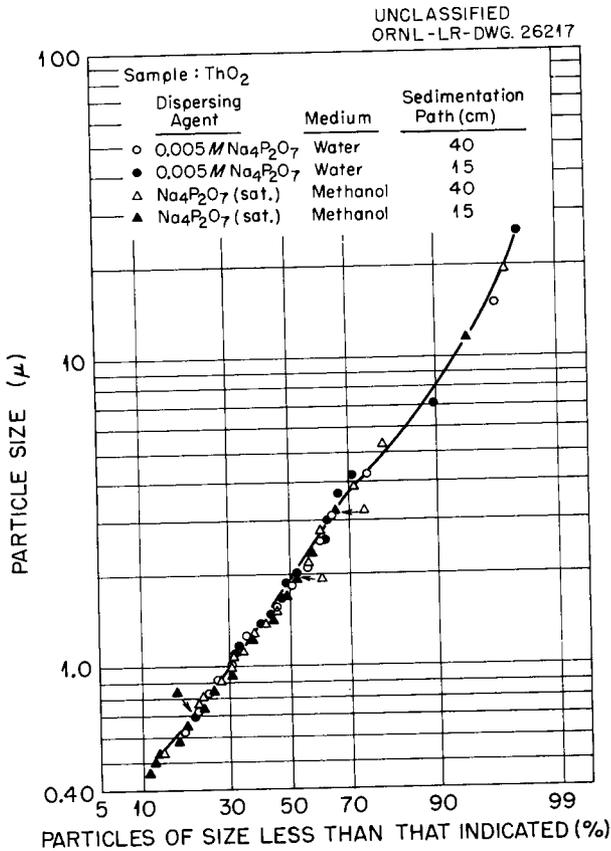


Fig. 10. Particle-Size Distribution of Thorium Oxide in Low-Viscosity Media.

equipment consists of a sedimentation tube and a rack to support a thallium-activated crystal of sodium iodide. The signal resulting from the radioactivity observed at any particular time of sedimentation is fed into a triple-discrimination unit, and the radioactivity that is observed for each specific gamma radiation is displayed on the strip chart of a Brown recorder. The observed radioactivity at any time of measurement is then correlated with the total radioactivity of the sample in order to estimate the concentration of particles of any given size. The particle size is calculated by means of Stokes' law, which relates the specific gravity of the particles, viscosity of the supporting medium, time of sedimentation, etc., to each other.

This activation analysis-sedimentation method is unique in that each component of the mixture

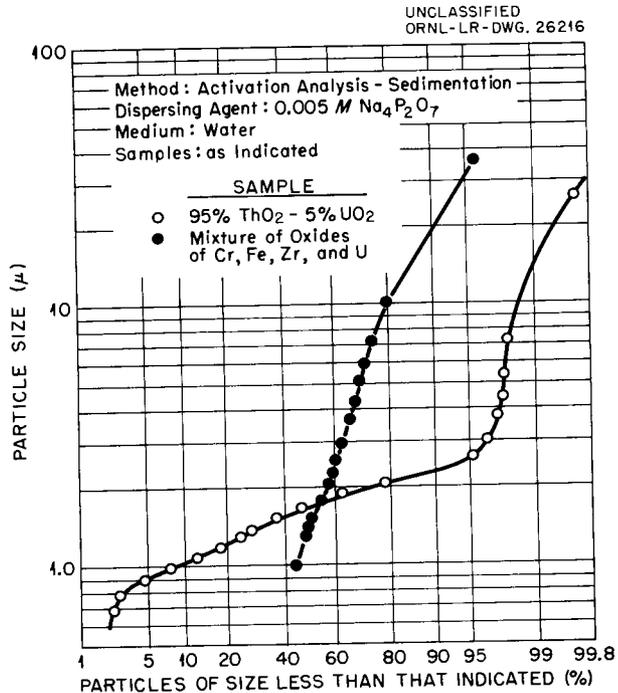


Fig. 11. Particle-Size Distribution of Multicomponent Systems Determined by Gross Activity Measurements.

can produce radionuclides that have characteristic decay rates and ionizing radiations (particularly gamma), and therefore each component of a multiple-component system can be differentiated. The analyses reported herein could have been made with a great deal more exactness if a gamma spectrometer of the multichannel (20 or more channels) type could have been used.

The technique of analysis and related information will be described in a forthcoming report. Typical examples of its application to the analysis of coprecipitated and autoclaved 95% thorium oxide-5% uranium oxide samples are given in Fig. 12. The results for the coprecipitated sample indicate nonhomogeneous behavior for each individual component of the mixture.

Figure 13 shows the results of the analysis of synthetic mixtures of the oxides of chromium, iron, zirconium, and uranium. These results indicate nonhomogeneous behavior for each component in sample B.

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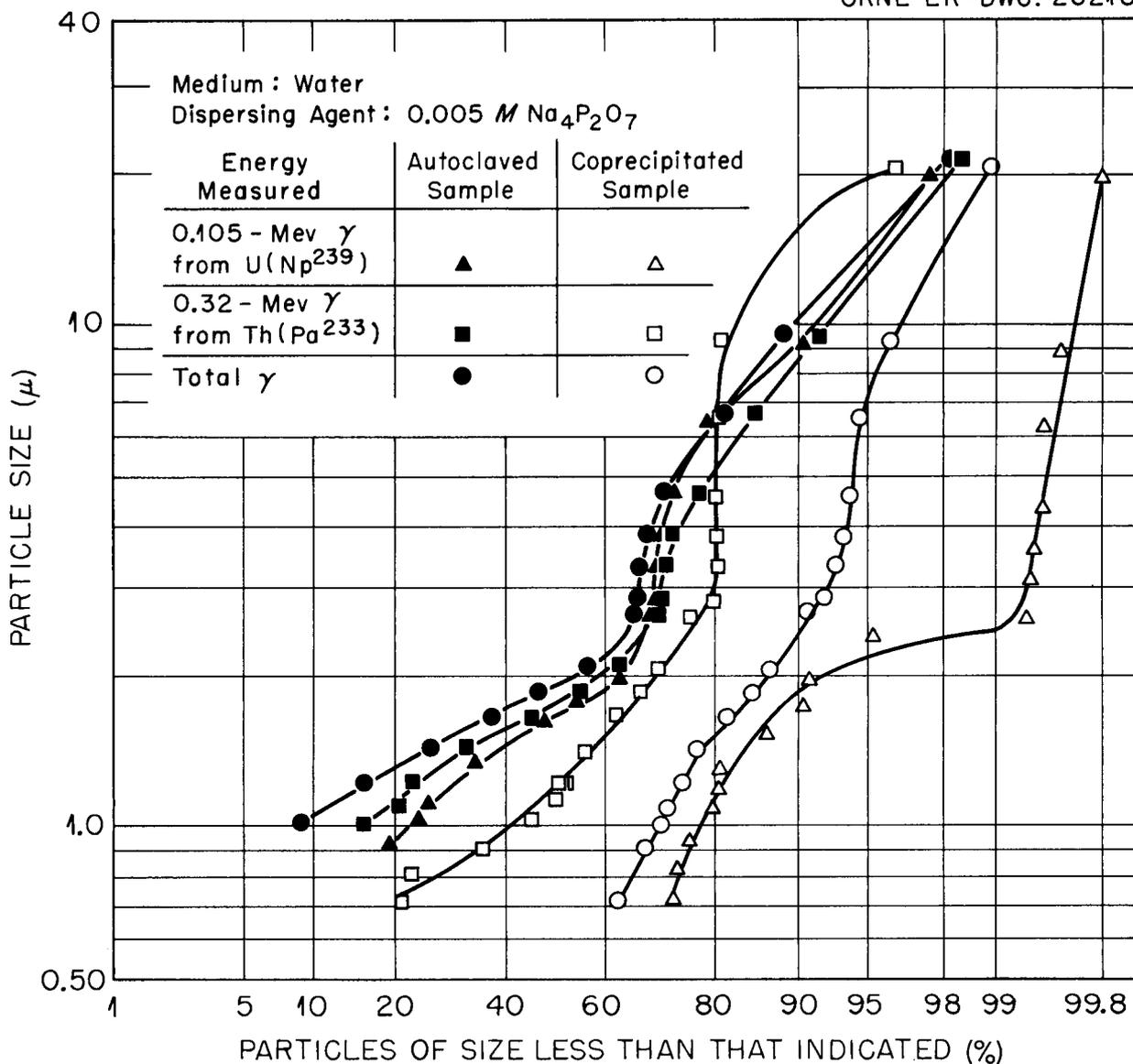


Fig. 12. Particle-Size Distribution of 95% ThO₂-5% UO₂ Determined by an Activation Analysis-Sedimentation Method That Makes Use of a Gamma Spectrometer.

Particle-Size-Distribution Analysis in the Submicron Range By Activation Analysis-Centrifugation Method

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

Particle-size-distribution analyses have been made in the submicron range on a variety of samples by an activation analysis-centrifugation

method.^{73,74} The activation by neutron irradiation of a particle to produce an induced radionuclide in a stable isotope of an element contained in that particle makes possible a very sensitive and

⁷³G. W. Leddicotte and S. A. Reynolds, *Neutron Activation Analysis*, ORNL CF-56-7-106 (July 20, 1956).

⁷⁴S. W. Martin, "Particle-Size Distributions of Pigment Suspensions: Determination with a Beaker-Type Centrifuge," *Ind. Eng. Chem. Anal. Ed.* 11, 471 (1939).

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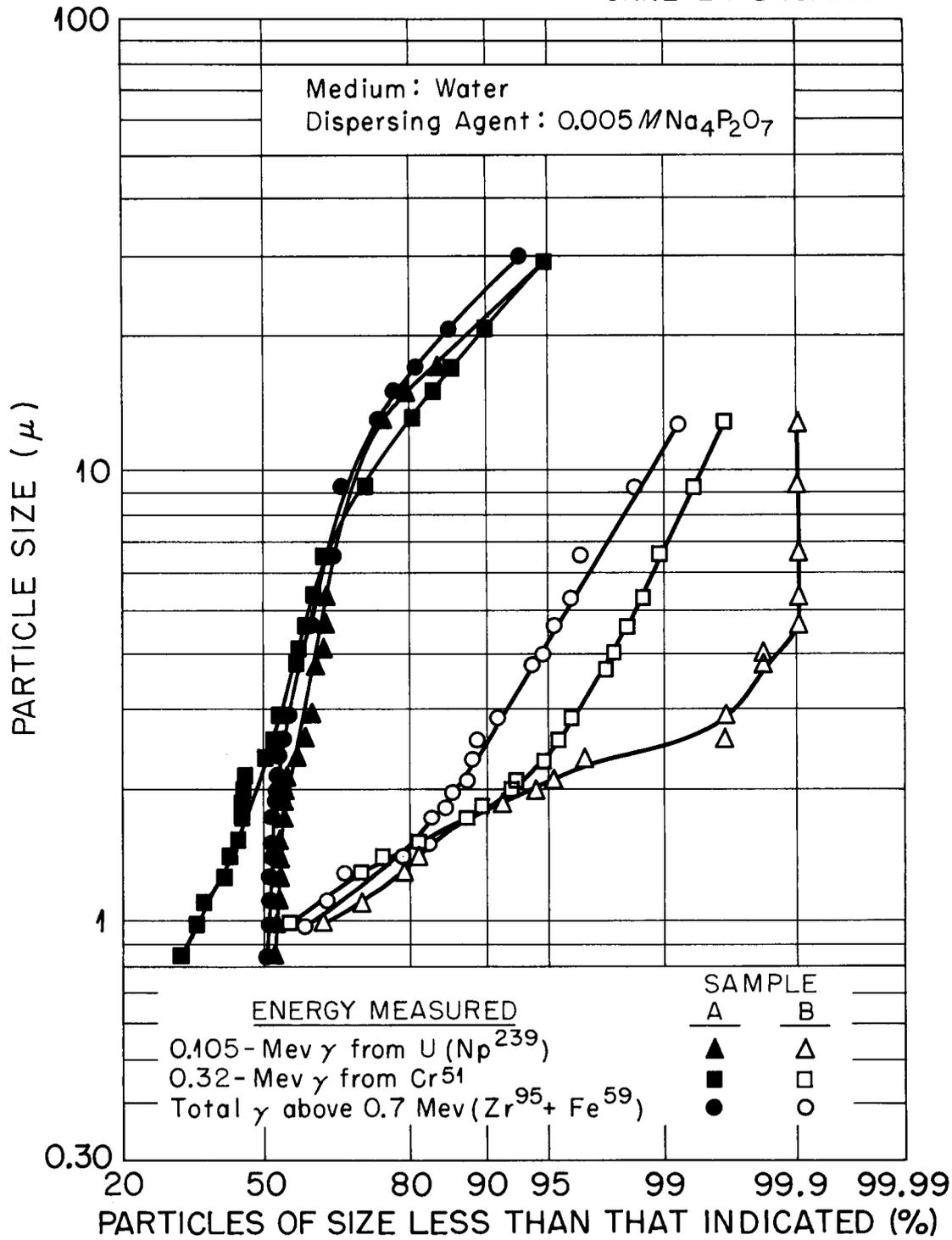


Fig. 13. Particle-Size Distribution of a Mixture of the Oxides of Chromium, Iron, Zirconium, and Uranium Determined by an Activation Analysis-Sedimentation Method That Makes Use of a Gamma Spectrometer.

specific measurement of the size of that particle and of particles of the same size in a heterogeneous distribution of particles that contain the stable isotope(s) of the element of interest. In effect, the radioactivity induced into a particle or particles and the measurement of the activity by some type of counter make possible determination of the concentration of particles of a definite size (in this instance, in the submicron range). The fractional concentration is the ratio of the radioactivity observed in the group of particles obtained for one set of conditions to the total radioactivity of the sample being analyzed.

The particle size can be calculated from the equation⁷⁴

$$(1) \quad d_s = \frac{6}{\Omega} \sqrt{\frac{n \ln R/S}{2(D_2 - D_1)t}}$$

where

Ω = angular momentum = 2π rps (revolutions per second),

d_s = particle diameter, μ ,

R = distance from the center of the centrifuge to the sampling point in the supporting medium, cm,

S = distance from center of centrifuge to the surface of the supporting medium, cm,

D_1 = density of supporting medium, g/cm^3 ,

D_2 = density of particles, g/cm^3 ,

t = time, sec,

n = viscosity of supporting medium, poises.

Since the only variables in an analysis are the time intervals for centrifugation and the speed of the centrifuge, it is possible to reduce Eq. 1 to

$$(2) \quad d_s = \frac{k}{\frac{\Omega}{2\pi} \sqrt{t}}$$

where k = a constant derived from all the terms in Eq. 1. For example, k for thorium oxide dispersed in a 0.005 M solution of sodium pyrophosphate and supported by water is 1.655×10^{-2} .

The centrifugation method is used for the analysis of the supernatant slurry obtained after the activation analysis-sedimentation assay is completed at about 0.70 μ . Measured portions of the slurry

are centrifuged at various speeds and for different time intervals (usually from 5 to 60 min at centrifuge speeds of 900 and 1900 rpm), after which an aliquot of the supernatant liquid from the centrifugation is transferred by means of a volumetric pipet to a counting tube (pyrex culture tube, 10 \times 72 mm) for the radioactivity measurement. The radioactivity measurements are made by means of a gamma scintillation counter; the percentage-undersize concentration of particles of a given size in the slurry is calculated by relating the observed radioactivity in each aliquot to the total amount of radioactivity of the sample. An International model 2 centrifuge is used. The activation analysis-centrifugation method can be used independently of the activation analysis-sedimentation method.

This method has been used⁷⁵ most often in the particle-size-distribution analysis of submicron particles in samples of thorium oxide that have previously been analyzed for particles in the micron range by the activation analysis-sedimentation method.⁷¹ The data of Table 8 show that the activation analysis-centrifugation method of particle-size-distribution analysis is applicable to the particle-size-distribution analysis of particles as small as 0.05 μ .

⁷⁵L. C. Bate and G. W. Leddicotte, *Determination of Submicron Particle Sizes by an Activation Analysis-Centrifugation Method*, ORNL CF-57-1-116 (Jan. 29, 1957).

Table 8. Calculated Particle Sizes for Thorium Oxide for Conditions Used in an Activation Analysis-Centrifugation Method

Length of Centrifugation (sec)	Particle Size at Indicated Centrifuge Speed (μ)			
	900 rpm	1280 rpm	1900 rpm	2350 rpm
300	0.64	0.45	0.30	0.24
600	0.45	0.32	0.21	0.17
1200	0.32	0.22	0.15	0.12
1800	0.26	0.18	0.12	0.10
2400	0.23	0.16	0.107	0.086
3600	0.20	0.13	0.095	0.077
7200	0.18	0.092	0.062	0.050

Typical data obtained in the analysis of thorium oxide by a combined activation analysis-sedimentation-centrifugation method are given in Fig. 14. In this application the thorium oxide was dispersed in 0.005 M solution of $\text{Na}_2\text{P}_2\text{O}_7$ and was supported in water. High-viscosity media can also be used; however, a recalculation of particle sizes will be required.

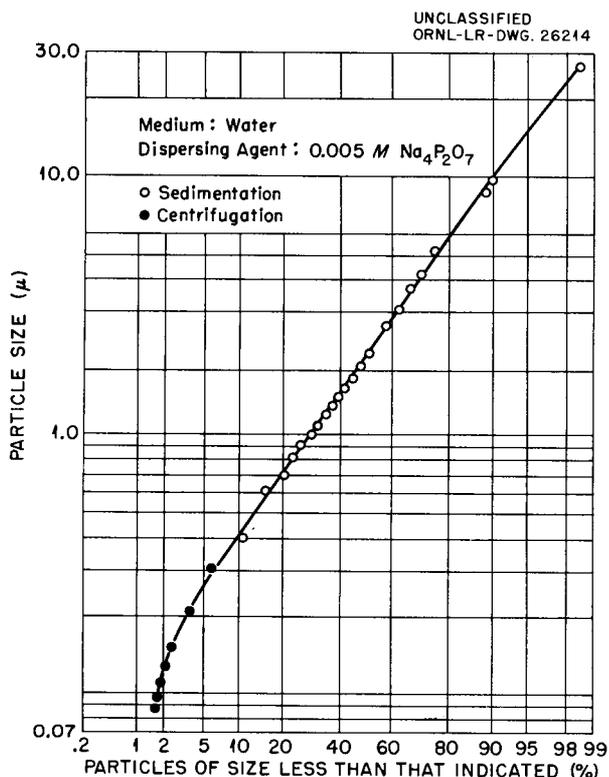


Fig. 14. Particle-Size Distribution of Thorium Oxide Determined by Activation Analysis-Sedimentation-Centrifugation Method.

In addition to thorium oxide, samples of mixed oxides of chromium, iron, zirconium, and uranium and of thorium and uranium have been analyzed by this method for particle-size distributions in the submicron range. Other applications are possible. In the analysis of multicomponent samples, gamma scintillation spectrometry can be substituted for gross gamma counting in order to establish the behavior of the individual components as specific radionuclides in the sample mixture.

New Applications of Activation Analysis

G. W. Leddicotte

Inquiries were received regarding the suitability of activation analysis for the determination of trace elements in silicon, steroids, animal feeds, and aluminum. Samples have been received and are now being analyzed by the activation analysis method.

MASS SPECTROMETRY

A. E. Cameron

Mass Spectrometry Research and Development

J. F. Burns

New Mass Spectrometer. - A 60-deg, 6-in. mass spectrometer was designed, built, and applied to the isotopic analysis of a large number of potassium samples. The spectrometer has operational characteristics comparable with the standard uranium assay instrument but its design is such as to give it a great deal more versatility. The signal-detection system can be used either to read the intensity of a single ion peak or to give directly the ratio of two peaks to four significant figures without interpolation. The collector end of the spectrometer tube has been enlarged so that adjacent isotopes of mass as low as 20 can be measured simultaneously and their ratio displayed directly on the recorder chart. All components of the spectrometer tube and vacuum system are readily accessible and can be easily replaced for studies involving component design and performance.

Two vibrating reeds, a magnet power supply, and the magnet itself were salvaged from an earlier instrument and a few of the other electronic components were obtained from surplus supplies for the uranium assay instrument. As a result, the spectrometer was built at a capital outlay of less than \$4000. It was placed in operation in approximately four months after space for its installation became available.

Potassium Analysis Program. - A potassium analysis program was carried out as a cooperative project with the U.S. Department of Agriculture. The purpose of the project was to evaluate the use of Rb^{86} as a "potassium isotope" in soil chemistry problems. It involved the measurement of the $\text{K}^{41}/\text{K}^{39}$ ratio of 72 samples of normal potassium and potassium enriched in the isotope

of mass 41. This analysis was carried out by the use of solid samples in the form of potassium phosphate; each sample was run on at least two different filaments. The instrumental influences were evaluated by means of a reference sample. If the corrected value of the two ratios obtained for a given sample differed by more than 0.2%, the sample was reanalyzed until consistent results were obtained. The data given in the tabulation below show the precision obtained.

Extreme Variation (%)	Number of Samples Having the Given Variation or Less
0.1	31
0.2	24
0.3	3
0.4	4
0.5	3
>0.5	7

All data except those which could be rejected for a definite cause, such as instrument instability, inability to properly focus the ion beam, etc., are included. Since, in the majority of cases, only two or three determinations were made, the reproducibility is indicated by the extreme variation instead of the standard deviation. The seven samples having greater than 0.5% extreme variation gave very poor reproducibility (extreme variation as great as 1.0%). Only with great difficulty could the samples be made to wet the filament. No attempt was made to purify these few samples because of the amount of extra testing that would have been required.

It is pointed out that these data were obtained as a result of completely independent determinations of the isotopic ratio and include all the variation that was introduced in coating the filaments, loading the sample into the spectrometer, working under slightly different vacuum conditions between determinations, removing and replacing the ion source, and the like. In the case of a single loading of the sample, the variation as determined by the ratio being read at different points along the trace was in the fifth significant figure.

