MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0250016 7

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

5

ORNL-2866
UC-4 Chemistry-General
TID-4500 (15th ed.)

ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

FOR PERIOD ENDING DECEMBER 31, 1959

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price $2.50. Available from the
Office of Technical Services
Department of Commerce
Washington 25, D.C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-2866
UC-4 Chemistry-General
TID-4500 (15th ed.)

Contract No. W-7405-eng-26

ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

For Period Ending December 31, 1959

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

DATE ISSUED

FEB 11 1960

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0250016 7

ANALYTICAL CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

SUMMARY

RESEARCH AND DEVELOPMENT

Analytical Instrumentation (X-10)

The following work was done in the In-Line Instrumentation Development program. A recording, high-sensitivity, controlled-potential, a-c polarograph was designed and constructed. The frequency of the modulating a-c voltage can be varied between 10 and 100,000 cps. The in-phase component of the a-c current is displayed on a recorder. This polarograph is being evaluated and will be applied to the determination of uranium(VI) in solutions of low uranium concentration. The flow colorimeter for the measurement of uranium at a concentration level of 50 g/liter is ready for plant installation. An improved design for a uranium colorimeter is being studied. A test loop for the investigation of the behavior of electrolytes in high concentrations and at frequencies up to 2000 Mc/sec has been built for radio-frequency monitor development. A single-beam gamma absorptiometer was operated on a flow-stream test loop that contained solutions of lead ions. Further study of the monitoring of uranium in radioactive streams is planned with a chopped-single-gamma-beam technique and with a dual-beam instrument. The monitoring of a waste stream at its surface for alpha emitters by means of a phosphor was tested for plant use but was rejected because of excessive maintenance requirements. A rotating-disk technique in which a liquid sample is taken, dried, and then alpha-counted is being examined. Three smooth-bore fluorothene-type monitors of gamma radiation have been installed and are operating in the Power Reactor Fuel Reprocessing Plant.

Developments in analytical instrumentation were as follows. A new high-resolution, high-sensitivity, scanning, recording flame spectrophotometer is being built. Several alternative components and techniques of measurement will be evaluated. Two ORNL model Q-1988 controlled-potential and derivative polarographs have been built by the Instrument Department. An electronic polarographic scanning circuit has been designed that has better performance than the usual motor-driven potentiometer scanner. With the polarographs, reducible species in concentrations less than 10^{-6} M can be measured. The resolution of derivative polarography has been shown to be superior to that of regular polarography. It was found that the magnitude of sporadic, nonreproducible noise pulses in the current through a standard D.M.E., which can be minimized by certain techniques, determines the useful limits of qualitative detection and quantitative measurement of polarography. Papers have been published that describe the polarograph and the results obtained with it. A spectrographic intensity-ratio analog computer has been designed and installed. The recorder can display as a function of time any one of the following: the instantaneous value of the intensity of light received by any of several multiplier phototubes, the time integral of any of these intensities, the ratio of the instantaneous signals from two phototubes, or the ratio of the integrated signals from two phototubes. The computer is being tested for the rapid spectrographic determination of oxygen in steels. Eight ORNL model Q-2005 automatic, electronic, controlled-potential coulometric titrators have been constructed by the Instrument Department. One of these titrators has been modified to have sensitivities of both five and fifty times that of the others for work with small amounts of high-equivalent-weight elements, such as plutonium. Papers that describe the titrators and applications of them have been published. A plastic-lined pipet is being designed that can be installed in the remotely servo-controlled pipetter. A chronopotentiometer has been built that has constant-current, potential-sensing, and timing circuits. The readout of transition time is obtained from a precision timer, which is actuated by the timing circuit. The cathodic-stripping voltammetry of the chloride ion has been studied by means of cathodic-stripping coulometry and chronopotentiometry. Chloride ion in the concentration range 0.07 to 35 μg/ml has been measured. A system has been devised that produces a mercury pool whose area is reproducible to $\pm 1\%$.

Inorganic Preparations (X-10)

The preparations for the Physics Division have shifted from the transition-metal halides to the nitrides of the rare-earth metals, and a program for the preparation of trimethyl borate containing

B^{10} from boron trifluoride etherate containing B^{10} is in progress. The high-purity lithium iodide program for the Neutron Physics Division and the fused salts program for the Metallurgy Division were continued. Single preparations of various fused salts and of compounds containing pure isotopes were made for the Chemistry Division.

Ionic Analyses (X-10)

The Ionic Analyses Group has continued its studies and development of methods in several areas of analytical chemistry. In the field of electrochemistry a coulometric titration method has been developed for the precise determination of plutonium. Two solvent extraction methods of separation of uranium(VI) prior to its coulometric determination have been studied. Polarographic and coulometric studies of neptunium have been started. A dropping mercury electrode (D.M.E.) for use in hydrofluoric acid solutions has been fabricated. A reduction wave for sulfite (sulfur dioxide) at the D.M.E. has been found to exist in aqueous hydrofluoric acid medium. A polarographic determination of technetium in uranyl oxide has been developed.

Automatic titrimetry work has resulted in methods for the determination of specific rare-earth elements and mixtures of strong and weak acids. A study was made of chemical changes in uranium trioxide–aluminum reactor fuel elements during heat treatment. The effect of radioactivity on the thermometric titration of acids was studied briefly.

Spectrophotometric studies of aqueous solutions of uranium, copper, and nickel were continued. The Oracle was used to resolve mathematically the uranyl ion spectral fine structure and to study the complexation of uranyl ion with sulfate. Spectral studies of scintillation crystals of europium-activated lithium iodide were continued. A spectrophotometric method was developed for the determination of iron in concentrated solutions of zinc bromide. The effect of Čerenkov radiation on spectrophotometric measurements has been considered.

The gas chromatography work has continued and studies were made of mixtures of nitric oxide, nitrogen dioxide, and nitrous oxide. A mathematical resolution of the 14 peaks in the gas chromatogram of a type of Amsco has been made.

Mass Spectrometry (Y-12)

A 6-in.-radius mass spectrometer and a 12-in.-radius mass spectrometer were built and put in operation in the service laboratory. Two double-stage instruments with digital readout are in operation in the Referee Analysis Laboratory.

Nuclear Analyses (X-10)

The application of nuclear methods of analysis was extended to the determination of trace and macro quantities of elements in many different materials; a tabular summary of this work is given. In addition, neutron-activation-analysis techniques were used to determine Li^6 and Li^6-to-Li^7 isotope ratios, metallic oxide and metallic film thickness, and particle-size distributions. Neutron-flux monitoring and the use of a radioactive tracer in the measurement of the surface area of uranium dioxide powders are discussed. Alpha, gamma, and neutron sources from Am^{241} were prepared for use in various analytical applications. An irradiation facility and analytical laboratory were established in the Oak Ridge Research Reactor building. Instruments for radioactivity measurements were improved or developed, for example, multichannel analyzers and a crystal discriminatory counter.

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

The complete unclassified *ORNL Master Analytical Manual* is now available in reprinted form (TID-7015) from the Office of Technical Services, Department of Commerce, Washington. Forty-seven new methods were added to the *Manual*; the Tables of Contents for three sections were brought up to date. The *Manual* was issued to eight new custodians.

Optical and Electron Microscopy (X-10)

The particle sizes and particle shapes of a large number of materials were studied; typical micrographs obtained in representative studies are shown. The nature of the materials for and after use in the GCR and in the molten-salt and thorium oxide slurry test loops was studied, and a specific comparison in one such study was made by means of electron micrographs. Identification work was done in connection with the NS "Savannah." The presence of bacteria in a tube that contained corrosion-inhibiting potassium dichromate solution

located adjacent to the Homogeneous Reactor was discovered. Assistance was given to the Physics Division in their work with single-crystal barrier counters and to the Biology Division relative to their studies of radiation effects on animal tissue. Changes were made in the circuitry of the Cintel Flying Spot resolver, and a device was fabricated to aid in measuring spot electron diffraction patterns. The contemplated improvements to the General Electric diffractograph are described.

Quality Control (X-10 and Y-12)

The Statistical Quality Control program was modified in keeping with revisions in the projects of other ORNL divisions, the result being that the scope of the control work was expanded while at the same time the frequency with which control analyses were made was decreased about one-third. The 1959 quality levels for all the service laboratories were essentially the same as those attained during the previous year.

Radiochemical Analyses (X-10)

A new isomer of yttrium has been identified, and the gamma radiations of Pm^{148} and of Sb^{124} have been studied. Eta values for U^{233}, U^{235}, and Pu^{239} have been measured. Liquid scintillation counting is being used for several purposes, and gamma spectrometry has been applied in new fields, making its usefulness even greater than before. New solvent-extraction methods in which amines and organophosphorus compounds are used have been developed.

Raw Materials Laboratory (Y-12)

The Raw Materials Laboratory studied the reaction of ceric sulfate with tartaric acid and found that, under the conditions of the test, 0.133 mmole of tartaric acid was reacted per milliequivalent of ceric sulfate. The resistance of two types of Tygon tubing and one sample of Duroflex plastic tubing to 14 specified chemical reagents was tested.

Reactor Projects Laboratory (Y-12)

The Reactor Projects Laboratory initiated a support program in analytical chemistry for the Gas-Cooled Reactor (GCR) Project. Gas chromatographic methods were developed for the determination of impurities in helium, which is to be used as a coolant in the GCR. Principal determinations are for nitrogen, oxygen, argon, hydrogen, carbon monoxide, carbon dioxide, methane, and water vapor. A system for the continuous monitoring of these impurities in helium was also designed in cooperation with the Instrumentation and Controls Division. The Greenbrier Chroma-matic 112 dual-column gas chromatograph was selected for this application. The fluorination procedure with potassium tetrafluorobromide was extended to the direct determination of total oxygen in reactor-grade uranium dioxide. The relative standard deviation based on duplicate analyses of 18 samples is 0.4%. The determination of carbon in uranium dioxide was also investigated to establish orders of precision and accuracy. The Leco automatic sulfur analyzer was applied to various metals and to beryllium oxide. The procedure for the dissolution of graphite in perchloric acid was improved. Research was continued on the spectrophotometry of molten fluoride salt systems; several new spectra were obtained. A spectrophotometric method for yttrium by use of pyrocatechol violet was devised. Solvent-extraction studies with organophosphorus compounds were continued. The extraction characteristics of antimony, arsenic, and zinc with tri-*n*-octylphosphine oxide were determined. A systematic investigation of tris(2-ethylhexyl)phosphine oxide as an analytical extractant was completed. A new extraction reagent, 1-phenyl-3-isohexyenyl-1-phospha-3-cyclopentene-*p*-oxide was evaluated. Infrared spectral studies of organophosphorus compounds were continued. Complexometric titration methods using disodium dihydrogen ethylenediaminetetraacetate were adapted for the determination of zinc, magnesium, and thorium in fluoride salts.

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

Extraction procedures were developed for concentrating titanium, nickel, chromium, and iron for spectrochemical analysis. Mannitol was found to prevent volatilization of boron during evaporation of acidic solutions of borates, even when fluorides were present. A procedure for dissolving niobium–rare-earth-element alloys was developed that does not require the use of hydrofluoric acid. The sensitivity of the determination of cesium by flame photometry was greatly enhanced in a 100-

to 200-ppm solution of potassium as potassium chloride in methanol. Development and organization is proceeding on a spectrographic facility for the analysis of human-tissue ash by means of a 42-channel spectrometer. X-ray absorption-edge spectroscopy has been successfully applied to the determination of zirconium in a variety of solutions by means of a single set of parameters. An electronic system for background correction with the photoelectronic spectrometer has been designed, built, and tested. The variability of several methods of solution analysis has been studied; the revolving-disk technique appears best at present. The electronic equipment for the determination of oxygen in metals has been installed on the Paschen spectrograph at the 60° slit position.

Thermal Breeder Reactor Projects Analytical Chemistry Laboratory (Y-12)

Studies were continued on the improvement or development of methods for the analysis of solutions of uranyl sulfate, thorium oxide, mixtures of thorium oxide with uranium oxide and other metallic oxides, slurries of thorium oxide–uranium oxide, and a number of other materials. In addition to the major constituents (thorium, uranium, and sulfate) a large number of minor constituents, principally additives and corrosion or erosion products of stainless steel and other materials used in the construction of test devices for studying reactor components and processes, were determined.

In the analysis of simulated Homogeneous Reactor fuel solutions of uranyl sulfate, high-frequency titrimetry was used for the determination of sulfate and free acid; a spectrophotometric method was developed for microgram or milligram quantities of osmium.

Methods developed or adapted for the analysis of thorium oxide alone or of mixtures of it with other oxides included flame photometric methods for palladium and iron; a derivative polarographic method for molybdenum in a nitrilotriacetic acid medium; a spectrophotometric method for uranium; and three procedures (volumetric, controlled-potential coulometric, direct coulometric oxidation) for establishing the uranium(IV)-to-uranium(VI) ratio.

Other methods studied included separation of fluoride from nitrate- or sulfate-containing solutions by pyrolysis; determination of microgram quantities of cobalt in aluminum by spectrophotometry; application of potentiometric titrimetry and flame photometry to the determination of rare-earth elements; simultaneous determination of two or more rare-earth elements; and direct titration of thorium with disodium dihydrogen ethylenediaminetetraacetate by means of xylenol orange as the indicator.

SERVICE ANALYSES

The Raw Materials Laboratory and the Miscellaneous Analyses Laboratory analyzed 10,900 samples, most of which were derived from solvent-extraction studies. The most commonly determined constituents were uranium, thorium, iron, molybdenum, vanadium, ammonia, sulfate, and carbonate. Specification tests of a variety of metals and nonmetals were conducted.

The Counting Laboratory processed 3150 samples. Radiochemical methods of separation and analysis were applied to the determination of plutonium, neptunium, americium, ruthenium, zirconium, niobium, total rare-earth elements, and gross gamma and gross beta activity. Nonradiochemical methods were used for the determination of uranium, iron, aluminum, thorium, sodium, and free acid.

Ionic service analyses were made relative to studies of HR fuels, the reprocessing of power-reactor fuels, the disposal of Purex wastes in salt mines, and the development of alloy-type fuel elements.

The Low-Radiation-Level Radiochemical Analytical Laboratory was occupied and put into service for the analysis of samples of very low levels of radiation. Equipment was designed and fabricated in order to lessen safety hazards and to promote greater efficiency. Since April 1, 1959, 1878 analyses were performed, primarily for the Health Physics Division.

During the past year the Analytical Mass Spectrometry Group has reported 70% more analyses from 63% more samples than in the previous year. Two gaseous-sample and three solid-sample mass spectrometers were in full-time use.

A total of 167,375 results was reported by the Process Analyses Laboratories for 16 divisions, the Chemical Technology Division and the Isotopes Division being the largest contributors. A brief statement of new developments in each laboratory follows.

The Special Analyses Laboratory determined the uranium-to-oxygen ratio and nitrogen in compacts of uranium dioxide. Rare-earth elements were titrated with disodium dihydrogen ethylenediaminetetraacetate by use of a recording potentiometric titrator. Irradiated stainless steels that contained boron were analyzed for B^{10} burnup. New equipment added was a Leco conductometric carbon analyzer, controlled-potential coulometric titrators, and two hot cells with 4-in.-thick lead walls and "wiggle tong" manipulators.

The Radioisotopes-Radiochemistry Laboratory developed a method for the determination of Pm^{147}. They have also adopted some new techniques in the determination of Tc^{99}. A 20-channel gamma scintillation spectrometer was put into service. In the future, a liquid scintillation counter will be used to determine C^{14} and S^{35}.

The Process Development Analytical Laboratory has developed a method for determining low concentrations of thorium in the presence of sulfuric acid and stainless steel and of aqua regia and stainless steel.

The High-Alpha Analytical Laboratory continued the work on preparations of neutron threshold detectors. A controlled-potential coulometer is being evaluated for use in determining plutonium. A new glove-box laboratory is being installed.

A coulometer has been put into use in the Pilot-Plant Control Laboratory for the determination of uranium in solutions of reactor fuels.

The Reactor Analyses Laboratory has put into use a new method for the determination of free acid in HRT type of samples. The coulometric determination of uranium and copper in a single aliquot has been extended to include the determination of nickel.

In the High-Radiation-Level Analytical Facility several modifications were made. An ultrasonic cleaner was installed for decontamination of apparatus. All manipulators were equipped with ambidextrous fingers, and other minor changes were made in the manipulators in order to lessen their down time.

The ORNL control program was expanded to include more complex synthetics. Seven simulated power reactor fuel reprocessing feeds, four HRT blankets, three HR-fuel-type solutions, and one standard solution for the spectrographic laboratory were prepared.

The Radiochemical Analyses Group made many gamma spectrometric determinations of fission products and other activities in a variety of materials. Special analyses for transuranic elements were made; fission products were identified and determined.

The Reactor Projects Laboratory analyzed many fused fluoride salts for component elements and corrosion products. Graphite rods impregnated with fused fluoride salts were analyzed in order to determine the depth of penetration of salts.

During 1959, 78,000 analyses were performed on 9958 samples in the Thermal Breeder Reactor Projects Analytical Chemistry Laboratory. Principal sample types, methods of analysis used, components determined, and physical measurements required are described.

CONTENTS

SUMMARY iii

RESEARCH AND DEVELOPMENT 1

Analytical Instrumentation (X-10) 1
In-Line Instrumentation Development 1
A-C Polarography 1
Flow Colorimeter 1
Radio-Frequency Monitor of Electrolytes in High Concentration 1
Single-Beam Gamma Absorptiometer 1
Monitors of Alpha Radiation 1
Monitors of Gamma Radiation 2
High-Resolution, High-Sensitivity, Scanning, Recording Flame Spectrophotometer 2
Controlled-Potential and Derivative Polarograph 2
Investigation of High-Sensitivity Polarography 3
Spectrographic Intensity-Ratio Analog Computer 3
ORNL Model Q-2005, Automatic, Electronic, Controlled-Potential Coulometric Titrator 3
High-Sensitivity Modification of ORNL Model Q-2005, Automatic, Electronic, Controlled-Potential Coulometric Titrator 4
Plastic Pipet for Remotely Servo-Controlled Pipetter 4
Chronopotentiometer 4
Cathodic-Stripping Voltammetry of Chloride Ion 5
Cathodic-Stripping Coulometry (Voltage-Step Method) 5
Chronopotentiometry (Current-Step Method) 5
Special Mercury-Pool Electrode for Voltammetry 5

Inorganic Preparations (X-10) 5

Ionic Analyses (X-10) 5
Controlled-Potential Coulometric Titration of Plutonium 5
Analysis of Product Solutions 6
Analysis of Dissolver Solutions 6
Future Program 6
Determination of Uranium(VI) in Dissolver Solutions by Extraction with Triisooctylamine and Controlled-Potential Coulometric Titration 6
Hexone Extraction of Uranium(VI) from Dissolver Solutions 7
Polarographic and Coulometric-Titration Study of Neptunium 7
Dropping Mercury Electrode for Polarographic Studies in Hydrofluoric Acid Media 8
Polarographic Determination of Sulfur Dioxide in Hydrofluoric Acid 8
Polarographic Determination of Sulfur Dioxide in Fluosulfonic Acid 9
Polarograph of Niobium 9
Determination of Technetium in Uranium Trioxide 10
Determination of Free Acid in Uranyl Sulfate Solutions by the Dowex 50 Resin Separation Procedure 10
Thermometric Titrations 11
Analysis of Bismuth Chloride 11
Automatic, Chelometric, Potentiometric Titrations by Use of a Mercury Indicator Electrode 11
Chemical Changes in the Reaction Between Purex Waste Solution and Sodium Chloride 11

Determination of the Oxygen-to-Uranium Ratio in Uranium Dioxide–Thorium Oxide 12
Chemical Changes in Uranium Oxide–Aluminum Reactor-Fuel Elements During Fabrication and Heat Treatment 12
Automatic Titration of Mixtures of Strong and Weak Acids 12
Program for Spectrophotometric Studies of Aqueous Solutions at Elevated Temperatures 13
Spectrophotometric Studies of the Sulfates of Uranium, Copper, and Nickel in Sulfuric Acid Solution 14
Mathematical Resolution of UO_2^{2+} Spectral Fine Structure 14
Correlation of Uranyl Spectra and Their Fine Structure with UO_2^{2+}-Sulfate Complexation 16
Calculated Effect of Čerenkov Radiation on Spectrophotometric Measurements 17
Spectral Study of Scintillation Crystals of Europium-Activated Lithium Iodide 17
Coulometric Determination of Europium in Europium-Activated Lithium Iodide Scintillation Crystals 17
Spectrophotometric Determination of Iron in Solutions of Zinc Bromide 18
Gas-Solid Chromatography 18
Determination of Gases in a Mixture of Nitric Oxide, Nitrogen Dioxide, and Nitrous Oxide 18
Analysis of Effluent Gases from a Sodium Carbonate Absorber After the Dissolution of Stainless Steel in Aqua Regia 18
Analysis of Off-Gases from Experimental Waste-Disposal Facilities in the Carey Salt Mines 19
Analysis of Off-Gases from the Charcoal Beds and from the Shield of the HRT 20
Mathematical Resolution of Overlapping Bands of Gas Chromatogram 20
Mass Spectrometry (Y-12) 20
Mass Spectrometry Research and Development 21

Nuclear Analyses (X-10) 22
Short-Half-Life Neutron-Activation Products Analysis Laboratory 22
Neutron-Activation Analysis 22
Quantitative Applications 22
Qualitative Applications 22
Neutron-Activation Analysis of Whole Milk for Stable Strontium 22
Neutron-Activation-Analysis Methods for Group VIII Elements 29
Analysis of Materials of Construction 30
Determination of Traces of Elements in Materials Containing Neutron-Absorbing Elements 30
Geochemical Applications of Neutron-Activation Analysis 30
Determination of Li^6 30
Determination of Film Thickness by Neutron-Activation Analysis 31
Measurements of Reactor Neutron Spectra 31
Particle-Size-Distribution Analysis 31
Preparation and Uses of Alpha, Gamma, and Neutron Sources from Am^{241} 32
Applications of Radioactive Tracers 32
Surface-Exchange Method for Determination of Surface Area of Uranium Dioxide Powder 32
Radioactivity Measurements 33
Multichannel Analyzers 33
Complement Subtraction Method of Gamma-Ray Spectrometry for the Quantitative Analysis of Complex Mixtures of Radionuclides 33

Crystal Discriminatory Counter 33
Neutron Activation Cross Sections 34

ORNL Master Analytical Manual (X-10 and Y-12) 36

Optical and Electron Microscopy (X-10) 36
Particle-Size Studies 36
Examination of Thin Films, Bulk Oxide Coatings, Corrosion Products, and Surface Structures 36
Single-Crystal, Surface-Barrier Type of Alpha Counters 40
Biological Studies 41
Instrumentation 41

Quality Control (X-10 and Y-12) 41

Radiochemical Analyses (X-10) 41
Nuclear Properties 41
New 3.1-h Isomer of Yttrium 41
Radiations from Pm^{148} 42
High-Energy Gamma Ray in the Decay of Sb^{124} 45
Measurement of Eta of U^{233}, U^{235}, and Pu^{239} by the "Manganese Bath" Technique 45
Measurement of Radioactivity 46
Liquid Scintillation Counting 46
Instrumental Methods 46
Gamma Scintillation Spectrometry 46
Fission Products 47
Radiochemical Determinations of Individual Rare-Earth Elements 47
Cyclotron Research 47
Studies of Neutron-Deficient Rare-Earth Nuclides 47
Solvent-Extraction Methods 47
Extractions from Acetate Solution with Triisooctylamine 47
Studies of Extractions with Triisooctyl Phosphorothionate 47
Participation in National Organizations 47

Raw Materials Laboratory (Y-12) 48
Oxidation of Tartaric Acid with Ceric Sulfate 48
Resistance of Tygon and Duroflex Plastic Tubing to Certain Chemical Reagents 48

Reactor Projects Laboratory (Y-12) 49
Gas Chromatographic Analysis of Helium 49
Direct Determination of Total Oxygen in Uranium Oxide 50
Automatic Conductometric Determination of Carbon 51
Dissolution of Graphite 51
Determination of Sulfur with a Leco Automatic Sulfur Titrator 51
Spectrophotometric Studies of Molten-Fluoride-Salt Systems 52
Spectrophotometric Determination of Yttrium with Pyrocatechol Violet 54
Solvent Extraction with Organophosphorus Compounds 54
Tri-*n*-octylphosphine Oxide 54
Tris(2-ethylhexyl)phosphine Oxide 55
Triphenylphosphine Oxide 56
Infrared Spectral Study of Phosphine Oxide Adducts 57
Infrared Spectral Study of Organophosphorus Compounds 57
1-Phenyl-3-isohexenyl-1-phospha-3-cyclopentene-*p*-oxide 57
Determination of Oxygen in Yttrium 58

Determination of Cadmium and Zinc in Fused Fluoride Salts 58
Complexometric Titration of Thorium 59
Flame Spectrophotometric Determination of Magnesium in Beryllium Oxide 59
Studies of Anodized Aluminum 60
Testing Laboratory 61

Spectrochemical and X-Ray Analyses (X-10 and Y-12) 62
Chemical Preparation of Samples (X-10) 62
Titanium 62
Boron 62
Dissolution of Niobium–Rare-Earth-Element Alloys Without Hydrofluoric Acid 62
Separation of Iron, Chromium, and Nickel from Niobium 62
Flame Photometry (X-10) 62
Cesium – Increase in Sensitivity 62
Tissue Analysis (X-10) 62
X-Ray Absorption and Fluoroescence – Extension of Wavelength Range (X-10) 63
X-Ray Absorption-Edge Analysis (X-10) 63
Electronic Background-Compensating System for Photoelectric Spectrometer (Y-12) 65
Investigation of Porous-Cup and Revolving-Disk Electrodes by Use of a Photoelectric Spectrometer (Y-12) 66
Improvements in Equipment for the Spectrometric Determination of Oxygen in Metals (Y-12) 66

Thermal Breeder Reactor Projects Analytical Chemistry Laboratory (Y-12) 68
Flame-Photometric Determination of Palladium in Thorium Oxide 68
Pyrolytic Separation of Fluoride from Nitrate- and Sulfate-Containing Solutions 68
Flame-Photometric Determination of Iron 68
Potentiometric Determination of Rare-Earth Elements 69
Evaluation of Flame Photometry for the Determination of Rare-Earth Elements 69
High-Frequency Titration of Sulfate and Free Acid in Solutions of Uranyl Sulfate 71
Polarographic Determination of Molybdenum 71
Spectrophotometric Determination of Osmium 71
Determination of Uranium(IV) in Thorium Oxide 72
Spectrophotometric Determination of Uranium(VI) 72
Determination of Uranium(IV)-to-Uranium(VI) Ratio in Thorium Oxide–Uranium Oxide Mixtures 72
Determination of Uranium(IV) by Direct Coulometric Oxidation 73
Spectrophotometric Determination of Cobalt in Aluminum 73
Simultaneous Extraction and Determination of Neodymium and Samarium 73
Complexometric Titration of Thorium by Use of Xylenol Orange as Indicator 74

SERVICE ANALYSES 75

General Services (Y-12) 75
Counting Laboratory 75
Miscellaneous Analyses Laboratory 75
Raw Materials Laboratory 77

Ionic Analyses (X-10) 77

Low-Radiation-Level Radiochemical Analytical Laboratory (X-10) 77
Special Equipment 79
Removable Sink Covers 79
Sample Holders for Use with the Low-Background Beta Counter 79

Dolly for the Scintillation Counter Shields 79
Vacuum Trap 79
Vacuum System for the Alpha-Range Analyzer 79
Counter Tables 79
Spectrometer Standards for Leaf Samples 80
Mass Spectrometric Analyses (Y-12) 80
Process Analyses (X-10) 80
High-Alpha Analytical Laboratory 80
High-Radiation-Level Analytical Facility (HRLAF) 81
Pilot-Plant Control Laboratory 81
Process-Development Service Laboratory 82
Radioisotopes-Radiochemistry Laboratory 82
Reactor Analyses Laboratory 82
Special Analyses Laboratory 82
Radiochemical Analyses (X-10) 83
Reactor Projects Laboratory (Y-12) 83
Thermal Breeder Reactor Projects Analytical Chemistry Laboratory (Y-12) 84
PRESENTATIONS OF RESEARCH RESULTS 85
ORGANIZATION CHART 99

RESEARCH AND DEVELOPMENT

ANALYTICAL INSTRUMENTATION (X-10)

D. J. Fisher

In-Line Instrumentation Development

J. W. Landry[1] T. S. Mackey[1]
R. W. Stelzner

A-C Polarography. – The construction of the prototype of the recording, high-sensitivity, controlled-potential, a-c polarograph[2] was completed. The instrument has a three-electrode system that consists of a saturated calomel reference electrode (S.C.E.), a dropping mercury electrode (D.M.E.), and a platinum-wire control electrode. The potential of the D.M.E. with respect to the S.C.E. is controlled at every instant of time by the feedback current of an operational d-c amplifier whose output is applied to the control electrode. The input to the control amplifier is the algebraic sum of a steady d-c voltage of either polarity (Initial Potential), a linearly increasing d-c voltage of either polarity (Electronic Scan), and a small sinusoidal voltage of selected amplitude in the range of either 0 to 10 mv or 0 to 100 mv. The frequency of the modulating a-c voltage can have a value in the range 10 to 100,000 cps.

First, the polarographic current is fed into a current amplifier having a low-sensitivity range of 1 to 2000 $\mu a/10$ mv and a high-sensitivity range of 1×10^{-4} to 5×10^{-1} $\mu a/10$ mv. Next, the a-c current is fed into a phase-discriminating circuit where the 90°-out-of-phase component of the current is rejected. The resultant in-phase component is displayed on a 10-mv Brown strip-chart recorder.

The evaluation of the instrument by means of solutions of cadmium(II) is in progress. After these tests are completed, the instrument will be used to determine uranium(VI) in solutions of low uranium concentration.

Flow Colorimeter. – The flow colorimeter[3] for the measurement of uranium in organic process streams at a concentration level of 50 g/liter is ready for installation on the ICP stream of the Metal Recovery Plant. A new design of uranium colorimeter that uses a chopped light beam produced by a chopper disk which contains blue and yellow filters is being investigated. The new design also permits the use of a single light source and a single detector.

Radio-Frequency Monitor of Electrolytes in High Concentration. – A test loop for the investigation of the behavior of electrolytes in high concentrations at frequencies up to 2000 Mc/sec has been built. A General Radio Company type 1218-A unit oscillator is used as the source of radio-frequency energy. The energy from the primary loop is coupled to the secondary loop by means of the closed loop that represents the solution.

Single-Beam Gamma Absorptiometer. – A single-beam gamma absorptiometer that uses a 10-mg quantity of Am^{241} as a source of 60-kev gamma rays and a scanning gamma spectrometer as a detector of gamma radiation was operated on a flowing-stream type of test loop. Solutions of lead nitrate were used as heavy-metal-ion absorption mediums. A straight-line calibration curve was obtained when the logarithm of the count rate of 60-kev gamma rays was plotted against the concentration of lead ions over the range of 0 to 300 g/liter. Variation in the flow rate of the stream within the range from 0 to 200 ml/min had no effect on the calibration. The investigation of a chopped-single-gamma-beam technique for measuring the uranium concentration of radioactive solutions of uranium and the construction of a dual-beam instrument are planned.

Monitors of Alpha Radiation. – The possibility of the monitoring of an alpha-bearing waste stream at its surface by means of a silver-activated zinc sulfide phosphor[4] at a level of radioactivity of 3000 alpha counts$\cdot$min$^{-1}\cdot$ml^{-1} has been tested. It was concluded that the quantitative results obtained were unreliable and that the operation of the monitor in a plant would require excessive maintenance. An attempt to determine the alpha-emitter content of such streams by measurement of the neutrons arising from (α,n) reactions was unsuccessful because the method was not sufficiently sensitive. A study is being made of a rotating-disk technique in which a liquid sample is taken

---

[1] Chemical Technology Division.

[2] M. J. Kelly *et al.*, "A-C Polarograph," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 13.

[3] *Ibid.*, "Colorimeter for Organic Process Streams," p 13.

[4] *Ibid.*, "Alpha Monitor," p 12.

and dried and the residue then counted for alpha particles.

Monitors of Gamma Radiation. -- Three smooth-bore fluorothene-type monitors of gamma radiation[5] have been installed in the Power Reactor Fuel Reprocessing Plant. These are located on the Head-End Aqueous Product (HAP) stream, the Second-Cycle Product (IIAP) stream, and on a waste stream. The monitor on the HAP stream has operated satisfactorily for six months, the other two monitors for about two months. The shielding of the detector head of the falling-stream type of monitor in the Metal Recovery Plant was insufficient, and the monitor has therefore been removed.

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

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

The new high-resolution flame spectrophotometer[6] has been designed and is being fabricated. It has evolved design-wise from older instruments.[7] In addition to the features previously described,[6] a means has been provided to measure spectral intensities from selected regions of the flame. The constituent circuits that have been constructed and tested operate satisfactorily.

Clairex type CL-3 cadmium selenide photoconductive cells were evaluated in the infrared spectral region. The response of these cells to changes in intensity at very low light levels was found to be too slow for use with a light chopper. The advantages of recording the time integral of radiant intensity as a function of time will be compared with those of recording the instantaneous radiant intensity as a function of time. The performance characteristics of the flame spectrophotometer will be established.

Controlled-Potential and Derivative Polarograph

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

The design of the model Q-1988 controlled-potential and derivative polarograph has been described.[8] Two of these polarographs have been fabricated by the Instrument Department of the ORNL Instrumentation and Controls Division. A set of mechanical and electronic drawings has been prepared. A procedure for checking out and testing the Q-1988 polarograph was written and was used to test two of these models. A paper that describes the results obtained with the prototype of the Q-1988 polarograph was written.[9] A new polarizing unit has been designed[9-11] and built that has electronic circuits for controlled-potential electrolysis, linear compensation, and potential scanning. The electromechanical polarizing unit that was in the prototype of the model Q-1988 polarograph has been replaced by the new unit. The circuit diagram of the polarograph with the electronic polarizing unit has been given to Westinghouse Electric Corporation, and it appears as Westinghouse drawing No. 549 D369 (7-31-59). The results of tests of the electronic-scanning circuit and of the linear-compensator circuit indicate that the performance of the new electronic polarizing unit is superior to that of the electromechanical polarizing unit.

The following conclusions can be made from results obtained by means of controlled-potential and derivative polarography. Controlled-potential electrolysis prevents *iR* losses from affecting wave shapes. Concentration measurements can be made in organic or aqueous solutions with a platinum-wire quasi-reference electrode used in place of a standard reference electrode. Waves of conventional shape and reproducible heights are obtained because no appreciable current is drawn through the reference electrode. A cell that contains as little as 0.3 ml of test liquid and that has a conventional D.M.E. and two bright platinum wires as quasi-reference and working electrodes

---

[5] *Ibid.*, "Gamma Monitors," p 12.

[6] D. J. Fisher, H. C. Jones, and M. T. Kelley, "High-Resolution, High-Sensitivity, Scanning, Recording Flame Spectrophotometer," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 17.

[7] M. T. Kelley, D. J. Fisher, and H. C. Jones, "High-Sensitivity, Recording, Scanning Flame Spectrophotometer," *Anal. Chem.* 31, 178 (1959).

[8] M. T. Kelley, H. C. Jones, and D. J. Fisher, "Controlled-Potential and Derivative Polarograph," *Anal. Chem.* 31, 1475 (1959).

[9] M. T. Kelley *et al.*, "Controlled-Potential and Derivative Polarography," to be published in *Proceedings, 2nd International Congress of Polarography, Cambridge, England*, Pergamon.

[10] M. T. Kelley, H. C. Jones, and D. J. Fisher, "Controlled-Potential and Derivative Polarograph," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 15–16.

[11] ORNL-LR-Dwg. No. 40086, "Circuits, Electronic Scan and Linear Compensator, Controlled-Potential and Derivative Polarograph, Polarizing Section."

can be used for polarographic concentration measurements. Reducible species in solution in concentrations as low as 10^{-6} *M* can be measured quantitatively; smaller concentrations can be detected. Certain reducible substances that cannot be determined in the same solution by regular polarography because their waves overlap severely can be determined by derivative polarography because their derivative peaks are resolved.

Investigation of High-Sensitivity Polarography

W. D. Cooke[12] D. J. Fisher
M. T. Kelley

The variables that restrict the useful lower limits of qualitative detection and quantitative measurement of polarography were investigated[13] with the prototype of the controlled-potential and derivative polarograph.[10] It was concluded that the chief cause of the limitations is the relatively large magnitude of the sporadic nonreproducible "noise" contained in the cell current when a conventional D.M.E. is used. Noise pulses can be minimized by drawing down to a smaller orifice diameter the tip of the capillary used for the D.M.E. or by using very dilute (10^{-4} *M*) supporting electrolyte.

Spectrographic Intensity-Ratio Analog Computer

H. C. Jones M. T. Kelley
D. J. Fisher R. E. Weekley

A readout instrument for use in the rapid spectrographic determination of oxygen and other gases in certain metals was mentioned previously.[14] This instrument, which chopped the light beams at different frequencies, was designed and fabricated and was tested to some extent. Separation of the two signal frequencies from a single multiplier phototube was accomplished by means of tuned amplifiers. The efficiency of separation was not determined before this design was discarded because it was decided that it might be necessary to measure the intensities of as many as six different light beams on a 21-ft-radius spectrograph. It is not expedient to measure a wide spectral range with a single phototube.

The instrument has been modified to a new design. It has two amplifier channels: a numerator channel and a denominator channel. Either of the two channels can be switched to receive as its input the output of any one of several multiplier phototubes. The phototubes receive their input from a 21-ft-radius Paschen-Runge spectrograph. The light beam is chopped at the input slit of the spectrograph by a slotted disk-type chopper. Each amplifier channel consists of two cascaded, a-c–coupled GAP/R amplifiers; a rectifier and filter; and a GAP/R K2-X amplifier stabilized by a K2-P amplifier, which combination is used as either an inverting d-c amplifier or as a time integrator. For increased sensitivity, a GAP/R USA-3 amplifier can be inserted in the numerator channel as a d-c voltage amplifier. The outputs of the two channels are divided by a potentiometric-recorder-type position servo, and either the ratio of the intensities of the two spectral lines of interest or the ratio of the time integrals of their intensities is continuously presented on the recorder chart. Also, the intensity, or the time integral of the intensity, of either of the spectral lines can be presented on the recorder chart by the use of a standard, Zener-diode-regulated voltage source as a reference (constant-denominator signal).

The computer has been installed, and tests are being made in the infrared spectral region by the use of two RCA type 7102 multiplier phototubes. The computer will be applied first to the determination of oxygen in steels.

ORNL Model Q-2005, Automatic, Electronic, Controlled-Potential Coulometric Titrator

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

The prototype of the ORNL model Q-2005 automatic, electronic, controlled-potential coulometric titrator has been described.[15] Eight titrators of this type have been constructed by the Instrument Department and are now in use. The titrators were checked out and tested according to the

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

[13] W. D. Cooke, D. J. Fisher, and M. T. Kelley, "Investigation of High-Sensitivity Polarography," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 16.

[14] H. C. Jones, D. J. Fisher, and M. T. Kelley, "Ratio Readout Recorder for the Spectrographic Determination of Oxygen in Metals," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 17.

[15] M. T. Kelley, D. J. Fisher, and H. C. Jones, "Automatic, Electronic, Controlled-Potential Coulometric Titrator," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 13–14.

procedure that was written specifically for the Q-2005 instrument. A complete set of mechanical and electronic drawings has been prepared. A method for the use of this instrument has been included in the *ORNL Master Analytical Manual.*[16] Papers that described the titrator[17,18] and applications of it[19–21] have been published.

High-Sensitivity Modification of ORNL Model Q-2005, Automatic, Electronic, Controlled-Potential Coulometric Titrator

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

One of the ORNL model Q-2005 controlled-potential coulometric titrators[17,18] has been modified for the determination of small amounts of high-equivalent-weight substances, for example, 1 mg or less of plutonium. For this, the sensitivity of the integrator has been increased fifty times. This increase was accomplished by changing the series resistor of the controlled electrode from a 10- to 50-ohm resistor in order to achieve a sensitivity multiplication of five times and by changing the input resistor of the integrator from a 400- to a 40-kilohm resistor in order to give a multiplication of ten times. The combined effect of these two changes is an increase in sensitivity of fifty times. For the titration of more than 1 mg of a substance, the five-times increase is used. A single-pole double-throw switch is used to change from the five-times to the fifty-times increase in sensitivity.

The method of adjusting the integrator drift was also changed slightly in order to shorten the time required for the adjustment. The full output of the integrating amplifier is switched to the readout device, and then drift is eliminated by adjustment of the integrator bias. One-tenth of the full output was previously used to monitor integrator drift.

Results obtained by W. D. Shults with the modified instrument have been reported.[22]

Plastic Pipet for Remotely Servo-Controlled Pipetter

D. J. Fisher

A remotely servo-controlled pipetter has been described in which the pipet is constructed of stainless steel and Teflon, both of which materials touch the liquid sample.[23–25] A plastic-lined pipet is being designed that can be installed in the servo-controlled pipetter in place of the stainless steel–Teflon pipet. It is for use with samples that attack stainless steel. Various volumes up to as much as 0.7 ml can be delivered from the pipet. Design suggestions were made by B. Cook and R. J. Fox of the Engineering and Mechanical Division and by H. C. Meyer and W. R. Musick.

Chronopotentiometer

W. L. Maddox D. J. Fisher

A versatile chronopotentiometer has been built. This instrument comprises constant-current, potential-sensing, and timing circuits, each made up of a GAP/R K2-X amplifier and an appropriate feed-back network. A constant current as large as 750 μa and of either polarity can be driven through the electrolysis cell. The current is not affected by changes in cell impedance. The polarity of the current can be reversed either automatically on a programed basis or at will by means of manual

[16] H. C. Jones, "Automatic Coulometric Titrator, ORNL Model Q-2005, Electronic, Controlled-Potential," Method Nos. 1 003029 and 9 003029 (8-17-59), *ORNL Master Analytical Manual*; TID-7015, sec 1.

[17] M. T. Kelley, H. C. Jones, and D. J. Fisher, "Electronic Controlled-Potential Coulometric Titrator," *Anal. Chem.* 31, 488 (1959).

[18] *Ibid.*, p 956.

[19] W. D. Shults and P. F. Thomason, "Controlled-Potential Coulometric Determination of Copper and Uranium," *Anal. Chem.* 31, 492 (1959).

[20] W. D. Shults, "Controlled-Potential Coulometric Determination of Europium," *Anal. Chem.* 31, 1095 (1959).

[21] W. D. Shults *et al.*, *Progress Report on the Analysis of Dissolver Solutions by Controlled-Potential Coulometric Titration*, ORNL-2776 (Sept. 14, 1959).

[22] M. T. Kelley, H. C. Jones, and D. J. Fisher, *Electronic Controlled-Potential Coulometric Titrator for Pu Analysis*, a paper presented at the Third Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 26–29, 1959.

[23] D. J. Fisher and R. B. Quincy, Jr., "Pipetter, Remotely Servo-Controlled," Method Nos. 1 003101 and 9 003101 (11-12-56), *ORNL Master Analytical Manual*; TID-7015, sec 1.

[24] L. G. Stang, Jr. (compiler), "Servo-Controlled Pipetters," *Hot Laboratory Equipment*, 2d ed., p 168–69, Technical Information Service, Washington, D. C., 1958.

[25] M. T. Kelley, H. L. Hemphill, and D. J. Fisher, "Servo-Controlled Pipetter for Precise Delivery of Microliter Drops," *Proceedings, Second Conference, Analytical Chemistry in Nuclear Reactor Technology, Instrumentation, Remote Control Techniques, and Nucleonics*, TID-7568 (Pt. 2), p 98–106 (April 1959).

controls. The readout of transition time is obtained from a precision timer actuated by the timing amplifier. Alternatively, the potential-time curve can be recorded oscillographically.

Cathodic-Stripping Voltammetry of Chloride Ion

W. L. Maddox

Cathodic-Stripping Coulometry (Voltage-Step Method). – The electronic coulometric stripper reported previously[26] has been modified in order to increase its range and accuracy. The modified instrument has been tested on solutions of chloride ion concentration ranging from 0.07 to 18 μg/ml.

Chronopotentiometry (Current-Step Method). – The chronopotentiometer (see "Chronopotentiometer," this report) has been tested by means of the cathodic-stripping determination of chloride ion. The relationship between chloride ion concentration and cathodic transition time, following a constant-current anodization, is linear in the chloride ion concentration ranges from 0.35 to 3.5 and from 3.5 to 35 μg/ml. The choice of experimental conditions determines the concentration range of a linear region.

Special Mercury-Pool Electrode for Voltammetry. The difficulty of reproducing the mercury-pool electrode has been a source of some trouble in the cathodic-stripping techniques. A simple system has been devised for producing a pool having an area of 0.53 $cm^2 \pm 1\%$.

INORGANIC PREPARATIONS (X-10)

D. E. LaValle

In the work for the Nuclear Physics and Neutron Diffraction Group of the Physics Division, emphasis has shifted to the preparation of the nitrides of the rare-earth metals. The nitrides of holmium, thulium, terbium, and erbium were prepared. Several problems in connection with the previous work for this group on the transition-metal halides have been satisfactorily concluded; a small single crystal of chromic chloride, $CrCl_3$, has been grown from the vapor phase by the use of a zone-refining apparatus. The preparation and structure of molybdenum trifluoride, MoF_3, have been satisfactorily resolved. The molybdenum trifluoride prepared here is rhombohedral, in distinction to the cubic structure reported by Gutmann and Jack for that which they prepared.[27]

In the high-purity lithium iodide program for the Neutron Spectroscopy Group of the Neutron Physics Division, two methods alternative to the standard chemical method of purification of lithium iodide are being tested: repeated crystallization and zone refining.

The preparation of fused salts for the High-Temperature Reactions Group of the Metallurgy Division continued; such mixtures and compounds as $NaAlCl_4$-$KAlCl_4$ eutectic, and the chlorides of bismuth, cadmium, and zinc were made.

The preparation of several gallons of the B^{10}-isotopic form of trimethyl borate, $(CH_3O)_3B^{10}$, from the B^{10}-isotopic form of boron trifluoride etherate, $(CH_3)_2O{\cdot}B^{10}F_3$, is in progress for the Nuclear Measurements for Reactor Design Group of the Physics Division.

The work for the High Temperature and Structural Chemistry Group of the Chemistry Division included such preparations as 100-g quantities of anhydrous fused $CaCl_2$ and $CeCl_3$ and smaller quantities of the alkali-metal halides.

Other preparations of interest were the isotopic compounds $Li_3^6N^{15}$ for the Nuclear Chemistry Group and anhydrous Li^7BrO_3 for the Radiation Chemistry Group, both of the Chemistry Division. Relative to the Gas-Cooled Reactor Project of the Reactor Chemistry Division, Cs_2O was prepared.

IONIC ANALYSES (X-10)

P. F. Thomason

Controlled-Potential Coulometric Titration of Plutonium

W. D. Shults

A method for the determination of plutonium by controlled-potential coulometric titration has been developed.[28] It is similar to that described by

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

[27] V. Gutmann and K. H. Jack, "The Crystal Structures of Molybdenum Trifluoride, MoF_3, and Tantalum Trifluoride, TaF_3," *Acta Cryst.* 4, 244 (1951).

[28] W. D. Shults *et al.*, "Progress Report on the Analysis of Dissolver Solutions by Controlled-Potential Coulometric Titration," ORNL-2776 (Sept. 14, 1959).

Scott and Peekema[29] and involves two electrolyses: a reduction of plutonium in its higher valence states to plutonium(III) at +0.575 v vs the S.C.E., then an oxidation of plutonium(III) to plutonium(IV) at +0.875 v vs the S.C.E. The current consumed during the oxidation is a measure of the total amount of plutonium present. Both electrolyses are made in 1 *M* perchloric acid and at a platinum-gauze electrode; 1 *M* hydrochloric or nitric acid can also be used. The total time required for the determination is 20 to 25 min. The precision obtained when standard solutions of plutonium were analyzed by this method is indicated in the tabulation below; no bias was detected.

Pu Tritrated (μg)	Relative Standard Deviation (%)
1000	0.1
250	0.3
50	1.5

Changes were made in the circuitry of the ORNL model Q-2005 titrator so that it could be used for this determination (see "High-Sensitivity Modification of ORNL Model Q-2005, Automatic, Electronic, Controlled-Potential Coulometric Titrator," this report). The performance of the modified instrument is still being evaluated. The construction of a titrator designed specifically for the determination of high-equivalent-weight elements, such as plutonium, is planned.

Analysis of Product Solutions. – Controlled-potential coulometric titration is being used for the determination of plutonium in plutonium nitrate product solution which derives from the Metal Recovery process. Nitric acid is used to destroy any excess reducing agent, which is often present. No interference is encountered from the impurities normally present in this type of sample. Revisions have recently been made to improve the precision and general performance of the method. Control data taken during a three-month period have shown that for ~ 1-mg quantities of plutonium the relative standard deviation of the original technique is 0.2%. Control data for the revised technique are not yet available.

Analysis of Dissolver Solutions. – The determination of plutonium in Purex-type dissolver solution by controlled-potential coulometric titration is being studied. The anion exchange procedure for plutonium separation (nitrate system)[30] has been adapted so that it can be used to separate and/or concentrate plutonium prior to its determination by coulometric titration.[28] Recoveries of 99.5% or so are obtained. The problem of resin degradation by chemical attack has not yet been solved; it is therefore necessary to destroy traces of organic material with hot concentrated perchloric acid before making the electrolyses. The entire procedure requires approximately 2 hr; the relative standard deviation for ~250-μg quantities of plutonium is 0.6%.

Future Program. – The following work is planned to complete this study: (1) final refinements in the procedure for product solution analysis, (2) application of the titration and/or separation-titration to the determination of plutonium in radioactive dissolver solution, and (3) evaluation of the high-sensitivity coulometric titrator that is to be designed and constructed specifically for the determination of high-equivalent-weight elements.

Determination of Uranium(VI) in Dissolver Solutions by Extraction with Triisooctylamine and Controlled-Potential Coulometric Titration

B. B. Hobbs

A modification of the procedure described by Moore[31] for the liquid-liquid extraction of uranium(VI) with triisooctylamine has been used to remove uranium(VI) from dissolver solutions. The uranium(VI) contained in a test portion of the dissolver solution, to which aluminum nitrate is added as salting agent, is extracted into a 5% solution of triisooctylamine in xylene. The uranium(VI) is then stripped into an aqueous solution that is 0.05 *M* in perchloric acid and 0.5 *M* in sulfuric acid and is determined by controlled-potential coulometric titration. Uranium(VI) in nonirradiated synthetic dissolver

[29] F. A. Scott and R. M. Peekema, "Analysis for Plutonium by Controlled Potential Coulometry," *Proc. U. N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 1958* 28, 573 (1958).

[30] J. L. Ryan and E. J. Wheelwright, "Recovery and Purification of Plutonium by Anion Exchange," *Ind. Eng. Chem.* 51, 60 (1959).

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

solutions of the Darex, Sulfex, and Zirflex types has been determined in this way. The results indicate that the relative standard deviation of the method is 0.2 to 0.4% and the error is +0.05 to −0.3% for quantities of uranium(VI) in the range from 2 to 10 mg.

The effects of fission products on the extraction, on the titration, and on the entire procedure will be studied. Also, the High-Radiation-Level Analytical Facility will be used to gather data on the effects of radiation and remotely controlled analytical operations on this procedure.

Hexone Extraction of Uranium(VI) from Dissolver Solutions

E. L. Blevins

Uranium(VI) has to be separated from dissolver solutions before it can be determined satisfactorily. Booman and Holbrook[32] reported a method for the determination of uranium(VI) by extraction with methyl iosbutyl ketone (hexone) and coulometric titration. Their method is free from a large number of interferences but is rather time-consuming because destruction of organic materials by a fusion technique is required prior to the coulometric titration. A modified procedure has been developed that is faster and is a useful supplement to other uranium separation methods. The procedure consists in the extraction of uranium(VI) into hexone from an "acid-deficient" aluminum nitrate solution of the sample, recovery of uranium(VI) from an aliquot of the organic phase, destruction of organic matter by wet ashing, and then dissolution and titration of the uranium(VI). The titration cell is a Vycor crucible in which both the wet ashing and the titration are made. The final solution is pretitrated coulometrically at +0.125 v vs a silver–silver chloride electrode and then is titrated at −0.3 v vs a silver–silver chloride electrode.

The procedure has been evaluated by analyzing standard solutions of uranium(VI); the results are shown in Table 1. These data indicate that the method has good precision and that the extraction, which must be made, does not affect the precision significantly.

With some final improvements this procedure can be applied to nonradioactive synthetic and to authentic dissolver solutions. At the present time, however, the application of anion exchange to the separation of uranium(VI) from dissolver solution is being studied.

Table 1. Precision of Hexone Extraction–Coulometric Titration of Uranium(VI)

Uranium Taken (mg)	Extracted	Number of Titrations	Relative Standard Deviation (%)
5.44	No	14	0.2
5.44	Yes	17	0.4
10.31	No	9	0.2
10.26	Yes	14	0.5

Polarographic and Coulometric-Titration Study of Neptunium

H. E. Zittel

Work has been initiated to further elucidate the polarographic and coulometric behavior of neptunium. Slee, Phillips, and Jenkins[33] studied the behavior of neptunium(IV) in various media at the D.M.E. Stromatt[34] has studied the coulometric behavior of the neptunium(V)-neptunium(VI) couple at a platinum-gauze electrode. Since neptunium ordinarily occurs in solution as neptunium(V), this study was undertaken to determine whether or not an electrometric method could be developed to measure the neptunium(V) concentration without prior treatment such as was necessary in the two studies mentioned.

A standard solution of neptunium was obtained from J. H. Cooper, and studies of the polarographic behavior of neptunium(V) in aqueous solutions of sulfuric, nitric, and perchloric acids have been started. No wave was found for neptunium(V) at potentials from 0 to −1.2 v vs the S.C.E. When neptunium(V) was reduced to neptunium(IV) with ferrous ammonium sulfate prior to the potential scan, a wave was found to exist for the neptunium(IV)-neptunium(III) reduction at approximately −0.4 v vs the S.C.E.; this finding substantiated the results of others.[33,34] When phosphoric acid was used as the indifferent

[32] G. L. Booman and W. B. Holbrook, "An Extraction, Controlled-Potential Coulometric Method Specific for Uranium(VI)," *Anal. Chem.* 31, 10 (1959).

[33] L. J. Slee, G. Phillips, and E. N. Jenkins, *The Determination of Small Amounts of Neptunium in Plutonium Metal*, AERE C/R-2819 (Mar. 1959).

[34] R. W. Stromatt, *Analysis for Neptunium by Controlled Potential Coulometry*, HW-59447 (Feb. 1959).

electrolyte, a wave developed at approximately −0.7 v vs the S.C.E. without the prior reduction of neptunium(V) that had been necessary in the other electrolytes. The wave is somewhat anomalous and has not yet been thoroughly analyzed. However, it has been found that an increase in the phosphoric acid concentration tends to cause the wave to assume a split-wave shape. It has also been found that the wave height is almost exactly twice that found when prereduction is made. The addition of various other mineral acids (e.g., sulfuric and nitric) to the phosphoric acid solution has the effect of shifting the $E_{1/2}$ without any appreciable effect on the wave height. The addition of perchloric acid does not cause this marked effect. This effect appears to be anionic in nature since salts of the mineral acids (e.g., sodium nitrate and sodium sulfate) when added to the phosphoric acid solution of neptunium(V) have approximately the same effects as the acids themselves.

Further polarographic work will be done to clarify the nature of the neptunium(V) reduction in phosphoric acid media, and coulometric studies will be carried out to establish the best condition for the coulometric determination of neptunium(V) by means of a mercury-pool electrode.

Dropping Mercury Electrode for Polarographic Studies in Hydrofluoric Acid Media

H. P. Raaen

Polarographic studies can provide valuable information about reactions in hydrofluoric acid media. Attempts to fabricate from Teflon a capillary that will simulate a glass capillary when used as a D.M.E. and that will be satisfactory in hydrofluoric acid media have been discussed.[35] Analytical problems related to the Fluoride Volatility Process re-emphasize the need for such a capillary. Several Teflon capillaries made by R. J. Fox of the Engineering and Mechanical Division were evaluated experimentally, and design modifications suggested from the experimental results were made. As a result, a Teflon capillary having a uniformly circular orifice 0.0025 in. in diameter was made by a simple and inexpensive fabrication procedure. The capillary behaved very similarly to a Sargent S-29419 "2-to-5 sec" glass capillary when used as a D.M.E. in 0.1 *M* potassium chloride. Minor improvements in the design of the capillary are to be made, and it is to be evaluated in hydrofluoric acid media over a wide range of hydrofluoric acid concentration and for long periods of time. The initial evaluation of this capillary indicates that further study of it is justified, especially since its behavior is superior to that found to be reported for any other capillary made from hydrofluoric acid–resistant material.[36–39]

Polarographic Determination of Sulfur Dioxide in Hydrofluoric Acid

H. P. Raaen

A polarographic reduction wave for sulfur dioxide (sulfurous acid, sulfite) in aqueous hydrofluoric acid solution has been found to exist at an $E_{1/2}$ in the region of −0.40 to −0.45 v vs the S.C.E. No report of this reduction wave has been located in the project or open literature, although the sulfite reduction at the D.M.E. has been reported previously for several supporting electrolytes other than hydrofluoric acid. The finding of the wave is of interest for the following reasons. Only a very limited amount of polarography has been done in hydrofluoric acid media, even in dilute aqueous solutions. The excellent form of the wave suggests that the suitability of aqueous hydrofluoric acid solutions as supporting media for polarographic determinations should be studied thoroughly over a wide range of hydrofluoric acid concentration and for a large number of reducible ions. The existence of the wave will provide a quantitative method for the determination of sulfur dioxide in hydrofluoric acid, the hydrofluoric acid itself acting as the supporting electrolyte; the method will be useful in analytical problems related to the Fluoride Volatility Process in which

[35] H. P. Raaen, "Polarography of Niobium in Ammonium Bifluoride," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 31–32.

[36] A. F. Clifford and G. Balog, *The Hydrogen Fluoride Solvent System; Polarographic Studies*, AECU-1491 (no date).

[37] A. F. Clifford and M. E. Runner, *The Acids of the Hydrogen Fluoride System; I. Progress Report for the Period September 1, 1950 to May 15, 1951. II. Renewal Proposal for the Period September 1, 1951 to August 31, 1952*, AECU-1711 (June 1951).

[38] A. F. Clifford and G. Balog, *The Hydrogen Fluoride Solvent System; Polarographic Studies*, AECU-2008 (Aug. 1951).

[39] V. S. Griffiths and W. J. Parker, "The Flowing Mercury Electrode in Polarography. Part I," *Anal. Chim. Acta* 14, 194 (1956).

the embrittlement of nickel by sulfur-containing impurities in hydrofluoric acid is of concern.

The wave appears to have excellent characteristics. The results of the thus far limited study of the wave indicate that it is well defined, the residual-current and limiting-current regions being very nearly parallel, and that it is usually free of maxima. The value of the $E_{1/2}$ appears to be reasonably constant. A linear relationship seems to exist between the sulfur dioxide (sulfite) concentration and the diffusion current. The lower limit of quantitative measurement is in the region of 10^{-5} *M* sulfite in the solution polarographed.

The experimental work done thus far has been with four lots of ~49% reagent-grade hydrofluoric acid and one lot of ~75% hydrofluoric acid that was prepared by gas-phase transfer from liquid hydrofluoric acid stored in a pressure cylinder. Both sulfurous acid and sodium sulfite were used in the identification of the wave and in the preliminary studies of the diffusion current–concentration relationship. A cursory comparison was made of the form of the wave and of the diffusion current–concentration relationship for 0.1 *N* solutions of hydrofluoric, hydrochloric,[40–42] and nitric acids[43] as supporting media. No major differences were observed.

The work will be continued in order to obtain accurate fundamental polarographic data for the sulfite reduction at the D.M.E. in aqueous hydrofluoric acid media and to develop a quantitative polarographic method for sulfur dioxide in hydrofluoric acid.

Polarographic Determination of Sulfur Dioxide in Fluosulfonic Acid

H. P. Raaen

Evidence has been obtained of the existence of a polarographic reduction wave for sulfur dioxide (sulfurous acid, sulfite) in aqueous fluosulfonic acid solution. No report of the existence of the wave has been found. Experiments will be made in order to prove or disprove its existence. If it exists, the possibility of using it as the basis for the quantitative polarographic determination of sulfur dioxide in fluosulfonic acid will be studied.

Polarography of Niobium

H. P. Raaen

The study of the polarography of niobium was continued. The objective has been to study individually and from a fundamental approach some of the variables that are believed to be elusive and critical in the definition of the conditions under which the polarographic determination of niobium in 2 *M* citric acid solution of pH 1 was achieved at very high sensitivity in one experiment.[44]

The instability of solutions of niobium is a major problem. The usual procedures for the preparation of standard solutions of niobium are cumbersome and result in a relatively large number of extraneous ions being present in the final solution. The possibility of preparing standard solutions of niobium by electrolytic dissolution of niobium metal into aqueous solutions of a chosen electrolyte was considered. By means of both suggestions and assistance from J. A. McLaren of the Chemical Technology Division, the electrolytic dissolution of niobium metal into aqueous solutions of oxalic acid and of oxalic acid and ammonium bifluoride was achieved. It is believed that the technique could be the basis for a simple and accurate method of preparing standard solution of niobium and should be applicable for many chosen electrolytes, the stability of the resulting solution of niobium being, of course, a function of the electrolyte. In the course of this limited experimentation, interesting observations were made regarding the electrolytic behavior of niobium that should be of value in the interpretation of polarographic results, for example, the cyclic formation of colored films on the surface of the strips of niobium sheet metal used as electrodes and the

[40] B. Gosman, "Polarographic Studies with the Dropping Mercury Kathode. – Part X – The Reduction of Sulfurous Acid," *Collection Czechoslov. Chem. Communs.* 2, 185 (1930).

[41] O. Ya. Batmanova, "Polarographic Determination of Sulfur Dioxide," *Gigiena i Sanit.* 12, 17 (1951).

[42] E. Zvinca-Selegean, L. Cariadi, and N. Racoveanu, "Determination of Sulfur Dioxide in Air by Polarography," *Rev. chim. (Bucharest)* 9, 39 (1958); [*Chem. Abs.* 53, 3991c (1959)].

[43] I. M. Kolthoff and C. S. Miller, "The Reduction of Sulfurous Acid (Sulfur Dioxide) at the Dropping Mercury Electrode," *J. Am. Chem. Soc.* 63, 2818 (1941).

[44] P. F. Thomason and H. P. Raaen, "Polarographic Behavior of Niobium in Citric Acid Medium," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 11.

spontaneous and rapid stripping of the film during the course of the electrolysis. The possibility of intriguing and fruitful research, both fundamental and applied, on the electrochemical behavior of niobium is indicated. The importance of such research is shown by the limit of information now available and by the significance of niobium in reactor technology.

In the one polarographic experiment[44] mentioned above, a number of substances other than citric acid and niobium were present that might have acted as catalysts in the polarographic redox reactions. Since one of them was nitric acid, the polarography of niobium in nitric acid media was studied briefly. Derivative polarographic techniques revealed that what appeared as a single wave by regular polarography was resolved into two peaks and that one of the peaks grew at the expense of the other with time. It was thought that a niobium amalgam, provided it could be prepared, could be used instead of mercury in the D.M.E. in nitric acid solution to gain fundamental information regarding the mechanisms of possible reactions between niobium and nitric acid, catalytic and otherwise. Some work of this nature is reported for amalgams of other metals.[45,46] Attempts were made to electrodeposit niobium from aqueous solution by several procedures reported in the literature, but no success was had with them; in fact, from experimental results, it is believed that one author mistook a deposit of platnium for niobium. This area of work deserves further careful study.