Thermal Diffusion

W. R. Rathkamp

Separation of Isotopes of Krypton. — A thermal diffusion plant has been constructed and is currently in operation for the separation of the isotopes

of krypton. This plant is composed of eight columns, each 20 ft long, connected in series by $\frac{1}{8}$ -in.-ID tubing. Each column consists of a $\frac{7}{16}$ -in.-ID copper tube within a 1-in.-ID, steel-pipe water jacket and a 0.020-in. Nichrome heater-wire supported along the axis of the tube by mica spacers. Transport of gas through the interconnecting tubes between columns is achieved by alternately compressing and expanding a pair of bellows connected, one at each of the extreme ends of the system, so as to slowly displace about 150 ml of gas (one cycle every 5 min) from one end of the system to the other. The operating pressure in the system is 5 psia, the hot-wire temperature is 800°C, and the cold-tube temperature is 15°C.

About 200 ml of krypton has been collected that has the mass-80 isotope enriched from 2 to 21%. Approximately 100 ml of krypton is available with Kr⁸⁶ enriched from 17.3 to over 75% concentration. This enriched Kr⁸⁶ is contained in the plant and is being built up by removing material from the light end of the system and periodically replacing this removed material with normal krypton.

Separation of Mass-36 Isotope of Argon. — A thermal diffusion plant for the separation of the mass-36 isotope of argon is also in operation. This system consists of eight columns that are almost identical in construction with those used in the krypton plant; however, because the concentration of A³⁶ in normal argon is so very low (only 0.34%), all eight columns are connected in parallel to a common reservoir at their bottom ends. Since argon is rather inexpensive, an intermittent feed system is used which alternately admits normal argon to the reservoir and bleeds the excess argon, depleted in A³⁶, out to the atmosphere on a 15-min cycle. Each column has at the upper end an individual, 500-ml receiver in which the A³⁶ isotope is concentrated. The operating pressure in the system is 1 atm, the hot-wire temperature is 800°C, and the cold-wall temperature is 15°C.

About 1000 ml of argon having the A³⁶ isotope enriched from 0.34 to over 20% is on hand. This material is now in the process of being separated from contamination (mainly air); when purified, it will be charged into a single column and taken to over 90% A³⁶.

Since several failures of the 0.020-in. Nichrome heater wires have been experienced, with embarrassing results, columns constructed with Calrod heaters are being evaluated. These heaters are

very rugged and foolproof and lend themselves to the simple and inexpensive construction of columns. By the use of Calrod units of $\frac{5}{16}$ -in. dia and 7-ft length, columns have been constructed which have either $1\frac{1}{16}$ -in.-ID or $1\frac{5}{16}$ -in.-ID cold-wall tubes. The larger size has been tested with argon and shows a unit separation factor comparable with that attained by means of hot-wire columns, a mass transport several times greater, and an equilibrium several times smaller than for hot-wire operation.

Both the $1\frac{1}{16}$ - and $1\frac{5}{16}$ -in.-ID Calrod columns are being operated with carbon monoxide in an attempt to separate the isotopes of both carbon and oxygen in a single plant. Preliminary results show that the separation factor for O^{16}/O^{18} is about the same as the separation factor for C^{12}/C^{13} in CO .

SPECTROCHEMICAL AND X-RAY ANALYSES

C. Feldman

Determination of Rare-Earth Elements

J. Y. Ellenburg⁷⁶

It was found that microgram amounts of rare-earth elements can be separated quantitatively from aluminum by treating the test solution with excesses of carbonate and phosphate at pH 11.5.

The Mitchell-Scott⁷⁷ procedure which makes use of 8-quinolinol and tannin was found to give quantitative recoveries of milligram amounts of rare-earth elements, tungsten, tantalum, niobium, and antimony.

Palladium proved to be an excellent internal standard for the determination of the rare-earth elements by the graphite-residue procedure.⁷⁸

Porous-Cup Excitation with Air-Interrupted Spark Source (C. Feldman). — Optimum sensitivity and line-to-background ratios for porous-cup work were obtained by using the following settings of the high-voltage spark section of the Jaco Varisource: voltage across transformer primary at the instant before breakdown of the auxiliary and analytical

gaps, 60 v; capacitance, 0.0025 μf ; inductance (excluding leads), 40 μh ; secondary resistance, none; breaks per half-cycle, 6; and radio-frequency current, 2.5 amp.

High-Radiation-Level Analytical Facility (HRLAF)

W. R. Musick

C. Feldman

Construction and instrumentation were completed on a facility for spectrographically analyzing highly radioactive materials (Figs. 15 and 16). This cell is located at the left end of a series of similar cells in the HRLAF. Samples, usually in liquid form, are received from adjacent cells. Any necessary chemical operations are performed in this cell by means of apparatus of special design. A Jarrell-Ash No. 1930 (Iowa State model) excitation stand is located in the cell and is operated by means of master-slave manipulators and externally controlled motors. Electrodes, filled inside the cell, are carried in disposable, plastic-tubing holders and are inserted into the clamps by means of manipulators. The exhaust stack can be swung over a sink that is located in the cell and can be flushed out with water coming from an externally controlled outlet, which is located at the inside, upper end of the stack.

Spectrum radiation emerges through a hole in the left wall of the cell, undergoes a 90-deg reflection by a front-surface mirror, and enters the spectrograph (see Fig. 16). A lead shield is placed so as to prevent radiation from entering the operating area. The spectrograph is a Jaco-Ebert instrument made with a 2.25-m focal length in order to permit simultaneous exposure of the entire spectral range. Ordinary analytical exposures are made in the second order of a 15,000-line-per-inch grating. When very high dispersion is needed, a 7,500-line-per-inch grating is used in higher (8 through 16th) orders, together with a vertical predispersing unit (Jaco Order-Shorter) on the optical bench (see Fig. 16).

X-Ray Diffraction

R. L. Sherman

J. C. McCown

An x-ray diffraction laboratory was established for identifying crystalline materials and determining mean particle size. Plans are being made for constructing shielded facilities for use in preparing highly radioactive samples and obtaining x-ray samples and obtaining x-ray patterns of them.

⁷⁶Present address: Southern Research Institute, Birmingham, Ala.

⁷⁷R. L. Mitchell and R. O. Scott, "Applications of Chemical Concentration by Organic Reagents to Spectroscopic Analysis," *Spectrochim. Acta* 3, 367 (1948).

⁷⁸C. Feldman and J. Y. Ellenburg, "The Chemical Isolation and Spectrographic Determination of Some Rare Earths in Purified Uranium and Thorium Preparations," a paper accepted for publication in *Anal. Chem.*

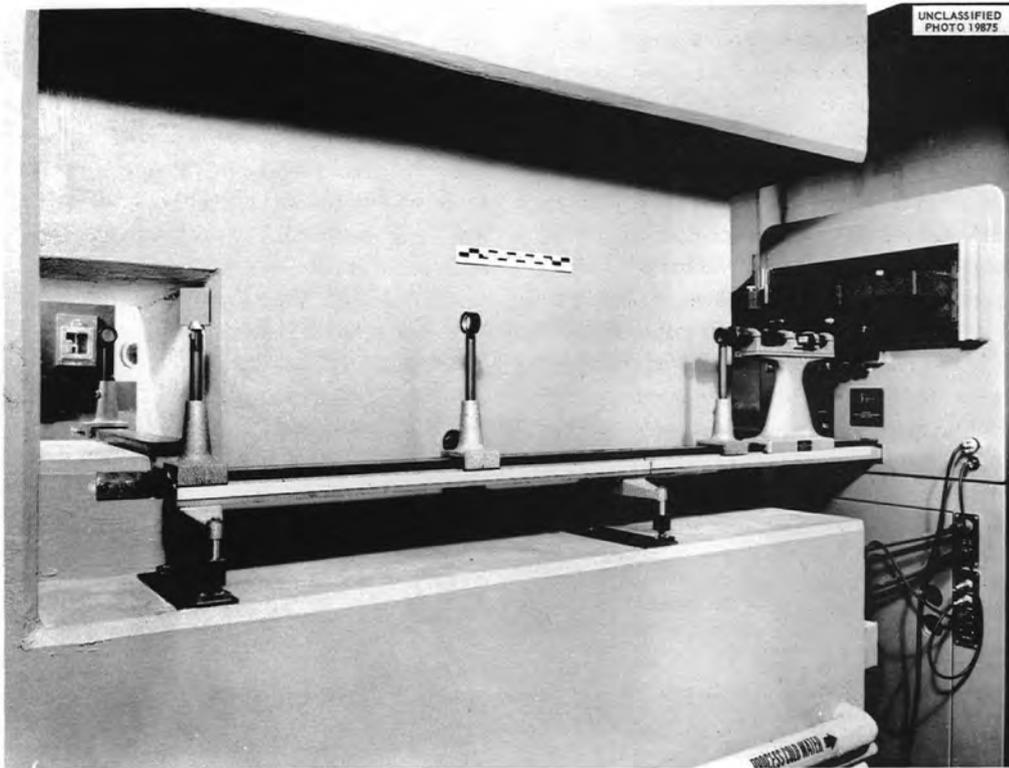


Fig. 15. Spectrograph, Power Source, and Shielded Cell for Use in Analyzing Highly Radioactive Samples (Front View).

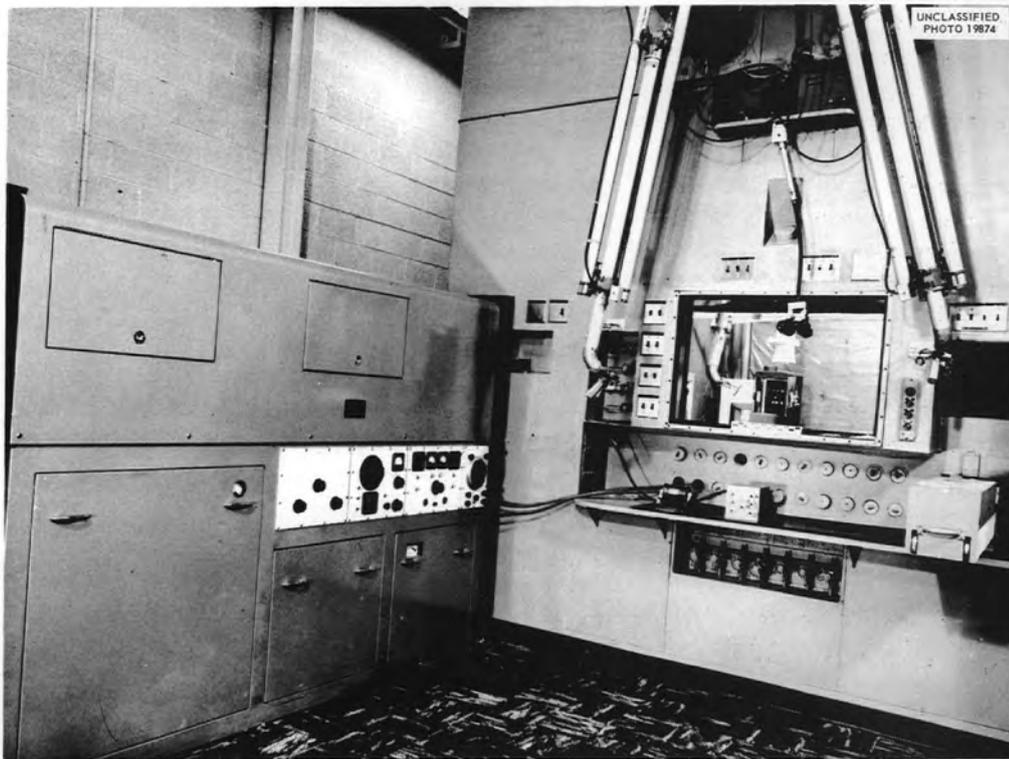


Fig. 16. Spectrograph, Power Source, and Shielded Cell for Use in Analyzing Highly Radioactive Samples (Side View with Radiation Shield Removed).

X-Ray Fluorescence

C. Feldman

Design of Solution Cell. — In order to avoid the problems of assuring sample homogeneity and obtaining valid standards for x-ray fluorescence measurements, it was decided to work with solutions as much as possible. Attempts to conserve intensity by making the top window of the cell out of cellulose tape were unsuccessful because of the lack of dimensional stability of the tape. A Lucite cell of the design shown in Fig. 17 was fabricated for this purpose.

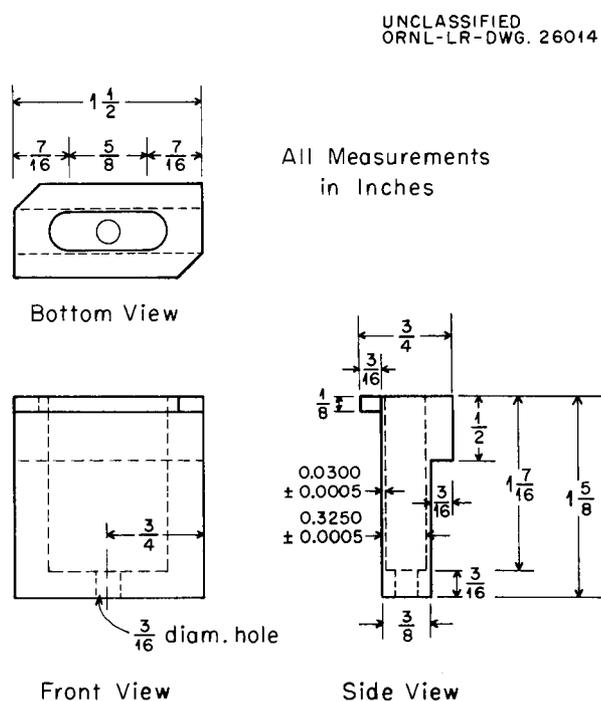


Fig. 17. Lucite Solution Cell for X-Ray Fluorescence.

The cell is used in the following way. While the cell is dry, the bottom face, which contains the oblong slot, is covered with $\frac{3}{4}$ -in.-wide Scotch tape. The cell is then inverted and filled, and the upper face is covered with Scotch tape. The tape will maintain a good seal for almost any solution for a few days, and for several weeks for most. After it is emptied, the cell can easily be cleaned with a brush to remove any solid material or hydrolysis products that may have accumulated.

Analysis of U-Nb-Zr Alloys. — Since there is a serious interference between the K_{α} line of niobium

and L_{β} line of uranium, uranium was removed, with tributyl phosphate, from solutions of samples of U-Nb-Zr alloys. Oxalate was added to the aqueous phase to prevent the extraction of zirconium. Rubidium was added to the aqueous solution as an internal standard. The optimum working concentration range is 0.5 to 5.0 mg of zirconium and/or niobium per milliliter, when 1% average deviation is desired. A detection limit lower than 0.5 mg/ml is possible at some cost in precision.

Analyses have also been performed for nickel and molybdenum in nickel-base alloys without chemical separation.

Flame Photometry

C. A. Pritchard

The enhancement of the intensity of the Li 6708 and Cs 8521 lines by several organic liquids was studied. The best sensitivity for lithium (0.00025 ppm or 2.5×10^{-10} g/ml) was obtained in a 95% solution of ethanol. The best sensitivity for cesium (1 ppm, or 1×10^{-6} g/ml) was obtained in 99% methanol. The RCA 6217 multiplier phototube was used at 6708 Å, and the Farnsworth 16 PML at 8521 Å.

INORGANIC PREPARATIONS

D. E. LaValle

The preparations of anhydrous, transition-metal halides for the Nuclear Physics and Neutron Diffraction Group of the Physics Division were continued. These preparations consisted of large amounts (150 g) of FeBr_2 and FeCl_2 for single-crystal growth, numerous smaller quantities of other halides, and several solid solutions (CoCl_2 - FeCl_2 , CoBr_2 - FeBr_2 , NiCl_2 - FeCl_2) in 25-g amounts by fusion in sealed, evacuated quartz tubes.

In another phase of the program several trifluorides were prepared: MnF_3 by the reaction of BrF_3 on $\text{Mn}(\text{IO}_3)_2$, and RuF_3 by the reaction of BrF_3 on ruthenium metal to produce RuF_5 and the subsequent reduction of the RuF_5 to RuF_3 with I_2 . A considerable amount of MoF_5 has been prepared and purified for the possible production of MoF_3 .

For the Nuclear Physics and Low Temperature Group, 10 g of anhydrous NdI_3 was made by the reaction of anhydrous AlI_3 and Nd_2O_3 .

Several grams of oxide-free arsenic and a similar amount of potassium azide (KN_3) were prepared

for the Atomic Beam Spectroscopy Group of the Physics Division.

In a program for the production of fused salts to be used as solvents by the High Temperature Reactions in Metals and Ceramics Section of the Physical Chemistry Group of the Metallurgy Division, numerous LiCl-KCl eutectics in quantities of 50 to 100 g were prepared in the anhydrous form, fused in HCl gas, and filtered. Single fused salts (LiCl and LiClO₄) were also prepared in 200-g quantities.

Several smaller preparations (~25 g) of fused RbNO₃, CsNO₃, and PbCl₂ were also made.

For the Nuclear Chemistry Group of the Chemistry Division, 100 g of potassium hexabromorhenate (K₂ReBr₆) was prepared by the reduction of K₂ReO₄ with chromous ion according to the method of Meloche and Martin.⁷⁹

Also, numerous experiments were carried out on the exchange of fluorine between HF and some fluorocarbons; HF that contained F¹⁸ was used. No exchange occurred.⁸⁰ In connection with this work some anhydrous CsF and a quantity of the fluorocarbon gas CH₃F were prepared.

The Thermochemistry and Calorimetry Group of the Chemistry Division was provided with 200 g of fused, filtered CsNO₃ made from CsBr.

A program has been initiated recently for the preparation of high-purity MgO and other materials for the growth of single crystals in connection with the high-flux, neutron-irradiation studies of the Solid State Division.

OPTICAL AND ELECTRON MICROSCOPY

T. E. Willmarth

H. W. Wright

T. G. Harmon

Optical and Electron Microscopy of Thorium Oxide

Electron microscopy, by providing the only direct means of observing individual particles of colloidal dimensions, has aided in establishing the correlation that exists between the particle size and shape and the rheologic characteristics and caking tendencies of thorium oxide. Many samples of this material, prepared by a variety of methods

and subjected to numerous tests and loop runs, have been studied. Among them was thorium oxide produced by laboratory methods designed to furnish spheroidal particles within a very limited range of particle size. Figure 18 shows an electron micrograph of thorium oxide prepared by stabilizing the solution with SiO₃²⁻, in a silicon-to-thorium ratio of ~1.

Microscopic observations of some samples of spheroidal particles of thorium oxide before and after sustained loop runs have indicated their susceptibility to degradation. During early studies of thorium oxide, it was found that many samples could not be dispersed by the usual techniques for study by electron microscopy. This was especially true of aggregates of tightly bonded particles. Unfortunately, the dispersing agents so widely used in optical and other types of study could not be employed because in the electron microscope, where a high vacuum and a heat-producing electron beam exist, the sample material is dried out, and the particles are drawn together in opaque masses. In order for particles to be observed as entities, they must be placed on the grids in a dispersed condition without the possibility existing that they can rejoin or aggregate during the drying process. With many materials this requirement can be met by mechanically mulling the powder in plastic, and dispersing the mixture as a thin film on water. Under certain conditions of preparation, especially where high calcination temperatures have been employed, thorium oxide becomes very friable and is easily degraded in particle size by such a method. Samples of this type can be prepared for electron microscopy by depositing a small amount of the powder in a test tube that contains approximately 10 ml of a 2.5% solution of Formvar in ethylene dichloride and lowering the test tube into a high-frequency (~500 kc) sound field that is produced by the ceramic transducer of a Brush hypersonic generator. At this frequency the agglomerates are broken up and dispersed in the viscous plastic medium without further degradation of the particles. After a 15- to 20-min exposure, a droplet of the suspension is cast on water, and portions of the resulting film are captured on microscope grids for examination. The technique has also proved useful for a wide variety of materials other than thorium oxide; Fig. 19 shows an electron micrograph of a dispersion of ZrO₂ that was prepared in this way.

⁷⁹V. W. Meloche and R. L. Martin, "Synthesis of Potassium Hexachlororhenate and Potassium Hexabromorhenate," *J. Am. Chem. Soc.* **78**, 5955 (1956).

⁸⁰T. A. Gens, *F¹⁸ Exchange Between Fluorocarbons and Some Fluorine-Containing Compounds*, ORNL-2363 (Aug. 22, 1957).