Hydrofluoric acid was another of the possible catalytic substances present. Niobium is readily soluble in hydrofluoric acid media if small amounts of nitric acid or hydrogen peroxide are present and if the solutions are relatively stable. It is of interest to study hydrofluoric acid both as a possible catalyst in the polarography of niobium in aqueous citric acid solution and independently as a supporting electrolyte. It has not been possible to determine whether niobium in aqueous hydrofluoric acid media gives a reduction wave, because all the hydrofluoric acid used has been found to contain sulfur dioxide (sulfurous acid, sulfite), which gives a reduction wave that would possibly mask other reduction waves (see "Polarographic Determination of Sulfur Dioxide in Hydrofluoric Acid," this report). When the problems associated with this impurity in hydrofluoric acid and with the lack of a satisfactory capillary for use as a D.M.E. in hydrofluoric acid media (see "Dropping Mercury Electrode for Polarographic Studies in Hydrofluoric Acid Media," this report) are solved, it will be established whether niobium gives a polarographic reduction wave in hydrofluoric acid media.

Determination of Technetium in Uranium Trioxide

F. J. Miller

The determination of microgram quantities of technetium in uranium trioxide was investigated. A procedure based mainly on previous work of other investigators was evolved. The procedure, which is described in detail elsewhere,[47] consists in the extraction of the tetraphenylarsonium chloride complex of technetium from an alkaline carbonate solution of the uranium trioxide into chloroform. The technetium(VII) is then stripped from the organic phase into a dilute aqueous solution of perchloric acid. The final determination is made by polarography. The necessity for using a correction factor to account for losses in extraction and backwashing was demonstrated by gamma counting with Tc^{95m} tracer.

Determination of Free Acid in Uranyl Sulfate Solutions by the Dowex 50 Resin Separation Procedure

F. J. Miller H. E. Zittel

A procedure which was suggested for obtaining the free-acid values of HRP fuel solutions[48] was studied to determine the optimum operating conditions. Possible methods of titration of effluent solutions were investigated. To summarize the investigation, which is reported elsewhere,[49] it

[45] I. M. Kolthoff and J. J. Lingane, *Polarography*, 2d ed., pp 197, 209, 387, Interscience, New York, 1952.

[46] R. E. Biggers, *Some Electrochemical Investigations with Dilute Bismuth Amalgams Used as Dropping Electrodes*, Chaps II and IV, Ph.D. Dissertation, Princeton University, October 1957.

[47] F. J. Miller, *The Determination of Technetium in Uranium Trioxide*, ORNL CF-59-10-27 (Oct. 9, 1959).

[48] L. O. Gilpatrick and H. F. McDuffie, *Free Acid Determination in Uranyl Sulfate Solutions by the Dowex-50 Resin Separation Procedure*, memorandum to M. T. Kelley, Dec. 12, 1958.

[49] F. J. Miller, *Evaluation of the Free-Acid Determination in Uranyl Sulfate Solutions by the Dowex-50 Resin Separation Procedure*, ORNL CF-59-10-112 (Oct. 27, 1959).

can be stated that the free acid present in a uranyl sulfate solution can be satisfactorily determined by passing a test portion of the solution through a column of Dowex 50 ion-exchange resin that has been loaded previously with lithium(I) ions. The hydrolyzable cations in the uranyl sulfate solution are exchanged for lithium(I) ions. The free acid is eluted from the column with a 0.05 *M* solution of lithium sulfate and is titrated automatically to a photometric end point by means of methyl red as an indicator. Persons in the Reactor Analyses Group were trained in the technique of the method and are presently using it as a standard procedure.

Thermometric Titrations

F. J. Miller

The thermometric titration of free acid in radioactive solutions has been successfully performed by members of the Reactor Analyses Group. It has been demonstrated that radioactivity does not affect the thermistor, at least over a short period of time, nor does its presence preclude the possibility of successful thermometric titrations. Results achieved in the thermometric titration of free acid have been comparable with those obtained by other methods. Because of the small amount of sample available and the low concentration of free acid present, it is doubtful that the thermometric method will be used on HRP fuel solutions except possibly as a check method to verify results obtained by other means.

Analysis of Bismuth Chloride

F. J. Miller

The analysis of bismuth chloride was studied as a part of a continued investigation of the stoichiometry of the bismuth halides. The analyses were performed by conventional methods; the chloride was determined by titration with a standard solution of silver nitrate, and the bismuth gravimetrically as bismuth phosphate.

Automatic, Chelometric, Potentiometric Titrations by Use of a Mercury Indicator Electrode

H. Kubota

The automatic, chelometric, potentiometric titration of metal ions with salts of ethylenediaminetetraacetic acid by means of a mercury indicator electrode[50] has been extended to the titration of milligram amounts of rare-earth elements. This method is especially useful for this quantity level of rare-earth elements because it is satisfactory in a region that is beyond the lower limit of quantitative measurement of spectrophotometric methods for such elements and because colorless rare-earth elements can also be determined. It is being used to determine the total rare-earth-element content of purified products from the Fission Products Separation plant. In order to remove citrate interference, the rare-earth elements are precipitated with oxalate, the mixture is centrifuged, and the precipitate is washed and redissolved in nitric acid. A few drops of peroxide are added to hasten the decomposition of the oxalate in warm nitric acid medium. The excess peroxide is destroyed by warming the solution in contact with platinum black before the titration for the total rare-earth elements is made.

Chemical Changes in the Reaction Between Purex Waste Solution and Sodium Chloride

H. Kubota

The feasibility of storing Purex waste solutions in deep salt (sodium chloride) mines, as has been proposed,[51] is being studied. It is pertinent to know what effects can be expected from the interaction between the acidic waste solution and sodium chloride. The investigation is being conducted along two lines: determination of the changes that take place in the solution during storage, and analysis of the effluent gaseous products. Conventional chemical methods are used for the analysis of the solution, whereas gas chromatography and infrared absorption techniques are used for the analysis of the gases.

Simulated Purex waste solution, about 7 *M* in nitric acid, was reacted with solid sodium chloride at 80°C. The main reaction was apparently that between nitric and hydrochloric acids, that is, the aqua regia reaction. The effects of the concentrations of acid, other cations, and various anions are being followed.

---

[50] H. Kubota, "Chelometric Titrations by Use of a Mercury Indicator Electrode," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 34.

[51] "The Disposal of Radioactive Waste on Land," *Natl. Acad. Sci.-Natl. Research Council, Publ. No.* 519, 6 (Apr. 1957).

The effluent gas from a reaction mixture contained in an all-glass system was found to contain chlorine and nitrosyl chloride in nearly equal amounts. Traces of moisture and of another gas, which appears occasionally up to a maximum concentration of 5 vol %, comprised the remainder of the gas. The gases obtained from a field test, also on simulated Purex waste solution, conducted in the Carey salt mines contained lesser amounts of nitrous oxide and carbon dioxide in addition to chlorine, nitrosyl chloride, and moisture.

Determination of the Oxygen-to-Uranium Ratio in Uranium Dioxide–Thorium Oxide

H. Kubota

The polarographic method of determining oxygen-to-uranium ratios of uranium dioxide[52] has been in established use for several months. A recent nuclear-fuel development is the use of uranium dioxide(5%)–thorium oxide(95%) pellets for which the oxygen-to-uranium ratio must be determined. The pellet is crushed in a vise, quickly transferred to a dissolver flask, and covered with phosphoric acid; the mixed oxides are dissolved by heating overnight at a gentle boil. The uranium(VI) in the solution is determined polarographically. The uranium(IV) in a portion of the same solution is oxidized to uranium(VI), and the total uranium is determined as uranium(VI). The oxygen-to-uranium ratio is calculated from the relative abundance of uranium(VI) to total uranium. This procedure circumvents the variation in the uranium dioxide content of the pellets. The presence of as much as 200 ppm of iron in the pellets did not affect the results. The iron appears to be retained in a state that does not cause oxidation of uranium(IV) during the dissolution.

Chemical Changes in Uranium Oxide–Aluminum Reactor-Fuel Elements During Fabrication and Heat Treatment

H. Kubota

The studies made of the chemical changes in uranium dioxide–aluminum (UO_2-Al) fuel elements during fabrication and heat treatment[53] have been extended to the uranium oxide–aluminum (U_3O_8-Al) system. The results show an initial reduction of U_3O_8 to UO_2 followed by the further reduction of UO_2 to give intermetallic compounds of uranium and aluminum. Since the latter reduction is in essence the reaction of uranium dioxide with aluminum, which has already been described, the rate of conversion of U_3O_8 to UO_2 was the main step followed in detail. After the removal of metallic aluminum by caustic dissolution and of intermetallic compounds by dissolution in dilute mineral acid, the mixed oxides were dissolved in phosphoric acid. The uranium(VI) content was determined polarographically if low and coulometrically if high. The uranium(IV) content was obtained by titration with a standard solution of ceric ion.

A uniform conversion of U_3O_8 to UO_2 with duration of heat treatment was observed with fuel plates from one batch. Similar trends were observed with other batches, but no constant rate of conversion with time was seen. As the bulk of the oxide was converted to UO_2, intermetallic uranium-aluminum compounds were observed to form before the reduction of U_3O_8 to UO_2 was complete.

Automatic Titration of Mixtures of Strong and Weak Acids

H. Kubota

The successive determination of a strong and a weak acid in mixtures of the two in an aqueous medium is theoretically possible if the pK values for the two acids differ by at least four units. In practical work, however, the differentiation is difficult when the difference in pK values is just about four. Such titrations can be improved by using a solvent that enhances the difference in acid strengths. Acetone has been found to be a good solvent for binary aqueous solutions of strong mineral acid and formic acid (pK = 3.75) or benzoic acid (pK = 4.2). For the determination of the same mixed acids in kerosene, a 1:4 methanol-acetone mixture was found to be a better matrix. The above-named solvent systems also increase the graphical magnitude of the

[52] H. Kubota, "Determination of the Oxygen-to-Uranium Ratio of Uranium Dioxide," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 33.

[53] *Ibid.*, "Study of Chemical Changes in UO_2-Al Reactor Fuel Elements During Heat Treatment at 600°C," p 33.

end-point break by a factor of nearly 2 over that of an aqueous system. By use of an automatic titrator the end points can be located with minimum error.

Program for Spectrophotometric Studies of Aqueous Solutions at Elevated Temperatures

R. E. Biggers J. M. Chilton[54]

The Analytical Chemistry and Chemical Technology Divisions are jointly making a spectrophotometric study of solution chemistry at temperatures up to at least 330°C and pressures up to 200 atm. This study supplements other high-temperature work at ORNL. It is anticipated that the necessary measurements can be made up to near the critical point (~370°C) in both water and deuterium oxide systems.

The chief advantage of the spectrophotometric technique at high pressures and temperatures is that it provides a means of determining not only equilibrium conditions but also chemical kinetics without the complexity and uncertainties that are associated with a method which requires withdrawing a large number of samples. Also, a great many of the constituents of a solution can be determined simultaneously by means of spectrophotometry. In view of the spectral character and considerable fine structure exhibited by members of the actinide, lanthanide, and transition-metal groups, it again appears to be the best technique.

The specifications for a spectrophotometric system capable of operating under these extreme conditions were drawn up. Negotiations are in progress between ORNL, a subcontractor, and the AEC for the modification of a Cary model 14PM instrument for this purpose. After some additional necessary development work, the instrument will serve as the essential part of an in-line analytical system for high temperature–high pressure processes and for various kinds of chemical research.

Among the most important parts of a spectrophotometric system and the most difficult to design and construct are the optical windows for the cells. Design and development work in addition to that already done at ORNL is necessary to provide cell windows that will be leak-proof at temperatures above 250°C. These considerations and the associated literature work have resulted in an extensive review and bibliography on the subject.[55]

Work on solutions of interest is in progress with a conventional Cary model 14PM spectrophotometer over the temperature range 0 to 100°C and at atmospheric pressure. While this work is being carried out, two modifications to the present system will be investigated. In one the spectrophotometric cell that contains the sample will be inserted in a circulating loop system operated at temperatures up to about 95°C in order to determine the feasibility of making spectrophotometric measurements on circulating streams with respect to thermal gradients, suspended solids, and dissolved gases. Techniques for minimizing or removing the effects of suspended solids and the formation of gas bubbles will be studied in order to establish the accuracy of analytical determinations under dynamic conditions. In the other modification the sample cell will be inserted in a pressurized loop operated at temperatures above 100°C. The pressurized loop will make possible the extension of the preliminary studies to higher temperatures and the use of gas overpressures.

A miniature loop circulating system has been designed for use with the conventional Cary model 14PM spectrophotometer and for operation at ~150°C and 80 to 100 atm; the detailed construction drawings have been prepared. The loop system is a completely integrated unit, identical in all general respects except size with a large pilot-plant-scale loop system. A study will be made of the dynamics of the loop operating conditions and how they affect the reproducibility and accuracy of absorption spectra of circulating streams at elevated temperatures. The loop has been designed in such a way that gas-liquid equilibration, bubble separation, and liquid-solid separation can be readily studied. Studies will be made of adsorption and ion-exchange processes as a function of temperature and of the distribution of an element between solid and liquid phases with typical ion-exchange resins and other insoluble materials, such as corrosion and oxide products, in contact with the circulating stream. It will also be

[54] Chemical Technology Division.

[55] R. E. Biggers and J. M. Chilton, *Review and Bibliography on: Design and Use of Windows for Optical Measurements at Elevated Temperatures and Pressures (1881–1959)*, ORNL-2738 (May 27, 1959).

possible to study corrosion rate under dynamic operating conditions.

A similar circulating system with glass cells will be used up to ~100°C at atmospheric pressure in order to obtain information on the dynamics of such a system. The general aims and details of this work have been reported in part.[56] When the high temperature–high pressure spectrophotometer is available, the phase changes that have been observed to occur in the fuel solution of the HRT will be studied. Whereas this instrument, as initially built, will not be suitable for operation with the HRT itself, it should provide basic information of great value in understanding the chemistry of such a complicated system.

In addition to serving as an analytical tool for such systems, the full-scale high temperature–high pressure instrument, when used with static cells and solutions that can be equilibrated with gas overpressures, will yield considerable basic data on the chemistry and spectral properties of aqueous solutions at elevated temperature. These studies will be carried out as a function of acidity, metal ion concentrations, temperature, and the presence of foreign ions and under various gas overpressures. The information obtained should be useful in predicting and correlating data on solubilities, adsorption processes, valence-state distributions, degree of hydrolysis, and oxidation-reduction reactions.

Spectrophotometric Studies of the Sulfates of Uranium, Copper, and Nickel in Sulfuric Acid Solution

R. E. Biggers J. M. Chilton

In the absorption spectroscopy of multicomponent systems at elevated temperatures, it is necessary to study each of the components as a function of numerous experimental variables before any measurements of component concentrations can be obtained.

A very thorough study is being made of the uranyl absorption spectra, both in the visible and ultraviolet regions. Work has been done on the uranyl perchlorate and uranyl sulfate systems. Also, the spectra of uranyl sulfate solutions that contained various amounts of excess sulfuric acid or uranyl oxide have been studied. It has been found that excess uranyl oxide (or a deficiency of sulfuric acid) has a pronounced effect on the spectrum of uranyl sulfate solutions; a deficiency of only 0.005 *M* sulfuric acid increases the height of the sharpest peak (~419 mμ) by a factor of ~30%. Excess sulfuric acid also increases the absorption peak heights, but to a smaller extent.

The effect of temperature on the absorption spectra of stoichiometric uranyl sulfate solutions and other solutions of various sulfate–to–uranyl oxide ratios has been studied over a range of about 5 to 97°C. Qualitatively, an increase in temperature changes the spectrum in the same way as a deficiency of acid. Gross spectral changes are observed; these include shifts in absorption-peak frequency, changes in band width, and large changes in intensity. Work is in progress to relate and correlate all the data observed with a consistent scheme for the hydrolysis and complexation of the uranyl ion in such systems. A mathematical method of treating the spectral data to obtain the absorption band parameters has been developed (see "Mathematical Resolution of UO_2^{2+} Spectral Fine Structure," this report).

The mutual influences of copper, uranium, and nickel on their spectra have also been studied. Interesting results have been observed in the copper-uranium system; the effect of copper sulfate on the uranyl spectrum is qualitatively similar to that of sulfuric acid, which indicates exchange of sulfate ion and resulting complexation changes. Simulated HRT-type solutions have also been studied; however, the major amount of work has been done with uranyl solutions that were stoichiometric or that contained excess acid, that is, in pH regions where hydrolytic problems are relatively insignificant.

Mathematical Resolution of UO_2^{2+} Spectral Fine Structure

R. E. Biggers J. M. Chilton

The resolution of the very complex fine structure of the absorption spectra of the uranyl ion has been achieved for the wavelength range between 3500 and 5000 Å by means of high-speed digital-computing techniques. Spectra of uranyl sulfate solutions were studied at 14 temperatures, from 5 to 97°C. Complete spectral resolutions were made at all

[56] R. E. Biggers and J. M. Chilton, *Proposed Program for Elevated Pressure and Temperature Investigations Using the Cary Spectrophotometer Now Located in Building 3508 at ORNL, Feb. 1, 1959 to July 15, 1960*, ORNL CF-59-2-17 (Feb. 5, 1959).

temperatures in order to determine the effect of variables on each of the electronic transitions of the uranyl ion. The ultraviolet and visible spectra of uranyl perchlorate solutions were also determined. Typical spectral absorbancy curves, together with the graphical plots of the absorption bands resolved from the curves, are shown for a uranyl sulfate solution and a uranyl perchlorate solution in Figs. 1 and 2, respectively.

The spectra were obtained with a Cary model 14PM automatic recording spectrophotometer, which effects the maximum degree of band resolution that can be expected of an optical instrument. From a summed spectrum thus obtained, it is impossible to measure with any reasonable certainty the parameters of a single absorption band, especially when the band overlaps two or three other bands on both sides of the band center, as is the case for uranyl spectra. The spectra for uranyl ion in sulfate systems represent the summed absorption (for each electronic transition) of the possible species uncomplexed UO_2^{2+}, UO_2SO_4, $UO_2(SO_4)_2^{2-}$, $UO_2(SO_4)_3^{4-}$, and any hydrolyzed species.

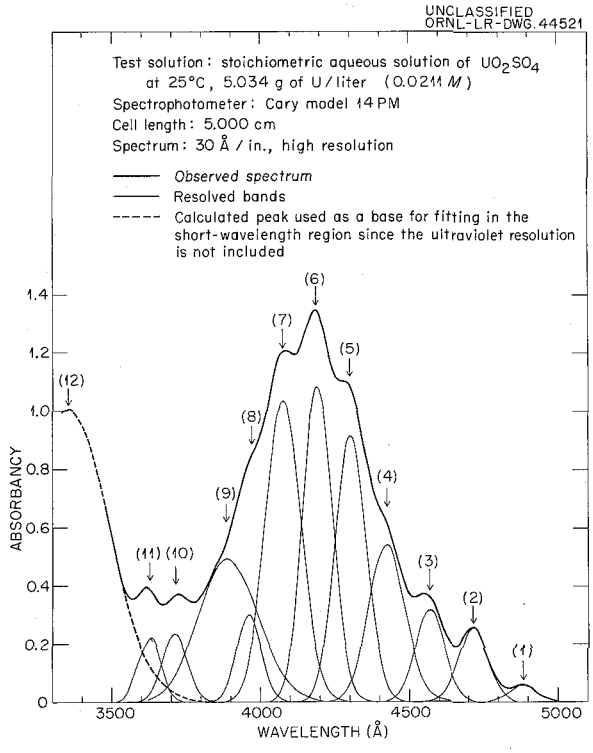

Fig. 1. Observed Spectrum of UO_2SO_4 and the Individual Bands Resolved by Use of the Oracle.

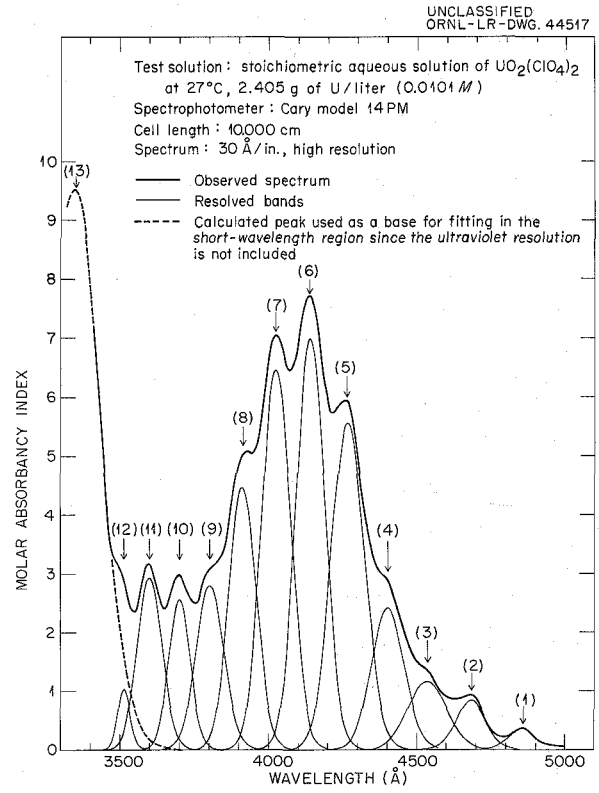

Fig. 2. Observed Spectrum of $UO_2(ClO_4)_2$ and the Individual Bands Resolved by Use of the Oracle.

An iterative, generalized, least-squares-fitting routine that was written for the Oracle[57] was modified for the purpose of resolving the uranyl spectra; a similar program is available for the IBM-704. A Gaussian function was found to be the single function that best represents the shape of a single spectral band; Jorgensen[58] also found this to be true. A resonance-type function was evaluated and found not to be as satisfactory. A more nearly theoretical correct model would probably be a function combining a Gaussian function with a small contribution from a resonance function. However, limitations in the memory capacity of the Oracle and the available IBM-704 prevent use of the double function. The computer program has been

[57] H. A. Levy and W. R. Busing, Chemical Physics Section, Chemistry Division, *ORACLE Least Squares II Code*, originally written for x-ray diffraction calculations.

[58] C. K. Jorgensen, "Studies of Absorption Spectra III. Absorption Bands as Gaussian Error Curves," *Acta Chem. Scand.* 8, 1495 (1954).

generalized so that the individual curves can be resolved from summed curves on the basis of any function by writing a subprogram to evaluate the function and the analytical derivatives with respect to each parameter. The Oracle program can analyze up to 21 peaks, and the variation of the parameters may be made in any combination up to 51 varied parameters.

Considerably more information about this work is given in a separate report.[59] Detailed discussions of the following are included: the procedure for the extraction of data for the computer from a spectral absorbancy curve; the evaluation and selection of the mathematical function; the iterative routine; the selection of the correct parameters; the determination of values for the parameters; the relative accuracy of the measurements of the parameters; the standard errors of the parameters; and the effects of experimental variables, such as temperature and acidity, on the uranyl spectra.

Correlation of Uranyl Spectra and Their Fine Structure with UO_2^{2+}-Sulfate Complexation

R. E. Biggers J. M. Chilton

The complicated nature of the spectrum of the uranyl ion is complicated even further by the effects of temperature and of solution changes, such as excess acidity or sulfate ion. For such systems, a determination of the distribution of uranium between the species, such as uncomplexed uranyl ion and the various sulfate complexes, at normal and elevated temperatures, in addition to a calculation of the concentration of other species present, would be very desirable. The experiments required to facilitate such calculations have been carried out, and an analysis of the data is in progress.

From an analysis of all the necessary equations that relate the light-absorption parameters of all species considered to be present, it has become evident that one should be able to calculate from accurate spectral data alone the concentrations of the species, and for the uranyl ion, the dissociation constants for the uranyl sulfate complexes up to $UO_2(SO_4)_3^{4-}$.

The spectra have been determined in the manner already discussed (see "Mathematical Resolution of UO_2^{2+} Spectral Fine Structure," this report). Most of the work has been carried out at a uniform uranium concentration of 5 g/liter (0.021 *M*). The spectrum of pure stoichiometric $UO_2(ClO_4)_2$ in solution was obtained from 3200 to 5000 Å, and then for $UO_2(ClO_4)_2$ solution that contained added hydrogen ion or sulfate ion to yield, in small steps, solutions of H^+(or SO_4^{2-})-to-U molar ratios of 1:1. Ionic strengths were maintained uniform at 0.3 with $NaClO_4$. Then stoichiometric UO_2SO_4 in solution was used, and the spectra were determined of solutions that contained added hydrogen ion (as $HClO_4$) and sulfate ion (as Li_2SO_4) up to H^+(or SO_4^{2-})-to-U molar ratios of 50:1, that is, $[H^+]$ (or $[SO_4^{2-}]$) $\cong$ 0.9 *M*, at an ionic strength of 3.0. Numerous intermediate concentrations were investigated for all series studied. Ionic strengths were balanced with $NaClO_4$. The ultraviolet spectra of the same series of solutions were also measured from 1900 to 3500 Å by means of cells of very short path length.

The calculations of the concentrations of the complexes present can be carried out and the spectrum of each complex determined if the values for the dissociation constants, *K*, for the complexes are known. These calculations have been made for some of the data obtained. Cubic and higher-ordered polynomials have been readily solved on the Oracle, which is used whenever possible to facilitate the calculations. It has become apparent from the calculations that the *K* values for the UO_2^{2+}-sulfate complexes reported in the literature have not been determined as accurately as is possible; in fact, there is very considerable variation among the reported values in the literature, and relatively large errors in the *K* values are quoted.

For the present work much more accurate *K* values are needed than those available. Enough spectral data have been obtained to evaluate simultaneously the concentration of the species present and the *K* values for the species. These data will, in turn, make possible the determination of the spectrum of each complex ion alone. Work is in progress on methods for the solution of the resulting complicated simultaneous equations by means of the Oracle or the IBM-704. In case this is not possible, additional experiments have been designed to permit the evaluation of the dissociation constants. The calculations can be performed at a very large number of wavelengths, and more accurate *K* values can be obtained.

[59] R. E. Biggers and J. M. Chilton, *Mathematical Resolution of UO_2^{+2} Spectral Fine Structure*, ORNL CF-59-12-83 (to be published).

It is believed that it will be possible to calculate from a single spectrum the distribution of uranium between complexed and uncomplexed species in any given solution at various temperatures, and in this way to ascertain the exact role of temperature, hydrolysis, etc., in the changing of the various parameters of the spectra. It should also be possible to make a theoretical treatment of the resolved spectral bands with respect to line broadening. This may yield information regarding the energetics of complexation from frequency shifts and the changing magnitude of the various separate electronic transitions, at the same time.

Calculated Effect of Čerenkov Radiation on Spectrophotometric Measurements

R. E. Biggers

The possibility of making spectrophotometric measurements on solutions so radioactive that they emit Čerenkov radiation is being considered, particularly in view of using the technique for the analysis of reactor-fuel streams. An effort was made to calculate the possible consequences of using such samples. Aqueous fuel solution from the HRT and the Cary model 14 spectrophotometer were chosen as the sample type and instrument on which to base the hypothetical calculation. Some of the system parameters chosen were essentially those anticipated in such a system, others represented the worst possible case, and still others those whose probability of encounter is reasonably good. Some of the factors considered in the calculation were delayed-neutron-, gamma-, and beta-source strengths for HRT fuel from the reactor that has been operated long enough for fission-product equilibrium to be obtained; source energies; reactor power level; cell geometry; maximum light levels of the photodetectors in the Cary model 14 spectrophotometer; wavelengths of the spectrophotometer's monochromatic light; spectral band widths; signal/noise ratios; sample absorbancy; types of detectors; slit widths and geometrical factors of the spectrophotometer; gamma-ray relaxation length effects; the spectral distribution of Čerenkov radiation; and the efficiency of light production for various gamma-ray energies.

The calculations show that for the conditions considered the Čerenkov radiation would impose a signal strength on the detector of 10 to 100 times that for zero-absorbancy operation, or up to 10,000 times that for an absorbancy of 2, which would completely preclude any spectrophotometric measurements. It will be possible to make spectrophotometric measurements on such solutions emitting Čerenkov radiation only if the spectrophotometric system is modified to provide monochromatization of the light between the sample and/or reference cells and the detector.

A more detailed discussion of this calculated effect and a possible method for minimizing or eliminating the problem are given in a recent report.[60]

Spectral Study of Scintillation Crystals of Europium-Activated Lithium Iodide

D. A. Costanzo

The study of the absorption spectrum of scintillation crystals of europium-activated lithium iodide[61] (0.025 to 0.1 wt % europium) has been continued. The absorption spectrum of a polished single crystal of anhydrous europium-activated lithium iodide was obtained by use of a Cary model 14PM automatic recording spectrophotometer. The polished crystals (1 cm × 1 cm × 2 mm) were coated with Dow Corning 200 fluid, mounted between cover glasses, and then sealed into position between the cover glasses with Apiezon Q compound. An intense and very broad absorption band of maximum at 4200 Å was found that is attributed to europium(II) in the crystal. The europium(III) has no absorbancy whatsoever.

An evacuable die has been designed and is under construction to press out transparent pellets of lithium iodide that contain $EuCl_2$ and $EuCl_3$. The spectral properties of the pressed pellets will be examined, and a quantitative study made.

Coulometric Determination of Europium in Europium-Activated Lithium Iodide Scintillation Crystals

D. A. Costanzo

The determination of total europium and europium(II) in scintillation crystals is achieved by

---

[60] R. E. Biggers, *Calculated Effect of Čerenkov Radiation on Spectrophotometric Measurements*, ORNL CF-59-12-84 (to be published).

[61] R. E. Biggers, "Spectral Studies of Eu^{2+}, Eu^{3+} and of Li^6I(Eu) Scintillation Crystals," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 37.

coulometric oxidation at a platinum electrode. Because of the oxidation of mercury in the presence of moderate concentrations of iodide ion, the coulometric method of Shults[62] for the determination of europium was modified.

To determine total europium, the scintillation crystal is dissolved in 0.1 *M* perchloric acid. The reduction of europium(III) to europium(II) is carried out at a mercury pool cathode at a controlled potential of –0.825 v vs the S.C.E. Immediately upon complete reduction of europium(III), a platinum electrode is immersed in the solution, and the europium(II) is oxidized at the platinum electrode at a controlled potential of –0.125 v. The oxidation occurs with 100% current efficiency. The platinum electrode is conditioned by electrolyzing it in a solution composed of 0.1 *M* perchloric acid and 1.0 *M* lithium iodide at a controlled potential of –0.125 v until oxidation ceases.

To determine europium(II) in a scintillation crystal of europium-activated lithium iodide, the crystal is dissolved in a 0.1 *M* solution of perchloric acid that has been deaerated for 5 min, and the europium(II) is oxidized at the platinum electrode at –0.125 v.

Spectrophotometric Determination of Iron in Solutions of Zinc Bromide

C. C. White

Iron causes turbidity in the concentrated solutions of zinc bromide (sp gr > 2.5) that are used in windows of hot cells, and therefore its determination is significant. The iron was determined satisfactorily by extracting it into a 50 vol % solution of acetylacetone in chloroform and measuring the spectral absorbancy of the extract at 440 mμ.[63] The pH of the aqueous phase was adjusted to 1 with hydrochloric acid. A number of other suggested procedures were tried directly on the sample solutions and on the sample solutions after removal of bromine; they were not satisfactory.

Gas-Solid Chromatography

A. D. Horton

Determination of Gases in a Mixture of Nitric Oxide, Nitrogen Dioxide, and Nitrous Oxide. – A detailed study of the behavior of the oxides of nitrogen on dry, Linde type 5A molecular sieves and on silica gel has been carried out. Stainless steel columns about 2 m long and ¼ in. in diameter were filled with 20- to 35-mesh, dry, molecular sieves or silica gel. The rate of flow of helium through the column and the reference side of the thermal conductivity cell was 250 cc/min. Studies were made at temperatures between 25 and 150°C.

The principal difficulty in the separation of these gases is the reaction of nitric oxide with nitrogen dioxide to form dinitrogen trioxide. The molecular sieves did not separate nitrogen dioxide from nitric oxide at any temperature, and it was found in later studies (see "Analysis of Effluent Gases from a Sodium Carbonate Absorber After the Dissolution of Stainless Steel in Aqua Regia," this report) that a portion of the nitric oxide reacted with the sieves.

The results of studies with silica gel, not yet completed, indicate that nitric oxide or dinitrogen trioxide emerges from the column at room temperature, independently of nitrogen dioxide or nitrous oxide. If the temperature of the column is raised rapidly to 100°C after the emergence of the nitric oxide, nitrous oxide and nitrogen dioxide will emerge separately. The reaction of nitric oxide with nitrogen dioxide at room temperature influences the resolution of the other oxides because it causes tailing of both the nitric oxide and the nitrogen dioxide peaks. It is evident that temperature programing, as well as studies of pressure and flow effects, will be necessary in order to obtain satisfactory separations.