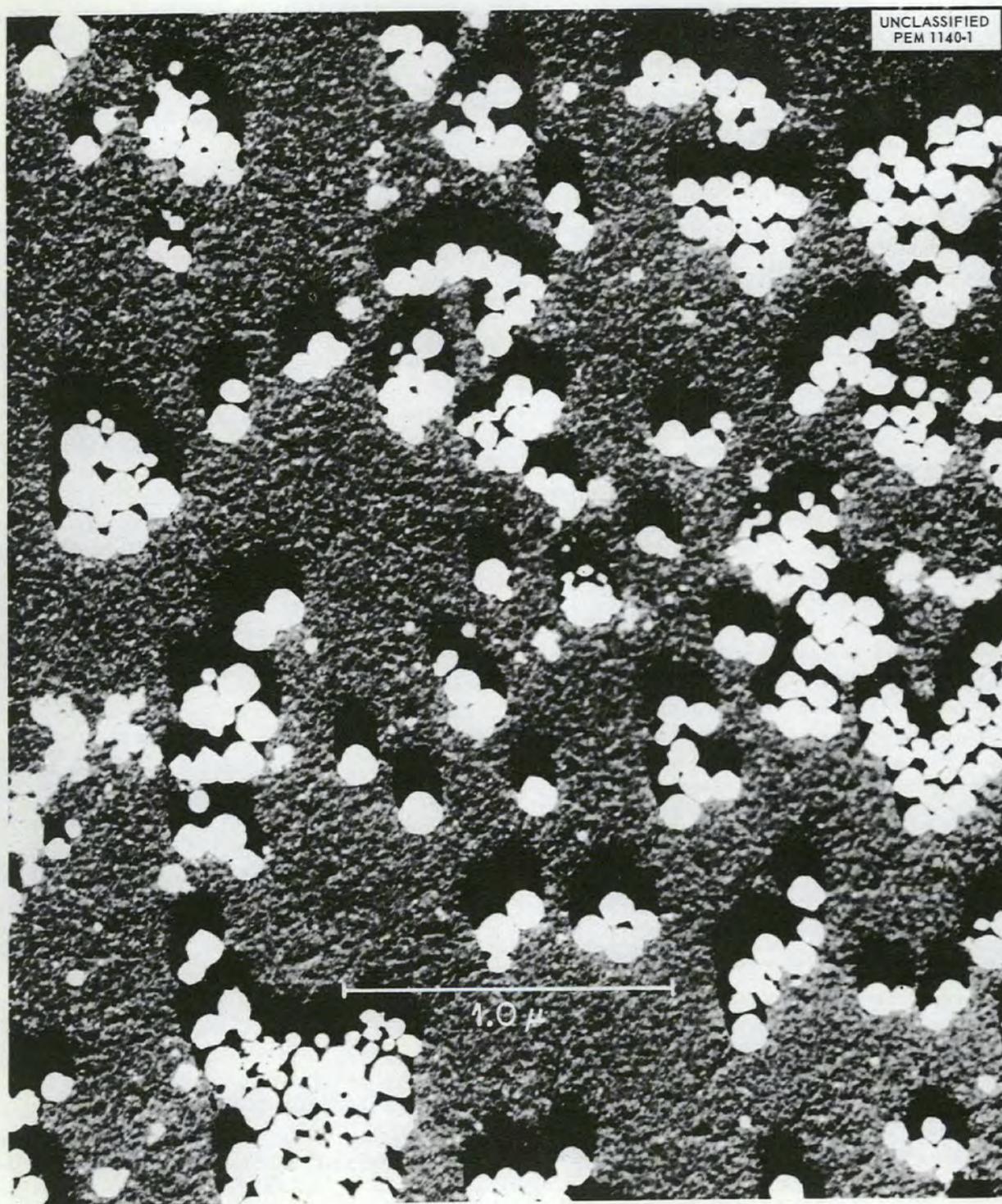


Fig. 18. Electron Micrographs of Davison Chemical Corp. ThO_2 Stabilized with SiO_3^{--} , in a Silicon-to-Thorium Ratio of ~ 1 . 60,000X; 60 mm = 1.0 μ . Reduced 8.5%.

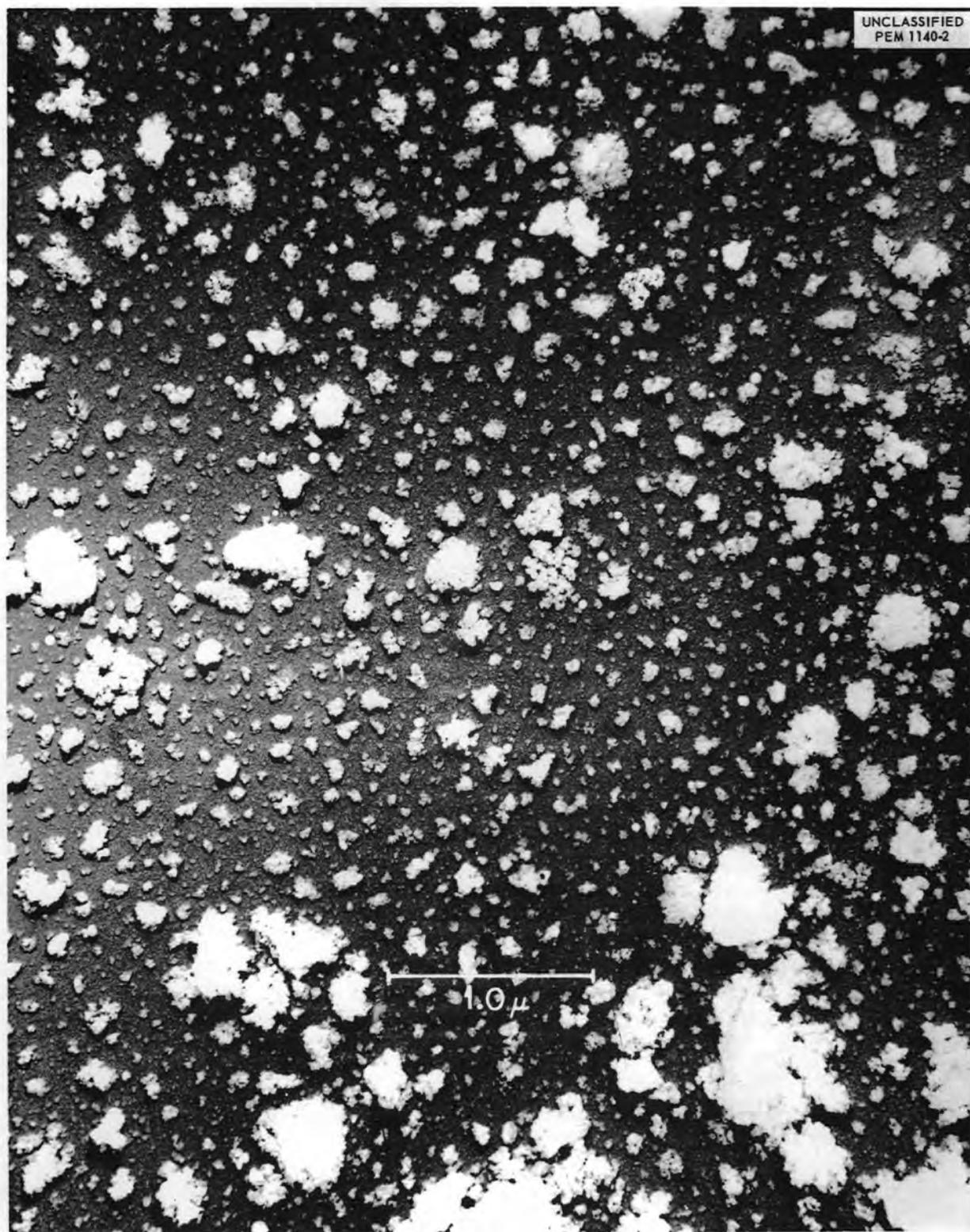


Fig. 19. Electron Micrograph of ZrO_2 Prepared for Electron Microscopy by Use of a 2.5% Solution of Formvar in Ethylene Dichloride. 40,000X; 40 mm = 1.0 μ . Reduced 13%.

Examination of Thin Films, Corrosion Products, and Surface Structures

Samples of foils of type 347 stainless steel, titanium, and Zircaloy-2 immersed in solutions of uranyl sulfate at 300°C in the Van de Graaff generator were examined by reflection electron diffraction in order to determine whether the oxide coatings of the metal foils that had been most directly exposed to the beam had undergone phase changes. Diffraction patterns taken before and after the experiment indicated that in all cases the oxides on both the exposed and unexposed samples were identical after the test.

The etched surfaces of single crystals of germanium were investigated in an attempt to determine why thin films of vapor-deposited indium contained on their surfaces were non-conducting. Reflection electron diffraction indicated the existence of a very thin layer of etch products which prevented the formation of a homogeneous, continuous film of indium. It was also learned that the deposition in vacuo of thin, nongranular films of evaporated indium is critically dependent on the pressure existing at the time of vaporization. More study is contemplated.

The corrosion products and surface structures of the following were studied: cadmium-plated bolts and nuts that had failed in service, the seal surfaces of valves where corrosion had been initiated, the interior surfaces of Zircaloy-2 capillary tubing that had broken during a test run, the interior surfaces of type 347 stainless steel exposed in a fused-salt bath of potassium chloride and lithium chloride, tungsten-plated type 316 stainless steel, samples of Hastelloy on which had been deposited a thin film of chromium and which had then been annealed, and nickel-plated Hastelloy.

Electron and Optical Microscopy of Crystallites, Metal Powders, and Exchange Resins

Many samples of crystallites, metal powders, and exchange resins were examined by microscopy. These included the following: thorium and aluminum coprecipitated as oxalates; thorium and uranium coprecipitated as oxalates; $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ precipitated from a solution of uranyl sulfate; alpha alumina; oxide mixtures containing various

percentages of ZrO_2 , Fe_2O_3 , and Cr_2O_3 ; $\text{UO}_2\text{C}_2\text{O}_4\cdot 3\text{H}_2\text{O}$; $\text{UF}_4\cdot \frac{3}{4}\text{H}_2\text{O}$; TiO_2 ; cuttings of uranium and brass taken from an automatic cutting machine; $\text{UF}_4\cdot 2.5\text{H}_2\text{O}$; Dowex 50X12, A-1X10, and 21 K ion-exchange resins; cuttings of type 316 stainless steel that contained abrasive material; boron; purified boron; ZrCl_4 ; ThSiO_4 ; and U_3O_8 from thermal precipitators.

Methods and Techniques

The General Electric diffractograph has been modified and improved by a Philips electron gun being substituted for the original gun. This was done by series-tuning the RF filament circuit supply to match the change in impedance caused by the greater length of cable lead to the Philips gun, changing the gun connections from a self-biased to a nonbiased position, and introducing a new series of apertures into the gun chamber. Figure 20 shows the modifications to the aperture. Verniers were added to the various tilt controls, and an aluminum-backed, fluorescent screen was substituted. The high-voltage output was brought up to the rated value of 50 kv. The changes result in a much more stable and critically controlled instrument.

The use of Faxfilm for negative replication of surfaces for electron microscopy as suggested by W. L. Ladd⁸¹ has been tried.

The possibility of using automatic techniques for measuring particle size from negatives obtained by electron microscopy has been investigated. The acquisition of a Cintel Flying Spot resolver was recommended and the purchase authorized.

ORNL MASTER ANALYTICAL MANUAL

Authors of Methods

H. P. Raen H. P. House

Forty new methods and revisions to 30 methods were issued to the *ORNL Master Analytical Manual* (see "Presentations of Research Results"). A large number of new methods are currently being processed for issue to the *Manual*. The new methods are the outcome of a part of the research

⁸¹W. L. Ladd, Ladd Research Inc., Roselyn Heights, N. Y., private communication to T. E. Willmarth, Sept. 11, 1957.

and development work of the Division. The revisions were made primarily to the radioisotope product analysis guides to bring the nuclear data up to date. Thirty-three new manuals were issued.

In April 1957 master copies of all the unclassified sections of the *Manual* were transmitted

to the AEC Technical Information Service Extension in Oak Ridge for reproduction and subsequent sale. Section 2, "Radiochemical Methods," which is the first of the sections to be reprinted, is now available for sale. The other sections should be forthcoming soon.

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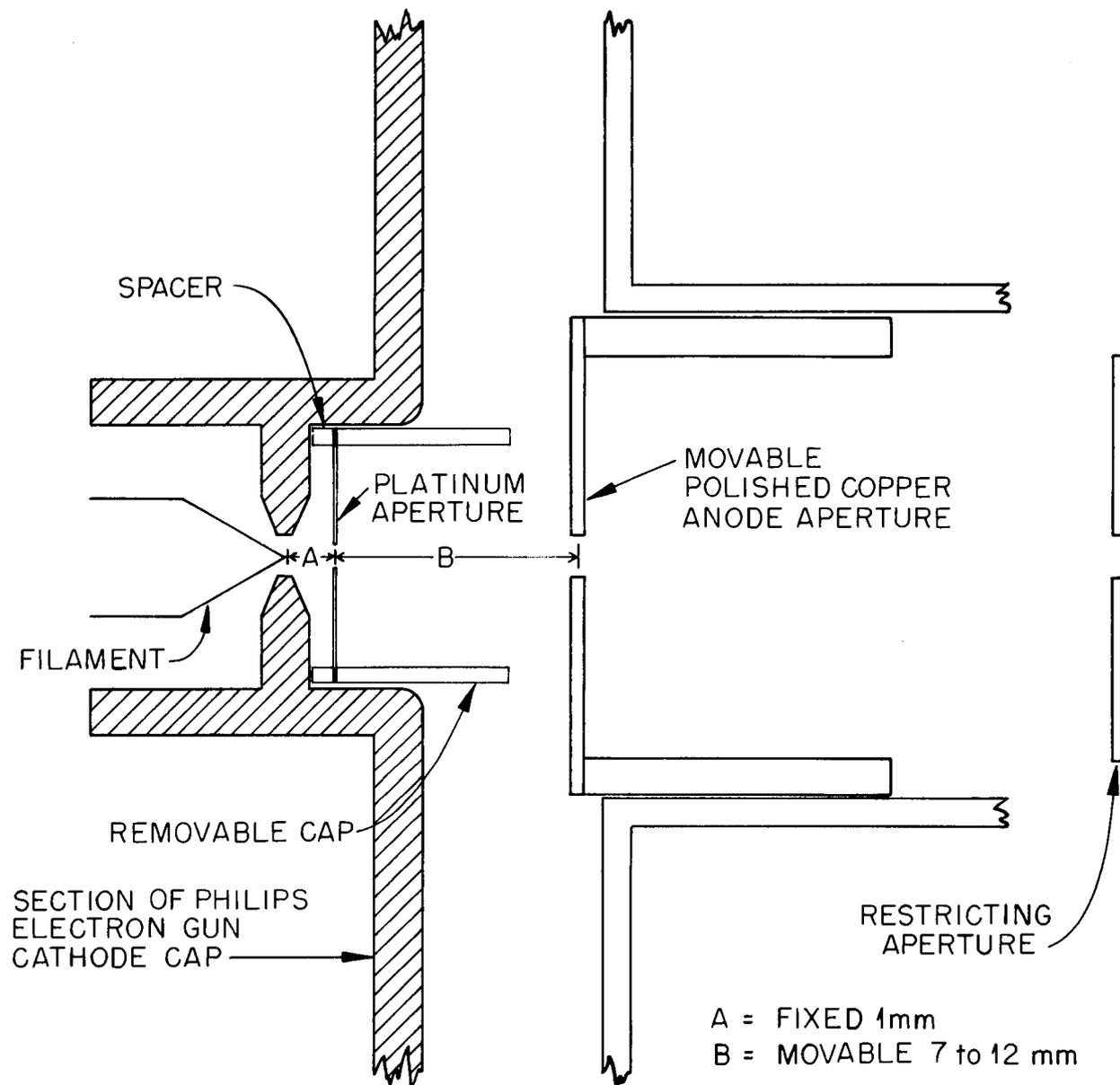


Fig. 20. Modifications to Philips Electron Gun for Use in the Gun Chambers of the General Electric Diffractograph.

SERVICE ANALYSES

A summary of the service analyses made at the X-10 laboratories of the Analytical Chemistry Division is given in Table 9.

IONIC ANALYSES

P. F. Thomason

The greater portion of the service work of the Ionic Analyses Group was for the Reactor Experimental Engineering Division relative to their corrosion studies. The service work for the Chemistry Division was made in order to support the research in high-temperature solubilities and the fundamental studies of ion exchange resins. The service work for the Chemical Technology Division was concerned with their dissolution studies of various fuel alloys. The methods that were used are contained in the *ORNL Master Analytical Manual*.

RADIOCHEMICAL ANALYSES

S. A. Reynolds

Over 71% of the service analyses made by the Radiochemical Analyses Group were performed for three ORNL divisions. For Chemical Technology, many measurements of ^{131}I in ceramic pellets were performed, as well as gamma spectrometric analyses. Work for the Health Physics Division included identification and measurement of activities in a variety of soil, plant ash, water, air filter, and other types of samples.

ACTIVATION ANALYSES

G. W. Leddicotte

Activation analysis has been applied to the determination of microgram and submicrogram amounts of elements in such materials as metals, alloys, minerals, soils, petroleum, plastics, glass, water, and biological specimens. The method has also been used to determine particle-size distributions in thorium oxide, uranium dioxide, zirconium oxide, a mixture of the oxides of thorium and of uranium, and a mixture of the oxides of chromium, iron, zirconium, and uranium.

MASS SPECTROMETRIC ANALYSES

J. R. Sites

The Analytical Mass Spectrometry Group was transferred to the Analytical Chemistry Division

on May 1, 1957. The major equipment of the group consists of one mass spectrometer for gaseous samples, two mass spectrometers for solid samples, and a gas-handling system for special samples. Qualitative and quantitative analyses are made for isotopes of an element, for molecular species from mixtures of compounds, and for purity of gases. For solid samples the preferred forms are element, oxide, and nitrate, or, in some cases, a halide. Gas samples can be submitted in break-seal or stopcock-type bulbs of volumes from a few to 100 ml and at pressures from atmospheric down to a few millimeters. When the contaminants in gases of high purity are to be sought, it is preferred that the sample be taken directly from the gas cylinder by means of the special gas-handling system. In some cases, solid samples can be spiked with separated stable isotopes in order to determine element concentration.

During the six months of operation in the Analytical Chemistry Division, the Analytical Mass Spectrometry Group has made 4302 analyses on 1369 samples.

LABORATORY CONTROL GROUP

L. T. Corbin R. B. Quincy, Jr.
G. R. Wilson A. F. Roemer, Jr.

The Chemical Technology Division submitted several samples that required new or modified analytical procedures. Determinations of fluoride and acid in the presence of zirconium have been requested. Fluoride in solid samples and in aqueous samples of low acidity was determined by means of a pyrolysis type of separation.¹ A Willard-Winter type still was set up for the determination of small quantities of fluoride in the presence of zirconium and nitric acid. The apparatus shown in the *ORNL Master Analytical Manual*² was modified to use a bath of boiling xylene instead of a heater to maintain the sulfuric acid and sample at constant temperature. The

¹R. H. Powell and O. Menis, *Separation of Fluoride from Inorganic Compounds by Pyrolysis*, a paper presented at the 132nd meeting of the American Chemical Society in New York City, Sept. 8, 1957.

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

Table 9. Summary of Analytical Service Work at X-10

Group Making Analyses	Number of Personnel		ORNL Requests for Analyses																				Other Requests for Analyses										Totals					
	Scientists	Technicians	Miscellaneous	Analytical Chemistry	Applied Nuclear Physics	Biology	Chemical Technology	Chemistry	Director's Department	Education	Electronuclear Research	Engineering and Mechanical	Finance and Materials	Health Physics	HRP	Instrumentation and Controls	Isotopes	Metallurgy	Operations	Physics	Reactor Experimental Engineering	Reactor Projects	Solid State	Amour Research Foundation	General Electric Co.	K-25	Miscellaneous	North Carolina State College	ORINS	Paducah	Pratt & Whitney Aircraft	University of California		University of Tennessee	Y-12			
Activation Analyses*	4	5	50	678	17		859	114						253	4		103	471	1	1154	6	162															2	3,878
Ionic Analyses*	7	1		62			395	466						20	29		82		55	557		42					4										2	1,708
Laboratory Control	3	6	4				26,689	223						52	23		12	219	1																			27,223
Optical and Electron Microscopy*	3	2		8			584	252						20	8		112	4	8	452	16	20													8	1,492		
Plutonium Isolation Laboratory	2	3					8,759	77			144			1		11			1	10		10															9,013	
Pilot-Plant Control	8	13					52,822								54				22	307		10															53,215	
Radiochemical Analyses*	4	1			4		333	37			47			372			17	75	96	442	1	54			14	2				4			114				1,612	
Radioisotope-Radiochemistry	3	17			1149		12,312	585						2056				16,054		243		410		350		491										33,650		
Reactor Analyses	7	7		2			245		44	3	24				16,344		3	40		18	5	80	23	5			27						9			16,872		
Special Analyses	9	10					16,249	438						3252		514	4069			1568		212														26,302		
Spectrochemical and X-Ray Analyses*	7	1		3	15	4	2,779	176	94		6			12		42	560	90	14	588	4	392														4,779		
Mass Spectrometry Analyses*	7	1		775			66	1131					24	10	12	555	1634		60		20															4,302		
Totals	64	67	54	1528	1181	8	122,092	3499	138	3	215	6	24	6048	16,474	42	1080	6592	16,976	235	5339	52	1392	23	369	6	491	27	3	4	12	9	114	10	184,046			

*These groups also do research and development work.

enthalpymetric titration procedure for the determination of free acid in the presence of zirconium that was developed by F. J. Miller (see "Enthalpymetric Determination of Free Acid in the Presence of Certain Hydrolyzable Ions," this report) has been used.

Coincident with the use of sulfuric acid to dissolve fuel elements, it became necessary to use something other than TBP-Amsco to extract the uranium prior to its fluorometric determination.³ In the presence of sulfuric acid, a 0.1 M solution of trioctylphosphine oxide in Amsco is used to extract the uranium. Since the oxidized forms of iron and chromium are also extracted by trioctylphosphine oxide, hydroxylamine hydrochloride is added to the aqueous phase, which is also 3 M in hydrochloric acid.

The Volatility Group of the Chemical Technology Division has requested the separate determination of uranium(IV) and (VI) in samples of sodium fluoride on which uranium hexafluoride has been adsorbed. Since the uranium(VI) compounds in these samples are water-soluble and the uranium(IV) compounds are water-insoluble, their separation is effected by leaching with water. The uranium(VI) is determined colorimetrically⁴ and the uranium(IV) volumetrically.⁵

PILOT-PLANT CONTROL LABORATORY

L. T. Corbin C. E. Lamb

The majority of the work done by the Pilot-Plant Control Laboratory was for the Chemical Technology Division relative to the Thorex, Metal Recovery, and Volatility processes. The methods that were used are contained in the *ORNL Master Analytical Manual* except for occasional minor modifications that were required in order to eliminate interferences.