Analysis of Effluent Gases from a Sodium Carbonate Absorber After the Dissolution of Stainless Steel in Aqua Regia. – The samples of effluent gases from a sodium carbonate absorber after the dissolution of stainless steel in aqua regia were found by gas chromatography to contain hydrogen, nitrogen, nitric oxide, carbon monoxide, nitrous oxide, and carbon dioxide. Chromatographic separations of these gases were carried out on a 1.6 m × ¼ in. stainless steel column filled with 20- to 35-mesh, Linde type 5A molecular sieves. After the samples from a dozen dissolution runs had been analyzed (see Fig. 3 for a typical chromatogram), attempts were made to identify the cluster of peaks obtained at elevated temperature. The gases that contributed this cluster of peaks were collected in a U-tube that was immersed in liquid nitrogen.

---

[62] W. D. Shults, "Controlled-Potential Coulometric Determination of Europium," *Anal. Chem.* 31, 1095 (1959).

[63] J. P. McKaveney and H. Freiser, "Analytical Solvent Extraction of Molybdenum Using Acetylacetone," *Anal. Chem.* 29, 290 (1957).

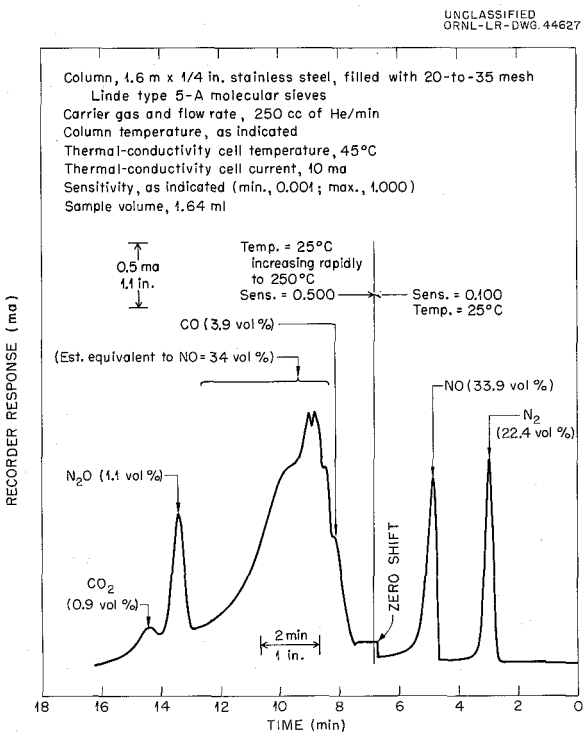

Fig. 3. Chromatogram of a Typical Nonacidic Gas Sample from the Dissolution of Stainless Steel in Aqua Regia.

Mass and emission spectra of the gases showed that the cluster was caused primarily by nitric oxide plus small amounts of carbon monoxide and water vapor. Apparently, a large portion of the nitric oxide was strongly absorbed at room temperature on selected sites in the molecular-sieve mass, thus producing low results for this gas. It was further established that the area of the cluster did not vary significantly with sample size. It is now possible to obtain the correct value for nitric oxide by analyzing a sample on both the molecular-sieve and the silica-gel columns.

Analysis of Off-Gases from Experimental Waste-Disposal Facilities in the Carey Salt Mines. – Simulated Purex waste solutions that contained 6 to 7 *M* nitric acid were dumped into stainless-steel-covered salt (sodium chloride) pits in mines of the Carey Salt Company at Hutchinson, Kansas. Gaseous products of the ensuing reaction were collected in liquid-nitrogen and carbon dioxide cold traps. The contents of these traps were analyzed. The principal gases obtained from the carbon dioxide cold traps were chlorine and nitrosyl chloride. An unknown gas, believed to be chlorine oxide (ClO_2), and carbon dioxide were also found. A typical chromatogram of gases from the carbon dioxide cold traps is shown in Fig. 4. The gases from the liquid-nitrogen cold traps were found to be principally air, plus various amounts of nitrous oxide and carbon dioxide. Nitrous oxide and carbon dioxide were determined by infrared analysis.

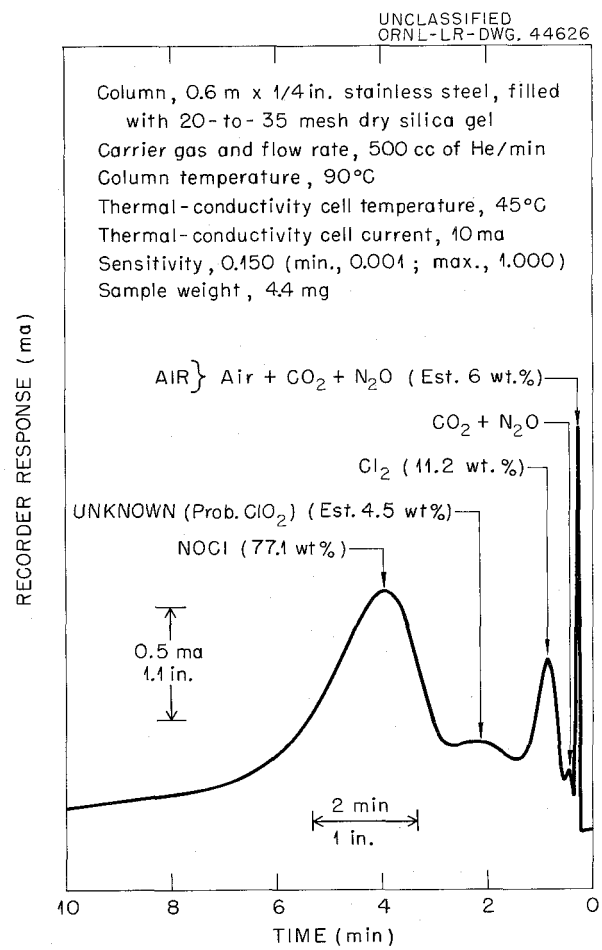

Fig. 4. Chromatogram of a Typical Sample from the Carbon Dioxide Cold Trap in the Off-Gas Lines of the Carey Salt Mine Pits.

The reaction of sodium chloride with synthetic Purex waste solutions was studied by the author and H. Kubota, using an all-glass system (see "Chemical Changes in the Reaction Between Purex Waste Solution and Sodium Chloride," this report). Carbon dioxide and nitrous oxide were not found in the off-gas.

Analysis of Off-Gases from the Charcoal Beds and from the Shield of the HRT. – During run 20 of the HRT, the contents of 23 samples of reactor off-gas and of 18 samples from the reactor shield were determined on a 1.6 m × ¼ in. molecular-sieve column.

The reactor off-gas was found to contain principally oxygen, with deuterium varying from <0.1 vol % after shutdown to 15.2 vol % at peak power; the average deuterium content was 5.3 vol %. The gas also contained carbon monoxide and carbon dioxide, usually in about equal concentrations, in the range from <0.01 to 3.2 vol %; 90% of the samples contained <1.0 vol % of these gases. A chromatogram of a typical off-gas sample is shown in Fig. 5.

Shield gas was found to be nitrogen-enriched air in which the oxygen content ranged from 3.2 to 22.0 vol %, the average being 11.0 vol %.

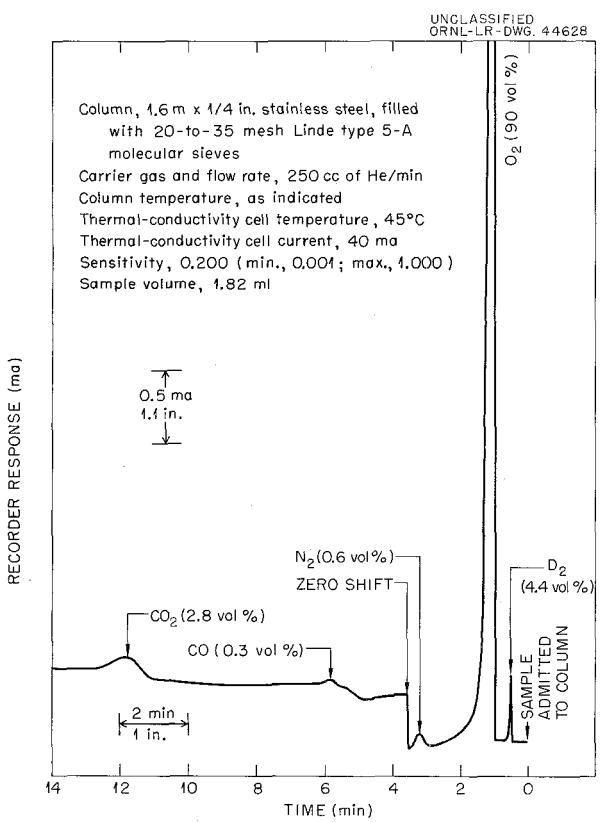

Fig. 5. Chromatogram of a Typical Off-Gas Sample from the Charcoal Beds of the HRT.

Mathematical Resolution of Overlapping Bands of Gas Chromatogram

R. E. Biggers A. D. Horton

High-speed digital-computing techniques have been used to resolve the bands corresponding to the 14 peaks of the gas chromatogram of an Amsco-type solvent.[64] It is very nearly impossible to resolve the bands by means of gas chromatography because of the proximity of the boiling points of the components associated with the peaks (166 to 205°C for the 14 peaks) and because of the similarity of structures and molecular weights of the components.

The Gaussian model was found to be suitable for the mathematical analysis of the gas-chromatogram peaks. The Oracle program for this function was available and was therefore used; however, it is possible to use other models for the peak shapes. The gas chromatogram of an Amsco solvent (125-82), together with the graphical plot of the mathematically resolved bands, is given in Fig. 6. Detailed information regarding the curve-fitting procedure and computing techniques[59] and a tabulation of the calculated parameters for the resolved gas-chromatogram bands have been reported.[65] The resolution of the bands, together with physical data already obtained,[59] is a significant contribution to the effort to define the composition of Amsco-type solvents.

MASS SPECTROMETRY (Y-12)

A. E. Cameron

Two new mass spectrometers were completed and are in operation in the Analytical Mass Spectrometry Laboratory. The new 12-in.-radius, 60°-deflection instrument is being used principally for uranium samples, whereas the 6-in.-radius, 60°-deflection one is being used for stable isotope measurements. In the Referee Analysis Laboratory, the two double-stage instruments are in operation. The second of these instruments uses inhomogeneous magnetic fields in both magnets. The inhomogeneity is that which doubles the geometrical radius, giving a working radius of 24 in., and

[64] A. D. Horton and W. H. Baldwin, "Distillation of Amsco 125-82 and Identification of Its Major Constituents," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 8–9.

[65] R. E. Biggers and A. D. Horton, *Mathematical Resolution of Overlapping Bands of Gas Chromatograms*, ORNL CF-59-12-85 (to be published).

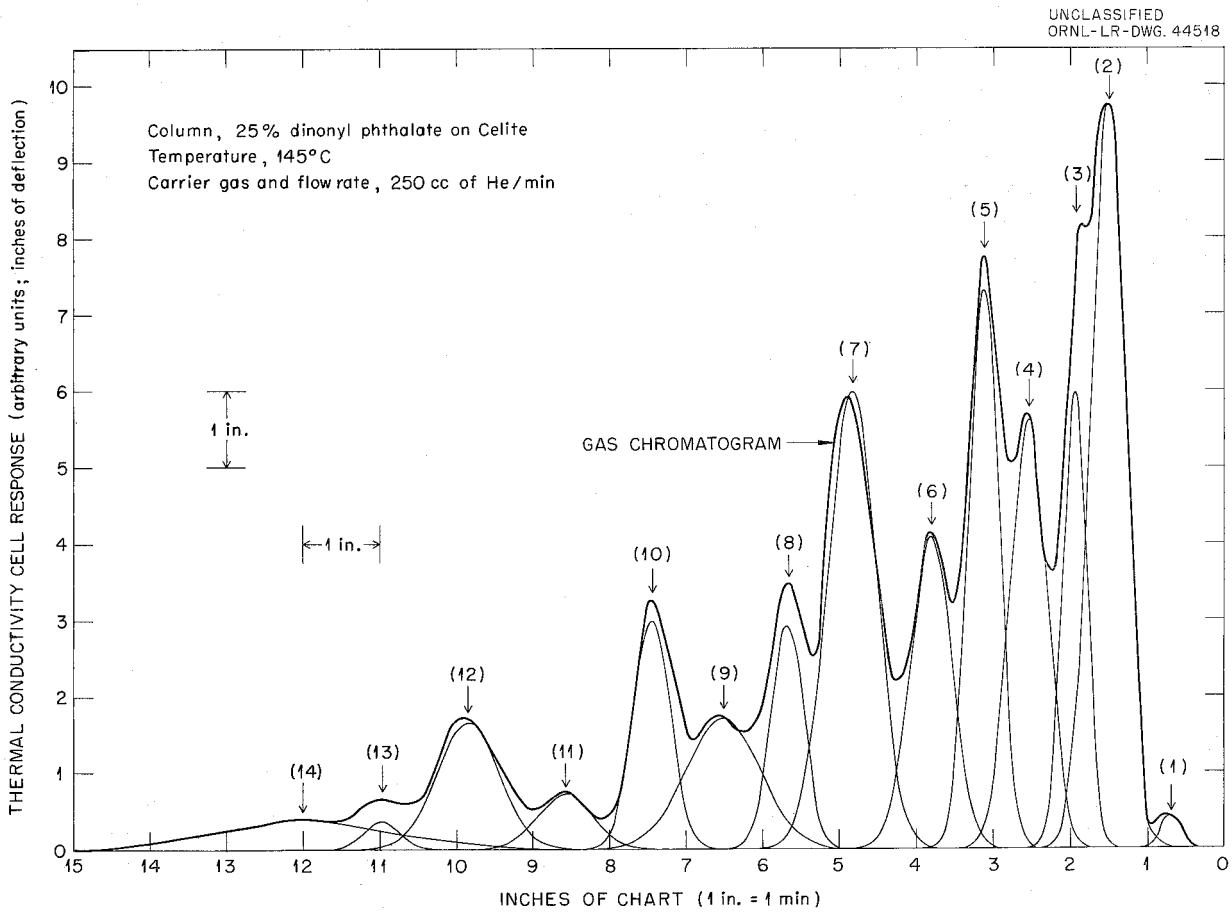

Fig. 6. Chromatogram of Amsco Solvent (125–82) and the Individual Bands Resolved by Use of the Oracle.

which gives maximum transmission because of coincidence of the z direction focusing with the normal focal point. A comprehensive mathematical analysis of the ion optics of this type of field was made by M. M. Bretscher this summer. The treatment indicates that the second-order aberrations are particularly troublesome in this type of instrument, and it is not yet clear whether the gain in dispersion exceeds losses in image definition caused by the aberrations. Contoured pole faces, which would have circular symmetry and are thus quite feasible to construct, would improve focusing.

The readout method in use on these instruments was adapted from that developed by G. W. Barton, Jr., at the Livermore Laboratory. Pulses from a secondary electron multiplier are stored in a 200-channel analyzer. The address scaler output is amplified and is used to sweep the high voltage so that each repetitive sweep causes the counts corresponding to a given accelerating voltage to be stored in the same channel. The mass spectrum is visible on the oscilloscope and is finally printed out on paper tape. Operation is proving to be very satisfactory. Heavy-element samples in amounts of the order of 10^{-9} g are adequate for good data collection.

Mass Spectrometry Research and Development

J. F. Burns

A survey of the literature on the application of mass spectrometry to the study of interactions of ions with gases was completed. Concurrently with this study, an attempt was made to design an experimental arrangement which would eliminate the ambiguities that beset this type of measurement.

No new approach was forthcoming, and it did not seem advisable to join the already large group of laborers in this field.

The appearance-potential apparatus previously used at K-25 has been reconditioned and revised. A design change that introduces the use of a chopper and tuned amplifier of a Perkin-Elmer infrared spectrometer is being tried to provide a-c detection of the essential signal. If successful, this change will reduce by a factor of 10 the time required to determine an appearance-potential curve. A systematic remeasurement of the more important of the electron energies that will produce appearance of ions from various molecules is of considerable importance. Such measurements should then be extended to include molecules for which no data are available.

NUCLEAR ANALYSES (X-10)

G. W. Leddicotte

Short-Half-Life Neutron-Activation Products Analysis Laboratory

G. W. Leddicotte

The Short-Half-Life Neutron-Activation Products Analysis Laboratory, which is equipped with an irradiation facility and a counting room, has been established by the Analytical Chemistry Division in the Oak Ridge Research Reactor building. The irradiation facility is a pneumatic-tube system capable of injecting a container into an area of neutron flux of $\sim 10^{14}$ neutrons·cm^{-2}·sec^{-1}. The laboratory is to be used in special activation-analysis studies made with radionuclides of very short half life (a few seconds to a few minutes). In addition, the 200-channel analyzer located in this area will be used to make analyses for reactor-operations and research groups. The plan of the area and its irradiation equipment are shown in Figs. 7 and 8, respectively.

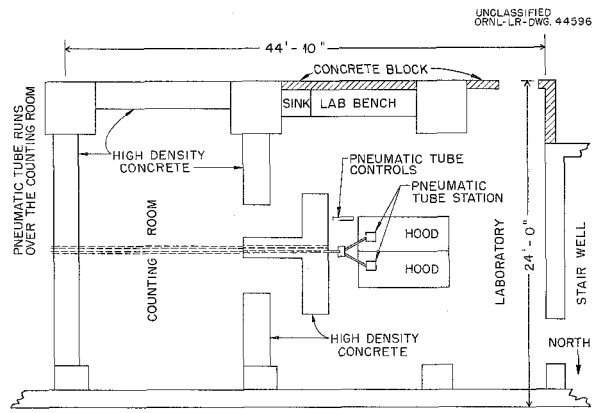

Fig. 7. Floor Plan of Short-Half-Life Neutron-Activation Products Analysis Laboratory.

Neutron-Activation Analysis

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

Quantitative Applications (G. W. Leddicotte, W. T. Mullins, R. L. Ferguson, J. F. Emery, L. C. Bate, J. E. Strain). – Microgram and submicrogram amounts of at least 45 elements have been determined in a variety of materials by means of neutron-activation analysis. The comparator-sample technique and both destructive and nondestructive methods have been used in this work. Typical results of these applications are summarized in Table 2. Those determinations believed to be of particular interest are discussed separately.

Qualitative Applications (G. W. Leddicotte, W. T. Mullins, R. L. Ferguson, J. F. Emery, L. C. Bate, J. E. Strain). – A variety of materials have been analyzed qualitatively by means of neutron-activation techniques. Either a radiochemical separation[66] was made before the radioactivity was measured or the radioactivity was measured directly. The types of material analyzed and the induced radioactivities observed are given in Table 3. In most instances, the induced radioactivity represents that radioactivity induced into microgram or submicrogram amounts of a stable element in the sample.

Neutron-Activation Analysis of Whole Milk for Stable Strontium (D. W. Moeller,[67] G. W. Leddicotte). The neutron reaction $Sr^{86}(n,\gamma)Sr^{87m}$ has been used to determine stable strontium in samples of whole milk from various sections of the United States. Following the neutron irradiation, the sample is treated with a 24 wt % aqueous solution of trichloroacetic acid to coagulate the fats, and it is then

[66] D. W. Moeller, *Radionuclides in Reactor Cooling Water – Identification Source and Control*, ORNL-2311, p 19 (June 12, 1957).

[67] U. S. Public Health Service, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

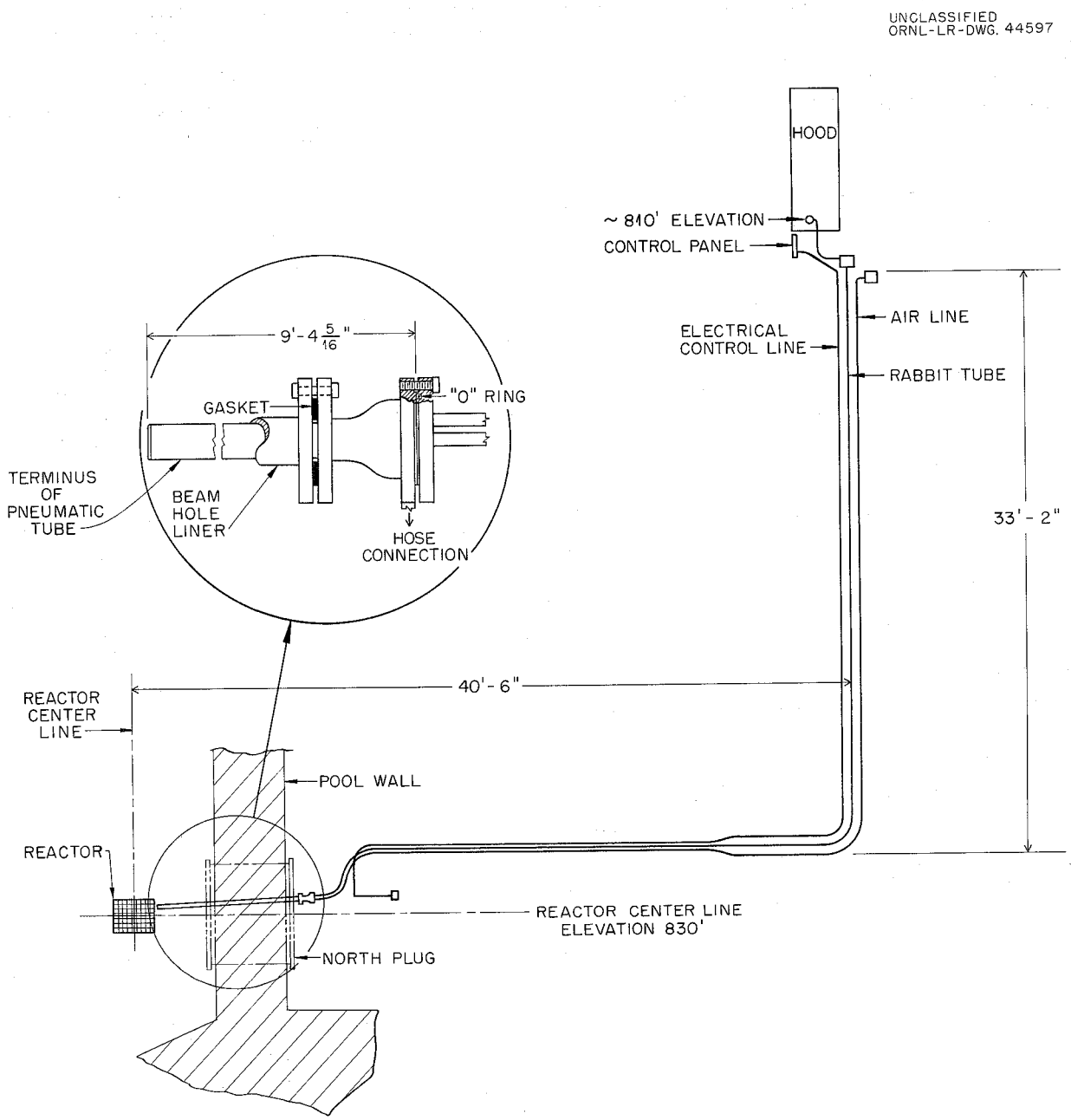

Fig. 8. Diagram of the Irradiation Facility in the Short-Half-Life Neutron-Activation Products Analysis Laboratory.

Table 2. Summary of Recent Quantitative Applications of Neutron-Activation Analysis

Element Determined	Induced Radionuclide	Technique[a]	Sample	Observed Concentration of Element Determined (μg/g or μg/ml)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
Al	Al^{28} (2.27 m)	ND	Water	0.03	0.03
			Cerium	600 to 5000	
			Titanium	10 to 20	
Sb	Sb^{122} (2.8 d) or Sb^{124} (60.9 d)	RC	Lithium hydride	0.1 to 1.0	0.005
A	A^{41} (110 m)	ND	Water	1 to 10	0.01
As	As^{76} (26.4 h)	RC	Alumina catalysts	1 to 3	0.001
			Animal tissue	0.03 to 10	
			Tobacco	0.03 to 30	
		ND	Naphtha	3 to 15	
			Petroleums	3 to 15	
Br	Br^{82} (35.87 h)	ND	Naphtha	3 to 15	0.001
Cd	Cd^{115} (53 h) or Cd^{115m} (43 d)	RC	Water	0.00003 to 0.03	0.01
Ca	Ca^{45} (164 d)	RC	Gallium arsenide	10 to 50	5.0
Cl	Cl^{38} (37.29 m)	RC	Amsco solvent	1 to 10	0.05
			Sulfuric acid	1 to 10	
			Gallium arsenide	0.4 to 4.0	
			Hydrazine	20 to 35	
Cr	Cr^{51} (27.8 d)	RC	Graphite	1 to 3	0.10
			Zirconium	1 to 10	
			Cerium	6 to 100	
Co	Co^{60} (5.24 y) or Co^{60m} (10.47 m)	ND	Graphite	0.4 to 2.0	0.05
			Stainless steel	10 to 60	
			Magnesium oxide	1 to 10	
			Zirconium	1 to 10	
			Aluminum	0.4 to 2.0	
			Aluminum alloys	150 to 3000	
			Inconel	700 to 1300	

Table 2 (continued)

Element Determined	Induced Radionuclide	Technique[a]	Sample	Observed Concentration of Element Determined (μg/g or μg/ml)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
Cu	Cu^{64} (12.8 h)	RC	Lithium hydride	<0.05	0.001
			Water	1 to 10	
			Titanium	2.0	
			Hafnium	2.0	
			Silicon	0.02 to 0.08	
			Trichlorosilane	60 to 100	
			Zirconium	3 to 15	
			Gallium arsenide	0.1 to 1.5	
Ga	Ga^{72} (14.3 h)	RC	Aluminum	60 to 220	0.001
Au	Au^{198} (2.70 d)	ND	Silicon	<0.001	0.001
			Metal film	200	
Hf	Hf^{181} (44.6 d)	RC	Zirconium	100	0.05
In	In^{116m} (53.99 m) or In^{114m} (50 d)	RC	Deep-sea sediments	0.1 to 1.0	0.0001
Ir	Ir^{192} (74.37 d)	RC	Deep-sea sediments	<0.01	0.0001
Fe	Fe^{59} (45.1 d)	RC	Graphite	30 to 100	2.0
			Zirconium	28 to 30	
			Titanium	100	
			Gallium arsenide	10 to 10^3	
			Cerium	75 to 240	
			Trichlorosilane	0.1 to 2.0	
La	La^{140} (40.22 h)	RC	Niobium	10^4	0.01
Mg	Mg^{27} (9.45 m)	ND	Gallium arsenide	10 to 100	2.0
			Titanium	10 to 100	
			Hafnium	10 to 100	
Mn	Mn^{56} (2.6 h)	ND	Cerium	2 to 4	0.0001
			Lithium hydride	0.1 to 1.0	
			Graphite	0.1 to 3.0	

Table 2 (continued)

Element Determined	Induced Radionuclide	Technique[a]	Sample	Observed Concentration of Element Determined (μg/g or μg/ml)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
Hg	Hg^{197m} (24 h)	RC	Biological materials	0.01 to 50	0.1
			Water	2 to 5	
			Paper	0.3 to 1.0	
			Oils	0.2 to 1.0	
			Silver	1 to 5	
			Organics	3 to 30	
Mo	Mo^{99} (66 h)	RC	Titanium	1 to 5	0.2
			Hafnium	1 to 10	
			Thorium bismuthate	0.9 to 200	
			Zirconium	1 to 50	
			Zirconium-cadmium alloys	0.1 to 1.0	
			Zirconium-gallium alloys	1 to 10	
Nb	Nb^{94m} (6.6 m)	ND	Thermocouple wire	10^3 to 10^4	1.0
			Stainless steel	10^3 to 10^4	
Ni	Ni^{65} (2.56 h)	RC	Titanium	1 to 10	0.1
			Hafnium	10 to 100	
			Zirconium	10 to 20	
			Silicon	1 to 10	
O	F^{18} (112 m)[d]	RC	Lithium	1 to 500	1.0
			Yttrium chloride	10^3	
			Yttrium fluoride	10^3	
			Yttrium-magnesium alloy	10^3	
Pd	Pd^{109} (13.5 h)	RC	Fissium alloys[e]	0.1 to 1.0	0.1
P	P^{32} (14.22 d)	RC	Metal sublimates	1 to 10	0.04
			Cerium	1 to 10	
			Ceramics	10 to 100	

Table 2 (continued)

Element Determined	Induced Radionuclide	Technique[a]	Sample	Observed Concentration of Element Determined (μg/g or μg/ml)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
K	K^{42} (12.52 h)	RC	Limestone	200 to 250	0.1
			Cement	10^3	
			Sand	10^4	
			Zinc ore	50 to 100	
Re	Re^{186} (88.9 h) or Re^{188} (16.7 h)	RC	Ores	0.1 to 10	0.01
Ru	Ru^{97} (2.88 d)	RC	Fissium alloys[e]	10 to 35	0.1
Sc	Sc^{46} (46 d)	RC	Graphite	1 to 10	0.01
			Deep-sea sediments	0.01 to 1.0	
Se	Se^{75} (121 d)	RC	Animal feeds	0.02 to 200	0.02
			Yeasts	0.03 to 2.0	
			Proteins	1 to 2	
Si	Si^{31} (2.62 h)	RC	Hafnium	10 to 100	1.0
			Zirconium	10 to 20	
Ag	Ag^{110m} (253 d)	RC	Silicon	0.1 to 1.0	0.1
Na	Na^{24} (14.97 h)	RC or ND	Water	1 to 2	0.007
			Gallium arsenide	100	
			Trichlorosilane	0.006 to 1.0	
			Limestone	100 to 200	
			Cement	700 to 1000	
			Zinc ore	0.1 to 1.0	
			Lithium hydride	0.1 to 1.0	
Sr	Sr^{87m} (2.8 h)	RC	Whole milk	10^3	0.5
			Strontium titanate	10^4	
S	S^{35} (87 d) or P^{32} (14.22 d)[f]	RC	Sodium fluoride–zirconium fluoride	90 to 3000	1.0
			Lead sulfide	10^4	
			Arsenic	2 to 4	

Table 2 (continued)

Element Determined	Induced Radionuclide	Technique[a]	Sample	Observed Concentration of Element Determined (μg/g or μg/ml)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
S	S^{35} (87 d) or P^{32} (14.22 d)[f]	RC	Indium arsenide	2 to 4	1.0
			Potassium hydroxide	2 to 15	
			Gallium arsenide	20 to 100	
Ta	Ta^{182} (111 d)	RC or ND	Zirconium	1 to 3	0.002
			Zirconium-cadmium alloys	1 to 3	
Te	Te^{129} (33 d)	RC	Arsenic trichloride	1 to 4	0.1
			Arsenic	1 to 4	
			Gallium arsenide	150 to 300	
Th	Pa^{233} (27.0 d)[g]	RC	Thorium sulfate	10^3 to 10^4	0.01
			Lithium fluoride–sodium fluoride–beryllium fluoride	10^3 to 10^4	
W	W^{187} (24.0 h) or W^{185} (75.8 d)	RC	Titanium	1 to 10	0.001
			Hafnium	1 to 2	
			Zirconium	5 to 15	
U	Np^{239} (2.346 d)[h] or Ba^{140} (12.80 d)[i]	RC	Reactor fuel elements	0.01 to 1.0	0.0001
			Limestone	1 to 10	
			Sand	1 to 10	
			Cement	10 to 30	
			Lithium fluoride–sodium fluoride–beryllium fluoride	1 to 10^4	
Zn	Zn^{69m} (13.8 h) or Zn^{65} (245 d)	RC	Water	5 to 150	0.02
			Gallium arsenide	0.2 to 2.0	
			Copper	10 to 65	

Table 2 (continued)

Element Determined	Induced Radionuclide	Technique[a]	Sample	Observed Concentration of Element Determined (μg/g or μg/ml)[b]	Estimated Limit of Measurement for Element Determined (μg)[c]
Zr	Zr^{97} (17.0 h) or Zr^{95} (65 d)	RC	Hafnium	3 to 10^4	0.2
			Fissium alloys[e]	1 to 2	
			Titanium	10 to 600	
			Lithium fluoride–potassium fluoride	10^3 to 10^4	

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

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

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

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

[e]An alloy composed primarily of U, plus small amounts of Ce, Mo, Ru, Pd, Zr, and Rh.

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

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

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

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

Table 3. Summary of Recent Qualitative Applications of Neutron-Activation Analysis

Material	Induced Radionuclides
Cement, limestone, sand	Na^{24}, P^{32}, Sc^{46}, Cr^{51}, Mn^{56}, Fe^{59}, Co^{60}, Cu^{64}, Zn^{65}, Th^{232}, U^{238}
Copper	Fe^{59}, Zn^{65}, Ag^{110m}
Graphite	Na^{24}, Sc^{46}, Cr^{51}, V^{52}, Mn^{56}, Fe^{59}, Co^{60}
Lithium hydride	Be^7, Na^{24}, K^{42}, Cr^{51}, V^{52}, Mn^{56}, Co^{58}, Fe^{59}, Co^{60}, Cu^{64}, Zn^{65}, As^{76}, Sr^{87m}, Sb^{124}, Ta^{182}, Hg^{197m}
Molybdenum	Mn^{56}, Zn^{65}, W^{187}
Tobacco	Na^{24}, P^{32}, Sc^{46}, Mn^{56}, Fe^{59}, Zn^{65}, As^{76}

filtered. The filtrate is further processed, and the strontium carrier and Sr^{87m} (2.8 h) are separated and finally precipitated as strontium oxalate. Typical results are given below:

Source of Sample	Strontium Concentration (mg/liter)
Fargo, N. Dak.	0.07
Los Angeles, Calif.	0.15
Austin, Texas	0.15
St. Louis, Mo.	0.16
Spokane, Wash.	0.29
Provo, Utah	0.55

Neutron-Activation-Analysis Methods for Group VIII Elements (C. E. Miller[68]). – An investigation of the application of neutron-activation analysis to the determination of a group of chemically similar

[68]ORINS participant from Florida State University, Tallahassee. Present address: Armour Research Institute, Chicago, Ill.

elements has been completed and reported;[69] the elements in Group VIII of the Periodic Table were chosen for this study. Problems of inducing radioactivity into these elements and the subsequent measurement of this radioactivity were studied. In addition, the use of different types of nuclear reactions and the interferences produced by some of these reactions in the determination of certain of these elements by activation analysis are described. The use of short-lived radioactive products in activation analysis is also described. The gamma-ray spectra of the radionuclides used in particular analyses are given in the report.

Analysis of Materials of Construction (G. W. Leddicotte, L. C. Bate). – Zinc ore concentrates, cement, limestone, and sand to be used as materials for the construction of a shielded target room for a nuclear-particle accelerator were analyzed by neutron-activation-analysis methods. Both qualitative and quantitative analyses were made, and nondestructive and destructive techniques were used. The complement subtraction method of gamma-ray spectrometry (see "Complement Subtraction Method of Gamma-Ray Spectrometry for the Quantitative Analysis of Complex Mixtures of Radionuclides," this report) was used in many of these analyses. Some of the data obtained in this work are shown in Tables 2 and 3. Additional information about this study will be presented in a formal report.

Determination of Traces of Elements in Materials Containing Neutron-Absorbing Elements (W. T. Mullins, G. W. Leddicotte). – Materials that contained elements which absorb thermal neutrons during an irradiation have been analyzed in a manner that appears to adequately minimize these self-absorption effects. In particular, samples of zirconium (97%)–cadmium (3%) alloys and of cadmium sulfide (~70% cadmium) are being analyzed for microgram quantities or less of sodium, iron, silver, silicon, copper, indium, and chlorine. Techniques of analysis are being studied. The effects of the attenuation of neutrons by the neutron-absorbing element cadmium on 100 μg of Na^{23} are shown in Fig. 9.

Geochemical Applications of Neutron-Activation Analysis (G. W. Leddicotte, J. F. Emery, A. P. Grimanis[70]). – Neutron-activation analysis has

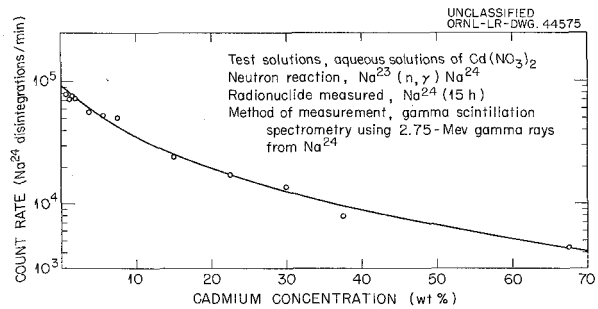

Fig. 9. Effect of Neutron Absorption by Cadmium on Determination of Na^{23} by Neutron Activation.

been used in studies of the composition of meteorites, ores, and deep-sea sediments. Typical results obtained in this work follow:

Material	Element Determined	Concentration (μg/g)
Iron meteorites	Re	0.1
Deep-sea sediments	Sc	0.01 to 0.9
	In	0.1 to 1.0
	Ir	0.01
Columbite ores	Re	0.1 to 2.0
Chromite ores	Re	1 to 30

Radiochemical separation and gamma-ray spectrometry were used in each of these determinations. In the rhenium determinations, the neutron reactions $Re^{185}(n,\gamma)Re^{186}$ and $Re^{187}(n,\gamma)Re^{188}$ were used, and the radioactive Re^{186}(92.8 h) and Re^{188}(16.7 h) plus the rhenium carrier were separated by extraction and final precipitation as tetraphenylarsonium perrhenate, $(C_6H_5)_4AsReO_4$.[71]

Determination of Li^6 (J. W. Winchester,[72] L. C. Bate, G. W. Leddicotte). – A method for determining the concentration of Li^6 in aqueous solutions by means of the nuclear reactions $Li^6(n,\alpha)H^3$ and $O^{16}(H^3,n)F^{18}$ has been tested. The induced 1.87-h F^{18} radioactivity decays with the emission

[69] C. E. Miller, *Neutron Activation Analysis Method for the Group VIII Elements*, ORNL-2715 (May 5, 1959).

[70] Alien guest from Greece.

[71] H. H. Willard and G. M. Smith, "Tetraphenylarsonium Chloride as an Analytical Reagent. Determination of Rhenium," *Ind. Eng. Chem., Anal. Ed.* 11(6), 305 (1939).

[72] Research participant from Massachusetts Institute of Technology, Cambridge.

of positrons. The annihilation gamma rays associated with the positrons were measured by means of a gamma counter. In these studies, the radioactivity per millimole of lithium in the solution was found to be independent of lithium concentrations below about 0.2 mole/liter. The limit of this method for the quantitative measurement of Li^6 is 0.0075 μmole. This method is suitable for the determination of Li^6/Li^7 isotope ratios. Details of the method are given elsewhere.[73]

Determination of Film Thickness by Neutron-Activation Analysis (J. W. Winchester, W. T. Mullins, H. W. Wright,[74] G. W. Leddicotte, R. E. Meyer,[75] L. C. Bate). – *Metal Oxide Films.* – Preliminary experiments have been conducted to evaluate the use of the nuclear reactions $Li^6(n,\alpha)H^3$ and $O^{16}(H^3,n)F^{18}$ to determine the thickness of metal oxide films on metals. The results of these experiments indicate that films of 1-Å thickness can be measured if the sample is irradiated in neutron fluxes of 10^{14} neutrons·cm^{-2}·sec^{-1} and a radiochemical separation of the induced F^{18} radioactivity from the bulk metal is made. Details of this investigation and some of the results obtained are reported elsewhere.[76]

Metal Films. – Experiments have been conducted to show the feasibility of using neutron-activation analysis to determine the thickness of a metal film evaporated onto another metal or ceramic base. In one series of experiments, the thickness of gold films evaporated onto a 1-cm^2 piece of aluminum was determined by means of the neutron reaction $Au^{197}(n,\gamma)Au^{198}$. The Au^{198} (2.69 d) radioactivity was measured by means of a nondestructive technique and a gamma-ray spectrometer. Films that contained 10^{-4} g of gold and had a thickness of ~700 Å were measured. The same techniques are feasible for determining the thickness of other metals that have been plated or evaporated onto metals or ceramics.

[73] J. W. Winchester, L. C. Bate, and G. W. Leddicotte, *Determination of Li^6 in Aqueous Solution by Neutron Activation Analysis*, ORNL CF-59-7-127 (July 10, 1959).

[74] Optical and Electron Microscopy Group.

[75] Chemistry Division.

[76] J. W. Winchester *et al.*, *Determination of Oxygen in Oxide Films by Neutron Activation Analysis*, ORNL CF-59-7-128 (July 15, 1959).

Measurements of Reactor Neutron Spectra (G. W. Leddicotte, W. T. Mullins, L. C. Bate, R. L. Ferguson). – The Nuclear Analyses Group has continued to assist research and reactor-operation personnel in monitoring the neutron flux in the irradiation facilities of the various ORNL reactors. Techniques similar to those described earlier[77] are used; these techniques have been improved through the use of gamma-ray spectrometry. In addition, a counter equipped with a scanning device (Fig. 10) has been provided to measure the radioactivity of the monitor wire as it moves continuously in front of the detector of the counter; previously the radioactivity in discrete segments of the wire was measured.

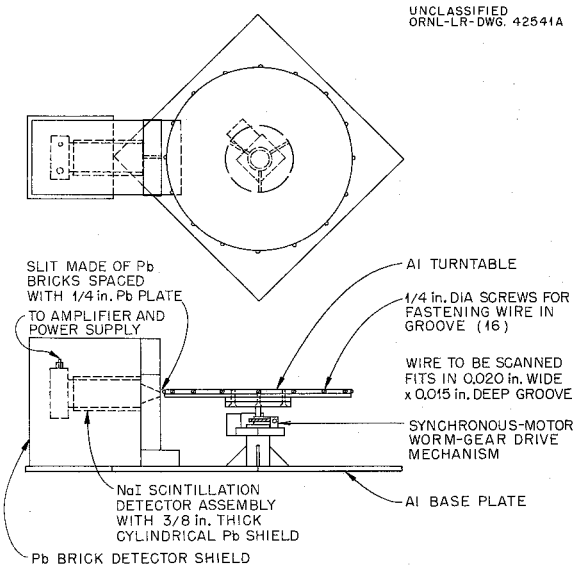

Fig. 10. Scanner for Measuring the Radioactivity of Monitor Wire.

Particle-Size-Distribution Analysis (L. C. Bate, W. J. Hampton, G. W. Leddicotte). – *Dispersants for Thorium Oxide.* – A study has been made of the usefulness of industrial dispersants as agents for coating particles of thorium oxide so that they will flow dispersed (nonagglomerated) in the dry state into a gas stream to be ignited in a gas flame. It is also desired that the dispersant be burned off during the ignition. The results of a study in

[77] G. W. Leddicotte and W. T. Mullins, "Measurements of Reactor Neutron Spectra," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 10.

which chemical agents, produced from the processing of wood pulp, and sulfonated hydrocarbons were used have been published elsewhere.[78] Some of the dispersants were reasonably satisfactory.

Analysis of Sieve-Sized Particles of Thorium Oxide. – High-viscosity mediums and sedimentation techniques have been used to determine the particle-size distributions of samples of thorium oxide in the particle-size range from 100 to 800 μ. Glycerol-water mixtures were used as the supporting mediums for sedimentation. The natural radioactivity of thorium in the particles was measured by gamma counting and was compared with the total radioactivity of the sample in order to obtain the concentration of particles of a given size; typical results obtained in this work are shown in Fig. 11. The techniques were similar to those reported elsewhere,[79] and the results will be published as a topical report.

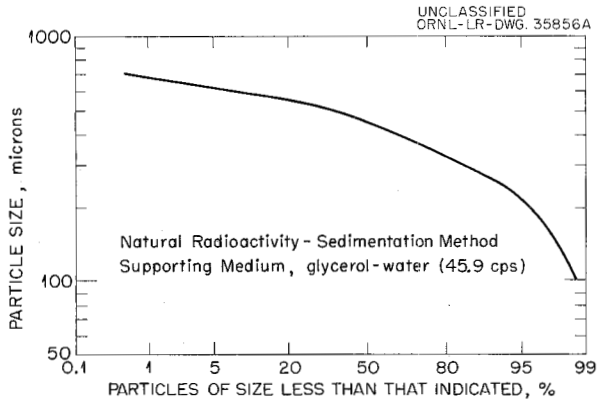

Fig. 11. Typical Results of Particle-Size-Distribution Analysis of Sieve-Sized Particles of Thorium Oxide.

Preparation and Uses of Alpha, Gamma, and Neutron Sources from Am^{241}

J. E. Strain J. H. Oliver
G. W. Leddicotte

Americium-241 is an artificially produced element, which has a half life of 458 y and decays to Np^{237} by alpha emission followed by low-energy gamma (0.0595 kev) emission from Am^{241}. The high specific activity of Am^{241}, 7.3×10^9 $d \cdot min^{-1} \cdot mg^{-1}$, together with its reasonably long half life, makes it ideally suited to the preparation of radioactive sources. Currently, Am^{241} is produced in high-flux reactors in multigram quantities by successive neutron reactions beginning with Pu^{239}:

$$Pu^{239} + n \longrightarrow Pu^{240} + n \longrightarrow Pu^{241} \xrightarrow{\beta} Am^{241}$$

In order to prepare a source, the Am^{241} must be separated from contaminant elements. The separation is made by adsorption of the thiocyanate complex of Am^{241} on Dowex 1, a strongly basic resin.[80] This separation is specific for the removal of rare-earth-element impurities and sodium. Americium-241 is eluted from the column with 3 *M* hydrochloric acid, and the excess ammonium thiocyanate is removed from this solution by evaporation with sulfuric acid. Americium hydroxide, $Am(OH)_3$, is then precipitated by ammonium hydroxide and is used to prepare either alpha, gamma, or neutron sources. Details of this separation and the techniques of preparing the sources will be reported elsewhere.

The alpha sources are used in an activation-analysis method for the lighter elements, such as beryllium. The gamma sources are used in gamma radiography and in the determination of voids in plastic and in metals. The neutron sources are used to study the concentration and homogeneity of distribution of boron in plastics and metals. The results of each of these investigations will be reported soon.

Applications of Radioactive Tracers

Surface-Exchange Method for Determination of Surface Area of Uranium Dioxide Powder (R. L. Ferguson, G. W. Leddicotte). – Applicability of the surface-exchange method to the determination of the surface area of uranium dioxide powder has been investigated. The basis of the method is the exchange reaction between nonradioactive ions on the surface of a solid and radioactive ions of the same species in solution. If a saturated solution of a nonradioactive solid is in contact with the same solid whose total surface area is to

[78] L. C. Bate and G. W. Leddicotte, *Study of Dispersant Agents for Thorium Oxide*, ORNL CF-59-8-43 (Aug. 7, 1959).

[79] G. W. Leddicotte and H. H. Miller, ORNL-1788, p 21–23 (classified).

[80] J. S. Coleman *et al.*, *Purification of Gram Amounts of Americium*, LA-1975 (Nov. 1955).

be determined and if a radioactive isotopic tracer of the same species is added to the saturated solution, the radioactivity of the solution being mixed with the solid will decrease with time. The initial and rapid decrease is due to an exchange reaction between the tracer species in solution and the nonradioactive species on the surface of the solid. The amount of radioactivity adsorbed during the initial exchange at the surface gives a measure of the surface area of the solid adsorbent. A report has been made of the use of U^{237} (6.75 d) tracer in determining the surface area of uranium dioxide powders having an area of 1.5×10^3 cm^2/g.[81]

Radioactivity Measurements

Multichannel Analyzers (G. W. Leddicotte). – Two 200-channel pulse-height analyzers, manufactured by Radiation Instrument Detector Laboratories (RIDL), Chicago, Ill., are now in operation. These analyzers have been equipped with 3×3 in. and $3 \times 3/32$ in. thallium-activated sodium iodide scintillation crystals and are used to measure the radioactivity of neutron-irradiated samples. One of these analyzers is used in the new Short-Half-Life Neutron-Activation Products Analysis Laboratory. The other is used in more routine applications and in particle-size-distribution analyses. Many of the results reported elsewhere in this report were obtained by means of these analyzers.

Complement Subtraction Method of Gamma-Ray Spectrometry for the Quantitative Analysis of Complex Mixtures of Radionuclides (L. C. Bate, G. W. Leddicotte). – Complex mixtures of radionuclides found in neutron-irradiated samples are now being analyzed quantitatively for individual components by a direct-radioactivity-measurement method. The Radiation Instrument Detector Laboratories model 34-2 multichannel pulse-height analyzer, which is equipped with "electronic subtraction" and dead-time correction devices, is used in this direct nonmathematical procedure. This analytical technique can be applied to any mixture of radionuclides in which a photopeak of the gamma radiation from some radionuclides of the mixture can be identified in the gamma spectrum displayed on the screen of the analyzer. The electronic subtraction device converts the information stored in each channel of the memory of the analyzer so that the information displayed on the screen is an inverted image of the gamma spectrum. If the gamma spectrum from a standard sample of a radionuclide is fed to the inverted (complemented) memory, the spectrum will be subtracted from the spectrum of the unknown sample, which was stored earlier in the memory. A complete removal from the spectrum of the inverted images of the photopeaks characteristic of the standard nuclide indicates the presence of that nuclide in the unknown mixture. This occurs when the number of counts from the standard nuclide is exactly equal to that which was stored in the memory before the inversion was made. Other radionuclides in the mixture can be identified in a similar manner. The data can be made quantitative by the use of standards of known disintegration rate and the dead-time correction device.

The quantitative determination of each component in mixtures of at least six components has been made in samples of irradiated graphite, tobacco, limestone, sand, and cement. The results of a typical analysis of tobacco by this method of radioactivity measurement are shown in Fig. 12. Additional information and data will be presented elsewhere.

Crystal Discriminatory Counter (J. F. Emery, G. W. Leddicotte). – A counter for measuring low- and high-energy gamma rays in the presence of each other has been developed. Known as a crystal discriminatory counter, it uses at least two scintillation crystals (at present, a 3×3 in. and a $3 \times 3/32$ in. thallium-activated sodium iodide crystal) and a pulse-height analyzer. In principle, high-energy gamma radiations do not always lose all their energy to a thallium-activated sodium iodide detector. The energy that is not absorbed in the crystal appears in the gamma spectrum as a Compton-recoil-electron continuum. Thus, the photopeak of a lower-energy gamma ray will appear on top of the continuum and in many instances cannot be seen because the continuum obscures it. Vary thin (wafer) crystals (thickness $\leq 1/8$ in.) as gamma-ray detectors offer several half-thicknesses to gamma rays having energies of 0.1 Mev or less; thus, such detectors can absorb about 90% of the gamma rays of these energies and will offer only

[81] R. L. Ferguson and G. W. Leddicotte, *Surface-exchange Method for Determination of Surface Area of UO_2 Powder*, ORNL CF-59-8-62 (Aug. 6, 1959).

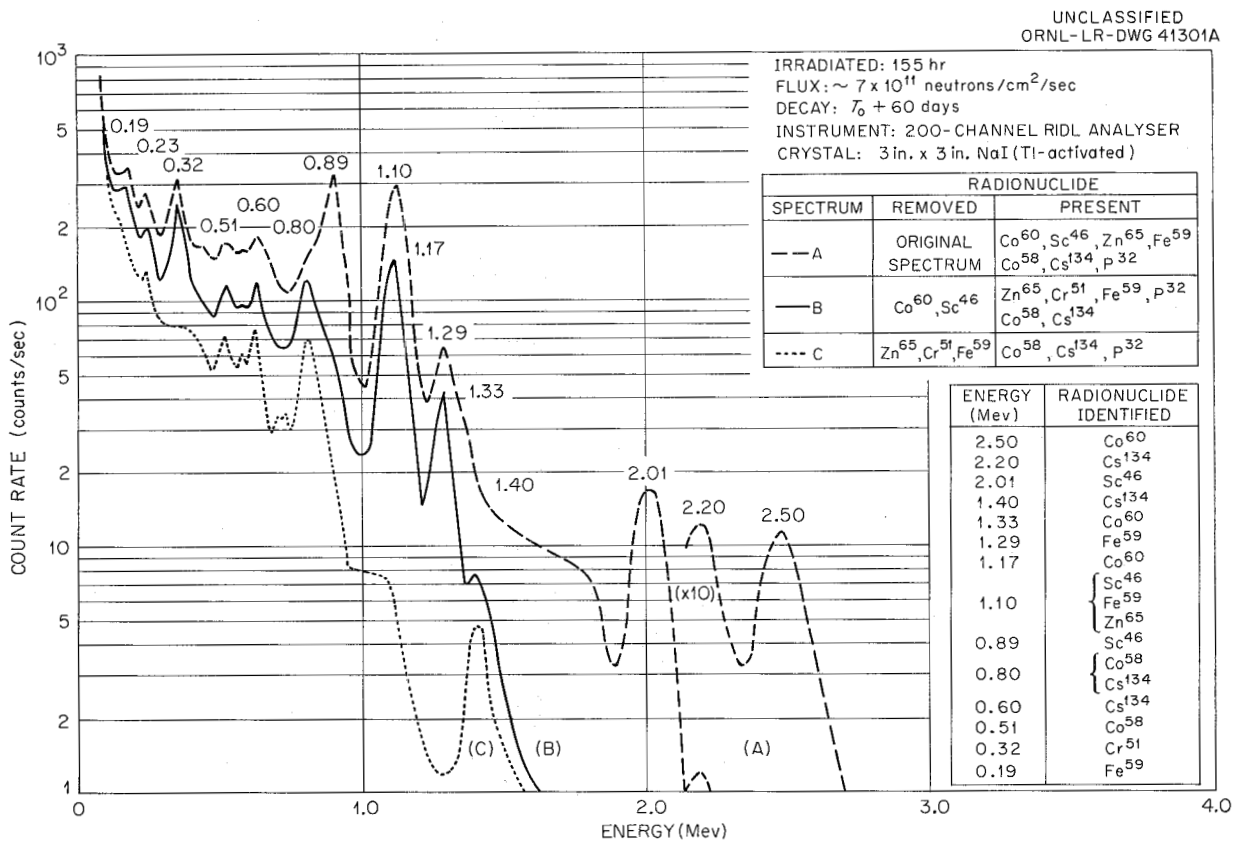

Fig. 12. Results of Analysis of Tobacco by Complement Subtraction Method of Gamma-Ray Spectrometry.

fractions of half-thicknesses to higher-energy gammas. For example, large or thick crystals (in this instance, 3 in. thick) offer two or three half-thicknesses to gamma rays of 1.0-Mev energy. Thus, by using discriminately a wafer crystal and a thick crystal in simultaneous operation, it is possible to obtain significant data from most radiation spectra.

This crystal discriminatory counter has already been used in the determination of radioisotopes of both short and long half lives. For example, it has been used in the determination of niobium in stainless steel, rhenium and lanthanum in niobium, cobalt in alloys, tellurium in arsenic, and selenium in biological materials. A schematic arrangement of the components of the counter is shown in Fig. 13. A report will be made of this device.

Neutron-Activation Cross Sections

C. E. Miller

The activation cross sections for the fast-neutron reactions $Fe^{54}(n,p)Mn^{54}$ and $Ni^{58}(n,p)Co^{58}$ were found to be 3.55 ± 0.18 and 5.35 ± 0.32 mb, respectively. The methods used for these measurements and information pertinent to them have been reported.[82]

[82] C. E. Miller, *Neutron Activation Analysis Method for the Group VIII Elements*, ORNL-2715, p 83 (May 5, 1959).

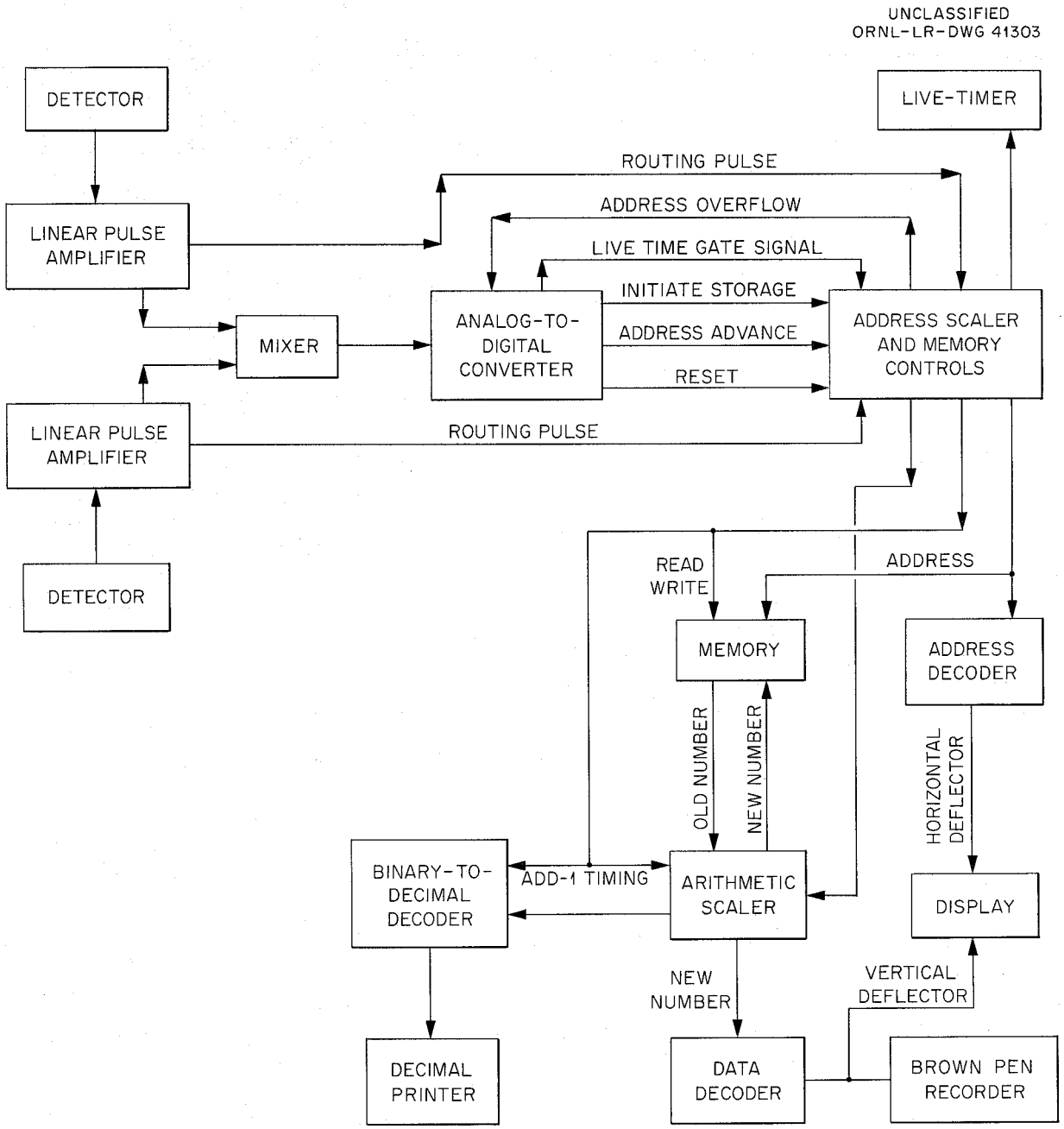

Fig. 13. Block Diagram of Crystal Discriminatory Counter Used with 200-Channel Analyzer.

ORNL MASTER ANALYTICAL MANUAL

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

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

The entire *ORNL Master Analytical Manual* is now available in reprinted form as document TID-7015 from the Office of Technical Services, Department of Commerce, Washington 25, D.C., as follows:

Section	Methods	Price
1	Ionic	$9.00
2	Radiochemical	6.50
3, 5	Spectrographic, Nuclear Analyses	4.50
9	Process	9.00

Announcements of the availability of the *Manual* have been sent to journals and publications in the field of analytical chemistry. The reprinting of the *Manual* has made it possible for the ORNL Analytical Chemistry Division to discontinue the maintenance of all copies of the *Manual* that were issued externally to Oak Ridge.

Forty-seven new methods were added to the *Manual* (see "Presentations of Research Results"); of these, nine were for the purpose of record only. These methods represent a part of the research and development work of the Division. The Tables of Contents for three parts of the *Manual* (that is, 1, "Ionic Methods"; 9 00, "General Process Methods"; and 9 08, "HRP Methods") were revised to bring them up to date. The *Manual* was issued to eight new custodians.

OPTICAL AND ELECTRON MICROSCOPY (X-10)

T. E. Willmarth

H. W. Wright T. G. Harmon

The Optical and Electron Microscopy Group has continued to obtain and interpret data from microscopic or electron diffraction studies of materials resulting from experiments or tests performed by other ORNL staff members or relative to outside allied projects. Results of such studies are communicated directly to the individuals or group concerned in the form of memorandum reports or micrographs with notations. Research efforts were confined to the development of methods or techniques for the preparation and observation of the materials presented for study. Because of the large number of these, only the types of materials are mentioned herein with the exception of specific reference to a few that are representative.

Particle-Size Studies. – The particle sizes and shapes of the following were examined: thorium oxides, uranium oxides, coprecipitated thorium oxides–uranium oxides, thorium oxides–aluminum oxides, thorium oxides–silicon oxides, thorium oxides–chromium oxides, aluminum oxides, magnesium oxides, boron nitrides, beryllium oxides, iron nitrate, chromium nitrate aerosols, and tungsten powder. The results of two such studies with the electron microscope, which may be of interest, are shown in Figs. 14 and 15.

Examination of Thin Films, Bulk Oxide Coatings, Corrosion Products, and Surface Structures. – Corrosion test specimens and metallic components from the Gas Cooled Reactor (GCR) and from the molten salt and thorium oxide slurry test loops have been examined to determine the nature of the physical changes produced in them by exposure in several environments under the various conditions of time and temperature. Surface observations are made directly by optical microscopy or by the use of shadow-cast replicas for electron microscopy. Transmission and reflection electron diffraction are used to identify the components of the surface layer (or layers). Numerous samples of Inconel, Hastelloy, Croloy 3M, Croloy 2¼, T-1 steel, DB-2 alloy, beryllium, and types 304, 310, 316, and 410 stainless steel as altered by specific tests have been examined in the manner stated. Typical results of this class of studies are the electron micrographs of stainless steel surfaces shown in Fig. 16. The surface components of both samples, though vastly different in appearance, were shown by electron diffraction to be identical in chemical composition. Another problem in which corrosion products were of interest concerned the particulate material entrapped in cloths and on filter papers used to wipe various surfaces of loop-tested valves for service in NS "Savannah." Particles were removed from the cloths and papers by ultrasonic techniques for electron diffraction studies.

Of possible interest in connection with the study of the corrosion of materials in a reactor environment was the discovery of bacteria in samples of

Fig. 14. Electron Micrograph of Thorium Oxide–Aluminum Oxide Produced from Thorium Nitrate and Aluminum Nitrate Nonahydrate Dissolved in Methanol, Asperated, and Burned in a Mixture of Oxygen and Propane Gas at 1500°C. Gold shadow-cast; 16,000X. Reduced 8%.