Some samples were received from the Volatility process to be analyzed for chromium⁶ in the

³R. L. Walker, "Uranium, Fluorometric Method," Method Nos. 1 219240 and 9 00719240 (7-10-53), *ORNL Master Analytical Manual*.

⁴U. Koskela and C. E. Lamb, "Uranium, Spectrophotometric Ammonium Thiocyanate Method," Method Nos. 1 219210 and 9 00719210 (11-12-53), *ORNL Master Analytical Manual*.

⁵C. A. Pritchard, "Uranium(IV), Volumetric Potassium Dichromate Method," Method Nos. 1 219272 and 9 00719272 (5-16-56), *ORNL Master Analytical Manual*.

⁶W. F. Vaughan, "Chromium, Spectrophotometric 1,5-Diphenylcarbohydrazide Method," Method Nos. 1 212110 and 9 00712110 (5-6-57), *ORNL Master Analytical Manual*.

presence of zirconium. In the analysis an excess of silver oxide⁷ was used to oxidize chromium(III) to chromium(VI) and the excess was destroyed by heating.

A buret having electromagnetically activated valves for filling and delivering titrant was installed on the Beckman model K automatic titrator unit in cell No. 3 of the HRLAF (see "Electric Buret for HRLAF," this report). Its use by remote control has increased the speed of titrating a sample and eliminated the use of a rubber-diaphragm valve and the need for periodic lubrication that is required by the conventional glass stopcock type of buret.

Analyses have been made in the HRLAF cells on radioactive solutions of ~10-ml volume and calculated activity of the magnitude of 25,000 r/hr at contact. Contaminant background radiation in the cells resulted from the receipt of sample bottles having contaminated surfaces, the discarding of radioactive solutions, the use of polyethylene and rubber lines in transferring radioactive wastes to the cell drain, and the use of equipment onto which radioactive materials had plated out. Some pieces of equipment that had contributed a substantial portion of the background radiation have been replaced with inexpensive equipment that can be rapidly disassembled and discarded.

ISOLATION ANALYSES

L. T. Corbin J. H. Cooper

The major portion of the work done by the Isolation Analyses Group was for the Chemical Technology Division relative to the Thorex process and to the plutonium-producer-blanket studies.

The Health Physics Division, in studying radiation dosimetry, requested assistance in preparing pellets of NpO_2 to be used as neutron-threshold detectors. The Chemistry Division isolated and purified Np^{237} and submitted it as a solution of the chloride. The solution was evaporated to dryness, and the chloride salt was calcined in a muffle furnace. The resulting NpO_2 powder was weighed out into small batches; each batch was packed into a small copper can, which was then

⁷J. J. Lingane and D. G. Davis, "Argentous Oxide as an Oxidimetric Reagent. Determination of Manganese, Cerium, and Chromium," *Anal. Chim. Acta* 15, 201 (1956).

soldered to prevent leakage. A total of 103 pellets of this type was made.

The study of the solubility of plutonium fluoride in fused-salt mixtures required analyses of these salts for total plutonium and plutonium in its various valence states. The salts, which are primarily mixtures of NaF and BeF₂, were dissolved by refluxing in a solution of AlCl₃ and H₂SO₄ under an inert atmosphere. The resulting solutions were immediately scanned on a Cary recording spectrophotometer. From the absorption spectra the percentages of plutonium(III) and plutonium(IV) were calculated. The total plutonium concentration was determined by existing methods.

A recording gamma scintillation spectrometer has been obtained by the Isolation Analyses Group and is used for the qualitative determination of gamma-emitting nuclides. A unique characteristic of this instrument is its low background and minimum electronic noise. The spectrometer was used extensively to make measurements from which decontamination factors in the Thorex process were calculated. By means of this instrument a decontamination factor can be obtained within a few minutes after a sample is received, in contrast with the hours required by the conventional radiochemical methods.

SPECIAL ANALYSES LABORATORY

L. T. Corbin W. R. Laing

A variety of analyses were performed by the Special Analyses Laboratory. Zirconium was determined in alloys by amperometric titration. Metal hydrides were analyzed for hydrogen by combustion, and rare-earth metals were analyzed for oxygen and nitrogen by vacuum fusion. An equilibrium pressure apparatus was constructed for use in the determination of hydrogen in titanium- and zirconium-base alloys. The types of samples on which surface area determinations are made were extended to include TiO₂, charcoal, molecular sieves, Raschig rings, UO₂ compacts, BeO, and silver wire. Polarographic methods were used to study the solubility and diffusion of nickel in lead. Chloride in solutions that contained high concentrations of iron, nickel, and chromium was determined by oxidation with potassium permanganate followed by distillation into potassium iodide solution. The plutonium plating service was continued and enlarged to include the plating of

neptunium. Corn shucks, cobs, stalks, and leaves were analyzed for potassium, sodium, calcium, magnesium, and iron. Off-gas samples from the Darex process were analyzed for nitrogen dioxide, chlorine, carbon dioxide, nitrous oxide, oxygen, hydrogen, carbon monoxide, and nitrogen. Boron separations and determinations were made successfully on stainless steel fuel elements, boron control rods, sections of test-loop walls, fluoride-salt mixtures, and alkali metals. Carbon and water in microgram quantities were determined in fluoride-salt mixtures.

RADIOISOTOPE-RADIOCHEMISTRY LABORATORY

E. I. Wyatt

R. R. Rickard H. A. Parker

The major portion of the radioisotope work during the past year was the assay of products for shipment. Emphasis was placed on the quick assay of products having half lives shorter than three days. The process control work was related primarily to the Thorex process, most of the work being done with single-channel gamma scintillation spectrometers. Many neptunium separations and subsequent alpha-pulse analyses were made for the Metal Recovery Group of the Chemical Technology Division.

Pretreatment procedures and adaptations of established radiochemical methods for the determination of trace quantities of fission products in large volumes of water are being developed. New analytical procedures for the determination of radoruthenium and the carbonate capacity of resins have been developed by R. R. Rickard and written for inclusion in the *ORNL Master Analytical Manual*.

The half lives of several radionuclides were determined; the data are presented in Table 10. The calculations were made by the method of least squares. All the radionuclides listed were either purified by chemical means or were checked for possible impurities by beta absorption studies that were made by means of the gamma scintillation spectrometer, or were both purified and checked. No impurities were observed either before or after the period during which the decay was observed.

Table 10. Observed Half Lives of Some Radionuclides

Radionuclide	Reaction Used To Produce the Radionuclide	Instrument Used	Period of Observation (Half Lives)	Observed Half Life
S ³⁵	S ³⁴ (n,γ)S ³⁵	PC*	4	89.0 ± 0.5 d
Ca ⁴⁵	Ca ⁴⁴ (n,γ)Ca ⁴⁵	PC	3	165.1 ± 0.7 d
Br ⁸²	Br ⁸¹ (n,γ)Br ⁸²	GIC**	5	35.55 ± 0.15 h
Y ⁹¹	U ²³⁵ fission	PC	2	59.1 ± 0.2 d
Nb ⁹⁵	U ²³⁵ fission	GIC	5	35.0 ± 0.1 d
Cd ¹¹⁵	Cd ¹¹⁴ (n,γ)Cd ¹¹⁵	GIC	5	53.5 ± 0.1 h
Sm ¹⁵³	Sm ¹⁵² (n,γ)Sm ¹⁵³	GIC	6	46.8 ± 0.1 h
Ir ¹⁹²	Ir ¹⁹¹ (n,γ)Ir ¹⁹²	GIC	5	73.9 ± 0.2 d

*2π beta proportional counter (flow type).

**High-pressure gamma ionization chamber.

HIGH-RADIATION-LEVEL ANALYTICAL FACILITY (HRLAF)

C. L. Burros

The HRLAF was operated successfully during the past year. Mechanical failures were normal, and all were minor in nature. The most frequent mechanical failures of the master-slave manipulators were the breaking of torsion springs in the inside flange assembly and the shearing of the tension cables that actuate the inside tongs. The American Machine and Foundry Co. has fabricated a stronger torsion spring, which is now being used as a replacement part. Larger pulleys with deeper grooves are being installed in order to decrease the shearing of the tension cables. Wrist-action binding in the master-slave manipulators has resulted when idle gear spindles worked loose in the differential housings. Threading the spindle and locking it in place in the differential housing by means of a machine screw and washer have eliminated this difficulty.

Additional equipment that has been provided in the HRLAF includes the Thorex overhead conveyor, a remote area radiation monitoring system, two mobile air monitors, and one Exide Light-guard. The Thorex conveyor connects the sample gallery of the pilot plant to the storage cell. This

conveyor facilitates the transfer of samples from the Thorex pilot plant to the HRLAF, where the samples are automatically unloaded in the storage cell. The remote area monitoring system measures the levels of radiation in the work cells and the surrounding area. Air monitors are located in the east and west zones to record the activity of the air. In case of power failure, the Lightguard automatically directs a beam of light to the east and south exits of the HRLAF.

The north and south sides of the loading dock were enclosed as an additional measure to control the spread of radioactive contamination.

REACTOR ANALYSES

U. Koskela L. G. Farrar

The HRP continued to furnish the majority of the samples analyzed by the Reactor Analyses Group. In March and in October the HRT was operated with natural uranium. Samples from this operation were analyzed on an around-the-clock basis. In addition, samples from the in-pile loop and bomb programs were analyzed. Radioactive thoria slurries have been separated, and the residues dissolved and analyzed for corrosion products and additives.

At the request of the AEC, solutions of uranium from the reactors located at North Carolina State

College, Armour Research Foundation, and the University of California Radiation Laboratory have been analyzed.

The training of personnel in the use of the equipment in the HRLAF is being continued preparatory to HRT power operations.

Analysis of Mixtures of Fluoride Salts

J. E. Attrill S. R. Dinsmore

The major portion of the work on the analysis of mixtures of fluoride salts has consisted in the development of methods for the determination of iron, nickel, and chromium in the mixtures. In accordance with the suggestions of various laboratory personnel⁸ (see "Determination of Nickel and Chromium in Mixtures of Fluoride Salts," this report) a number of colorimetric and polarographic analyses have been made on synthetic salts. Radioactive tracers were used to check the reproducibility and sensitivity of the methods. It has been shown that radiation affects a number of the colorimetric determinations. Attempts will be made to determine the magnitude of this interference and to develop correction factors so that more reliable results can be obtained.

Determination of Dissolved Oxygen in Water

R. E. Corcoran

The corrosion problem in the steam system of the HRT is more serious than it is in conventional steam plants because of the generation of oxygen and the presence of stainless steel in the HRT heat exchangers.⁹ Consequently, a method was needed for the determination of very small concentrations of dissolved oxygen in water. The method studied was a modification of the Winkler method, that is, the Schwartz-Gurney modification B,¹⁰ which uses a potentiometric titration. The method depends upon the release of free iodine in amounts equivalent to the dissolved oxygen in the sample and the measurement of the iodine by

titration with a standard solution of sodium thiosulfate.¹¹

The equipment consisted of a Leeds & Northrup pH meter used as a potentiometer, a straight, platinum wire electrode, a standard calomel half-cell,¹² and a 250-ml, tall-form beaker fitted with a No. 12 rubber stopper having holes for the electrodes and a buret. The system was enclosed to prevent volatilization of the iodine. A 1-ml Greiner microburet was used to deliver the titrant.

A standard iodine solution was used in the experimental work.¹³ Satisfactory results were obtained in the range of 10 to 100 ppb of dissolved oxygen. Actual HRT samples have not been available to date.

Controlled-Potential Coulometric Titrator

L. G. Farrar

A controlled-potential coulometric titrator¹⁴ has been used for the determination of copper(II) and uranium(VI) in nonradioactive HRT solutions. A comparison of the results obtained by coulometric titration and by gravimetric analysis showed a deviation between the two of approximately 1%. The coulometric titrator has been adapted for use in the analysis of HRT fuel containing fission and corrosion products. An assembly has been built for the HRLAF. A topical report of the work has been written and a paper is being prepared for submission to *Analytical Chemistry*.

Preparation of Samples for Isotopic Analysis

L. G. Farrar C. P. Baker S. R. Dinsmore

Stainless steel fuel elements of the type used in the APPR contain a matrix of FeB, BN, or B₄C associated with uranium. Burnup of the uranium is calculated from the B¹⁰/B¹¹ ratio in a used fuel element.

The boron compounds were separated from the stainless steel by dissolution with nitric acid,

¹¹American Public Health Association, *Standard Methods for the Examination of Water and Sewage*, 9th ed., p 106, American Public Health Association, New York, 1946.

¹²G. A. Perley, "Determination of Dissolved Oxygen in Aqueous Solutions," *Ind. Eng. Chem. Anal. Ed.* 11, 240 (1939).

¹³C. K. Talbott, "Oxygen in Water, Spectrophotometric Modified Winkler Method," Method Nos. 1 215810 and 9 00715810 (5-21-56), *ORNL Master Analytical Manual*.

¹⁴H. C. Jones and M. T. Kelley, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 12 (classified).

⁸A. D. Horton, Ionic Analyses Group; R. S. Pressly, Operations Division; R. P. Shields, Solid State Division; private communications to J. E. Attrill.

⁹H. A. McLain, *Treatment of the HRT Steam System Water*, ORNL CF-56-11-132 (Nov. 29, 1956).

¹⁰T. H. Daugherty, "Technique in the Determination of Dissolved Oxygen," *Am. Soc. Testing Materials, Proc.* 37(Pt. II), 615 (1937).

the residue was fused with potassium sulfate, and the melt was treated with HF at low temperatures to form potassium fluoroborate.¹⁵ The B¹⁰/B¹¹ ratio was determined in the potassium fluoroborate by mass analysis in the Y-12 Special Assay Laboratory.

Automatic Potentiometric Titration of Free Acid in Uranyl Sulfate Solutions

J. L. Mottern

The titrant-delivery unit described by Maddox¹⁶ was modified by substitution of a motorized Lab-Jack¹⁷ for the manual assembly to position the sample. The unit has been tested and has the advantage of being eight times more sensitive than the ORNL model Q-1728 titrant delivery unit. The new assembly is much easier to use with master-slave manipulators.

The method for determining free acid in uranyl sulfate solutions consists in a modification of two methods.^{18,19} The sample is added to an ethyl alcohol (65%)-saturated potassium oxalate

¹⁵The various methods used were suggested by C. F. Leitten of the Metallurgy Division, J. G. Morgan of the Solid State Division, and W. D. Harman of Y-12.

¹⁶W. L. Maddox, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 12 (classified).

¹⁷D. J. Fisher and E. B. Wagner, "Motorized Lab-Jack," *Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1955*, ORNL-1973, p 5.

¹⁸P. F. Thomason, *Micro Oxalate Method for the Determination of Nitric Acid* (Nov. 1, 1948), in files of P. F. Thomason.

¹⁹W. N. Carson, Jr., *Microtitration of Free Acid in Uranyl Nitrate Solutions*, HW-29455 (Oct. 1, 1953).

(35%) solution and is titrated with a standard solution of sodium hydroxide, approximately 0.1 N. An aqueous sample of volume up to 0.5 ml and containing 0.005 to 0.015 meq of acid can be titrated satisfactorily.

Determination of Lithium in Beryllium Metal

J. L. Mottern

An analysis was made for the purpose of determining Li⁶/Li⁷ ratios in beryllium shim rods from the MTR. The radioactive beryllium was dissolved in 5% sulfuric acid, and the solution was analyzed by means of the ORNL model Q-1457 flame photometer. The lithium content ranged from 0 to 10 ppm, a range too low for isotopic analysis.

Modified pH Electrode Assembly

J. Slessinger, Jr. U. Koskela

The pH electrode assembly²⁰ for the HRLAF proved to be unsatisfactory over a long period of usage. The up-and-down travel of the motorized Lab-Jack¹⁷ was too erratic to allow safe positioning of the sample with respect to the electrode. An electric screw-jack²¹ was substituted most satisfactorily.

²⁰U. Koskela and J. Slessinger, Jr., *Anal. Chem. Semiann. Prog. Rep. April 20, 1956*, ORNL-2070, p 30 (classified).

²¹Designed by H. L. Hemphill, Solid State Division. No report; briefly mentioned in *Anal. Chem. Quar. Prog. Rep. Sept. 26, 1952*, ORNL-1423, p 41 (classified).

ANALYTICAL CHEMISTRY DIVISION — Y-12 SITE

RESEARCH AND DEVELOPMENT

HRP ANALYTICAL CHEMISTRY

O. Menis

Removal of Fluoride from Inorganic Material
by Pyrolysis

R. H. Powell

Experimental work was continued on a pyrolytic method for the separation of fluoride from thorium oxide that is contaminated with small amounts of inorganic fluorides.¹ Improvements have been devised whereby it has become possible to increase significantly the rate of release of fluoride and to extend the application of the pyrolysis method to the removal of fluoride from refractory materials, such as clays and glasses, which hitherto have been considerably difficult to analyze for fluoride.

In the report of earlier work mention was made that it is unnecessary to use steam to release fluoride from sodium fluoride since the fluoride can be released by pyrolysis in a stream of dried oxygen; thus dilution of the solution used to absorb the volatile fluoride condensate is avoided. Furthermore, a fused-silica rather than a nickel or platinum apparatus was demonstrated to be entirely satisfactory. More recent studies have shown that if moist oxygen (0.01 to 0.02 g of H₂O per liter) is used to purge the system, the rate of release of the fluoride is greatly accelerated and also that other oxides, notably WO₃ or V₂O₅ as shown in Fig. 21, can be substituted advantageously for U₃O₈ as accelerators to promote the release of fluoride. For example, the fluoride can be completely removed from 100 mg of sodium fluoride by mixing the sodium fluoride with ~3 g of WO₃ and then pyrolyzing the mixture in a stream of moist oxygen at 825°C for about 10 min. The fluoride is absorbed in a dilute solution of sodium hydroxide and determined either by acidimetric titration, if no other volatile, acidic products are produced during the pyrolysis, or by spectrophotometric titration with a solution of thorium nitrate in which titration alizarin red S or Thoron

is used as the indicator. As little as 10 µg of fluoride, as NaF, can be separated by pyrolysis and titrated spectrophotometrically with a relative standard deviation of 5%. When the pyrolytic method was applied to the separation of 75 mg of fluoride as NaF (mixed with U₃O₈), the average fluoride recovery for five determinations was 99.5% and the relative standard deviation was 0.1%, whereas with WO₃ added to the sample the average recovery was 99.9% and the relative standard deviation was 0.2%. Macroquantities of fluoride were determined by the method of acidimetry.

As a consequence of further study, it has been established that fluoride can be separated from a number of readily decomposable, inorganic fluorides by pyrolysis in a stream of moist oxygen without the addition of any accelerator. Examples

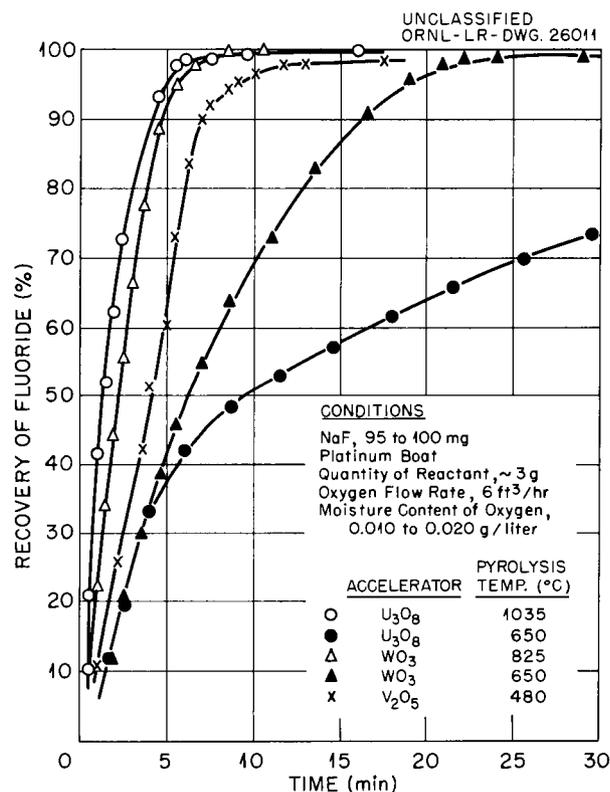


Fig. 21. Rate of Recovery of Fluoride as a Function of the Accelerator and Temperature of Pyrolysis.

¹R. H. Powell, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 44 (classified).

of this type of fluoride, together with the optimum temperature and the time required for the complete recovery of fluoride, are given in Table 11.

Table 11. Optimum Conditions of Temperature and Time Required To Pyrolyze Various Fluoride Compounds

Compound	Temperature (°C)	Time (min)
$\text{ThF}_4 \cdot x\text{H}_2\text{O}$	800	20
$\text{AlF}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$	900	20
$\text{ZrF}_4 \cdot x\text{H}_2\text{O}$	650	10
$\text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O}$	800	10
UF_4	800	20
NpF_4	700	20

In the application of this method to the removal of fluoride from a number of clays and related materials under study for use as suspending agents for slurries of thorium oxide, it was found that the usual procedure is inadequate. A novel and simple, yet effective, method was developed whereby the fluoride can be completely volatilized from refractory materials within 1 hr. In this procedure a flux, Na_2WO_4 , is used to decompose the refractory material. To the flux is added an accelerator, WO_3 , which is soluble in the flux at elevated temperatures, in order to promote the release of the fluoride. Samples mixed with Na_2WO_4 and WO_3 are dehydrated by being heated in a stream of helium gas at 400°C in the pyrolysis apparatus, after which the pyrolysis is continued in moist oxygen at 325°C . The fluoride is completely removed within 1 hr, absorbed in a dilute solution of sodium hydroxide, and then determined as previously described. Sodium metavanadate, NaVO_3 , can be substituted for the mixture of Na_2WO_4 and WO_3 ; this compound apparently serves the dual purpose of flux and accelerator. This procedure was tested by means of two samples from the National Bureau of Standards, namely, opal glass No. 91 and phosphate rock No. 56B. In each case the results were in excellent agreement with the values assigned by the Bureau. As a consequence of the foregoing, this procedure

has been applied to the analysis of a number of clays and related materials. The application of the new procedure results in considerable saving of time, as compared with the time required with classical methods.²

Polarographic Determination of Zinc

R. G. Ball

D. L. Manning

In the application of a polarographic method to the determination of zinc in solutions of uranyl sulfate, zinc is first separated from the uranium by extraction, in the presence of carbonate, into a chloroform solution of diethyldithiocarbamate at a pH of 8. The zinc is then extracted into 0.01 M HCl, following which it is measured polarographically. The method, based on the reduction of zinc(II) to metallic zinc, which exhibits a half-wave potential of approximately -1.0 vs the S.C.E., is applicable to the determination of zinc in concentrations of the order of $0.5 \mu\text{g}/\text{ml}$. The relative standard deviation is about 5%.