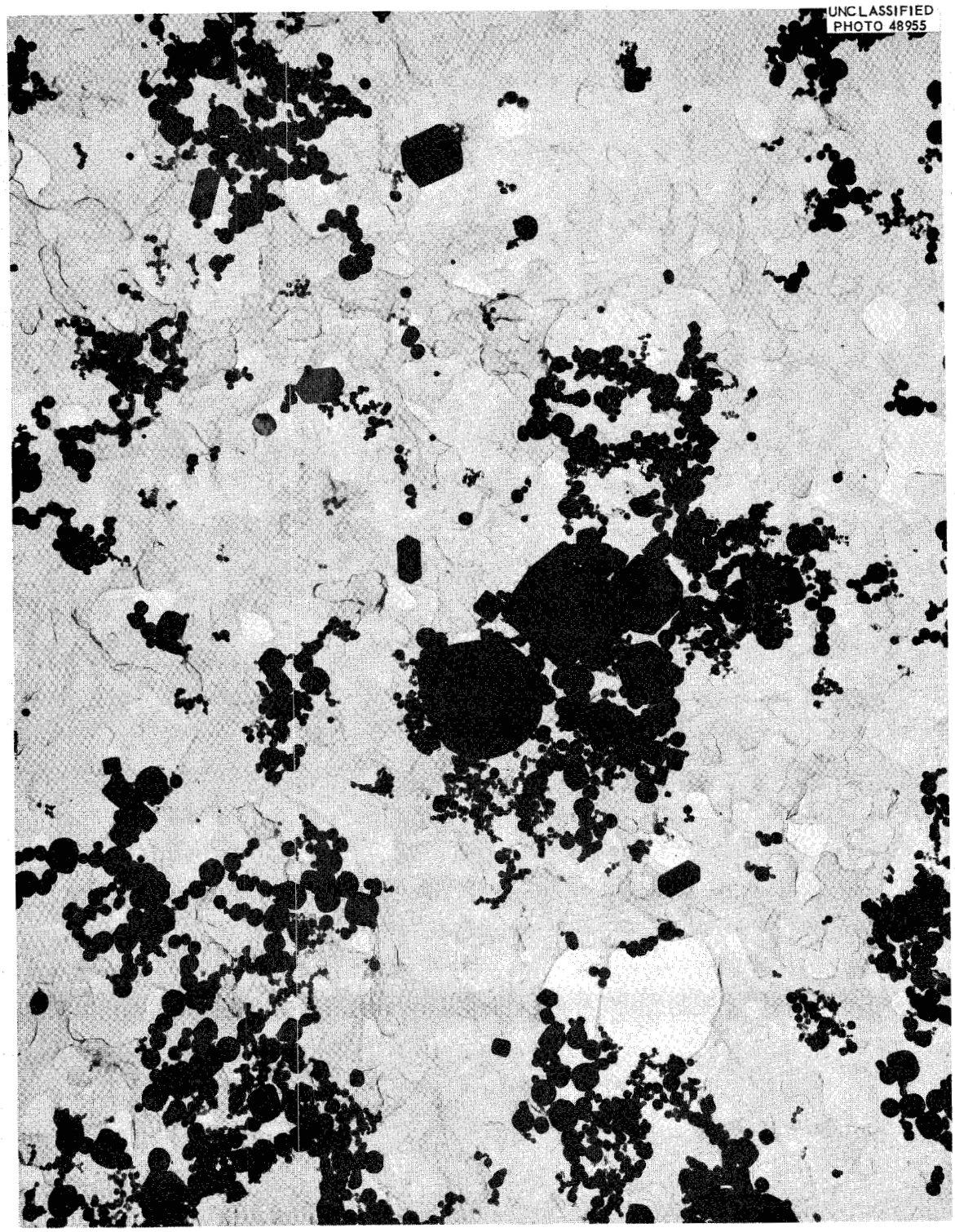

Fig. 15. Photomicrograph of Uranium Oxide Collected as Smoke from Nonirradiated Uranium Burned in Oxygen at 1300°C; Oxygen Pressure, 1050 cc/min. Collection on 0.45-μ Millipore filter; carbon film strip; 20,000X. Reduced 13.5%.

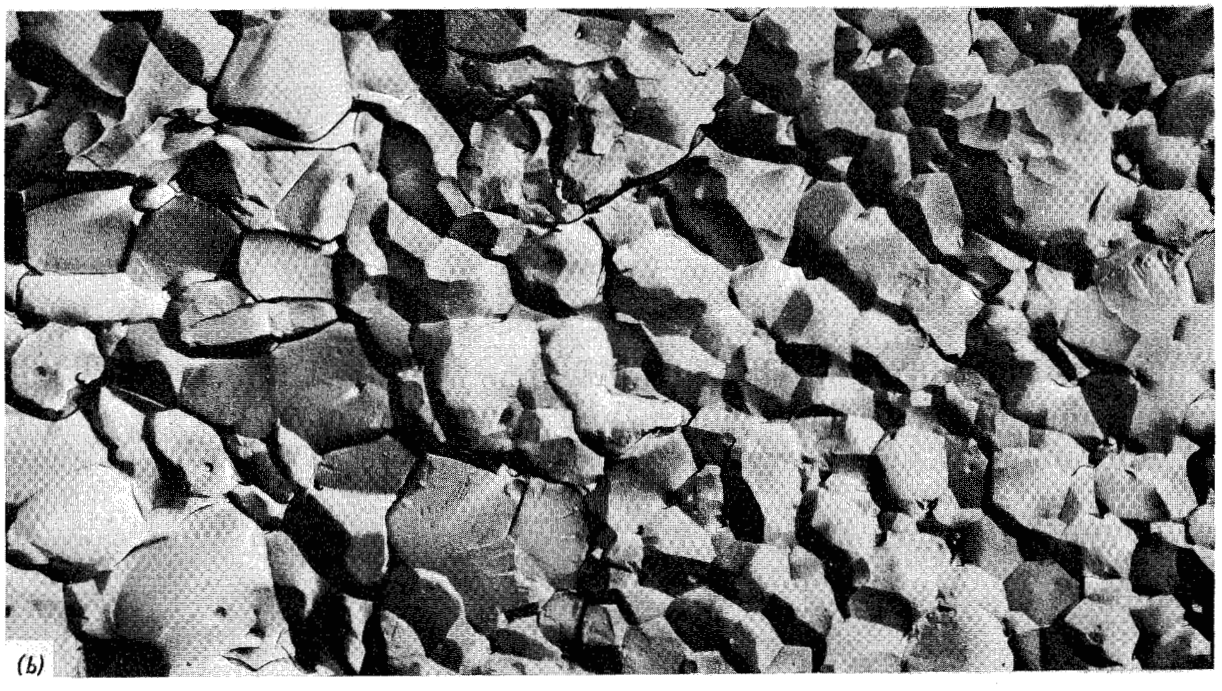

Fig. 16. Electron Micrographs of Surfaces of Type 304 Stainless Steel. (*a*) Oxidized 24 hr at 1500°F. (*b*) Oxidized 24 hr at 1700°F. Faxfilm-carbon replicas; chromium shadow-cast; 8,000X. Reduced 9%.

a corrosion-inhibiting solution of potassium dichromate used in a tube that contained the mechanism to raise and lower recording instruments behind the neutron shield of the Homogeneous Reactor. The bacteria appeared to be associated with the Tygon-sheathed cables used and apparently thrived in the liquid medium. Two of the species observed are shown in Fig. 17.

Single-Crystal, Surface-Barrier Type of Alpha Counters. – Work with members of the Physics Division on the construction of single-crystal, germanium, surface-barrier-type counters for alpha radiation and fission fragments was successfully completed and reported.[83] In an extension of this

[83] F. J. Walter *et al.*, *A Study of Germanium Surface Barrier Counters*, ORNL CF-58-11-59 (Nov. 28, 1958).

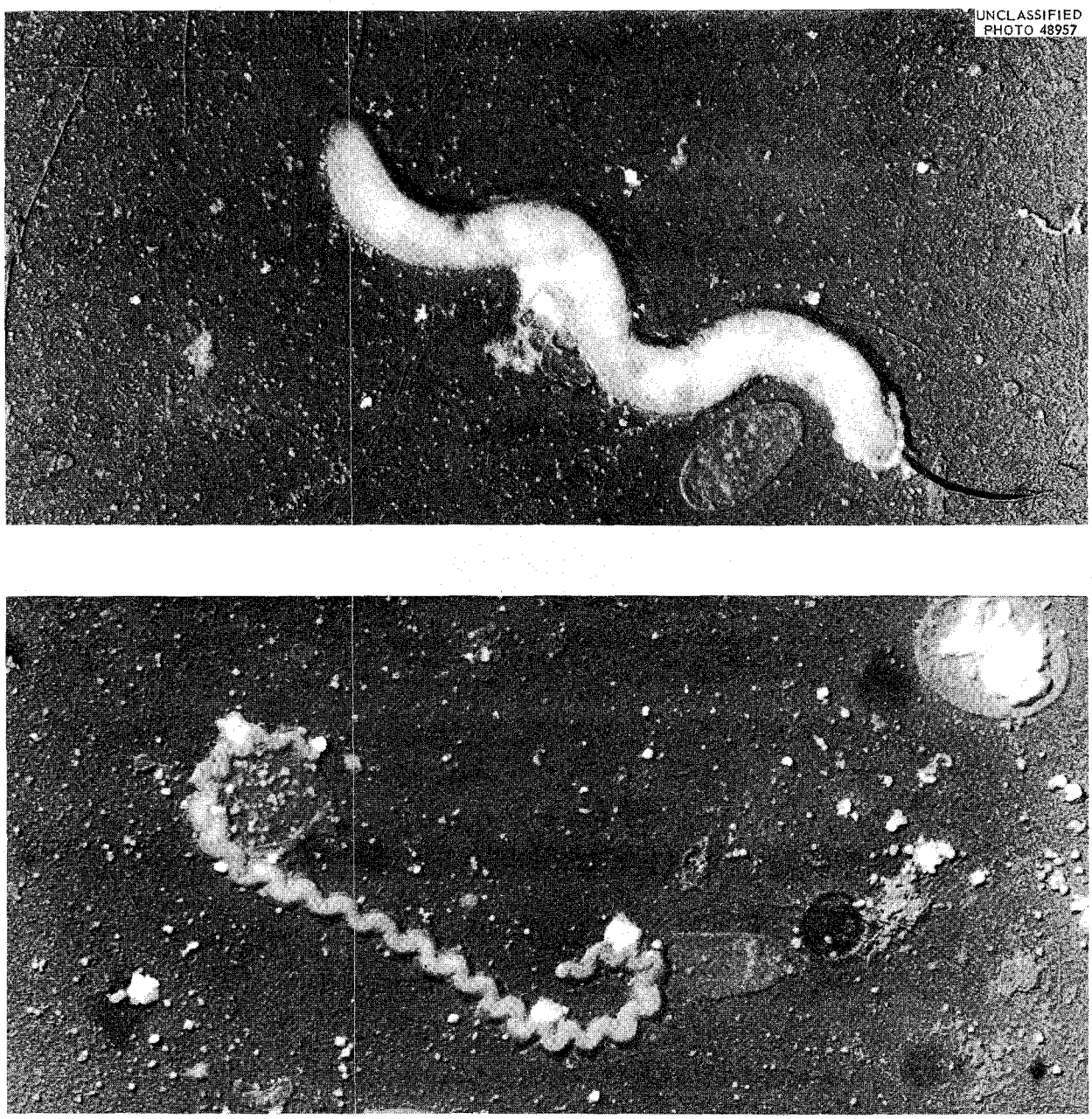

Fig. 17. Electron Micrographs of Types of Bacteria Found in a Corrosion-Inhibiting Solution Used in the HR. Chromium shadow-cast; 26,000X. Reduced 19%.

work, J. L. Blankenship of the Instrumentation and Controls Division is being assisted in the preparation of barrier-type diodes of various new designs.

Biological Studies. – Increased assistance in the way of electron microscopy has been given to the Biology Division in their studies of radiation effects on animal tissue. These have included studies of changes in the ultra structure of the glomerulus vessels of the mouse kidney induced by radiation and by normal aging, the effects of radiation on the mouse liver and intestines, and exploratory studies of the effect of radiation on various internal organs of grasshoppers.

Instrumentation. – The Cintel Flying Spot resolver, an instrument for electronically sizing and counting particles, has been modified by the addition of protective circuitry for the scanning tube when it is being used with plates or films. A new holder for plates has been built that eliminates charge effects at the face of the scanning tube. These effects have been the source of erroneous counts under certain circumstances.

A device has been designed and fabricated which is useful in measuring Laue spot electron diffraction patterns where only a relatively few crystals are contributing to the pattern. The original photographed spot pattern is projected in the darkroom on an unexposed lantern slide that is rotating at a fixed speed. This procedure produces a pattern that is made up of easily measured continuous lines and indicates at once which spots are related. Arrangement has also been made by means of a shaped slit to accommodate for the usual variation in the density of the original plate caused by the primary beam intensity and scatter at the center of the pattern.

The redesign and conversion of the 50-kv power supply and lens system of the General Electric diffractograph to a Philips variable power supply (40 to 100 kv) which uses a Philips electron gun and lens system is in progress. Higher accelerating voltages have been found to be necessary, but unobtainable with the original power supply, in photographing diffraction patterns from bulk oxides made up of large crystallites. The redesigned instrument should provide the necessary optima for the crystalline surfaces being investigated.

QUALITY CONTROL

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

Revisions in the projects of other ORNL divisions and the subsequent changes in the work loads of the service laboratories in the Analytical Chemistry Division during 1959 necessitated more extensive adjustments than usual in the Statistical Quality Control (SQC) programs. To compensate for the changes in the work loads, some programs were discontinued, others were curtailed, and still others were expanded to include additional methods of analysis. The frequency with which control analyses were made consequently decreased about one-third while the scope of the control work was being expanded. In 1958,[84] over 12,000 analyses were made in connection with about 65 control programs, whereas only 8310 control results were secured during the present 12-month period for 85 programs. The distribution of these 8310 determinations, by laboratory, is shown in Table 4; a similar compilation, by analysis, is given in Table 5.

The extensive adjustments[85] in these programs did not significantly affect the quality of the work. As is shown in Table 4, the quality levels for all laboratories in 1959 equaled or exceeded, with one exception, the levels for 1958. The over-all average for all laboratories remained unchanged at 92%.

RADIOCHEMICAL ANALYSES (X-10)

S. A. Reynolds

Nuclear Properties

New 3.1-h Isomer of Yttrium (W. S. Lyon, J. S. Eldridge, L. C. Bate[86]). – A new 3.1-h isomer of yttrium has been found by irradiating yttrium with neutrons in ORNL reactors. Yttrium has only one stable isotope, and the well-known 64-h Y^{90} is found by neutron capture. Yttrium-90 is a pure beta emitter; consequently, it was with some surprise that two gamma-ray photopeaks were observed when neutron-irradiated yttrium oxide,

[84] R. L. McCutchen, B. J. Ginocchio, and C. D. Susano, "Quality Control," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 51.

[85] M. T. Kelley, *Statistical Quality Control Report Analytical Chemistry Division, January through September, 1959*, ORNL CF-59-10-120 (Oct. 15, 1959).

[86] Nuclear Analyses Group.

Table 4. Summary by Laboratory of Distribution of Control Determinations for October 1958 Through September 1959

Laboratory	Number of Control Determinations		Quality Level (%)*	
	Total	Outside Fixed Limits	1958	1959
Pilot Plant Control	2589	281	81	89
Reactor Analyses	757	123		84
High-Alpha Analytical	268	68	90	75
Special Analyses	1129	60	93	95
Process-Development Analytical	1290	64	95	95
Reactor Projects Analytical	233	2	98	99
Thermal Breeder Reactor Project Analytical Chemistry	979	13	98	99
Raw Materials	813	30	93	96
Miscellaneous Analyses	252	10	89	96
Total	8310	651	Av 92	Av 92

*Per cent of control data inside fixed limits.

Y_2O_3, was examined with a 3 × 3 in. crystal of thallium-activated sodium iodide and a 20-channel analyzer. These two gamma rays have energies of 210 and 480 kev and decay with a half life of 3.1 ± 0.1 h. The results of gamma-gamma coincidence experiments indicate the two gamma rays to be in coincidence; absolute intensity measurements, however, indicate that the ratio $(\text{intensity})_{210\gamma}/(\text{intensity})_{480\gamma} = 1.22$. The activity is isotopic with yttrium as proved by chemical purifications by means of ion exchange. Irradiations made with and without cadmium shielding have eliminated the possibility of an $(n,2n)$ reaction giving rise to the 3.1-h activity and of it being isomeric with Y^{88}. Yttrium-89 has a 16-s isomer (910 kev), which is the daughter of Zr^{89}; in addition, Y^{89} has been produced by inelastic scattering on yttrium. Swann and Metzger[87] have studied this isomer by inelastic-scattering techniques and have found no activity of energy lower than 910 kev. These results, together with cross-section measurements, seem to eliminate Y^{89} as the source of the observed gamma rays.

On the basis of the data obtained, it is concluded that the activity is an isomer of Y^{90} and that the ratio σ of 64-h Y^{90}/σ of 3.1-h Y^{90} has the following values:

Type of Irradiating Neutron	σ of 64-h Y^{90} / σ of 3.1-h Y^{90}
Thermal	~750
Reactor	~600
Epicadmium	~100

Radiations from Pm^{148} (J. S. Eldridge, W. S. Lyon). – Promethium-148 is found in short-cooled fission-product mixtures as a result of the neutron-capture reaction on Pm^{147}. As a requirement for the detection and determination of Pm^{148} in Pm^{147} products, it was necessary to undertake a study of the properties of Pm^{148} since the literature at the time of this study showed very little information concerning this nuclide. The 42-d isomer of

[87] C. P. Swann and F. R. Metzger, "Production of Y^{89m}, Ba^{137m}, and Hg^{199m} by Inelastic Neutron Scattering," *Phys. Rev.* 100, 1329 (1955).

Table 5. Distribution of Control Results for October 1958 Through September 1959

Type of Method	Constituent	Number of Control Programs		Number of Control Results	
Colorimetric (spectrophotometric)	Aluminum	1		10	
	Chromium	4		369	
	Iron	6		498	
	Molybdenum	1		57	
	Nickel	4		393	
	Nitrate	1		37	
	Phosphate	2		15	
	Thorium	16		1286	
	Uranium	9		2742	
	Vanadium	4		56	
			48		5463
Coulometric	Copper	5		256	
	Nickel	3		205	
	Uranium	7		399	
			15		860
Electrogravimetric	Copper	1		109	
			1		109
Fluorometric	Uranium	7		1056	
			7		1056
Potentiometric	Free acid	1		135	
	Sulfate	1		156	
	Uranium	1		175	
			3		466
Volumetric	Aluminum	2		11	
	Iron	1		15	
	Thorium	2		117	
	Uranium	4		205	
	Vanadium	2		8	
			11		356
Total			85		8310

Pm^{148} is listed as a class B nuclide.[88] Subsequent to the start of this investigation, the decay of Pm^{148} has been reported by Bhattacherjee and co-workers.[89] However, there is considerable discrepancy between the values found by them for half lives and gamma intensities and those found in the present study.

Promethium-148 was produced by the (n,γ) reaction on Pm^{147} and by a proton bombardment of a target of enriched Nd^{148} in the ORNL 86-Inch Cyclotron. The products from these reactions were purified by means of ion-exchange techniques, and the nuclides were studied for characteristic

[88] D. Strominger, J. M. Hollander, and G. T. Seaborg, "Table of Isotopes," *Revs. Modern Phys.* 30, Pt. 2, 585 (1958).

[89] S. K. Bhattacherjee, B. Sahai, and C. V. K. Baba, "Decay of Pm^{148}," *Nuclear Phys.* 12, 356 (1959).

properties. Decay measurements were made by the use of G-M counters, scintillation detectors, and a gamma ionization chamber. Scintillation spectrometry was performed by the use of techniques described by Heath.[90] The gamma-ray energies and their intensities were measured in a 3 × 3 in. thallium-activated sodium iodide crystal spectrometer equipped with a 20-channel pulse-height analyzer. The resolution for 0.662-Mev Cs^{137} gamma rays was 7.6%. Some beta-gamma and gamma-gamma coincidence experiments were also performed.

The decay of the Pm^{148} sources was followed on several instruments for periods as long as 250 days. The decay curves were resolved into 5.41 ± 0.05 d and 41.8 ± 0.5 d half-life components. The decay curves obtained by means of G-M counters showed a greater abundance of the 5.4-d component than did the curves run on the gamma ionization chamber. This indicates a high beta branching, which is not followed by gamma emission, in the 5.4-d component.

The gamma-ray spectrum associated with the 5.4-d isomer is shown in Fig. 18 (the contribution to the spectrum from the 42-d isomer has been subtracted). The prominent gamma rays belonging to this isomer are seen to have energies of 0.55, 0.91, and 1.46 Mev. Gammas of weaker intensity, that is, 0.29, 0.42, and 0.63 Mev, are also seen.

The gamma-ray spectrum associated with the 42-d nuclide is shown in Fig. 19. This spectrum was made on the reactor-produced material. This material showed no gamma-emitting contaminants 244 days after its production. A similar spectrum made on the cyclotron-produced material showed the presence of gamma contaminants as soon as 84 days after production. These contaminants have approximate energies of 0.47, 0.62, and 0.69 Mev. These gamma rays probably arise from Pm^{144} and/or Pm^{146} produced by the (p,n) reaction on the small amounts of Nd^{144} and Nd^{146} in the enriched Nd^{148} target. The different gamma-ray energies and relative intensities associated with each isomer are summarized in Table 6.

[90] R. L. Heath, *Scintillation Spectrometry — Gamma-Ray Spectrum Catalogue*, IDO-16408 (July 1, 1957).

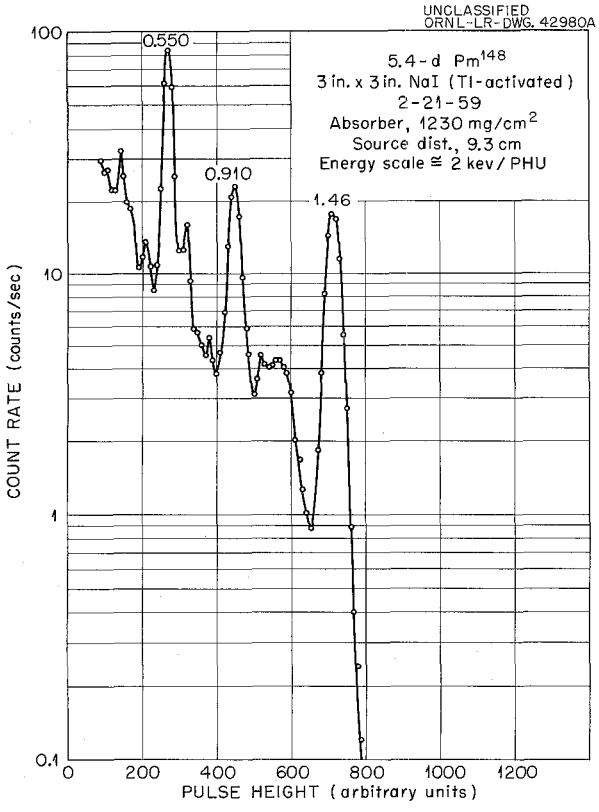

Fig. 18. Gamma-Ray Spectrum of 5.4-d Pm^{148}.

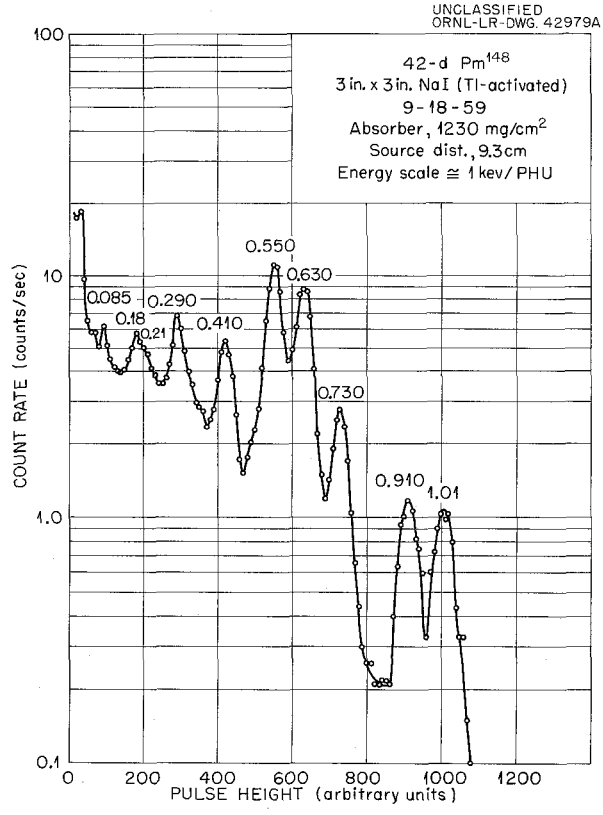

Fig. 19. Gamma-Ray Spectrum of 42-d Pm^{148}.

Table 6. Gamma Energies and Relative Intensities of Pm^{148} Isomers

Gamma Energy (Mev)	Relative Intensity
42-d Isomer	
0.085	2
0.180	6
0.210	2
0.290	14
0.420	21
0.550	100
0.630	83
0.730	38
0.910	21
1.01	21
5.4-d Isomer	
0.290	10
0.420	8
0.550	100
0.630	10
0.910	50
1.46	80

Bhattacherjee and co-workers[89] report gamma rays having energies of 1.20 and 1.76 Mev with relative intensities of ~ 3 and <1, respectively, in the 42-d isomer. An experiment was performed to determine whether the 1.20- and 1.76-Mev gamma rays were real or coincidence-summing peaks. The gamma spectrum was determined at two distances: 9.3 and 3.0 cm. The ratio of the 1.20-Mev peak relative to others at 3.0 cm was very much greater than it was at 9.3 cm. The 1.76-Mev gamma was not detected. A calculation was made for coincidence summing of the 0.55- and 0.63-Mev peaks, and the summing was found to account for 80% of the observed 1.18-Mev peak. It was concluded from this calculation that there is little, if any, real 1 18-Mev gamma radiation and that the observed peak at 1.18 Mev is due to coincidence summing of the 0.63- and 0.55-Mev gamma rays, which were found to be in coincidence by gamma-gamma coincidence measurements.

The analysis of the data is continuing, and a complete report will be submitted for publication. The help of R. S. Pressly of the Isotopes Division, who supplied the neutron-irradiated Pm^{147} and Nd^{148} target material, and also that of T. H. Handley, who arranged for the preparation and separation of the (p,n)-produced Pm^{148}, is acknowledged.

High-Energy Gamma Ray in the Decay of Sb^{124} (W. S. Lyon). – Antimony-124 is often used as a neutron source by means of the (γ,n) reaction on beryllium. In order to measure yields and cross sections from this reaction, the number and abundances of the gamma rays above the threshold for this reaction must be known. Tabulated nuclear data[88] indicate that uncertainty exists concerning the number and abundances of high-energy gamma rays in the decay of Sb^{124}; hence it was of interest to remeasure these branchings by the use of gamma scintillation spectrometry and 4π-beta–gamma coincidence counting. The high-pressure ionization chamber was calibrated for Sb^{124} by means of the 4π-beta–gamma coincidence counting of an aliquot of a standard solution of Sb^{124} and then measuring another larger aliquot in the chamber. Pieces of antimony metal were irradiated, cooled for a number of months to allow short-lived activities to decay, and then read in the ion chamber to obtain disintegration rate. The high-energy gamma spectrum was then obtained by use of a 20-channel analyzer and a 3 × 3 in. crystal of thallium-activated sodium iodide. Data were taken at 9.3, 14.9, and 21.9 cm in order to observe the effects of summing; in each instance, the effect believed to arise from coincidence summing was calculated and corrected for. As a result of this work, the high-energy gamma rays in Sb^{124} and their abundances are believed to be as follows:

Gamma Energy (Mev)	Number of Gamma Rays / Number of Beta Rays
1.69	0.49 ± 0.02
2.09	0.07 ± 0.03
2.32	0.007 ± 0.003

Measurement of Eta of U^{233}, U^{235}, and Pu^{239} by the "Manganese Bath" Technique (R. L. Macklin,[91] G. DeSaussure,[92] J. D. Kington,[92] W. S. Lyon). – Six months of full-time work was spent on the "eta project." A complete account of the work will be published elsewhere; a brief abstract of the methods used follows.

[91] Physics Division.

[92] Neutron Physics Division.

The absolute values of eta for U^{233}, U^{235}, and Pu^{239} were measured directly by a method of total absorption in which relative counting is used and some minor corrections are made. A beam of thermal neutrons is introduced in the center of a 1-m-dia sphere that is filled with an aqueous solution of manganous sulfate, $MnSO_4$ ("manganese bath"). The beam is first made to activate the manganese bath directly; then it is totally absorbed in a sample of the isotope under investigation whose fission neutrons then activate the bath. The ratio of the activities measured under the two conditions is equal to eta, except for small corrections. Values for eta obtained (corrected to 2200 m/sec) were 2.30 ± 0.02 for U^{233} and 2.07 ± 0.02 for U^{235}. The values of the small corrections to be applied to the value of eta for Pu^{239} have not yet been established.

Measurement of Radioactivity

Liquid Scintillation Counting (J. S. Eldridge). The use of the liquid scintillation spectrometer for the determination of beta emitters has continued, and new procedures have been developed. Many situations exist in which the determination of a radionuclide is made difficult by the presence of solids, volatile components that contain the radioactivity, or extraneous alpha or beta activities which would be counted in a gross-activity detector.

The liquid-scintillation-counting technique has been applied to the determination of P^{32}-labeled tributyl phosphate relative to the Chemical Technology Division's studies of the solvent extraction of thorium. Some of the tributyl phosphate solutions contained thorium in concentrations as high as 40 g/liter.

Sulfur-35 has been determined with a counting efficiency greater than 50%; this work was done in connection with the Chemical Technology Division's kinetic studies by means of ion exchange. The samples consisted of individual beads of ion-exchange resin in an eluant that was 0.4 ml of 1 *N* H_2SO_4. Some samples contained 0.3 mg of natural uranium in addition to the S^{35} activity.

Sulfur-35 has also been determined in product samples from the Isotopes Division. The S^{35} products have consisted of elemental sulfur dissolved in benzene, as well as the usual $H_2S^{35}O_4$ products.

An experiment was performed to determine the feasibility of assaying $BaC^{14}O_3$ products by use of the liquid-scintillation technique. The usual procedure had been to dissolve a weighed portion of the desired $BaC^{14}O_3$ product in a solution of tetrasodium ethylenediaminetetraacetate from which the C^{14} could be evolved as $C^{14}O_2$ into an ionization chamber.[93] The time required to make the measurements by means of the ion-chamber technique was excessively long. It was found that an aliquot from the solution containing the $BaC^{14}O_3$ could be placed directly in the proper scintillator solvent from which the C^{14} activity could be determined with a considerable saving of time. A comparison of a result obtained (by H. A. Parker, Radioisotope-Radiochemistry Laboratory) by use of the ionization chamber with one obtained by means of the liquid-scintillation technique follows:

Ion-chamber assay	0.248 mc/mg
Liquid-scintillation assay	0.254 mc/mg

Promethium-147 in radioisotope product samples has also been determined by means of the liquid-scintillation technique.

Instrumental Methods

Gamma Scintillation Spectrometry (T. H. Handley, J. S. Eldridge, W. S. Lyon, S. A. Reynolds). – Many types of samples were analyzed by means of gamma scintillation spectrometry. Most were complex and contained several radionuclides. The determination of individual nuclides in fission-product-gas samples was based on the careful choice of photopeaks for measurement and on the proper timing of counting to differentiate between radionuclides of different half lives. Subtraction techniques, as described by Heath,[90] were used when necessary. The radionuclides found and reported were Kr^{85}, Kr^{85m}, Kr^{87}, Kr^{88}, Rb^{88}, Xe^{133}, Xe^{135}, Xe^{135m}, and Cs^{138}.

The Health Physics Division submitted a series of samples of filters and charcoal traps that were taken from gas exhaust stacks in various areas of ORNL. Gamma spectrometric methods were used to identify and to determine quantitatively the following nuclides in these samples: Zr^{95}-Nb^{95},

[93] E. I. Wyatt, "Carbon-14, Beta Ionization Chamber Method," Method No. 9 0733172 (3-19-53), *ORNL Master Analytical Manual;* TID-7015, sec 9.

Ru^{103}-Ru^{106}, I^{131}, I^{133}, I^{135}, Cs^{137}, Ba^{140}-La^{140}, Ce^{141}-Ce^{144}, and the daughters of Th^{228}.

Fission Products

Radiochemical Determinations of Individual Rare-Earth Elements (T. H. Handley). – A radiochemical method for the determination of the individual long-lived rare-earth-element fission products has been developed. The method is based on data published by Peppard[94] and coworkers on the use of di-2-ethylhexylphosphoric acid for the extraction of rare-earth-element activities. Separations of cerium, promethium, and yttrium have been made with good decontamination factors and adequate yields. The method will be described in an open-literature publication.

Cyclotron Research

T. H. Handley

Studies of Neutron-Deficient Rare-Earth Nuclides. – Work is continuing in cooperation with members of the Electronuclear Research Division and with K. P. Jacob and J. W. Mihelich of the University of Notre Dame on the investigation of neutron-deficient rare-earth nuclides. The separations chemistry, preparation of sources, and some of the gamma spectrometry are performed by the Analytical Chemistry Division. Studies with permanent-magnet spectrographs are being made by the Electronuclear Research Division. Some of the coincidence scintillation spectrometry, the application of theory, and the interpretation of the data are done at the University of Notre Dame. Results of the work will continue to be reported in the open literature. Two papers, "Electron Capture Decay of Tm-168 and Tm-166," and "Nuclear Levels Populated by Radioactivities of Light La and Ta Isotopes," have been submitted to *The Physical Review* for publication.