Further tests have shown that zinc can be determined in solutions of pH as low as 1. These results demonstrate a definite advantage of the high-sensitivity, derivative polarograph (ORNL model Q-1673), which is used in this work, inasmuch as the zinc wave is not completely resolved from the hydrogen reduction wave, at a pH of 1, by a polarograph of the more conventional type.

Extraction and Spectrophotometric Determination of Molybdenum

G. Goldstein

D. L. Manning

A method was developed for the spectrophotometric determination of molybdenum in slurries of thorium oxide, in solutions of uranyl sulfate, and in samples of steel. In this method the molybdenum is extracted from a strongly acidic solution into a solution of α -benzoinoxime in chloroform, after which a complex between molybdenum and quercetin (3,3',4',7-pentahydroxyflavone) is formed by the addition of an ethanolic solution of quercetin to a portion of the organic extract. The molybdenum concentration is calculated from the absorbancy of the solution of the yellow complex, which is measured at a wavelength of $420 \text{ m}\mu$.

²R. P. Hollingworth, "Spectrophotometric Determination of Fluorine in Rocks," *Anal. Chem.* **29**, 1130 (1957).

The optimum molybdenum concentration range was found by the method of Ringbom³ to be 0.1 to 2.0 $\mu\text{g}/\text{ml}$. Of a large number of substances examined, only tungsten and vanadate interfere in the method; the elements ordinarily present in slurries of thorium oxide do not interfere.

Flame Photometric Determination of Lanthanum

T. C. Rains J. A. Dean⁴

The work on the flame photometric method for the determination of lanthanum was continued⁵ and

³A. Ringbom, "Über die Genauigkeit der colorimetrischen Analysenmethoden I," *Z. anal. Chem.* 115, 332 (1939).

⁴Consultant, University of Tennessee.

⁵T. C. Rains, *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1956*, ORNL-2218, p 44 (classified).

was extended to include the oxide bands of lanthanum that are formed at longer wavelengths (Fig. 22). Additional experiments were carried out to establish the effectiveness of organic solvents in enhancing the sensitivity and in eliminating various interferences. This work was carried out in conjunction with similar work done at the University of Tennessee. At the University, a Beckman model DU instrument has been used, whereas in the HRP laboratory, an ORNL high-sensitivity, single-beam, grating flame photometer is being used. The latter instrument was found to be more applicable in the red region of the spectrum; however, for measurements in the blue region of the spectrum; however, for measurements in the blue region, the use of the Beckman instrument leads to greater resolution. In both cases, however, the sensitivity of the method was increased 100-fold

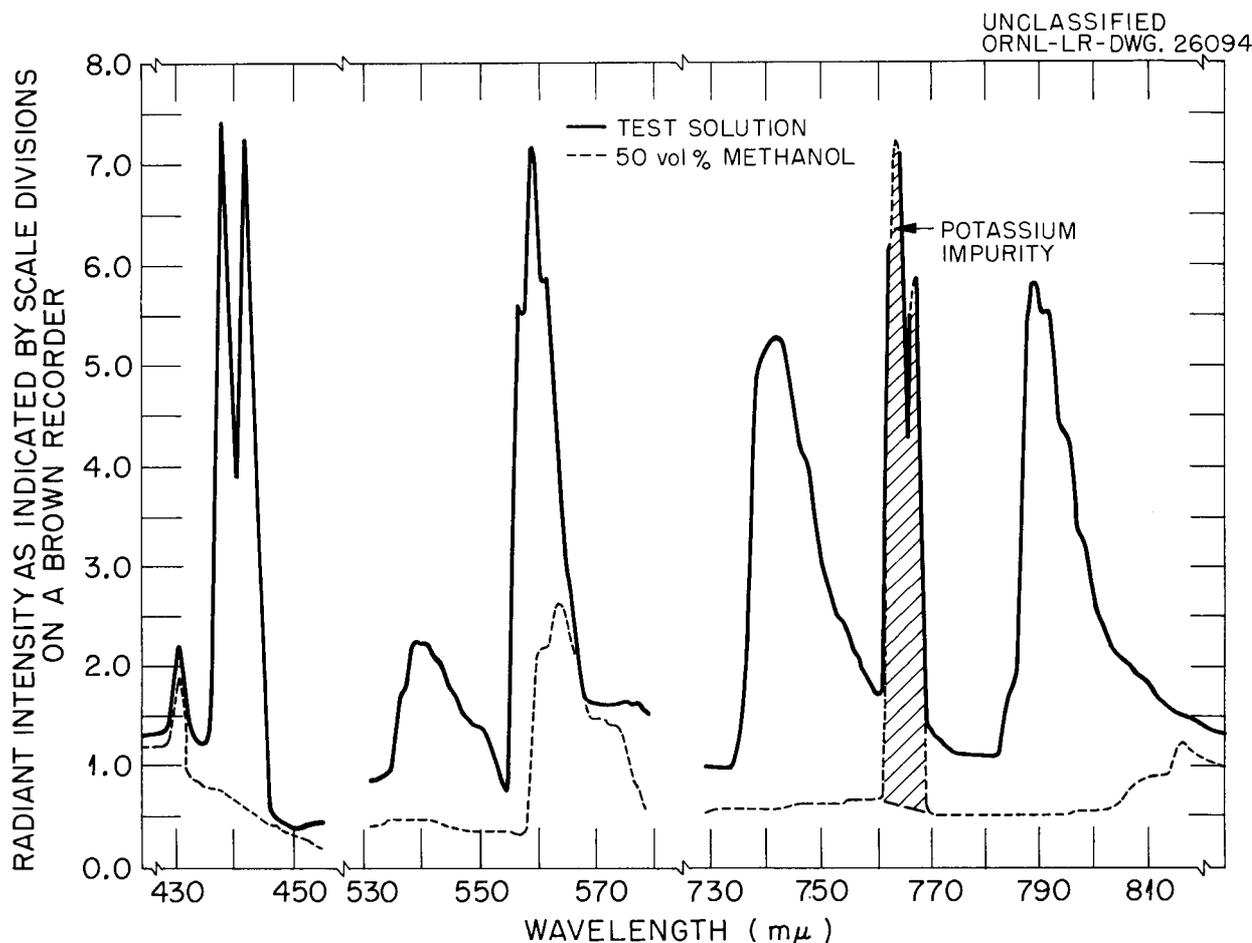


Fig. 22. Emission Spectrum of Lanthanum Oxide, LaO . In the wavelength regions 435 to 500 $\text{m}\mu$ and 532 to 580 $\text{m}\mu$, the test solution was 100 μg of La per milliliter of 50 vol % methanol; in the region 730 to 820 $\text{m}\mu$ it was 20 μg of La per milliliter of 50 vol % methanol.

by measuring the radiant intensity of the lanthanum oxide from an organic medium. From 2 to 20 $\mu\text{g}/\text{ml}$ of lanthanum can be determined with a relative standard deviation of 5%. Of 30 elements tested as possible interferences, many were found to interfere in aqueous or in 50% methanol media when the concentration of any one of these elements exceeded 100 $\mu\text{g}/\text{ml}$; however, interference from most of these elements can be avoided by the extraction of the lanthanum from a 1 M acetate solution, buffered at pH 5, into a 0.1 M solution of thenoyltrifluoroacetone (TTA) in hexone and the subsequent measurement of the radiant intensity of the lanthanum in the hexone solution. Almost all the interfering elements

either remain in the raffinate or do not interfere when the measurement of radiant intensity is made on the organic phase. Titanium and aluminum are exceptions; they interfere when present in concentrations exceeding that of lanthanum. Fluoride and phosphate inhibit the extraction of lanthanum.

In the separation of lanthanum from interfering substances it was noted that the acetate concentration has a marked effect on the degree of extraction of lanthanum into hexone solutions of TTA (Fig. 23). As the acetate concentration increases, the pH at which complete extraction of lanthanum can be achieved likewise increases. Advantage can be taken of this effect when large quantities of thorium or uranium must be removed,

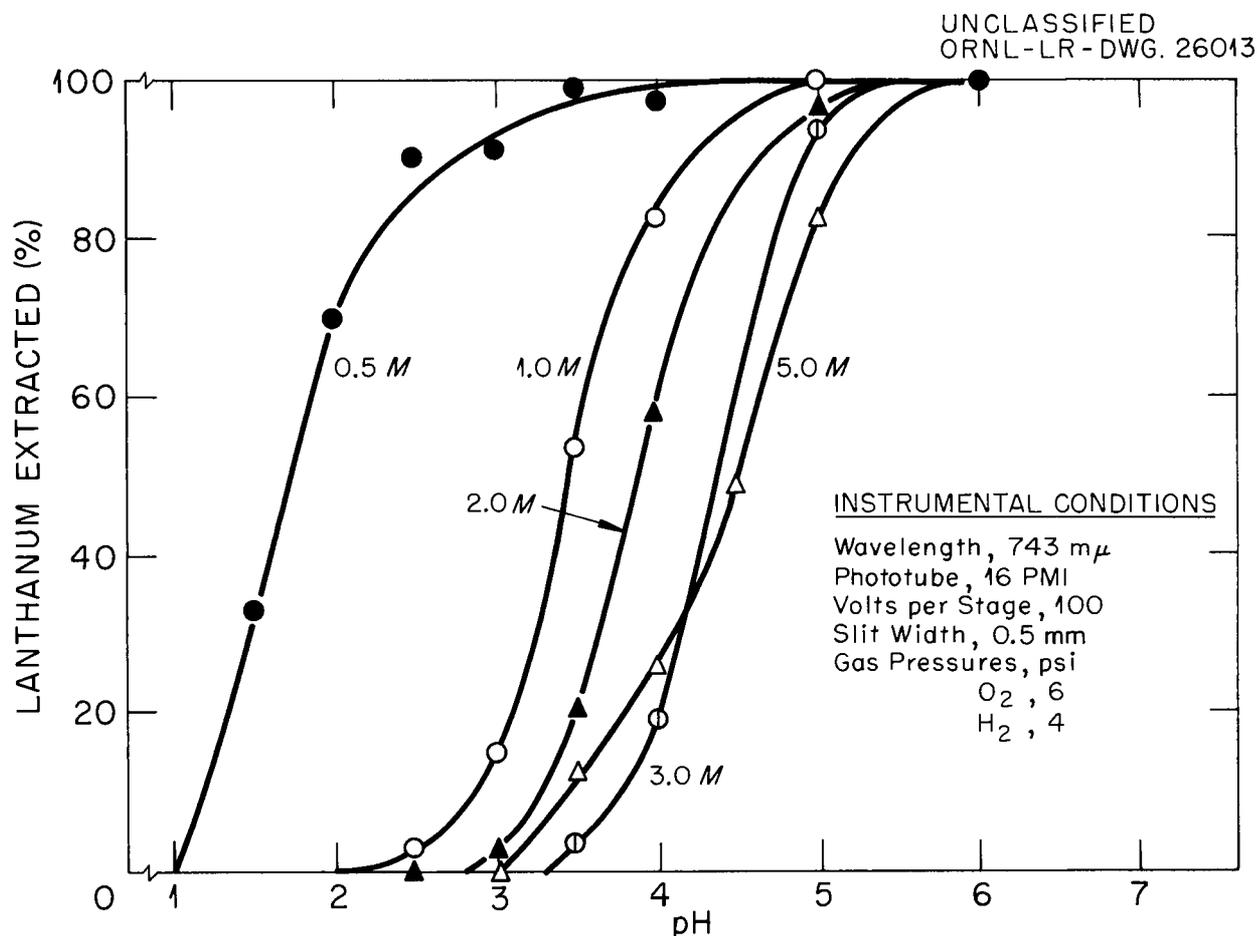


Fig. 23. Effect of Acetate Concentration of Aqueous Phase at Various pH Values on the Extraction of Lanthanum into a 0.1 M Solution of Thenoyltrifluoroacetone (TTA) in Hexone. The conditions were: phase ratio (vol), 1:1; aqueous phase, La concentration, 20 $\mu\text{g}/\text{ml}$; acetate ion concentration (M), as shown; pH, as above (adjusted by addition of CH_2ClCOOH or $\text{CH}_3\text{COONH}_4$); organic phase, 0.1 M solution of TTA in hexone.

since, at a pH of 1.5 and an acetate concentration of 1 M, lanthanum cannot be extracted, whereas both thorium and uranium are extractable into a hexone solution of TTA from this medium.

Spectrophotometric Determination of Aluminum in Thorium Oxide

G. Goldstein D. L. Manning

A solvent-extraction procedure was developed for use in the isolation and subsequent spectrophotometric determination of low concentrations of aluminum in slurries of thorium oxide that are contaminated with additives, corrosion products of steel, and other impurities. The isolation of aluminum is achieved by first extracting a dilute perchloric acid solution of the slurry with a chloroform solution of TTA, followed by an extraction of aluminum with a chloroform solution of 8-quinolinol in the presence of peroxide and nitilotriacetic acid at a pH of 8.0. The aluminum-8-quinolinol complex in the chloroform phase is measured either spectrophotometrically at a wavelength of 390 m μ or fluorometrically, depending upon the quantity present. The method is satisfactory for the estimation of aluminum in concentrations ranging from 0.2 to 3 μ g/ml in the final solution used for the absorbancy measurement. A concentration as small as 0.04 μ g/ml can be measured fluorometrically. The relative standard deviations are approximately 3 and 5%, respectively. The use of this procedure effectively eliminates the interferences of iron, thorium, titanium, uranium, zirconium, vanadium, and molybdenum. The interferences of copper, zinc, and nickel are eliminated by washing the chloroform phase, which contains the aluminum, with a dilute solution of sodium cyanide prior to making the absorbancy measurement. If manganese and cobalt are present in addition to the above-mentioned interferences, it is necessary to use an alternative procedure, which consists in an extraction with TTA at a pH of 1.5 followed by a diethyldithiocarbamate extraction in the presence of tartrate at a pH of 8.0. By application of this scheme of separation, the difficulties due to interferences usually encountered in the fluorometric determination of aluminum are eliminated.

Flame Photometric Determination of Aluminum

T. C. Rains

A direct, flame photometric procedure was developed whereby aluminum can be determined in slurries of impure thorium oxide and other materials at a concentration level not less than 10 ppm. In order to attain the requisite sensitivity and to eliminate interferences from thorium and a number of other elements, the aluminum is extracted from an acetate-buffered solution into a 0.1 M solution of TTA in hexone, after which the radiant intensity of the aluminum is measured. The radiant intensity is enhanced approximately 100-fold by the use of an organic medium (hexone) rather than an aqueous medium. Either the atomic line at 396 m μ or the molecular A10 band at 484 m μ can be used for the measurement of the radiant intensity; the sensitivity of the former measurement is 0.5 μ g/ml per scale division, whereas that of the latter is 0.25 μ g/ml per scale division. Aluminum in concentrations from 5 to 50 μ g/ml can be satisfactorily determined with a relative standard deviation of 10%.

The study of interferences showed that uranium(VI), chromium(VI), thorium, potassium, calcium, magnesium, barium, and iron(III), each in concentrations of 1 mg/ml or less, do not interfere. Sodium, lithium, and titanium interfere in concentrations greater than 0.04 mg/ml, whereas molybdenum, tungsten, copper, and nickel interfere when present in concentrations in excess of 0.02 mg/ml.

Spectrophotometric Determination of Microgram Quantities of Titanium in Thorium Oxide

I. B. Rubin T. C. Rains

A modification of a method proposed by Szarvas and Csiszar⁶ for the spectrophotometric determination of titanium was applied to the estimation of microgram quantities of titanium in slurries of thorium oxide. A perchloric acid solution of

⁶P. Szarvas and B. Csiszar, "Colorimetric Determination of Small Amounts of Titanium(IV) in the Presence of Large Amounts of Iron(III)," *Magyar Kem. Folyoirat* 61, 50 (1955).

thorium oxide is buffered with an acetic acid-acetate buffer at a pH of 5, disodium ethylenediaminetetraacetate is added to complex thorium and iron, and then disodium-1,2-dihydroxybenzene-3,5-disulfonate (Tiron) is added to develop the intensely yellow-colored complex of the titanium. After the solution is diluted to 25 ml, the absorbancy, from which the concentration of titanium is calculated, is measured at 380 m μ in a 5-cm cell. The absorbancy measurement must be made vs a sample blank because iron also forms a colored complex with disodium ethylenediaminetetraacetate. For greatest accuracy a slight correction for the reagent blank must also be made. Beer's law is obeyed over the titanium concentration range 0.05 to 2 μ g/ml of solution on which the absorbancy is measured. From 1 to 10 μ g of titanium in a volume of 25 ml can be determined with a relative standard deviation of 5%. The presence of 100 to 400 mg of thorium in the final 25-ml volume of solution used for the absorbancy measurement causes a positive error of the order of 5%. Titanium in the concentration range 3 to 6 ppm in a number of samples from HRP test loops of thorium oxide slurries has been determined by this method.

Distribution of Hydrazine in Thorium Oxide Slurries

T. C. Rains I. B. Rubin

The spectrophotometric method of Watt and Chrisp⁷ was found to be satisfactory for the determination of small amounts of hydrazine in slurries of thorium oxide. Tests conducted at room temperature and at normal pressure indicate that about 30% of the hydrazine is adsorbed on the thorium oxide and that about one-half the hydrazine can be desorbed by shaking the slurry with the chromogenic reagent, *p*-dimethylaminobenzaldehyde, that is used in the spectrophotometric determination.

Polarographic and Beta-Counting Determination of Technetium

R. G. Ball D. L. Manning

Polarographic and beta-counting methods were applied to the determination of microgram quantities

of technetium in solutions of uranyl sulfate. By means of the polarographic method in which the diffusion current of the pertechnetate ion is measured at an $E_{1/2}$ of -0.68 v vs the S.C.E., concentrations of technetium in the range 2.0 to 8.0 μ g/ml can be determined with a relative standard deviation of the order of 1%. Concentrations of technetium as small as 0.2 ppm can be estimated if a 5-ml sample is used.

In the counting procedure the beta activity of Tc^{99} ($t_{1/2} = \sim 2 \times 10^5$ y) is measured with a Geiger-Mueller counter. No prior separation is required, since technetium is the only beta emitter present. For samples of 1-ml volume or less, concentrations of technetium as small as 0.1 ppm can be determined by this method.

Determination of Sulfate by Indirect, Potentiometric Titration

I. B. Rubin T. C. Rains

An indirect, potentiometric titration method was developed for the determination of microgram quantities of sulfate. In this procedure a standard solution of barium perchlorate in excess of that required to precipitate the sulfate is added, after which the excess barium is determined by potentiometric titration with a standard solution of disodium ethylenediaminetetraacetate; a mercury indicator electrode⁸ is used to detect the end point. It was established experimentally that, for best results, the precipitation of sulfate should be made from a slightly alkaline solution at room temperature and that an excess of 300 to 500 μ g of barium should be added. From 100 to 800 μ g of barium can be determined with a relative standard deviation of 5% if the titration is made with a 0.002 M solution of disodium ethylenediaminetetraacetate in 50% methanol at a pH of 9.5 to 10 and if the solution that is to be titrated contains one drop of a 0.01 M solution of mercuric ethylenediaminetetraacetate. From 125 to 600 μ g of sulfate can be estimated by this indirect procedure with a relative standard deviation of 5%. Phosphate in any quantity and fluoride in quantities greater than 400 μ g interfere.

⁷G. W. Watt and J. D. Chrisp, "A Spectrophotometric Method for the Determination of Hydrazine," *Anal. Chem.* 24, 2006 (1952).

⁸R. W. Schmid and C. N. Reilley, "A Rapid Electrochemical Method for the Determination of Metal Chelate Stability Constants," *J. Am. Chem. Soc.* 78, 5513 (1956).

Determination of Lower Limit of Quantitative Measurement of Potassium by Flame Photometry

T. C. Rains

In the operation of certain test loops a solution of potassium sulfate was being circulated so that it could be ascertained whether any of this solution was leaking into a high-pressure water system located back of the pumps on the loops. It was established that an analytical procedure suitable for the measurement of changes in potassium concentration of the order of $0.1 \mu\text{g/ml}$ could be used to detect any such leakage. The limit of sensitivity for potassium attainable by flame photometry by use of the ORNL model Q-1457A flame photometer, with the 16PMI photomultiplier tube, was found to be $0.003 \mu\text{g/ml}$ per scale division. Therefore changes in the potassium concentration of the order of $0.02 \mu\text{g/ml}$ can be detected, that is, approximately one-fifth of the minimum change adjudged necessary to indicate and evaluate leakage in the loop systems.

Determination of Cerium in Solutions of Uranyl Sulfate by Redox Titration

D. L. Manning

A redox titration procedure for macroquantities of cerium⁹ was adapted to the determination of microgram quantities of cerium. Cerium(III) is oxidized to cerium(IV) by titration with a standard solution of potassium permanganate, $\sim 0.0002 N$. The end point of the titration is established photometrically. From 50 to 200 μg of cerium in a volume of 40 ml can be determined by this procedure with a relative standard deviation of about 6%. Uranium does not interfere; consequently, no separation of it is required.

Spectrophotometric Determination of Arsenic in Solutions of Uranyl Sulfate

D. L. Manning

A spectrophotometric¹⁰ method was applied to the determination of arsenic in concentrations from 5 to 100 $\mu\text{g/ml}$ in solutions of uranyl sulfate. Arsenic(V) is reacted in a 0.15 M sulfuric acid

solution with ammonium molybdate, thereby forming a heteropoly arsenomolybdic acid. The arsenomolybdic acid is reduced with 1,2,4-aminonaphthol-sulfonic acid to molybdenum blue. The concentration of arsenic is calculated from the absorbancy measurements, which are made at a wavelength of 840 $m\mu$. Uranium does not interfere in this method and therefore requires no prior separation. Arsenic in concentrations from 0.2 to 4 $\mu\text{g/ml}$ in the solution used for the absorbancy measurement can be determined by this method with a relative standard deviation of $\sim 3\%$.

Spectrophotometric Determination of Cobalt in Slurries of Thorium Oxide

G. Goldstein

D. L. Manning

A very sensitive method was desired for the determination of cobalt in concentrations of the order of 1 ppm or less in slurries of thorium oxide in order to indicate whether excessive corrosion of pump components was occurring in a closed, high-pressure system. A survey of chromogenic reagents for cobalt indicated that 1-(2-pyridylazo)-2-naphthol (PAN) appeared to possess the specified sensitivity and selectivity.¹¹ These properties were confirmed experimentally. It was found that as little as 0.5 μg of cobalt(III) can be determined by reacting it with PAN at a pH of 5, extracting the green cobalt-PAN chelate into 5 ml of chloroform, and measuring the absorbancy of the extract at 640 $m\mu$. In applying this procedure to the analysis of impure thorium oxide for cobalt, the cobalt is separated from thorium and other substances by making the test solution 10 M with HCl, heating the solution to 80°C, and then passing it through a column of an anion exchange resin (Dowex 1, 50 to 100 mesh, chloride-form).¹² The cobalt is retained on the resin, whereas thorium and also aluminum, nickel, titanium, chromium(III), and manganese(II) are contained in the effluent. The cobalt is eluted with 3.5 M HCl, following which the acid is removed by evaporation of the eluate to near dryness. The residue is then dissolved in dilute HCl, and the solution is

⁹T. L. Marple, E. P. Przybylowicz, and D. N. Hume, "Photometric Titration of Cerium(III)," *Anal. Chem.* 28, 1892 (1956).

¹⁰E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2d ed., p 178, Interscience, New York, 1950.

¹¹K. L. Cheng and R. H. Bray, "1-(2-Pyridylazo)-2-naphthol as a Possible Analytical Reagent," *Anal. Chem.* 27, 782 (1955).

¹²K. A. Kraus, F. Nelson, and G. W. Smith, "Anion-Exchange Studies. IX. Adsorbability of a Number of Metals in Hydrochloric Acid Solutions," *J. Phys. Chem.* 58, 11 (1954).

buffered with an acetate-citrate buffer at pH 4.5 to 5.0. The cobalt-PAN chelate is formed, after which the absorbancy is measured as previously described. Beer's law is obeyed over the range 0.5 to 7 μg of cobalt in the final solution used for the absorbancy measurement. The relative standard deviation is of the order of 10% at this concentration level, although under ideal conditions a relative standard deviation of 5% can be attained. Of a large number of elements tested for interference, copper alone interferes in the determination; however, even copper can be tolerated in concentrations that do not exceed that of the cobalt.

Pyrolytic Separation and Spectrophotometric Determination of Ruthenium

R. H. Powell R. G. Ball
D. L. Manning

A method was devised for the separation of 10 to 100 μg of ruthenium as a nitroso salt, chloride, or sulfate from uranyl sulfate and its subsequent spectrophotometric determination. Decomposition of the nitroso salt and volatilization of the ruthenium are accomplished by pyrolysis for 1 hr at 1000°C in a stream of moist oxygen. The ruthenium is absorbed and reduced to the trivalent state in 1 M HCl that is saturated with sulfur dioxide. Following the addition of β -nitroso- α -naphthol, the solution is placed in boiling water for about 10 min to accelerate the development of the blue ruthenium- β -nitroso- α -naphthol complex and to expel excess sulfur dioxide. After the solution is cooled, the absorbancy of this complex, from which the ruthenium concentration is calculated, is measured at 560 $m\mu$. Ruthenium in concentrations from 0.2 to 6 $\mu\text{g}/\text{ml}$ in the solution used for the absorbancy measurement can be determined by this method with a relative standard deviation of $\sim 3\%$.

Flame Photometric Determination of Ruthenium

T. C. Rains

It was established experimentally that ruthenium in fairly low concentrations can be determined by flame photometry by measurement of the radiant intensity of aqueous solutions of either a ruthenium nitroso salt or ruthenium chloride at 373 $m\mu$. Over the ruthenium concentration range of 10 to 50 $\mu\text{g}/\text{ml}$, the radiant intensity is a linear function of concentration. Since ruthenium in the

form of a nitroso salt can be determined by this method, the method offers an advantage over colorimetric methods which are not applicable unless the stable nitroso salt is first decomposed. Uranium in concentrations greater than 2 mg/ml interferes with the flame photometric determination of ruthenium because of background radiation. Iron also interferes because of a series of iron lines located in the spectral region used for the ruthenium determination.

METHODS DEVELOPMENT GROUP

J. C. White

Extraction of Elements from Acidic Solutions with Tri-*n*-octylphosphine Oxide (TOPO) in Cyclohexane

J. C. White W. J. Ross C. A. Horton

Study of the applicability of tri-*n*-octylphosphine oxide (TOPO), $n\text{-(C}_8\text{H}_{17}\text{)}_3\text{PO}$, in cyclohexane for the solvent extraction of certain cationic elements from acidic solutions was continued. The two principal objectives of this investigation are to gain information on the extractability of particular metals and to apply this characteristic to useful separations by solvent extraction. To date, extraction data have been obtained for uranium, molybdenum, bismuth, zirconium, thorium, niobium, tantalum, titanium, iron, and chromium. Final reports on the solvent extraction of chromium¹³ and iron¹⁴ have been published. Short summaries of the data on the solvent extraction of the other metals are included in the following paragraphs. Comparisons of the extraction coefficients for some of these metals as a function of acid concentration are shown in Figs. 24 and 25.

Zirconium. - Zirconium is extracted exceedingly well from either nitric or hydrochloric acid by TOPO in cyclohexane. The extraction is decidedly acid-dependent; for example, the extraction coefficient increases sharply from about 20 in 1 M acid to around 1000 in 7 M acid. Similar enhancement is also achieved in chloride or nitrate systems by increasing the concentration of the anion and maintaining the acid concentration constant at 1 M.

¹³J. C. White and W. J. Ross, *Extraction of Chromium with Trioctylphosphine Oxide*, ORNL-2326 (July 9, 1957).

¹⁴W. J. Ross and J. C. White, *The Solvent Extraction of Iron with Tri-*n*-octylphosphine Oxide*, ORNL-2382 (Sept. 26, 1957).

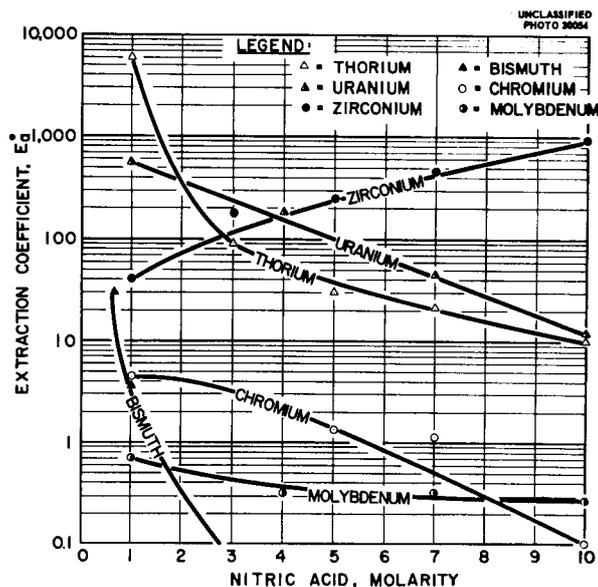


Fig. 24. Results of the Extraction of Some Metal Ions by 0.1 M Tri-*n*-octylphosphine Oxide in Cyclohexane from Nitric Acid Solutions.

The loading value of 0.5 mmole of TOPO is 25 mg of zirconium. The molar ratio of TOPO to Zr is 2; the formula of the species extracted from chloride solution is $ZrCl_4 \cdot 2[n-(C_8H_{17})_3PO]$. As much as 20 mg of zirconium can be extracted completely in 5 min from 7 M HCl, whereas 15 mg is separated to an extent that exceeds 99% in acidic solutions (1 M) that contain 7 M nitrate. The extraction from chloride and nitrate solutions remains essentially complete at a phase ratio, V_a/V_o , of 20. Relatively no extraction of zirconium occurs in systems that contain substances which form stable complexes with zirconium. Separation of zirconium from solutions of certain anions, such as sulfate and tartrate, is enhanced, however, by the addition of chloride or nitrate to give 7 M solutions and adjustment of the acidity to at least 1 M, to the degree that complete extraction can be achieved. No such effect was observed on the addition of chloride or nitrate to fluoride solutions of zirconium. Extraction of zirconium from perchlorate systems is readily achieved; however, the resulting extract frequently consists of two immiscible organic phases, which thereby reduce the possibility of the extracted metal being completely recovered.

Molybdenum. - Molybdenum(VI) is extracted readily by TOPO in cyclohexane from acidic

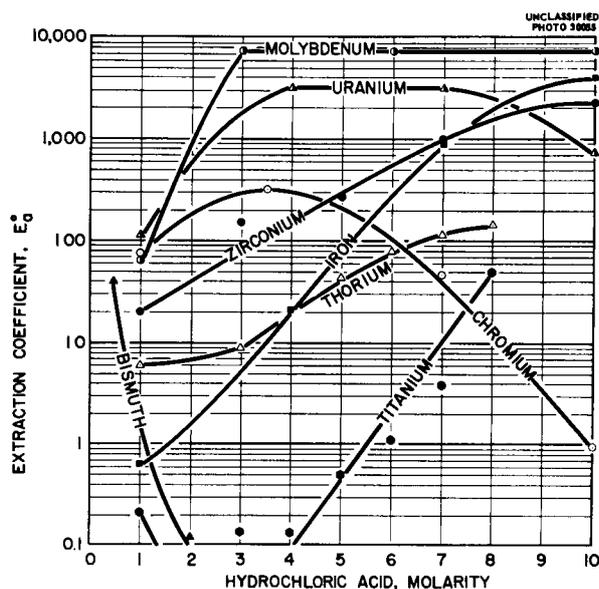


Fig. 25. Results of the Extraction of Some Metal Ions by 0.1 M Tri-*n*-octylphosphine Oxide in Cyclohexane from Hydrochloric Acid Solutions.

chloride solutions over a wide range of acid concentration (0.1 to 10 M). Extraction coefficients of the order of several thousand were observed for solutions of hydrochloric acid more concentrated than 3 M. The extractability is great, that is, 25 mg of molybdenum from 5 M HCl per 0.5 mmole of TOPO. In a single equilibration of approximately 10 min, 8 mg of molybdenum can be extracted completely from a solution that is 3 to 10 M in HCl with 0.5 mmole of TOPO at phase ratios (V_a/V_o) as high as 20. The extracted species is probably $MoO_2Cl_2 \cdot 2[n-(C_8H_{17})_3PO]$. Molybdenum is essentially inextractable from acidic sulfate, nitrate, or perchlorate solutions; however, by the addition of sufficient chloride ions, molybdenum can be extracted from these solutions. Molybdenum can be re-extracted easily from the organic phase by equilibration of this phase with 2 M NH_4OH .

Uranium. - The extent to which uranium(VI) is extracted from acidic solutions varies with the type, as well as the concentration, of acid. In chloride systems the maximum extraction coefficients are obtained in 4 to 10 M HCl; in these systems as much as 19 mg of uranium(VI) is extracted completely by 0.5 mmole of TOPO. The extraction coefficient of uranium in nitrate systems decreases somewhat as the concentration of acid

increases. In 1 M HNO₃ as much as 40 mg of uranium is extracted by 0.5 mmole of TOPO to an extent that exceeds 99%. In hydrochloric or nitric acid systems the loading capacity of 0.5 mmole of TOPO is 55 to 60 mg of uranium(VI). Equilibrium is attained within several minutes. The extractable species are believed to be UO₂Cl₂·2[n-(C₈H₁₇)₃PO] and UO₂(NO₃)₂·2[n-(C₈H₁₇)₃PO]. Uranium(VI) is extracted to a much lesser degree from sulfate and perchlorate solutions and is essentially completely retained in the aqueous phases of phosphate systems. The addition of chloride or nitrate to these solutions materially increases the degree of extraction.

Bismuth. — The extraction of bismuth from solutions of hydrochloric or nitric acid is characterized by its strong dependence on acid concentration. For example, bismuth is readily extracted (to the extent of about 9 mg per 0.5 mmole of TOPO) from 0.2 M HNO₃ or HCl. When the acid concentration exceeds 1 M, however, the extraction is decreased by a factor of about 10. Only a few micrograms were extracted from a 20-ml solution of 5 M HCl or HNO₃ that contained 1 g of bismuth. This "negative acid-concentration coefficient" of extraction is useful in the separation of bismuth from uranium by extraction with TOPO in cyclohexane.

Thorium. — A study of the extraction of thorium from acidic solutions into solutions of TOPO in cyclohexane is now in progress. Initial results show that thorium is extracted in various degrees from chloride, nitrate, sulfate, and perchlorate media. The extraction coefficient of thorium is enhanced in hydrochloric acid systems and is decreased in nitric acid when the concentration of acid is increased. The loading capacities of 0.5 mmole of TOPO in chloride and in nitrate systems are 35 and 39 mg of thorium, respectively. These values indicate an extracted species that has a ratio of three moles of TOPO per mole of thorium; the formula for this species is probably ThCl₄·3[n-(C₈H₁₇)₃PO]. In 7 M HCl systems as much as 14 mg of thorium is extracted to a degree that exceeds 99%, whereas the extraction of 20 mg is 95% complete. The optimum HNO₃ concentration is 1 M; in such systems 23 mg is extracted completely, but as much as 32 mg is 95% extracted. Extraction of thorium from sulfate solutions is of a very low degree. In perchlorate systems the values for the extraction coefficient pass through

a minimum in 3 M acid media, whereas the maximum value that has been obtained in 1 M HClO₄ is approximately half that found in 7 M HCl systems.

Niobium. — Niobium(V) is extracted only from those hydrochloric acid solutions in which a sufficient concentration of some complexing agent, such as oxalic, tartaric, citric, or lactic acid, is present. The standard solutions of niobium used in this work were either 0.33 M in tartaric acid or 0.2 M in lactic acid. A maximum in the degree of extraction of niobium as a function of hydrochloric acid concentration was observed at 4 M HCl, where the extraction was more than 99% complete. Extraction does not occur in the presence of nitric acid. In sulfuric acid, hydrolysis occurs too rapidly to permit useful application of this acid.

Tantalum. — The extraction of tantalum follows the same pattern as that of niobium except to a lesser extent. In 6 M HCl–0.2 M lactic acid, about 60% of 5.5 mg of tantalum was extracted, which is the maximum for any system tested to date. These tests are being made with Ta¹⁸¹ tracer.

Titanium. — Titanium is extracted from either strong sulfuric or hydrochloric acid solutions. For complete extraction (>98%), the sulfuric acid concentration must be at least 7 M; hydrochloric acid should be at least 8 M. In more dilute acid solutions the degree of extraction decreases sharply. The presence of 0.5 M tartaric acid has no depressing effect on the extraction. The molar ratio of titanium to TOPO is 2, and therefore the postulated formula of the extracted species is TiOSO₄·2[n-(C₈H₁₇)₃PO].

Formation of Colored Species with Tri-*n*-octylphosphine Oxide (TOPO) in Cyclohexane Solutions

J. C. White W. J. Ross J. P. Young

Several applications were made of the extraction characteristics of TOPO dissolved in cyclohexane. A method¹⁵ was developed and tested for the extraction of a few micrograms of chromium from highly concentrated solutions of alkali metals, derived from the dissolution of NaK, and for the

¹⁵C. K. Mann and J. C. White, *Extraction of Chromium with Trioctylphosphine Oxide from Acidic Solutions of Alkali Metal Salts and Its Determination in Situ as the Chromium-Diphenylcarbazine Complex*, ORNL CF-56-10-86 (Oct. 23, 1956).

determination of the chromium as the diphenyl-carbazide complex, which was formed directly in the organic extract. The same general approach, in which the formation and development of the colored species were carried out in the organic extract ("nonaqueous colorimetry"), was successfully applied to the separation and determination of uranium.¹⁶ This success in applying nonaqueous colorimetry to the cyclohexane-TOPO-metal extracts has led to similar investigations in other systems. Progress along these lines is reported in the following paragraphs.

Zirconium-Pyrocatechol Violet. - The blue color of the zirconium-pyrocatechol violet complex was used in the development of a sensitive method for the direct, spectrophotometric determination of zirconium in organic extracts that contain TOPO. This method is based on the absorbancy of the zirconium-pyrocatechol violet complex at a wavelength of 660 $m\mu$ in a TOPO-cyclohexane-ethanol medium. The molar absorbancy index for this complex is 38,500. The absorbancy of the complex conforms to Beer's law up to a zirconium concentration of 1 $\mu\text{g}/\text{ml}$. In order to eliminate the interference of several elements that can also be extracted in this medium, zirconium is extracted into 0.01 *M* TOPO from aqueous solutions that contain ammonium thiocyanate and that are 7 *M* with respect to hydrochloric acid. The method is useful for the separation of zirconium from large amounts of aluminum, uranium, vanadium, iron, and chromium, and for its subsequent determination. Moderate amounts of thorium do not interfere. Equal amounts of molybdenum, by weight, are tolerable. Titanium and hafnium interfere with the method. Zirconium can be determined in the presence of milligram quantities of phosphate and sulfate. This method has the advantage, common to most extraction methods, that zirconium can be extracted from a given volume of its aqueous solution into a smaller volume of organic solvent. The relative standard deviation for the determination of zirconium by this method is less than 3%.

Zirconium-Alizarin. - The zirconium-alizarin reaction was applied to a cyclohexane solution of TOPO. The organic extract was diluted with acetone until the concentration of zirconium was

less than 140 $\mu\text{g}/\text{ml}$. A test portion was then transferred to a 10-ml volumetric flask and was combined with 4 ml of a 0.05% (w/v) solution of alizarin in ethanol, following which the solution was diluted to volume with ethanol. The intensity of the red zirconium-alizarin color was measured after 1 hr at 525 $m\mu$ vs a reference solution that was treated in the same manner as the sample. Beer's law was adhered to when the zirconium concentration of the final solution was less than 15 $\mu\text{g}/\text{ml}$. The color faded only slightly after the initial hour. The molar absorbancy index was 7000 at 525 $m\mu$. Iron(III) and uranium(VI) do not interfere when present in amounts equal to the zirconium content; however, chromium in an amount equal to that of the zirconium increases the absorbancy by approximately 10%.

Thorium-Alizarin. - The thorium-alizarin reaction is carried out as described above for zirconium-alizarin. The complex conforms to Beer's law in thorium concentrations up to 11 $\mu\text{g}/\text{ml}$. The absorbancy is measured at 535 $m\mu$, at which wavelength the molar absorbancy index is 12,000. Maximum color, which is stable for at least 1 hr, is developed immediately after the test portion and alizarin are mixed. Zirconium in the same solution, as well as other extracted substances that react with alizarin, interferes.

Titanium Thiocyanate. - Titanium thiocyanate extracts into a 0.01 *M* solution of TOPO in cyclohexane as an intensely colored complex. A possible method of determining titanium by measurement of the absorbancy of titanium thiocyanate in cyclohexane is being evaluated. It has been found that the titanium thiocyanate is extracted equally well from either 7 *M* HCl or 6 *M* H₂SO₄. The molar absorbancy index of the complex is approximately 42,000 at a wavelength of 432 $m\mu$. The absorbancy of the complex is stable for at least 4 hr and conforms to Beer's law for concentrations of titanium as high as 1.5 $\mu\text{g}/\text{ml}$. Other studies of the effect of thiocyanate on the extraction of cations from solutions of hydrochloric acid into cyclohexane which contains TOPO have shown that the extraction of many cationic substances, for example, uranyl, ferric, vanadyl, and vanadate, is grossly hindered under these conditions, whereas zirconium is extractable, but as a colorless complex. Aluminum does not extract into cyclohexane solutions of TOPO. This proposed method for the determination of titanium should therefore be both highly selective and very sensitive.

¹⁶C. A. Horton and J. C. White, *Separation of Uranium by Solvent Extraction with Tri-n-octylphosphine Oxide and Its Direct Colorimetric Determination with Dibenzoylmethane*, ORNL CF-57-7-43 (July 15, 1957).

Crouthamel *et al.*¹⁷ have described an extremely sensitive spectrophotometric method for the determination of titanium with thiocyanate in an acetone-aqueous medium. They stated, however, that the development of the color of the titanium complex requires a precisely controlled procedure. The results that have been obtained to date by extracting the titanium complex with cyclohexane-TOPO have not indicated any such limitations.