Solvent-Extraction Methods

Extractions from Acetate Solution with Triisooctylamine (F. L. Moore). – A new and rapid method for the liquid-liquid extraction of uranium(VI) and plutonium(VI) from an aqueous solution of acetate is based on the use of triisooctylamine dissolved in xylene or in another organic solvent. Uranium(VI) and/or plutonium(VI) are separated from thorium, alkali elements, alkaline-earth elements, rare-earth elements, zirconium, niobium, ruthenium, iron, protactinium, americium, and other elements that do not form anionic species under the conditions described. The technique can be used in the range from submicro to macro quantities of uranium. Several practical applications of the method in radiochemical analyses and purifications are proposed. A paper that describes the method in detail has been submitted to *Analytical Chemistry* for publication.

Studies of Extractions with Triisooctyl Phosphorothionate (T. H. Handley, J. A. Dean[95]). – Triisooctyl phosphorothionate, $(C_8H_{17}O)_3PS$, the octyl derivative and sulfur analog of the well-known and widely used tributyl phosphate (TBP), possesses solvent properties and extraction characteristics that differ markedly from those of tributyl phosphate. The present investigation has revealed the extractability of silver(I) and mercury(II) under various conditions of acidity, salt concentration, and concentration of triisooctyl phosphorothionate. Particularly attractive is the fact that the extractions take place from aqueous solutions that are 3 to 9 *M* in nitric acid into carbon tetrachloride that contains 30 to 60% (*v/v*) of triisooctyl phosphorothionate. The effect of variation of acid concentration of the aqueous phase has been studied in nitric acid, sulfuric acid, hydrochloric acid, and acetic acid media. The mechanisms of the silver(I) and mercury(II) extractions have been studied in considerable detail, and the solvation numbers for silver and mercury have been determined.

Participation in National Organizations

W. S. Lyon S. A. Reynolds

The authors are, or have been, associated with the following national organizations.

ASTM Committee E-10, Radioactive Isotopes

Subcommittee II (Dosimetry, Fuel Burnup). – This committee is engaged in writing a handbook and exploring new methods of dosimetry. The fuel burnup group of this subcommittee is compiling methods for burnup determination and will issue a standard method for this determination.

[94] D. F. Peppard, G. W. Mason, and S. W. Maline, "The Use of Dioctyl Phosphoric Acid Extraction in the Isolation of Carrier-Free ^{90}Y, ^{140}La, ^{144}Ce, ^{143}Pr, and ^{144}Pr," *J. Inorg. & Nuclear Chem.* 5, 141 (1957).

[95] Consultant, University of Tennessee.

Two interlaboratory check samples for use in method evaluation have been issued to the laboratories represented in the group. W. S. Lyon is a member of this subcommittee.

Subcommittee III (Task Group on Radioisotope Methods and Specifications). – W. S. Lyon is head of this group, which has as its objective the writing of specifications for the preparation of radioisotopes for sale and of the methods of specification analysis for the isotopes.

ASTM Committee D-19, Industrial Water

S. A. Reynolds is a member of three task groups of this committee: measurement of radioactivity of industrial water, applications of radioactive tracers, and sampling radioactive water.

American Standards Association Committee N 5.4, Use and Handling of Radioisotopes and High-Energy Radiation

Specifications are being written for unsealed sources of radiation, methods are being written for "Safety and Working Hygiene," and standards for a radioisotope laboratory are being prepared. In addition, standard methods of assay and the best values for decay data are being sought. W. S. Lyon is a member of this committee.

National Research Council Subcommittee on Measurements and Standards of Radioactivity

S. A. Reynolds is a member of this subcommittee, the functions of which are defined in its name.

National Committee on Radiation Protection and Measurements (NCRP)

S. A. Reynolds served as a member of a task group of this organization. The group prepared "A Manual of Radioactivity Procedures," to be published in the near future.

RAW MATERIALS LABORATORY (Y-12)

L. J. Brady

Oxidation of Tartaric Acid with Ceric Sulfate

The reaction of ceric sulfate with tartaric acid has been used as the basis of a method for estimating the concentration of tartrate in acidic aqueous solutions and in organic extracts. An aliquot of the solution that contains from 1 to 15 mg of tartaric acid is reacted with 25 ml of an ~0.05 *N* standard solution of ceric sulfate at approximately 25°C for 1 hr. The excess ceric sulfate is then determined by back titration with an ~0.05 *N* standard solution of ferrous sulfate.

Two series of tests were made on solutions that contained 3, 7.5, and 15 mg of tartaric acid. Under the conditions of the test, the ratio of millimoles of tartaric acid to milliequivalents of ceric sulfate was 0.133. The relative standard deviation of the results of this test was 2%.

It was established experimentally that ceric sulfate does not react to a significant extent with a solution of di-2-ethylhexylphosphoric acid–tributyl phosphate in petroleum distillate (Amsco), which solution is under test by the Chemical Technology Division as an extractant for metals complexed with tartrate, if the di-2-ethylhexylphosphoric acid has been purified. Ceric sulfate does react with an Amsco solution of unpurified di-2-ethylhexylphosphoric acid that contains tributyl phosphate. It appears, therefore, that if such a solution of *purified* di-2-ethylhexylphosphoric acid is used as an extractant, the ceric sulfate method can be used to estimate the tartrate in the organic phase, as well as in the raffinate, and the distribution ratio for this component can be thus established. Other constituents oxidized by ceric sulfate must be absent. Further tests will be made in order to determine the reaction rate and effect of temperature on the oxidation reaction.

Resistance of Tygon and Duroflex Plastic Tubing to Certain Chemical Reagents

L. J. Brady

Three specimens of plastic tubing (type R 3603 Tygon, type S-22-1 Tygon, and Duroflex vinyl plastic) were subjected to test by a modification of the ASTM test D543-56T.[96] Specimens (1.5-in. lengths) of the tubing were submerged in each of the following 14 reagents: 3 and 30 vol % sulfuric acid, 10 wt % sodium hydroxide, 95 vol % ethyl alcohol, 10 wt % sodium chloride, 10 vol % nitric acid, 10 vol % hydrochloric acid, 5 vol % acetic acid, 10 vol % ammonium hydroxide, 3 vol % hydrogen peroxide, tributyl phosphate (30 vol %)–Amsco (70 vol %), saturated solution of oxalic

[96] "Resistance of Plastics to Chemical Reagents," ASTM Designation D 543 – 56 T, *1958 Book of ASTM Standards*, part 9, p 453, American Society for Testing Materials, Philadelphia, 1958.

acid, gasoline, and tributyl phosphate. The weight and the volume of each specimen were determined prior to exposure and after an exposure period of 14 days.

Changes in the weights of the specimens varied from a loss of 34% in ethyl alcohol to a gain of 89% in the tributyl phosphate–Amsco mixture. Volume changes varied from a loss of 39% to a gain of 124% in these same solutions.

It was apparent within the first 24 hr that none of the specimens of plastic behaved satisfactorily in tributyl phosphate. All the specimens underwent a marked increase in weight and volume, and by the end of the test period they were no longer intact in the form of tubing but appeared as gelatinous globules which occupied volumes many times those of the original specimens.

The attack of both ethyl alcohol and gasoline caused all the specimens to lose weight and volume, to become inflexible, and to undergo a significant loss in transparency.

Tygon type S-22-1 decreased markedly in volume, lost flexibility, and became opaque during prolonged contact with the 10 wt % solution of sodium hydroxide, effects not observed to a significant extent with the other types of plastic.

In general, the resistance of the plastic samples to the other reagents tested was adequate. No significant changes were observed during prolonged exposure tests which would prevent their use under conditions requiring contact with these reagents for extended periods of time.

REACTOR PROJECTS LABORATORY (Y-12)

J. C. White

Gas Chromatographic Analysis of Helium

A. S. Meyer, Jr. I. B. Rubin

The development of methods for the determination of various impurities in helium, which will be used as the coolant in the Gas-Cooled Reactor, was initiated. The helium will be subject to contamination by gases from various sources: gases desorbed from graphite, inleakage of steam and atmospheric gases, and reaction products of these contaminants with heated graphite. The principal contaminants include nitrogen, oxygen, argon, hydrogen, carbon monoxide, carbon dioxide, methane, complex mixtures of higher hydrocarbons, and water vapor. During this period most samples were derived from graphite-evaluation studies in which graphite was heated in vacuo and from thermal convection loops.

The analyses were performed by means of a Perkin-Elmer model 154 vapor fractometer by injecting a sample of gas into a stream of helium carrier gas which passes through an 8-ft.-long column of $\frac{3}{8}$-in.-dia stainless steel tubing packed with Linde type 5A molecular sieves. This column absorbs polar compounds, such as water and carbon dioxide, essentially irreversibly but provides a clean-cut separation of hydrogen, oxygen and argon together, nitrogen, carbon monoxide, methane, and some other light hydrocarbons. The concentrations of the separated constituents are determined by comparing the thermal conductivity of each of the eluted gases with that of the carrier gas by means of a conductivity cell equipped with thermistor elements. More complex equipment, which has a dual-column valve, is being purchased to provide a means for the simultaneous determination of carbon dioxide and the gases mentioned above by performing a preliminary separation with a column packed with either silica gel or activated charcoal.

Because of the low pressure of the samples from the graphite-evaluation program, a special technique has been developed for the addition of these samples to the chromatographic column. The samples are submitted in glass bulbs of 200- or 1000-cc capacity at pressures as low as 100 μ. After being dried over anhydrous magnesium perchlorate, the mixture of gases is transferred to an evacuated system of calibrated volume in which the total pressure of the gas is determined with a McLeod gage. Subsequently, the entire sample, or a suitable aliquot, is transferred by a two-stage pumping operation over mercury to a 1-cc sample loop, which is mounted between two three-way stopcocks. By appropriate manipulation of the stopcocks, the stream of carrier gas is switched from a bypass loop through the sample loop to inject the sample onto the column as an integral plug with only momentary interruption of the flow of the carrier gas. Sample volumes of 20 to 500 μl have been analyzed by this technique. The relative standard deviation in the determination of nitrogen, oxygen, carbon monoxide, and methane for sample volumes between 100 and 500 μl is about 2%.

Samples from the thermal convection loops, which are submitted under positive pressure, are injected more simply by expanding the gas to atmospheric

pressure in a calibrated sample loop and switching the stream of carrier gas through the calibrated loop. For samples of 3- to 5-cc volume, separated on 3-ft columns, concentrations of nitrogen, oxygen, carbon monoxide, and methane below 50 ppm can be determined. The sensitivity for the detection of hydrogen is less by a factor of about 20 because its thermal conductivity is similar to that of the carrier gas.

Other determinations that have been carried out with this apparatus include the depletion of oxygen from a sample of air; inert gases in helium; and hydrogen, oxygen, and nitrogen in radiolysis products of aqueous solutions.

A system, based largely on gas chromatographic techniques, for the continuous monitoring of impurities in helium has been designed jointly by the Analytical Chemistry Division and the Instrumentation and Controls Division. In this system the concentration of water is continuously determined with a Consolidated Electrodynamics Corporation moisture monitor. The other six major contaminants will be determined by means of a Greenbrier Instruments, Inc., Chroma-matic 112, dual-column gas chromatograph that can be programed to analyze separate samples at intervals of from 10 min to 1 hr. At a preselected interval this instrument injects a reproducible volume of a dried sample stream into a stream of helium carrier gas, which is directed through successive columns, the first packed with silica gel and the second with Linde type 5A molecular sieves, and then through a thermal conductivity cell. The first column serves to separate carbon dioxide from the remaining constituents (hydrogen, oxygen, nitrogen, methane, and carbon monoxide), which are fractionated on the second column. When all the constituents except carbon dioxide have entered the molecular-sieve column, the dual-column valve is actuated to isolate this column and to route the carbon dioxide directly to the detector. After the carbon dioxide has been eluted and measured, the dual-column valve is returned to its original position, and the components absorbed on the molecular-sieve column are eluted. By this technique each contaminant is uniquely isolated, except oxygen, which is accompanied by any argon that may be present. The instrument is actuated by a multicam programed timer to carry out in proper sequence the operations normally performed by the analyst, for example, balancing the thermal conductivity bridge, zeroing the recorder, actuating the sampling and dual-column valves, and selecting attenuator circuits for the signal produced by each eluted component. A stepless attenuator, which can be adjusted to record data in terms of per cent or other appropriate concentration units, is provided for each of the six contaminants.

The analytical system is being installed on the test facility of the materials compatibility low-pressure loop in which specimens of structural alloys will be maintained in an atmosphere of constant composition by the deliberate addition of contaminants. At the completion of the above test, the system will be redesigned for multipoint sampling and used to evaluate the efficiency of a helium purification system.

Direct Determination of Total Oxygen in Uranium Oxide

A. S. Meyer, Jr. G. Goldberg

The fluorination procedure[97] has been adapted for the direct determination of total oxygen in uranium dioxide. This investigation is part of the program designed to establish accurate and precise values for the oxygen-to-uranium (O/U) mole ratio in reactor-grade uranium dioxide, UO_2, fuel pellets. The determination is carried out by reacting samples of UO_2 with molten potassium tetrafluorobromide, $KBrF_4$, in order to evolve oxygen and any contaminant nitrogen quantitatively as the elemental gases. The evolved gases are confined over mercury in a calibrated volume above a Toepler pump and are measured by determining their pressure with a differential manometer. The apparatus has been modified by the addition of a supplemental volume of confining space, which is terminated by capillary tubes for precise definition of the volume between the Toepler pump and the original measuring chamber. In addition, a sampling port has been provided so that, after measurement, the evolved gases can be analyzed by mass spectrography or gas chromatography to correct for traces of nitrogen that is derived from nitrides in the sample. With the increased volume of confining space, more precise measurements of gas volumes are possible, and samples of UO_2 as large

[97] A. S. Meyer, Jr., and G. Goldberg, "Determination of Oxides in Fluoride Salts," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 68.

as 80 mg can be analyzed; thus the errors introduced by weighing and incomplete transfer of the sample to the reactor are minimized. For samples from which only small volumes of gas are evolved, the level of mercury can be raised to confine the gas in the original volume so that the sensitivity of the method does not suffer as a result of this modification.

The relative standard deviation based on the results of duplicate determinations of the ratio for 18 samples of UO_2 (~50 to 150 mg) is 0.4%. This precision makes the method suitable for determining whether the O/U mole ratio falls within the acceptable range of 2.00 to 2.03 which has been established for UO_2 fuel pellets.

The determination of the O/U mole ratio is to be required on an excessively large number of pellets; hence, a rapid method is also highly desirable. Since only nine analyses can be completed per 8-hr shift when three reaction vessels are used, plans are under way to use an all-Teflon system in order to reduce materially the time per analysis. In this system, bromine trifluoride, BrF_3, will be substituted for $KBrF_4$, and the reaction will be carried out at 100°C. Another advantage of the Teflon unit will be the elimination of blanks since no prior fluorination of the system is necessary.

Other analyses that have been performed by the fluorination method in this period include the determination of oxygen in copper, nickel, aluminum, yttrium-magnesium alloys, uranium tetrachloride, molybdenum disulfide, and the fluorides of iron, chromium, and nickel and the determination of oxygen and nitrogen in uranium nitride and terbium nitride.

Automatic Conductometric Determination of Carbon

J. E. Attrill

The Leco conductometric carbon analyzer has been used successfully for the determination of carbon in iron, steel, copper, lead, tin, zinc, uranium dioxide, berrylium oxide, and silicon dioxide. Of these materials, the refractory oxides inhibit the induction heating and thus require large amounts of accelerator, which necessitates care to ensure that the zirconia crucible does not collapse under these operating conditions. The order of precision to be expected in the analysis of uranium dioxide for carbon in the range of 0.05 to 0.002% is being studied. Blanks are found to be large and erratic. Attempts to use quartz and platinum liners inside a quartz-encased carbon crucible, which could be used repeatedly and thus result in a negligible blank, have so far been unsuccessful because of the difficulty of attaining high temperatures without breakage of the crucibles.

Dissolution of Graphite

J. E. Attrill

A large number of graphite samples were received that had been subjected to prolonged contact under various temperatures and pressures with molten fluorides of beryllium, thorium, and uranium. The molten fluoride penetrates the graphite to various degrees. The extent of penetration is determined by analyzing successive millings from the graphite for beryllium, thorium, and uranium.

Cursory tests proved that it was not feasible to leach the salts from the graphite by prolonged refluxing with nitric acid. Combustion methods were unsatisfactory because the beryllium salt is somewhat volatile and thus the quantitative collection of the salts is impractical. On the basis of these findings, wet oxidation with concentrated boiling perchloric acid was used. By means of the addition of about 2 to 10 mg of solid chromic oxide as a catalyst, complete dissolution of as much as 10 g of graphite was achieved in about 3 hr. In the absence of the chromic oxide, 12 to 24 hr would be required for the dissolution. Attempts to dissolve graphite in perchloric acid under reflux conditions were unsuccessful. After dissolution is successfully achieved, the excess acid is evaporated, and the three metals are determined by conventional spectrophotometric methods.

Determination of Sulfur with a Leco Automatic Sulfur Titrator

J. E. Attrill

Sulfur is now being determined by means of a Leco automatic sulfur titrator in conjunction with an induction furnace. Both these instruments were purchased from Laboratory Equipment Corporation. The sample is burned in a porous zirconia crucible in the presence of iron and tin as accelerators. A stream of oxygen is passed through the system to hasten the burning of the sample and to sweep the released gases to the titrator. All the sulfur in the sample burns to sulfur dioxide in the furnace

and the sulfur dioxide is carried to the titrator by the stream of oxygen. The gas enters a titration vessel that contains hydrochloric acid, potassium iodide, starch, and enough standard solution of potassium iodate to release some free iodine and thus to turn the solution blue. As the sulfur dioxide is swept through the cell, it bleaches the color and more iodate solution is added automatically to restore the blue color of the solution to its original intensity. The chemical reactions are

$$KIO_3 + 5\,KI + 6\,HCl = 3\,I_2 + 6\,KCl + 3\,H_2O$$

$$SO_2 + I_2 + 2\,H_2O = H_2SO_4 + 2\,HI$$

When all the sulfur has been released, the blue color no longer fades, and the amount of iodate titer added is read on a buret. The buret is calibrated directly in per cent sulfur within the range from 0.000 to 0.200%, based on a 1-g sample. However, the range can be extended either by using a sample of different size or by changing the titer of the iodate solution.

Advantages of this method are the speed with which a large number of analyses can be made (each analysis can be completed in 5 to 10 min); dissolution of the sample is eliminated; insoluble sulfur compounds are easily decomposed; and there is no long initial warmup period as is required with a resistance furnace. The maximum temperature reached with this induction furnace is 1700 to 1800°C. It therefore appears that sulfur can be determined in any material that melts below this temperature or that becomes soluble in the molten accelerator. Volatile organic samples can also be analyzed by this method if a preignition system is added to the induction furnace.

The main disadvantage has been the refractory behavior of certain oxide samples and the large amount of accelerator that is thereby required to bring the sample to a sufficiently high temperature. This high temperature in turn may cause localized overheating within the crucible and subsequent breakage of the crucible, which might allow the molten metal to be released in the system and to cause breakage of other components.

Spectrophotometric Studies of Molten-Fluoride-Salt Systems

J. P. Young

The high-temperature cell assembly that was described previously[98] has been fabricated and used in obtaining absorption spectra of various metal ions dissolved in several molten fluoride salts. The furnace can be heated to temperatures as high as 780°C; a water jacket efficiently maintains the outer shell of the apparatus at temperatures below 25°C. The spectra are recorded on a Cary model 14-M recording spectrophotometer, which can be easily converted from normal to high-temperature operation in less than a minute. In obtaining spectra, the molten-fluoride-salt solutions are contained either in a crystalline magnesium oxide cell or as a pendent drop in a platinum tube (0.4 cm in diameter, 1 cm long). The general characteristics[99] of the crystalline magnesium oxide spectrophotometric cell have limited the usefulness of this type of sample confinement. Most of the spectra were obtained by means of the pendent-drop technique.

From spectra that were obtained with drop-shaped samples of didymium glass and with drops of aqueous solutions of several rare-earth elements that were confined in pendent-drop-type containers, it was proved that reproducible and valid spectra can be obtained with pendent drops. This technique can therefore be used for qualitative spectral identification. It is not possible, however, to control accurately the quantity of sample held as a pendent drop; also, minor variations in the placement of the drop in the light path of the spectrophotometer can result in changes in the optical response of a sample of pure solvent; therefore, in order to provide quantitative spectral data, two parameters of the drop must be known, namely, the optical path length of the drop and the absorbancy of the pure solvent. A method for the determination of the path length of a pendent drop in the platinum tube has been developed. By means of the following equation, the path length of an aqueous pendent drop can be calculated with a relative standard deviation of about 2%:

$$\text{P.L.} = \frac{V}{0.95\pi R^2} - 0.078 \ ,$$

where

P.L. = the optical path length,

[98] J. P. Young, "Spectrophotometry of Molten Fluoride Salts," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 70.

[99] J. P. Young and J. C. White, "A High-Temperature Cell Assembly for Spectrophotometric Studies of Molten Fluoride Salts," *Anal. Chem.* 31, 1892 (1959).

V = volume of the drop = weight/density,

R = radius of the platinum tube.

This expression was derived from a series of experiments in which the spectra of a number of pendent drops of an aqueous solution of praseodymium nitrate were treated statistically and compared with known absorbancy characteristics of this solution. Because of the extremely sharp peaks of the praseodymium spectrum, it was possible to extrapolate the reference absorbancy of each sample drop. The same type of study is being made with solutions of praseodymium fluoride in the molten eutectic of LiF-NaF-KF (46.5-11.5-42.0 mole %). Preliminary comparisons of the data from the aqueous solution and molten-fluoride-eutectic solution indicate that the expression for the determination of path length will vary with solvent and is probably related to surface tension and density. Other than by extrapolation of the reference absorbancy curve under a particular absorption peak, no way to compare the absorbancy of a sample directly with the absorbancy of a solvent has been developed as yet.

The prime purpose of this molten-salt spectrophotometry project is to investigate the possibility of spectrophotometric measurements in molten fluoride salts. The various solvents that have been investigated include LiF-NaF-KF (46.5-11.5-42.0 mole %), NaF-ZrF_4 (50-50 mole %), LiF-NaF-ZrF_4 (33.3-33.3-33.3 mole %), and LiF-BeF_2 (63-37 mole %). The solvent of chief interest has been the alkali-metal fluoride eutectic. The two solvents that contain zirconium were studied in an attempt to verify the presence of a di- or a trivalent zirconium salt in these eutectics. No unique spectra were obtained, but rather the results of this study indicated that the original solvent was not free from transition-metal impurities, which would possibly interfere with the detection of the desired component. The general field of interest is shifting to the BeF_2-containing solvents since studies in this field will be more in line with the present emphasis of the molten-salt power reactor program. The high-temperature cell assembly is being modified somewhat to prevent any accidental release of toxic BeF_2 vapor.

One of the more interesting of the spectra that have been obtained is the spectrum of UF_4 in LiF-NaF-KF (Fig. 20). When this spectrum was obtained, the solution was maintained at a temperature of approximately 570°C. The spectrum of

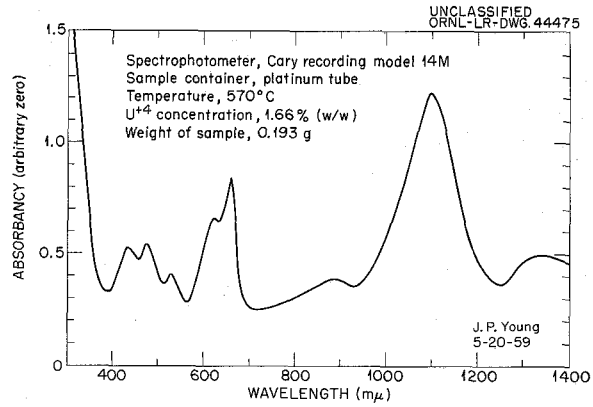

Fig. 20. Spectrum of UF_4 in Molten LiF-NaF-KF.

UF_4 resembles a spectrum of UCl_4 in LiCl-KCl that was reported by Gruen and McBeth.[100] Uranium tetrafluoride exhibits peaks at 658 and 1100 mμ and a shoulder at 615 mμ, compared with UCl_4, which exhibits peaks at 655 and 1090 mμ and a shoulder at 605 mμ. The fluoride salt also has peaks at 428, 470, and 530 mμ; in this region UCl_4 presents a broad absorbancy with peaks at approximately 450 and 480 mμ. Both UF_4 and UCl_4 exhibit an absorption minimum at 710 mμ. When the absorbancy of UF_4 at 710 mμ was taken to be the absorbancy of the solvent and when the concentration of UF_4 and the density and weight of the molten fluoride solution were known, it was possible to estimate the molar absorbancy index for the 1100-mμ peak of UF_4 to be 15; this value compares favorably with the molar absorbancy index value of 13 reported for the 1090-mμ peak of UCl_4. Spectra have been recorded for NiF_2, CoF_2, CrF_3, PrF_3, and UO_2F_2 when dissolved in the LiF-NaF-KF eutectic. The characteristics of these spectra will be described in forthcoming publications.

Some work has been carried out in an effort to find organic chromogenic reagents that will be useful for spectrophotometric determinations in molten salts in general and in molten fluoride salts in particular. It could be assumed that such methods would be extremely sensitive because little or no dilution of a solid sample would be involved in the determination. Both alizarin and

[100] D. M. Gruen and R. L. McBeth, "Oxidation States and Complex Ions of Uranium in Fused Chlorides and Nitrates," *J. Inorg. & Nuclear Chem.* 9, 290 (1959).

alizarin red S were found to be soluble in molten LiCl-KCl (mp = 350°C) and LiF-NaF-KF (mp = 459°C). These organic compounds volatilize from either molten solvent but are noticeably more stable in the lower-melting LiCl-KCl. The resultant spectrum of this solution at ~400°C exhibited a peak at 557 mμ. Qualitative tests have shown that zirconium ion precipitates alizarin in LiCl-KCl. This fact could conceivably be used in developing a sensitive method for the determination of heavy-metal ions in alkali-metal chlorides. The porphyrin class of organic compounds constitutes another possible type of chromogenic reagents for use in molten-salt media. Cursory work with phthalocyanine has indicated that this compound is not soluble in molten alkali-metal halides; however, derivatives of phthalocyanine or porphyrin might be synthesized which would be soluble.

Spectrophotometric Determination of Yttrium with Pyrocatechol Violet

J. P. Young R. G. Ball

Pyrocatechol violet has proved to be a very sensitive chromogenic reagent for the spectrophotometric determination of small concentrations of yttrium. The molar absorbancy index of the yttrium–pyrocatechol violet complex is 25,900 at the wavelength of maximum absorbancy, 665 mμ. The absorbancy of the complex conforms to Beer's law up to the yttrium concentration of 1.8 mg/ml in the final test solution. The procedure necessitates the formation of the yttrium–pyrocatechol violet complex in a chloride solution, the pH of which is maintained at 8.5 ± 0.1. Under these conditions, the color of the yttrium complex is unaffected by the presence of large concentrations of nitrate or sulfate ions; small concentrations of fluoride ion can also be tolerated. The alkaline-earth elements and moderate amounts of zinc do not seriously affect the determination of yttrium. If a preliminary group separation is made by means of an extraction with tri-*n*-octylphosphine oxide in cyclohexane, the method is useful for the determination of yttrium in the presence of large concentrations of iron(III), uranium(VI), zirconium(IV), molybdenum(VI), thorium(IV), tin(II) and (IV), and other ions that are extractable with tri-*n*-octylphosphine oxide. If cyanide is present in the final test solution, moderate amounts of nickel do not interfere.

The rare-earth elements, when treated according to this procedure, probably can be determined with a sensitivity, on a molar basis, equal to that for yttrium. The method is about 20% less sensitive for scandium. These elements therefore interfere seriously with the determination of yttrium; however, this method could be used to determine individual rare-earth elements if suitable separations were made. Other ions that were found to interfere are vanadium and large amounts of beryllium and aluminum. A final report is being prepared which will describe this method in detail.

Solvent Extraction with Organophosphorus Compounds

W. J. Ross

Tri-*n*-octylphosphine Oxide. – The extraction studies with tri-*n*-octylphosphine oxide have been continued in order to determine the extraction characteristics of antimony, arsenic, and zinc in acidic solutions. These elements are not extracted from solutions of nitric or sulfuric acid into cyclohexane solutions of this reagent unless chloride ion is also present in the aqueous phase. In Fig. 21 the extraction coefficients for these metals are plotted as a function of the hydrochloric acid molarity of the aqueous phase.

Both antimony(III) and antimony(V) are extracted from acidic chloride solutions by means of tri-*n*-octylphosphine oxide although the extractability is dependent on the concentration of hydrochloric acid (or chloride ion). Antimony(V) forms an insoluble hydrolytic species in systems that contain less than 2 *M* hydrochloric acid. The extraction of antimony(III) is not affected by as much as 5 *M* sulfuric acid but is seriously impaired by nitric acid. Both nitric acid and sulfuric acid reduce the extractability of antimony(V).

Arsenic(III) is partially extracted from acidic chloride solutions but is not extracted from nitrate or sulfate solutions. Arsenic(V) is not extracted from acidic solutions with tri-*n*-octylphosphine oxide.

The extraction of zinc from chloride solutions is complicated by the formation of insoluble adducts in systems that contain more than 2 *M* hydrochloric acid. No extraction occurs in nitrate or sulfate systems.

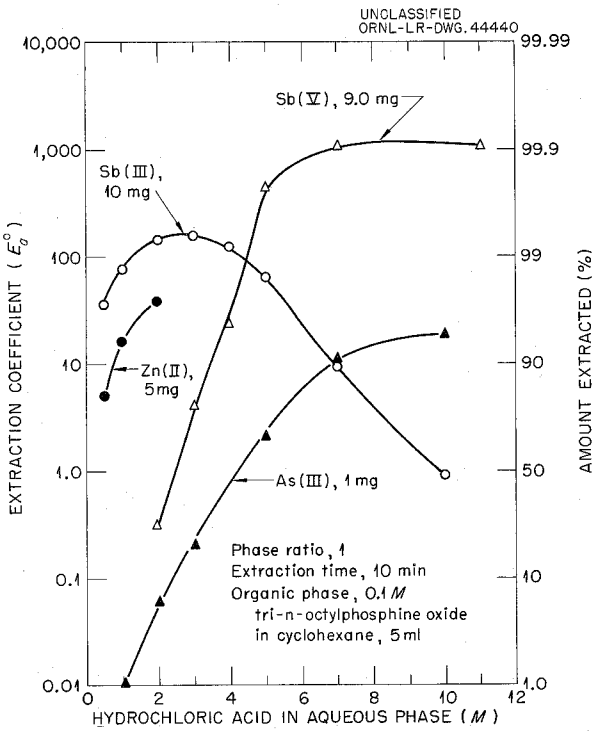

Fig. 21. Extractability of Antimony, Arsenic, and Zinc from Hydrochloric Acid Solutions with Tri-*n*-octylphosphine Oxide.

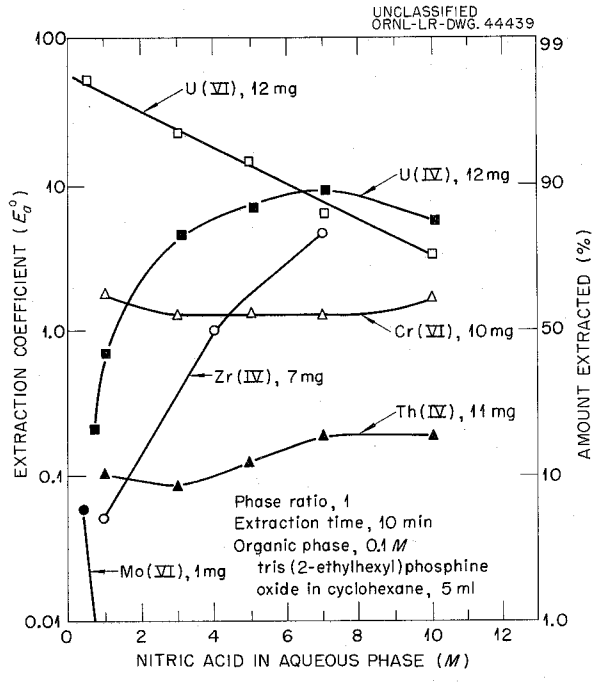

Fig. 22. Extractability of Elements from Nitric Acid Solutions with Tris(2-ethylhexyl)phosphine Oxide.