Extraction of Acids by Tri-*n*-octylphosphine Oxide (TOPO) in Cyclohexane Solution

J. C. White

W. J. Ross

Tri-*n*-octylphosphine oxide in cyclohexane functions as an extractant only from acidic solutions. Experiments were therefore conducted to determine the degree of extraction of common mineral acids as a function of the acid concentration of the solution being extracted. This concentration was varied from 0.5 to 7 *M*. In all tests 1 mmole (10 ml of a 0.1 *M* solution of TOPO in cyclohexane) of extractant was used. The results are plotted in Fig. 26.

¹⁷C. E. Crouthamel, B. E. Hjelte, and C. E. Johnson, "Thiocyanate Spectrophotometric Analysis of Titanium, Vanadium, and Niobium," *Anal. Chem.* 27, 507 (1955).

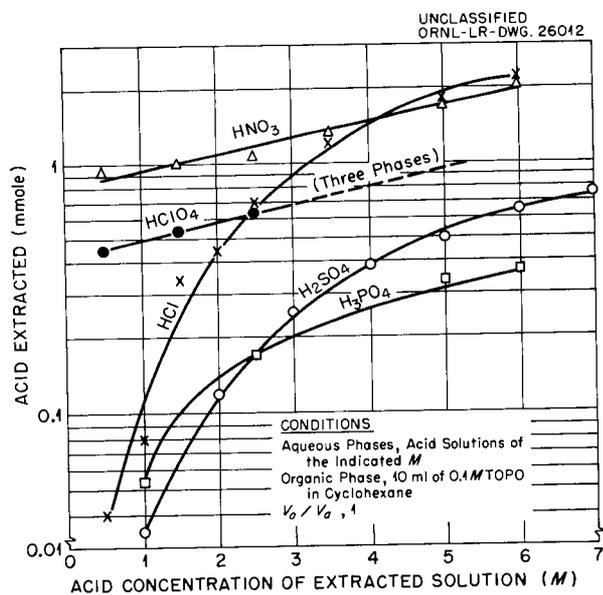


Fig. 26. Effect of Acid Concentration on the Extraction of Mineral Acids from Aqueous Systems into a Solution of Tri-*n*-octylphosphine Oxide in Cyclohexane.

The acids fall into two groups on the basis of rate of extraction. The slopes of the extraction curves for hydrochloric, sulfuric, and phosphoric acids are similar but differ widely from those for nitric and perchloric acids. The mole ratio of acid to TOPO at saturation is 1, except for nitric and hydrochloric acids, for which the ratio is greater than 2 at the 6 *M* level.

The solubility of the TOPO-acid adduct in the cyclohexane phase varies with the acid used. For example, the perchloric acid adduct precipitates at 3 *M* HClO₄, whereas the sulfuric acid adduct precipitates at about 8 *M*. Nitric and hydrochloric acids form more soluble adducts. Usually, these acids also represent the systems most favorable for the extraction of cationic substances.

The absorption spectrum of a cyclohexane-TOPO-acid solution is important because many of the applications of this reagent involve direct absorbancy measurements in the organic phase. Cyclohexane was chosen as diluent since it has a low cutoff in the ultraviolet region at approximately 220 *mμ*. In Fig. 27 the absorption spectra of cyclohexane-TOPO-acid solutions are given over the wavelength range from 190 to 300 *mμ*. No absorption of significance was observed in the visible or near-infrared regions of the spectrum; furthermore, in the region shown, no absorption maxima of any consequence were observed, although the cutoffs vary. The utilitarian value of these solutions as reference solutions is obvious.

Infrared Absorption Spectra of Trialkylphosphine Oxides¹⁸

C. A. Horton

As is shown in Fig. 28, the infrared spectrum of a film obtained by the evaporation of a solution of TOPO in cyclohexane shows a band at 8.8 *μ* that is attributable to the phosphorus-oxygen binding. This band was not observed in the spectrum of a film remaining after the evaporation of a TOPO-cyclohexane extract that contained iron; instead, a new, broad absorption band appeared at 9.3 *μ*. The spectrum of a film that remained from a similar extract of uranium showed a similar band at 9.1 *μ*. The shift that occurs in the wavelength of the maximum absorbancy is due to the presence of metals and indicates complexation of the cation

¹⁸L. L. Burger, *The Esters of the Acids of Phosphorus as Solvents*, HW-44888 (Jan. 3, 1957).

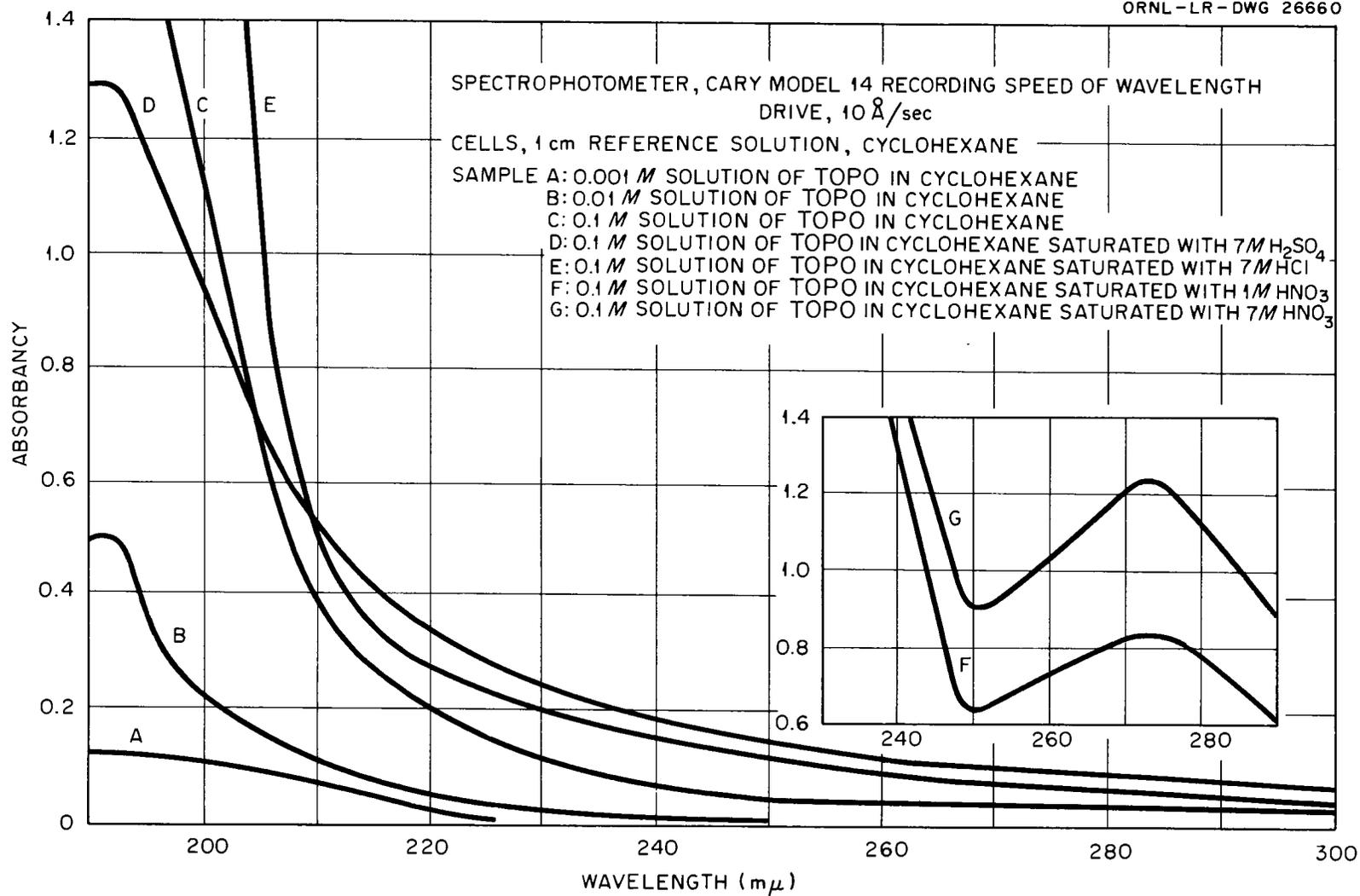


Fig. 27. Ultraviolet Absorption Spectra of Cyclohexane-Tri-n-octylphosphine Oxide-Acid Solutions.

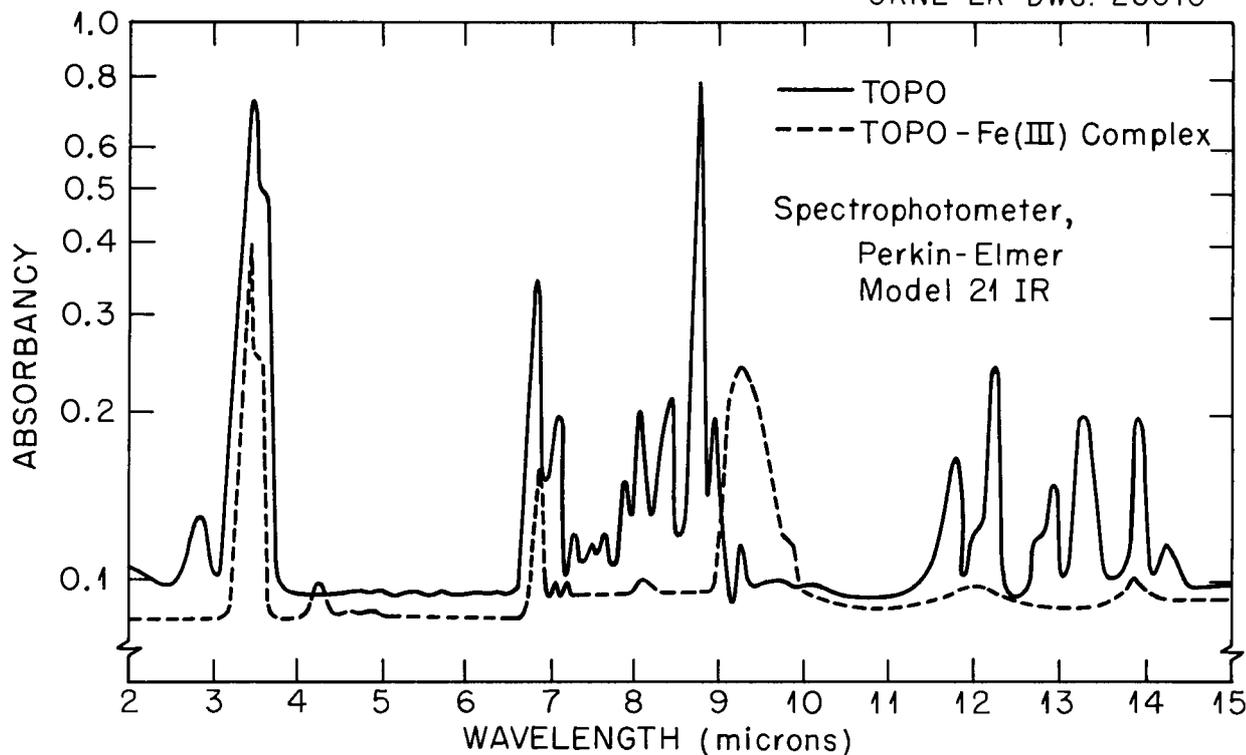
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Fig. 28. Infrared Absorption Spectra of Tri-*n*-octylphosphine Oxide and Its Iron(III) Complex. The substances examined were the films remaining after the evaporation of solutions of TOPO or TOPO-Fe(III) in cyclohexane.

with the phosphoryl-linked oxygen atom. The infrared spectra of tricaprylphosphine oxide and tris-2-ethylhexylphosphine oxide show the band at about 8.5μ that is typical of phosphorus-oxygen binding.

Spectrophotometric Determination of Iron in Hydrocarbon Solutions of Di(2-ethylhexyl) Phosphoric Acid with *o*-Phenanthroline

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

A method was developed for the spectrophotometric determination, by means of *o*-phenanthroline, of iron in di(2-ethylhexyl) phosphoric acid (DEHPA) extracts of sulfate leach liquors of uranium ores. These samples are the extracts obtained when iron was extracted from aqueous solutions of sulfuric acid of pH 1, which are 1 *M* in total sulfate, into 0.1 *M* solutions of DEHPA in kerosene or Varsol.¹⁹

Iron(III) is reduced to iron(II); then the iron(II)-*o*-phenanthroline complex is formed directly in the DEHPA extracts without previous destruction of the organic material. The procedure of Smith and Richter²⁰ for the determination of iron in aqueous media was taken as a guide for the choice of the reducing agent and the concentrations of reagents that were used in the development of the color.

Of the solvents investigated as media for the color development, isopropyl alcohol and acetone were found to be the most satisfactory. Isopropyl alcohol was selected as a diluent because of its lower volatility. A slightly higher molar absorptivity index (12,600) of the complex was measured in the organic media than the highest (11,100) index that has been reported for the complex in water at the absorption maximum of $510 m\mu$, which remains unchanged regardless of solvent. A solution of

¹⁹C. A. Blake, K. B. Brown, and C. F. Coleman, ORNL-1903 (June 21, 1955) (classified).

²⁰G. F. Smith and F. P. Richter, "Phenanthroline and Substituted Phenanthroline Indicators," p 94, The G. Frederick Smith Chemical Co., Columbus, Ohio, 1944.

hydroquinone in isopropyl alcohol is used for the reduction of the iron(III) to iron(II) prior to the formation of the iron(II)-*o*-phenanthroline complex by the addition of an ethanolic solution of *o*-phenanthroline. The color of the iron(II)-*o*-phenanthroline complex in isopropyl alcohol develops completely after 2 hr; however, the period of color development is shortened to 30 min by the addition of small amounts of alcohol-soluble acids and bases, such as acetic acid and pyridine. Since a small decrease in molar absorptivity index was observed with the addition of pyridine, acetic acid was selected as the preferred reagent. Stronger acids, such as chloroacetic acid, were no more effective than glacial acetic acid.

The iron in DEHPA extracts which is to be determined by this method may be contained in a test portion of 4 ml or less of any hydrocarbon. Volumes of test portions greater than 4 ml exceed the solubility of the hydrocarbons in isopropyl alcohol.

Uranium and vanadium have also been reported to be extractable from aqueous sulfate solutions into hydrocarbon solutions of DEHPA.¹⁹ Uranium in concentrations of 1 mg/ml causes no interference in this method for the determination of iron, but vanadium in concentrations greater than 4 $\mu\text{g/ml}$ leads to serious interference.

The iron(II)-*o*-phenanthroline complex in isopropyl alcohol obeys Beer's law in the concentration range from 0.2 to 5 $\mu\text{g/ml}$; the relative standard deviation of the method is 2%. This method is simple and rapid and offers many advantages over conventional methods; for example, it eliminates the time-consuming separation steps, such as oxidation of the organic material and stripping of the organic phases with a solution of carbonate.

Oxidation of Chromium with Argentic Oxide

J. P. Young J. R. French

The oxidation of chromium with argentic oxide, Ag_2O , prior to the spectrophotometric determination of chromium with diphenylcarbazide was investigated. Lingane and Davis,²¹ who have discussed argentic oxide as an oxidimetric reagent, reported that the oxidation of chromium(III) to chromium(VI)

²¹J. J. Lingane and D. G. Davis, "Argentic Oxide as an Oxidimetric Reagent. Determination of Manganese, Cerium and Chromium," *Anal. Chim. Acta* 15, 201 (1956).

occurs almost instantaneously in the presence of argentic oxide.

For the oxidation of microgram quantities of chromium, 100 mg of argentic oxide is added to approximately 30 ml of the solution that contains chromium. The solution is then heated to boiling and is maintained at that temperature for 5 min in order to reduce the excess of argentic ion. The resultant chromium(VI) can then be determined spectrophotometrically with diphenylcarbazide. Oxidation with argentic oxide can also be applied to the determination of chromium²² as the diphenylcarbazide complex in a TOPO-benzene solution.

This method of oxidation requires less time than does the method which is based on the oxidation with perchloric acid, because the latter method requires complete dehydration of the sample. Oxidation of microgram quantities of chromium by either reagent appears to be complete. The relative standard deviation for the determination of chromium by the perchloric acid method has been reported to be 2%;²³ the relative standard deviation for the determination of chromium by the argentic oxide method also was found to be 2%.

Determination of Uranium Metal in the Products of the Reaction Between Uranium Hexafluoride and Metallic Sodium

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

Samples of material that had been produced by the reduction of UF_6 with metallic sodium were analyzed for uranium metal content according to the procedure of Meyer *et al.*²⁴ These samples contained the reaction products UF_4 , UF_3 , U^0 , and NaF . This method is based on the conversion of uranium metal to the hydride and the subsequent oxidation of the hydride to water and mixed oxides of uranium. The water is determined by measurement of its pressure in a known volume.

In order to ensure representative sampling, the uranium metal in the entire sample was converted to the hydride so that the sample could be thoroughly

²²C. K. Mann and J. C. White, *Extraction of Chromium with Trioctylphosphine Oxide from Acidic Solutions of Alkali Metal Salts and Its Determination in Situ as the Chromium-Diphenylcarbazide Complex*, ORNL CF-56-10-86 (Oct. 23, 1956).

²³R. L. McCutchen, private communication to J. P. Young, Oct. 1957.

²⁴A. S. Meyer, Jr., B. L. McDowell, and J. C. White, ORNL-2003 (Dec. 5, 1955) (classified).

pulverized. All grinding and transfer operations were carried out in a vacuum dry box. A modified combustion tube was designed which could be loaded in the dry box and sealed for transfer to the apparatus. Because of the presence of inert material, NaF, it was necessary to modify the original apparatus in such a way that the sample could be placed in a loosely fitted platinum liner in the platinum combustion boat. As a consequence of the lower heat capacity of the thin-walled platinum liner, the samples were heated to a temperature sufficient to guarantee complete reaction during the oxidation of the hydride. Uranium metal was determined in concentrations of 0.5 to 35% in samples that weighed 100 to 500 mg.

Spectrophotometric Determination of Microgram Quantities of Aluminum in Sulfuric Acid Solutions with Pyrocatechol Violet

J. P. Young J. R. French

A method for the spectrophotometric determination of aluminum in sulfuric acid solutions was developed that is based on the absorbancy of the aluminum-pyrocatechol violet complex at a wavelength of 582 $m\mu$. The molar absorbancy index for this complex is 54,000. The absorbancy of the complex obeys Beer's law for concentrations of aluminum as high as 0.2 $\mu\text{g/ml}$. Milligram amounts of uranyl ion do not interfere. Aluminum can be determined directly in solutions that contain iron, nickel, chromium, molybdenum, and niobium provided that the metal-to-aluminum ratio is not greater than 1. Weight ratios of iron-, nickel-, chromium-, or molybdenum-to-aluminum as high as 10 are tolerable if the sample solutions are electrolyzed at a mercury cathode prior to the determination of aluminum. Titanium and zirconium interfere seriously in this method because they also form complexes with pyrocatechol violet.

Spectrophotometric Determination of Vanadium by the Benzohydroxamic Acid Method

J. P. Young J. R. French

The method of Wise and Brandt²⁵ for the spectrophotometric determination of vanadium(V) with benzohydroxamic acid was evaluated for application

²⁵W. M. Wise and W. W. Brandt, "Spectrophotometric Determination of Vanadium(V) with Benzohydroxamic Acid and 1-Hexanol. Application to Steels and Crude and Residual Oils," *Anal. Chem.* 27, 1392 (1955).

to sulfate solutions that contained uranium, iron, nickel, chromium, molybdenum, titanium, and aluminum.

Oxidation of the vanadium(IV) to vanadium(V) was accomplished by the use of argentic oxide, a more rapid method of oxidation than the usual oxidation with perchloric acid. The lower limit of the method was extended to the determination of as little as 3 μg of vanadium in 100 ml of aqueous solution by extraction of the complex into 5 ml of 1-hexanol, rather than into 20 ml as is recommended. As much as 40 μg of vanadium as the complex is extracted into 5 ml of 1-hexanol during an equilibration period of 30 sec. Uranium, titanium, and aluminum, in concentrations which exceeded the expected concentration of these substances in the samples of sulfate solutions, do not interfere with the determination of vanadium.

Spectrophotometric Determination of Nickel with 4-Isopropyl-1,2-cyclohexanedionedioxime

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

A method for the spectrophotometric determination of nickel with 4-isopropyl-1,2-cyclohexanedionedioxime has been developed. Hooker and Banks²⁶ described the preparation of the reagent and its original application to the determination of nickel. In that procedure the chelate complex of nickel(II) with 4-isopropyl-1,2-cyclohexanedionedioxime is formed in a nearly neutral, acetate-buffered solution and is extracted with several portions of chloroform. The combined chloroform extracts are diluted to an appropriate volume, after which the absorbancy of the solution is measured at a wavelength of 385 $m\mu$. In this medium the complex obeys Beer's law for concentrations of nickel from 1 to 15 $\mu\text{g/ml}$.

In order to increase the sensitivity of the method by the use of very large V_a/V_o ratios, organic compounds that are less water-soluble than chloroform were investigated. Xylene proved to be a much better extractant than chloroform. The molar absorbancy index for the chelate at the absorption maximum of 385 $m\mu$ was unaffected by the solvent, but the extraction coefficient of the chelate was vastly different in chloroform (300) and xylene

²⁶D. T. Hooker and C. V. Banks, *Preparation, Properties, and Analytical Applications of Some Substituted Alicyclic Vic-Dioximes*, ISC-597, pp 11, 17 (March 1955).

(5000). In view of this very high extraction coefficient of the complex in xylene, it is possible to determine concentrations of nickel of less than 0.5 ppm in a 5-g sample.

Iron(II) and (III), cobalt(III), and copper(I) are reported to cause serious interference in the method. Methods for the elimination of these interferences have been developed. Iron, oxidized to the ferric state, is "masked" with fluoride. When cobalt(III) is present, its interference is eliminated by the addition of cyanide and peroxide to the neutral or basic solution in order to convert cobalt(III) to the very stable cobaltcyanide complex. Prior to the color development, the less stable nickel cyanide complex is decomposed by the addition of formaldehyde.²⁷ The reported procedure for the elimination of the interference of copper(I) by complexing it with thiocyanate in order to prevent its extraction as the dioxime complex is not applicable if either cobalt or iron, or both, is present with the copper, because the masking techniques for their elimination preclude the reduction of copper(II) to copper(I). The interference of copper(I) is eliminated by washing the extract of the nickel and copper chelates with a weakly acidic solution of hydrogen sulfide which is formed by heating a solution of stabilized thioacetamide (Sulfi-Down, distributed by the A. Daigger & Co., Chicago, Ill.) to 80°C. The copper is transferred to the aqueous phase and is precipitated as the copper(II) sulfide. When the solution is neutralized and excess reagent is added, any nickel that has accompanied the copper to the aqueous phase is re-extracted.

This method has proved to be applicable to the determination of microgram quantities of nickel that have been completely extracted into 5 ml of xylene from volumes of aqueous solutions of as much as 1 liter. The relative standard deviation of the method is 5% when all masking techniques are included as a part of the procedure.

Organic Preparations

R. E. Feathers W. J. Ross

Tris-2-octylphosphine Oxide. – Tris-2-octylphosphine oxide was prepared by the reaction of 2-octylmagnesium bromide with phosphorus oxychloride.

²⁷F. Feigl and H. J. Kapulitzas, "Über den Nachweis und die Bestimmung von Nickel neben viel Kobalt und Dimethylglyoxim," *Z. anal. Chem.* 82, 417 (1930).

A 30-g portion of final product having a boiling point of 142°C at 0.2 mm pressure was prepared. The specific gravity at 20°/20°C was 0.8946; the refractive index at 20°C was 1.4623.

Tris-2-ethylhexylphosphine Oxide. – Tris-2-ethylhexylphosphine oxide was prepared by the reaction of 2-ethylhexylmagnesium bromide with phosphorus oxychloride. The final product (40 g) had a boiling-point range of 156 to 166°C at 0.2 mm. The specific gravity at 20°/20°C was 0.9248, and the refractive index at 31°C was 1.4593.

Tri-*n*-octylphosphine Oxide. – Tri-*n*-octylphosphine oxide was prepared by the reaction of *n*-octylmagnesium bromide with phosphorus oxychloride. The purification of the final product was carried out by the method proposed by Ross.²⁸ By this method 530 g of TOPO having a melting point of 49.5 to 51.0°C was prepared.

A second batch of tri-*n*-octylphosphine oxide was synthesized by the modified procedure of Rainey *et al.*²⁹ The yield was 45% based on the amount of POCl₃ that was used (0.8 mole). The melting-point range of the final product was 51.5 to 52.0°C. The amount of titratable impurities was 0.3%, thereby indicating that the final product of TOPO was 99.7% pure.

4-Isonitroso-1-phenyl-3-methyl-5-pyrazolone.³⁰ – A 76-g portion of 4-isonitroso-1-phenyl-3-methyl-5-pyrazolone was prepared by dissolving 1-phenyl-3-methyl-5-pyrazolone in concentrated hydrochloric acid and then precipitating it with a solution of sodium nitrite. The material had a melting-point range of 154.4 to 156.5°C.

4-Isopropyl-1,2-cyclohexanedionedioxime.²⁶ – 4-Isopropyl-1,2-cyclohexanedionedioxime was prepared by oxidizing 4-isopropyl-cyclohexanol to 4-isopropyl-1,2-cyclohexanedione and converting the dione to 4-isopropyl-1,2-cyclohexanedionedioxime. Approximately 6 g of the reagent having a melting-point range of 182 to 184°C was prepared.

²⁸W. J. Ross, "Preparation of Trioctylphosphine Oxide," *The Use of Trialkylphosphine Oxides as Extractants in the Fluorometric Determination of Uranium*, ORNL-2161, p 22–24 (Nov. 1, 1956).

²⁹W. T. Rainey and J. M. Schmitt, "Preparation of Trioctylphosphine Oxide," *Prog. Rep. on Raw Materials Aug. 1957*, ORNL-2399, p 7–9.

³⁰L. Knorr, "Synthetische Versuche mit dem Acetessigester," *Ann. Chem. Liebigs* 238, 137 (1887).

RAW MATERIALS ANALYTICAL CHEMISTRY

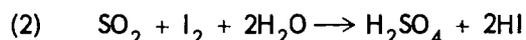
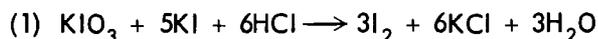
L. J. Brady

Determination of Sulfur Dioxide Absorbed in
n-Butyl Alcohol Solutions of Amines

L. J. Brady

E. C. Lynn

Samples that consisted of sulfur dioxide absorbed in an *n*-butyl alcohol solution of aniline and of other amines were analyzed to determine the concentration of sulfur dioxide. The principle applied in making the analysis is the oxidation in acidic solution of sulfur dioxide by iodine according to the following equations:



Iodine is produced by the reaction of potassium iodide and potassium iodate in acidic solution. The iodine thus formed reacts with the sulfurous acid as the sulfur dioxide is collected and oxidizes it to sulfuric acid. An excess of iodine is indicated by the blue starch-iodine complex formed in the solution in the absorption vessel.

The apparatus, consisting of a distilling flask, a condenser, and an absorption vessel, is so constructed that the rate of evolution of sulfur dioxide from the sample can be controlled. Nitrogen gas, introduced into the distilling flask through a gas-inlet tube, is bubbled through the sample and sweeps the sulfur dioxide that is evolved at room temperature into the solution of potassium iodide. The sample is then treated with 5 to 10 ml of 20 v/v % hydrochloric acid and heated to boiling for release of the sulfur dioxide that is not evolved at room temperature. As the sulfur dioxide reacts with the iodine in the absorption vessel and destroys the blue starch-iodine color, more potassium iodate is introduced until the blue color is restored. When all the sulfur dioxide has reacted, as is indicated by a stable blue solution, the volume of standard potassium iodate solution is recorded, and from this volume the concentration of sulfur dioxide in the sample is then calculated. The method has a relative standard error of 2% at the 95% confidence level.

Comparison of Two Methods for the Decomposition
of Di-2-ethylhexyl Phosphoric Acid and the
Conversion of the Phosphorus
to Orthophosphate

L. J. Brady

E. C. Lynn

In order to determine the adequacy of the nitric acid-perchloric acid decomposition step in the method for the spectrophotometric determination of phosphate as the phosphovanadomolybdate when applied to the analysis of samples that contain di-2-ethylhexyl phosphoric acid (Di2EHPA), two test samples were prepared both by this method and by an alternative method based on combustion of the sample with sodium peroxide in a Parr bomb. The latter method of oxidation, although more time consuming and less applicable to routine operation, does ensure complete conversion of the phosphorus to inorganic phosphate and, therefore, can be used as a basis for evaluation of the effectiveness of the acid-decomposition method.

The effectiveness of the oxidation of the sample with nitric and perchloric acids, as compared with that of the sodium peroxide-Parr bomb oxidation, is shown by the data given below:

Method of Decomposition	Phosphorus as PO_4^{---} (%)	
	Test A	Test B
$\text{HNO}_3\text{-HClO}_4$	31.8	32.5
$\text{Na}_2\text{O}_2\text{-Parr bomb}$	31.6	32.5
Difference	0.2	0.0

It is apparent from the results of these tests that acid oxidation with boiling perchloric acid is completely effective in the decomposition of Di2EHPA and in the conversion of the phosphorus to orthophosphate, in which form it can be determined spectrophotometrically as the phosphovanadomolybdate complex.

Determination of Bismuth with Disodium
Ethylenediaminetetraacetate

L. J. Brady

J. M. Peele

The method reported by Fritz³¹ was adapted to the determination of bismuth in acidic raffinate

³¹J. S. Fritz, "Titration of Bismuth with Ethylenediaminetetraacetic Acid," *Anal. Chem.* 26, 1978 (1954).

solutions that are derived from studies of the application of solvent extraction to the separation of uranium from bismuth. This method, based on the titration of from 5 to 20 mg of bismuth with disodium ethylenediaminetetraacetate, was used as a replacement for the more time-consuming gravimetric method. In the determination a test portion of sample that contains from 5 to 20 mg of bismuth is transferred to a 100-ml beaker; then 0.5 to 0.8 g of thiourea is added. After the thiourea has dissolved, the sample is diluted to 50 ml with water, following which the acidity of the solution is adjusted to a pH of 1.7 ± 0.3 . The solution is titrated with a standard solution of disodium ethylenediaminetetraacetate, $\sim 0.02 N$. The end point is indicated by the disappearance of the yellow color that is characteristic of the bismuth-thiourea complex. The relative standard deviation of the method is less than 1%.

Spectrophotometric Determination of Phosphate in Vanadium Oxide

L. J. Brady

J. R. Lund

The spectrophotometric molybdenum-blue method for the determination of phosphate in uranium oxide, which is described by Rodden,³² has been adapted for the determination of phosphate in vanadium oxide, V_2O_5 . When the method as written is applied without modification, a significant correction must be made in compensation for the increase in absorbancy that is caused by the reduced vanadium species at the wavelengths at which the absorbancy of the molybdenum-blue complex is measured. The alteration of the method by extraction of the molybdiphosphoric acid with an organic solvent prior to the reduction of the sample with hydrazine sulfate or with stannous chloride does not circumvent this difficulty, because the vanadium, which is present as vanadium(V) at this step in the procedure, is extracted along with the phosphate. If, however, the vanadium and molybdiphosphoric acid are reduced with sulfite and hydrazine sulfate prior to the extraction, the molybdenum-blue complex can be extracted into *n*-butyl alcohol without interference from vanadium, since the reduced vanadium species is not extractable into *n*-butyl alcohol.

³²C. J. Rodden (Editor-in-Chief), *Analytical Chemistry of the Manhattan Project*, p 326, McGraw-Hill, New York, 1950.

QUALITY CONTROL

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B. J. Ginocchio

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Only minor changes were made in the scope of the control program for the laboratories of the Analytical Chemistry Division at both the X-10 and the Y-12 Sites. The control work was expanded, in one or two cases, to include certain analyses that heretofore had not been included in the control program. In keeping with the main purpose of this work, however, improvements in methods of analysis and in procedural details that are associated with these methods were emphasized. In general, the quality of the work in these laboratories has been maintained at a satisfactory level.

Although only 5% of the results that are evaluated for control purposes are expected to fall outside the established control limits, 10% of these values at the X-10 Site and 8% at the Y-12 Site were found to be outside the limits. This higher percentage of unsatisfactory results is attributed to one or two programs in which some difficulty in maintaining the precision of the analyses was encountered.

The distribution by laboratory of the 13,403 determinations that were evaluated for control purposes in the X-10 and Y-12 laboratories is given in Table 12. For the purpose of comparison, a similar compilation for 1956 is included.

Table 12. Summary of Determinations Evaluated for Control Purposes

Laboratory	Number of Determinations	
	1956	1957
X-10 Site		
Building 3019	7,436	7,264
Building 3508	340	476
Building 3550	1,199	1,193
Building 4500	1,621	1,387
	10,596	10,320
Y-12 Site		
Building 9201-2	640	355
Building 9204-1	719	727
Building 9733-4	828	2,001
	2,187	3,083
Grand total	12,783	13,403

In connection with the Statistical Quality Control Program, experimental data that were pertinent to, but not a part of, the program were also evaluated. The results of studies undertaken in connection with the control program are summarized below, whereas pertinent information derived from other investigations is presented in other sections of this report.

Analysis of UO_3 .³³ – When the results of a recent cooperative analysis of UO_3 , New Brunswick Laboratory (NBL) analyzed sample No. 18, were reviewed, it was apparent that certain discrepancies in the values reported by the different laboratories were attributable to moisture pickup by the sample prior to analysis.

For the purpose of illustrating the effect of moisture content on the reliability of the results that are obtained for materials of this type, the uranium results for a sample of UO_3 (NBL analyzed sample No. 18) were evaluated on an "as-received," a "moisture-equivalent," and a "moisture-free" basis. The uranium content of this sample was also estimated by difference (100% minus the sum in the per cent of the impurities), in order to show the high degree of reliability that can be attained when this method is used for establishment of the concentration of a major constituent of a high-purity material. Particular emphasis is being placed on the importance of moisture content when the proposed standard sample is of high purity and is hygroscopic.

Determination of Molybdenum by the Butyl Acetate–Thiocyanate Method. – Tests were made at 10 to 15°C and at room temperature for the purpose of determining the effect of temperature on the extraction of the molybdenum-thiocyanate complex and, subsequently, on the reliability of the molybdenum results by the butyl acetate–thiocyanate method. Temperature was found to

have little effect; consequently, it was recommended that future analyses for molybdenum by this method be made at room temperature.

Determination of Nitrate by the Phenoldisulfonic Acid Method. – In connection with the phenoldisulfonic acid method for the determination of nitrate, a literature search was made for information on sources of error in this procedure. A review of these findings was presented in which the recommended procedure for preparing the reagent and the most probable sources of error in the method were given.

Fluorometric Determination of Uranium. – A number of investigations were made with an ORNL model Q-1165 fluorophotometer preparatory to substitution of this instrument for the Photovolt fluorophotometer used for the fluorometric determination of uranium in the Raw Materials Laboratory at the Y-12 Site. Certain operational difficulties were overcome after the effect of different extractants and fluxes on the phosphors was ascertained. As a result of these investigations, a 10:90 mixture of tributyl phosphate (TBP) and Varsol was selected as a suitable extractant, and a flux composed of LiF and NaF was found to yield satisfactory phosphors. Sometime later, tri-*n*-octylphosphine oxide (TOPO) was substituted for TBP as an extractant for uranium.

The reproducibility of results for uranium in the concentration range of 1 to 3 $\mu\text{g}/\text{ml}$ and for a random selection of samples that were examined in duplicate was found to be about 10% at the 95% probability level.

Determination of Uranium by the Stannous Chloride–Thiocyanate Method. – The absorbancy measurements for duplicate analyses of a random selection of samples that had been analyzed for uranium by the stannous chloride–thiocyanate method were evaluated in order to determine the reproducibility of these measurements. The degree of reproducibility, expressed as the limit of error of one measurement at the 95% probability level, was found to be 3%.

³³C. D. Susano and R. L. McCutchen, *Evaluation of Data for Standard Samples with Both Moisture-Content and Methods of Analysis as Determinable Factors*, ORNL CF-57-10-108 (Oct. 21, 1957).

SERVICE ANALYSES

A summary of the analytical service work at the Y-12 Site is given in Table 13.

HRP ANALYTICAL CHEMISTRY

O. Menis C. K. Talbott F. L. Layton

During 1957, some 15,000 samples, which represent a 20% increase over the number handled during the preceding year, were analyzed by the staff of the HRP Analytical Chemistry Laboratory. Solutions of uranyl sulfate and solutions of uranyl sulfate that contained copper sulfate or lithium sulfate were analyzed most frequently for uranium, iron, nickel, chromium, and chloride and only occasionally for 32 other elements, of which the most common were the alkali and alkaline-earth elements, the transition elements, elements of the platinum group, elements in groups I and IV, and the halides. The hydrogen ion concentration of a large number of these solutions was also measured, and the concentrations of dissolved oxygen and carbon dioxide were determined in solutions of

uranyl sulfate. Thorium oxide and other compounds of thorium were analyzed for thorium and for impurities similar to those which are found in solutions of uranyl sulfate. In addition, the lead content of thorium oxide was determined, and slurries of thorium oxide were analyzed for dissolved hydrogen, oxygen, and carbon dioxide. Measurements were also made of the particle-size distribution of thorium oxide in a large number of slurries during this period.

Iron, nickel, and chromium were determined in 2 M aluminum nitrate, in 20% magnesium chloride, and in 1 M, 7 M, and 5% solutions of nitric acid. Less frequently, these solutions were analyzed for aluminum, chromium(VI), copper, nitrate, and free acid. The density of the solutions was also measured. Other work included the determination of conductance, pH, uranium, sulfate, and chloride on samples of steam condensate, the establishment of the strength of solutions of hydrogen peroxide, and the evaluation of the chloride content of a number of organic dyes and inks. Methods used

Table 13. Summary of Analytical Service Work at Y-12

	Number of Persons		ORNL Requests for Analyses							Others Requesting Analyses		
	Scientists	Technicians	Aircraft Reactor Engineering	Chemistry	Chemical Technology	Metallurgy	Reactor Experimental Engineering	Isotopes	Y-12	Miscellaneous		
Laboratory Making Analyses			Number of Results Reported									Totals
Raw Materials and Miscellaneous	5	12	46	10,801	24,496	265	538	1201	789	219	38,355	
HRP	13	10					82,600				82,600	
9201-2	13	5	5345	8,098		281	2,824			663	17,211	
Totals	31	27	5391	18,899	24,496	546	85,962	1201	789	882	138,166	

ANALYTICAL CHEMISTRY PROGRESS REPORT

for the various determinations may be summarized as follows:

Method	Constituent
Titrimetric	
Visual indicator	Th, SO_4^{--} , excess acid
Colorimetric	U(IV), Bi, F
Potentiometric	Ce, Br, I, Cl
Spectrophotometric	Fe, Ni, total Cr, Cr(VI), Al, Co, Cu, Mg, Mo, Ti, Zr, Si, As, Sb, Pt, Ru, Au, NO_3^- , PO_4^{---}
Flame photometric	Ba, Ca, Na, K, Li, Ag, B
Polarographic	Sn, Zn, Hg, Pb
Gasometric	H_2 , O_2 , CO_2
Electrogravimetric	Cu
Beta counting	Tc

RAW MATERIALS ANALYTICAL CHEMISTRY

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J. R. Lund J. M. Peele

The staff of the Raw Materials Analytical Chemistry Laboratory analyzed a total of approximately 15,000 samples which were derived from the continuing studies of solvent extraction with amines and organophosphorus compounds. The acid-leach solutions and organic samples that result from tests being made in the Chemical Technology Division to evaluate new extractants for uranium were analyzed for that element by volumetric, spectrophotometric, and fluorometric methods. In view of the high degree of extractability of uranium into cyclohexane solutions of tri-*n*-octylphosphine oxide (TOPO), the extraction step which precedes the fluorometric measurement of uranium was altered by the substitution of this solution of TOPO for tributyl phosphate (TBP) as the extractant. This change in the extraction step has resulted in a significant reduction in the time that is required to make the analysis, since evaporation and careful adjustment of the acid concentration of the samples are no longer critical factors. In the modified procedure, uranium is extracted directly from an aqueous solution that is 5 M in nitric acid into the cyclohexane solution of TOPO. During the course of the year the flux material used in the fluorometric method for uranium was

changed from the mixture of Na_2CO_3 - K_2CO_3 -NaF to that recommended by DeSesa,¹ that is, 2% LiF-98% NaF. The fluorometric procedure as now constituted, with the change in the flux material and extractant, is most satisfactory, particularly from the standpoint of time and simplicity, even though no gain in precision and accuracy has been realized. In addition to being analyzed for uranium, the sulfate leach liquors and solutions of organic extractants were analyzed for a variety of substances, such as molybdenum, vanadium, iron, aluminum, sulfate, phosphate, chloride, nitrate, and ammonia.

Flame photometric methods were applied to the determination of strontium and cesium in both aqueous and organic media. The technique of the addition of an internal standard, described by Chow and Thompson,² was used to make these analyses independent of the chemical and physical conditions of the solutions under test. In addition, physical measurements, such as specific gravity, viscosity, surface tension, and interfacial tension, were made on a number of solutions that are under test as possible large-scale extractants for uranium and thorium. Spectrophotometric methods were applied in determining the concentrations of a variety of constituents less commonly requested; these included zirconium, tungsten, niobium, nickel, cobalt, and tantalum. The coulometric method for the determination of water, described by Meyer and Boyd,³ was also applied in the determination of water in samples of a variety of possible extractants that were dissolved in several organic diluents.

MISCELLANEOUS ANALYSES

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A total of 9500 samples, approximately double the number of samples that were analyzed during the preceding year, was analyzed in the Miscellaneous Analyses Laboratory. The major portion of these samples continued to be derived from

¹F. A. Centanni, A. M. Ross, and M. A. DeSesa, *The Fluorimetric Determination of Uranium*, WIN-34 (Feb. 10, 1956).

²T. J. Chow and T. G. Thompson, "Flame Photometric Determination of Strontium in Sea Water," *Anal. Chem.* 27, 18 (1955).

³A. S. Meyer, Jr., and C. M. Boyd, *The Determination of Water by Coulometric Titration*, ORNL-1899 (June 9, 1955).

studies of various chemical exchange reactions as applied to isotopic enrichment. Flame photometric methods were utilized extensively. In addition, a large number of samples were prepared for isotopic assay by methods which are based on the separation of desired components from various contaminants and the final conversion of the purified material to its iodide salt. A large number of analyses were made on samples that were derived from the production of N^{15} by the Nitrox system.⁴ Gasometric methods were applied to the measurement of the concentration of "inert" gas in the gaseous phase of the Nitrox column, as

⁴N. C. Bradley and G. M. Begun, *Chemical Separation of Isotopes Section, Semiann. Prog. Rep. June 30, 1956*, ORNL-2176, p 16-19 (classified).

well as to the determination of the ratio of NO to NO_2 in mixtures of these oxides.

Many specification analyses were made on ferrous and nonferrous metals. In addition, screening tests of a number of paints and inks used in marking metals were conducted in order to determine their chloride content. These tests for chloride are made by mixing the sample with mineral oil and then burning it in an atmosphere of compressed oxygen in a Parr bomb. The chloride, which is released as a result of this ignition, is dissolved in a solution of sodium carbonate, which is placed inside the bomb prior to combustion of the sample. The concentration of chloride is subsequently determined by volumetric methods.

ANALYTICAL CHEMISTRY DIVISION