Tris(2-ethylhexyl)phosphine Oxide. – The extraction characteristics of 49 elements in acidic solutions have been determined for possible application of tris(2-ethylhexyl)phosphine oxide, $[C_4H_9CH(C_2H_5)CH_2]_3PO$, in cyclohexane as an analytical extractant. Of the elements investigated, 17 were found to be extracted, to varying degrees, from solutions of hydrochloric, nitric, and sulfuric acids. This reagent is a more selective extractant than is its straight-chain isomer, tri-*n*-octylphosphine oxide. The extraction behaviors of antimony(III), gallium(III), germanium(IV), gold(III), hafnium(IV), indium(III), and titanium(IV) were not investigated quantitatively; however, each of these elements is extracted by this reagent, especially from solutions of high hydrochloric acid concentration.

In acidic sulfate solutions, only chromium(VI) is extracted by tris(2-ethylhexyl)phosphine oxide. The extraction is quantitative from 5 *M* sulfuric acid in a single, 10-min equilibration.

Five elements are extracted from nitric acid solutions with this phosphine oxide (Fig. 22); however, only uranium(VI) is extracted to a degree greater than 98% in a single equilibration. Uranium(IV) is partially oxidized to uranium(VI) in these media; the uranium(IV) is incompletely extracted, whereas the uranium(VI) is believed to be completely extracted.

The characteristics of eleven elements that are extractable in chloride–tris(2-ethylhexyl)phosphine oxide systems are shown in Fig. 23. The degree of extraction of each element is a function of the concentration of hydrochloric acid and reflects the concentration of extractable species in the aqueous phase. Some of the extracted species have been identified as

$$UO_2Cl_2 \cdot 2\{[C_4H_9CH(C_2H_5)CH_2]_3PO\} ,$$

$$UCl_4 \cdot 2\{[C_4H_9CH(C_2H_5)CH_2]_3PO\} ,$$

$$SnCl_4 \cdot 2\{[C_4H_9CH(C_2H_5)CH_2]_3PO\} ,$$

$$FeCl_3 \cdot 2\{[C_4H_9CH(C_2H_5)CH_2]_3PO\} ,$$

$$ZrCl_4 \cdot 2\{[C_4H_9CH(C_2H_5)CH_2]_3PO\} ,$$

$$H_2Cr_2O_7 \cdot HCl \cdot 3\{[C_4H_9CH(C_2H_5)CH_2]_3PO\} .$$

Maximum extractability of tin(IV), uranium(VI),

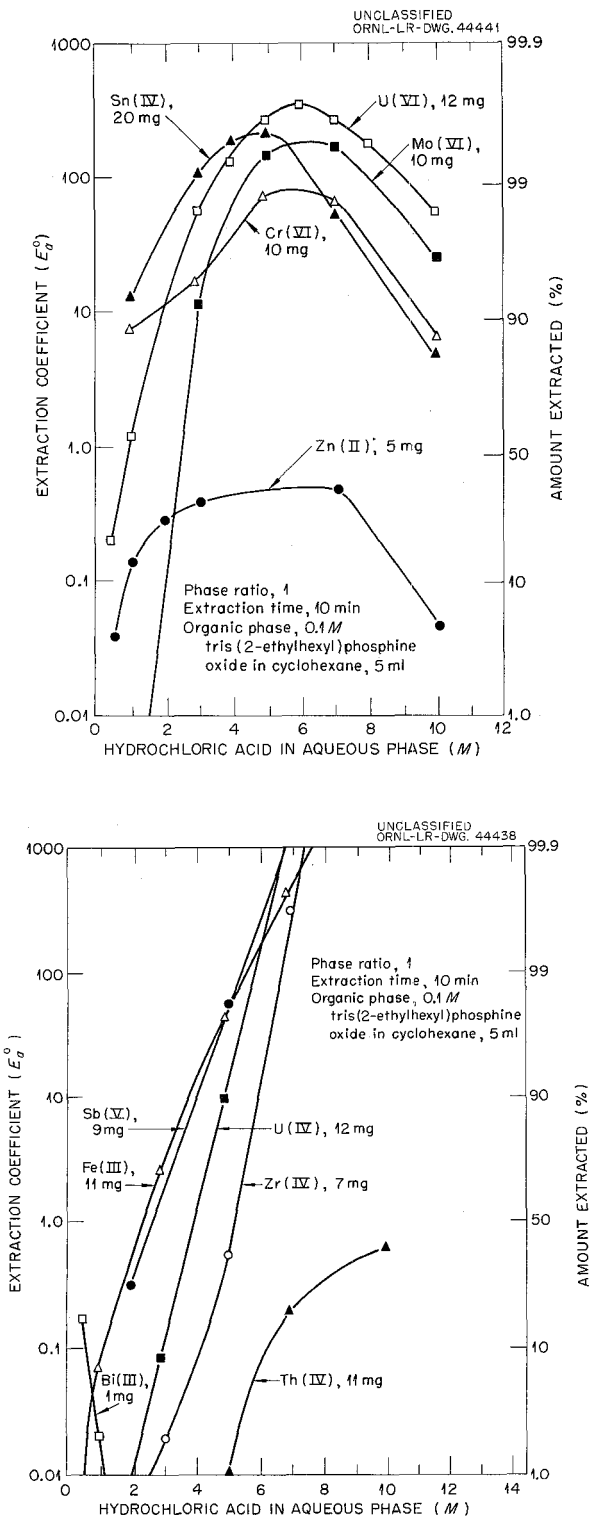

Fig. 23. Extractability of Elements from Hydrochloric Acid Solutions with Tris(2-ethylhexyl)phosphine Oxide.

molybdenum(VI), chromium(VI), and zinc(II) occurs in systems which are 4 to 6 *M* in hydrochloric acid. The existence of these maxima indicates that metal-chloride species are formed in the aqueous phase with chloride-to-metal ratios both greater and less than that of the extractable species. The linear relationship that is revealed between the extraction of iron(III), antimony(V), uranium(IV), zirconium(IV), and thorium(IV) (Fig. 23) indicates that the formation of the extractable species is favored continually by an increase in the chloride concentration of the aqueous phase.

A relatively high degree of selectivity can be achieved through variation of the chloride concentration in the presence or absence of nitrate or sulfate. For example, uranium(VI) is essentially the only element that is extracted by tris(2-ethylhexyl)phosphine oxide from a solution that is 0.5 *M* with respect to both hydrochloric and nitric acid. Similarly, uranium(VI) is separated from uranium(IV) and thorium by extraction from dilute hydrochloric acid solution. Uranium(VI) can be determined *in situ* by measuring the absorbancy of the organic phase at 230 mμ. The extraction of tin(IV) is seriously impaired by nitric acid; however, complete extraction is achieved from solutions that contain 1 *M* hydrochloric and 3 to 7 *M* sulfuric acid. Antimony(V) is hydrolyzed and precipitates during the extraction of solutions that are less than 2 *M* in hydrochloric acid. Because of the low degree of extraction, zinc does not form an insoluble adduct with this reagent as it does with tri-*n*-octylphosphine oxide systems.

Chromium(III), iron(II), and arsenic(V) are not extracted from acidic solutions with tris(2-ethylhexyl)phosphine oxide, whereas arsenic(III) is extracted from only very concentrated solutions of hydrochloric acid.

Triphenylphosphine Oxide. – A qualitative survey was carried out to determine the extent to which 41 elements were extracted from 1 and 7 *M* solutions of hydrochloric acid into a 0.1 *M* solution of triphenylphosphine oxide in cyclohexane or benzene. This reagent was found to be unsatisfactory as an extractant because of the insolubility of its metal chloride adducts in the organic solvent.

Infrared Spectral Study of Phosphine Oxide Adducts

C. A. Horton

Studies of the infrared spectra of tri-*n*-octylphosphine oxide adducts were continued.[101] The adducts are obtained by the equilibration of a solution of tri-*n*-octylphosphine oxide in cyclohexane with an aqueous solution that contains the appropriate metal ions and acids, followed by evaporation of the diluent from a few drops of the extract placed on salt (sodium chloride) plates. New adducts studied included those from the aqueous systems: 2.5 *M* phosphoric acid, 2.5 *M* perchloric acid, cerium(IV) in 2.5 *M* sulfuric acid, cerium(IV) in 2.5 *M* hydrochloric acid plus sulfate, uranium(IV) in 2.5 *M* sulfuric acid, and uranium(IV) in 2.5 *M* hydrochloric acid plus traces of sulfate.

The spectra of tris(2-ethylhexyl)phosphine oxide and of its uranium(IV) and (VI) adducts were obtained for comparison with the spectra of tri-*n*-octylphosphine oxide and its uranium(IV) and (VI) adducts. For all the adducts of both tri-*n*-octylphosphine oxide and tris(2-ethylhexyl)phosphine oxide except that of phosphoric acid, the phosphoryl stretching vibration disappeared from the position noted for an untreated phosphine oxide, and new bands were noted at lower frequencies. Bands due to the polyatomic anions were observed again in the new spectra. These changes are similar to those reported earlier for other tri-*n*-octylphosphine oxide adducts[101] and for bis-(2-ethylhexyl) complexes of phosphoric acid.[102] The spectra of uranium(IV) adducts differed from the spectra of uranium(VI) adducts. When the uranium(IV) adducts stood, their visual colors and infrared spectra slowly took on the spectral character of the uranium(VI) adducts. Considerable differences in the wavelengths of the absorption peaks of the adducts of the two different valence states of uranium would allow at least qualitative detection of the two in the presence of each other.

The nitrate-extracted adducts of tri-*n*-octylphosphine oxide previously recorded show one band attributable to the ionic nitrate group and two or more attributable to metal-coordinated nitrato groups.[103]

A report is being prepared that will describe all the infrared work on the metal and acid adducts of phosphine oxide.

Infrared Spectral Study of Organophosphorus Compounds

C. A. Horton

The extraction of uranium and of other metals by organophosphorus extractants is often greatly influenced by the presence of impurities in the extractant. Infrared examination helps to assess the purity and the success of chemical or distillation purification processes of such organophosphorus extractants.

Various organophosphorus samples were examined in carbon tetrachloride or carbon disulfide solution over the 2- to 15-μ region by means of an Infracord infrared spectrometer. From the infrared spectra, structural groups were partially identified as either major or minor components of the samples by use of prior correlations of band positions with functional groups. The change in intensity of impurity bands was also noted after chemical or vacuum-distillation purifications. Much of the work was with tributyl phosphate and some of its possible impurities. The study will be described in detail in a report now being prepared. Any further work will require preliminary concentration of impurities by ion-exchange, chromatographic, electrophoretic, or selective-solvent-extraction techniques.

1-Phenyl-3-isohexenyl-1-phospha-3-cyclopentene-*p*-oxide

R. J. Baltisberger[104]

Through the courtesy of the E. I. du Pont de Nemours and Company, Inc., a generous supply of 1-phenyl-3-isohexenyl-1-phospha-3-cyclopentene-*p*-oxide was received to determine its feasibility as an analytical reagent in separations by solvent extraction. The compound is a stable liquid with a high boiling point (176 to 177°C at 0.26 mm)

[101] J. C. White, "Reactor Projects Laboratory," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 60–73.

[102] D. F. Peppard and J. R. Ferraro, "The Preparation and Infrared Absorption Spectra of Several Complexes of Bis-(2-ethylhexyl)-phosphoric Acid," *J. Inorg. & Nuclear Chem.* 10, 275 (1959).

[103] B. M. Gatehouse, S. E. Livingston, and R. S. Nyholm, "Infrared Spectra of Some Nitrato and Other Oxy-anion Coordination Complexes," *J. Inorg. & Nuclear Chem.* 8, 75 (1958).

[104] Summer employee from the University of Wisconsin, Madison.

and is soluble in aromatic hydrocarbons. Its extraction characteristics are very similar to those of tri-*n*-octylphosphine oxide. In general, it is several orders of magnitude less efficient than tri-*n*-octylphosphine oxide, however. The major advantage of it is that it is made from readily obtainable, inexpensive starting materials, and thus its potential cost would be in the category of bulk chemicals rather than of reagent chemicals. The cyclic addition of myrcene to dichlorophenylphosphine with subsequent hydrolysis gives the product 1-phenyl-3-isohexenyl-1-phospha-3-cyclopentene-*p*-oxide. Myrcene is available for 50¢ per pound, and dichlorophenylphosphine for 75¢ per pound.

A complete report of the extraction characteristics of this reagent is being prepared.

Determination of Oxygen in Yttrium

R. F. Apple

The inert-gas fusion method was evaluated for the routine conductometric determination of oxygen in yttrium. The determination of carbon dioxide by absorption in a solution of barium hydroxide and measurement of the change in the conductance of the solution was first proposed by Cain and Maxwell.[105] Modifications of this method that make it suitable for the determination of oxygen and illustrations of the apparatus required for its use have recently been published.[106] The method is based on the evolution of oxygen from the sample at its fusion temperature and the subsequent reaction of the oxygen with carbon to form carbon monoxide. After it passes through a purifying train, the carbon monoxide is converted to carbon dioxide by the action of specially prepared iodine pentoxide, and the resultant carbon dioxide is swept into a column of barium hydroxide solution where it effects a change in the conductance of the solution. The change in conductance is measured in ohms, and the amount of oxygen equivalent to it is determined from a graph prepared by determining the oxygen content of NBS standard sample No. 1040. Although any one of a number of metals can be used as bath material (solvent for the sample), only platinum was used in this work. This method has also been applied to the determination of oxygen in zirconium, beryllium, copper, uranium, and uranium nitrides. Concentrations of oxygen in the range from 0 to 0.4 mg per sample have been determined. The Leco oxygen analyzer No. 534-300 was used throughout this work, and the relative standard deviation of the results is about 7%.

[105] J. R. Cain and L. C. Maxwell, "An Electrolytic Resistance Method for Determining Carbon in Steel," *J. Ind. Eng. Chem.* 11, 852 (1919).

[106] *Manual for the Operation of Leco Oxygen Analyzer No. 534-300*, Laboratory Equipment Corp., St. Joseph, Mich., Apr. 1958.

Determination of Cadmium and Zinc in Fused Fluoride Salts

R. F. Apple

A complexometric titration method has been developed and evaluated for the determination of cadmium and zinc in $LiF-BeF_2-UF_4-ThF_4$ (67-18.5-0.5-14 mole %) to which cadmium oxide, CdO, or zinc oxide, ZnO, has been added. Both cadmium and zinc form stable complexes in acidic media with disodium dihydrogen ethylenediaminetetraacetate; complexation is indicated by xylenol orange.[107] Cadmium is titrated at a pH of 5.5, and zinc is titrated at a pH of 5.0. The sharpness of the indicator change at the end point is enhanced by the addition of excess titrant and back-titration of the excess with an ~0.01 *M* standard solution of copper(II). When the titrations are performed with an ~0.01 *M* standard solution of disodium dihydrogen ethylenediaminetetraacetate, at least 3 mg of cadmium or 2 mg of zinc should be present in order to obtain a satisfactory titration. Thorium and components added to the salt mixture, such as rare-earth-element fluorides, that are known to interfere with the titration are effectively removed by the addition of excess masking agent, fluoride ion. Of the other cations that could interfere, only those of iron, nickel, chromium, and copper were evaluated since these metals constitute the bulk of the corrosion products in the sample. The sum of the concentrations of the corrosion materials in $LiF-BeF_2-UF_4-ThF_4$ rarely exceeds 1000 ppm. Macro amounts of these cations definitely interfere, however. The relative standard deviation of the method for macro amounts of cadmium and zinc is about 1%. Based on standards, the results of these determinations are accurate to within ±2%.

[107] *The EDTA Titration*, The J. T. Baker Chemical Company, Phillipsburg, N. J., Nov. 1957.

Complexometric Titration of Thorium

R. F. Apple

A chelometric titration method for the determination of thorium was developed specifically for application to mixtures of fluoride salts, such as $LiF-BeF_2-UF_4-ThF_4$ (67-18.5-0.5-14 mole %). Thorium forms a stable complex with disodium dihydrogen ethylenediaminetetraacetate in acid media and can be determined by the direct titration technique of Körbl and Pribil[108] in which xylenol orange is used as indicator. When the titrations are performed with an ~0.01 *M* standard solution of disodium dihydrogen ethylenediaminetetraacetate, at least 3 mg of thorium should be present to obtain a satisfactory titration. The sharpness of the color change of the indicator at the end point is enhanced by adjusting the pH to 4.0, adding excess disodium dihydrogen ethylenediaminetetraacetate solution and back-titrating the excess with an ~0.01 *M* solution of copper(II). Some products added to the fused fluoride salt mixtures, such as CeF_3 and other rare-earth-element fluorides, interfere. The thorium is extracted from a 7 *M* hydrochloric acid solution with tri-*n*-octylphosphine oxide.[109] Cerium(III) and other rare-earth elements remain unextracted in the aqueous phase. Thorium is then back-extracted into 0.3 *M* sulfuric acid and subsequently titrated with a solution of disodium dihydrogen ethylenediaminetetraacetate; xylenol orange is used as indicator.

The limit of quantitative measurement of the method was extended to micro quantities of thorium contained in graphite rods. Following the dissolution of the graphite in perchloric acid, as little as 200 μg of thorium can be determined by adding an excess of an ~0.001 *M* standard solution of disodium dihydrogen ethylenediaminetetraacetate and back-titrating this excess with an ~0.002 *M* standard solution of copper(II) to the color change of xylenol orange indicator.

Of the common cations that could interfere with the titration of macro quantities of thorium by this method, only iron, nickel, chromium, and copper have been studied because these metals are the corrosion products usually present in the sample and their total concentration rarely exceeds 1000 ppm. In the titration of micro quantities of thorium with disodium dihydrogen ethylenediaminetetraacetate, the perchloric acid used to dissolve the graphite contains sufficient iron to interfere. The addition of ascorbic acid reduces iron(III) to iron(II) of which as much as 60 μg can be tolerated in the analysis. The relative standard deviation of the method for macro quantities of thorium is about 1%. Based on standards, the results of these determinations are accurate to within ±1%.

A paper that describes this work has been submitted to *The Chemist Analyst* for publication.

[108] J. Körbl and R. Pribil, "Xylenol Orange: New Indicator for EDTA Titration," *Chemist Analyst* 45, 102 (1956).

[109] J. C. White, "The Use of Tri-*n*-Octylphosphine Oxide in Analytical Chemistry," *Symposium on Solvent Extraction in the Analysis of Metals*, ASTM Special Technical Publication No. 238, American Society for Testing Materials, Philadelphia, 1958.

Flame Spectrophotometric Determination of Magnesium in Beryllium Oxide

R. F. Apple

A flame spectrophotometric method for the determination of micro amounts of magnesium in reactor-grade beryllium oxide is being evaluated. The background produced by beryllium is so pronounced that separation of at least the major portion of the beryllium is necessary before the flame photometric technique can be applied. Magnesium is separated from beryllium by means of a modification of the procedure used by Luke and Campbell[110] which is based on precipitation with ammonium hydroxide in the presence of excess disodium dihydrogen ethylenediaminetetraacetate. Magnesium forms a soluble complex with disodium dihydrogen ethylenediaminetetraacetate in basic solution, whereas beryllium is unique in that it does not form a complex with this reagent in acidic or basic media. After the magnesium is separated from the beryllium, it is determined in the basic medium by means of a flame spectrophotometer; the emission peak at 285 mμ is used. On the basis of the limited number of results obtained, the method appears to be satisfactory; the relative standard deviation is better than 10%. The accuracy and the sensitivity are being evaluated; it is probable that the method will be useful for the determination of less than 50 ppm of magnesium in beryllium oxide.

[110] C. L. Luke and M. E. Campbell, "Photometric Determination of Magnesium in Electronic Nickel," *Anal. Chem.* 26, 1778 (1954).

Studies of Anodized Aluminum

H. L. Holsopple, Jr.

Experiments were conducted at the request of the Electronuclear Research Division to determine the optimum anodizing conditions for aluminum alloy 6061 for producing a thin oxide film of high density, reasonable durability, and high electrical insulating characteristic. A previous report[111] contains results of a literature survey concerning anodizing and oxide treatments for aluminum.

A study was made of the major variables involved in the formation and dissolution of the oxide coating; a sulfuric acid electrolyte was used. The factors examined experimentally were: electrolyte temperature, time of anodization, electrolyte concentration, and current density. Reports have been prepared which contain accumulated data, both tabular and graphical, that show the relationships of the variables.

The temperature of the electrolyte was shown to be the most critical factor in determining the final physical characteristics of the anodic coating. Figure 24 shows how, other conditions being constant, as the temperature was increased the coating ratio (that is, weight of Al_2O_3 film on electrode to weight of Al removed from electrode) decreased. At the higher temperatures, more aluminum was dissolved and the coatings became more porous, with consequent decrease in abrasion resistance and poorer electrical insulating characteristics. The concentration of the sulfuric acid is important in that harder, denser (higher coating ratio) coatings were formed at the lower acid concentrations and at the lower temperatures.

Each 10°F temperature rise resulted in a considerably lower equilibrium value. The data plotted in Fig. 25 indicate that the equilibrium weight of the coating is reduced by about one-half for every 10°F rise in temperature.

[111] H. L. Holsopple, Jr., *Survey of Anodizing Processes for Aluminum*, ORNL CF-59-8-132 (Aug. 27, 1959).

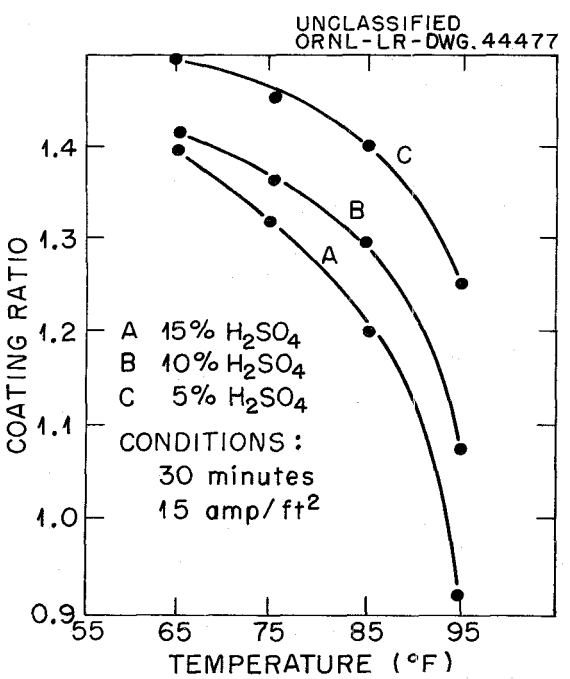

Fig. 24. Variation of Coating Ratio with Electrolyte Temperature.

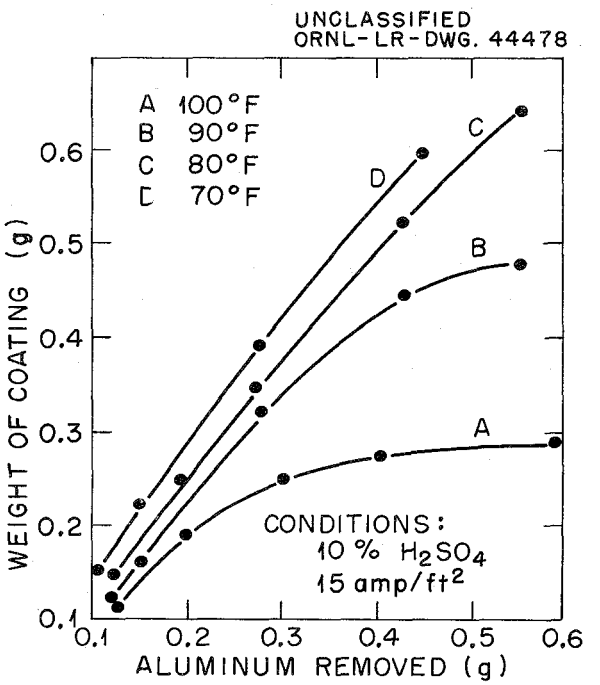

Fig. 25. Relation Between Aluminum Removed and Weight of Coating Formed.

The rate of formation of the anodic coatings was found to be primarily a function of current density as shown in Fig. 26. Other factors affect formation rate only insofar as they affect current density. Thus, at higher current densities thicker coatings were produced in a shorter time than at lower current densities.

The amount of aluminum metal removed was shown to be a measure of the ampere-minutes

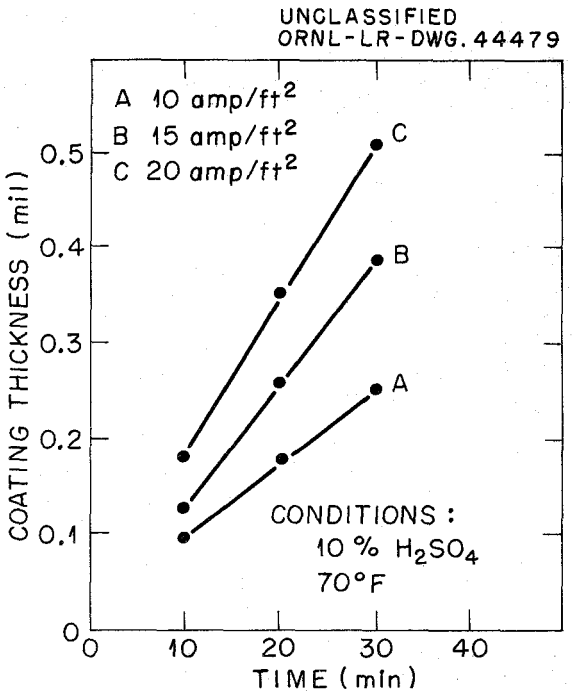

Fig. 26. Variation of Coating Thickness with Time.

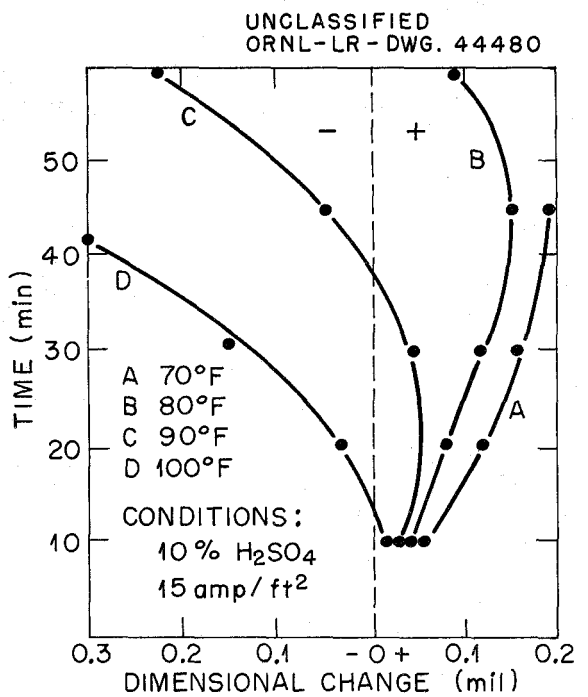

Fig. 27. Effect of Time and Temperature on Dimensional Change.

used in the electrolysis. The average amount of metal removed per ampere-minute was 0.0006 g in 10% sulfuric acid at 70°F.

The highest coating ratios were obtained for the shortest periods of time; thus it was indicated that coatings which remain in contact with the electrolyte are gradually dissolved. This was proved by measuring the amount of alumina dissolved in 10% sulfuric acid solution after various periods of time.

The lower solubility of alumina at lower temperatures resulted in higher coating ratios with, consequently, a smaller over-all dimensional change in the part anodized. Dimensional changes as a function of variations in the temperature of the electrolyte are illustrated in Fig. 27. It is obvious that dimensional decrease occurred sooner and to a greater degree at higher temperatures than at lower ones.

Experimental results indicated that, for coatings of greatest dielectric strength, anodization should be carried out at 20 amp/ft^2 for 30 min in 10% sulfuric acid solution at 70°F.

Testing Laboratory

C. D. Susano H. L. Holsopple, Jr.

The Testing Laboratory was established as a separate entity in May 1959, for the purpose of the specification analysis of materials. Samples of white toilet soap and drafting tape have been received from the Inspection Engineering Department with requests to check the conformance of these materials to Carbide and federal specifications.

Tests made on the soap included the determination of alcohol-insoluble matter, free alkali, volatile content, and total anhydrous soap. The soap met the chemical requirements of specification No. 08-AB-003 ("Carbide and Carbon Chemicals Company, 1955"). Samples of drafting tape from four different vendors were submitted for comparison. Tests were conducted for tensile strength, ultimate elongation, adhesion to steel (initial, after humidity test, and after accelerated aging), and adhesion properties under condition of pressure and temperature (block test). The samples from two vendors conformed to specification No. 10-AE-003 ("Carbide and Carbon

Chemicals Company, 1955"). Three samples did not fully meet specifications.

Methods were evolved for rapidly differentiating between the following base-metal thermocouples: iron-Constantan, Chromel-Alumel, and copper-Constantan.

Procedures were outlined for the spot-test identification of wrought aluminum alloys and wrought magnesium alloys and for differentiating between type 200 and type 300 stainless steel.

In addition, facilities were established and reagents prepared for carrying out tests on anodized aluminum. The "Standard Method of Test for Weight of Coating on Anodically Coated Aluminum" (ASTM Method B 137-45) was used to determine the weight and thickness of oxide on aluminum.

SPECTROCHEMICAL AND X-RAY ANALYSES

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

Chemical Preparation of Samples (X-10)

C. Feldman P. V. Hoffman
C. A. Pritchard M. Murray

Titanium. – Titanium is not extracted by triisooctylamine from 9 *M* aqueous hydrochloric acid solution; the separation of titanium from zirconium is thereby possible. The titanium–hydrogen peroxide complex is extracted by trioctylphosphine oxide.

Boron. – The presence of mannitol prevents the loss of boron during evaporation of neutral or acidic aqueous solutions of borate, even when hydrofluoric acid is present. A report of this work has been issued.[112]

Dissolution of Niobium–Rare-Earth-Element Alloys Without Hydrofluoric Acid. – A 1-g sample is dissolved in molten ammonium bisulfate[113] at ~300°C. The melt is cooled and dissolved in water, and the solution is treated with ammonia. The precipitate thus obtained is dissolved in a mixture of oxalic and nitric acids.

Separation of Iron, Chromium, and Nickel from Niobium. – When niobium is extracted into methylisobutyl ketone (hexone) from aqueous 6 *M* sulfuric acid–10 *M* hydrofluoric acid solution, iron, chromium, and nickel remain quantitatively in the aqueous phase. This separation facilitates their determination when they are present in niobium at trace levels.

Flame Photometry (X-10)

C. Feldman C. A. Pritchard

Cesium – Increase in Sensitivity. – A synergistic enhancement of cesium radiation was obtained by combining the use of methanol as a solvent[114] with the addition of potassium as an enhancing agent.[115] Each of these treatments separately enhanced cesium radiation approximately sixfold compared with the radiation from cesium in aqueous neutral chloride solution. When potassium was present in a concentration of 100 to 200 ppm in a methanol solution of the chlorides, however, a 30-fold increase was obtained. Full-scale deflection was easily obtained at a cesium concentration of 2 μg/ml. This increase in sensitivity is helpful in reducing the size of sample needed for the flame photometric determination of total cesium in highly radioactive solutions of Cs^{137}.

Tissue Analysis (X-10)

S. R. Koirtyohann C. Feldman

Procedure development and organizational work were begun on a new facility for the spectrometric analysis of human-tissue ash. A direct-reading spectrometer (Applied Research Laboratories industrial research quantometer, provided with 33 fixed channels and 9 movable channels) was acquired and put in operation. Efforts are now being made to lower detection limits while retaining good resolution, that is, to reduce the exit slit/entrance slit ratio to ~1.5 while retaining the 20-μ entrance slit. At present, the detection limits of the spectrometer for most elements are three to five times the limits of the photographic method.

[112] C. Feldman and P. V. Hoffman, *Retention of Boron with Mannitol During the Evaporation of Acid and Acid-Fluoride Solutions*, ORNL CF-59-11-87 (Nov. 17, 1959).

[113] C. Feldman, "Ammonium Bisulfate as Fusion Agent for NaF-ZrF_4-UF_4 Fuels and Other Substances," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 73.

[114] C. A. Pritchard, "Flame Photometry," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 44.

[115] E. A. Fabrikova, "Increasing the Sensitivity and Accuracy of the Determination of Cesium in Minerals by the Flame Photometric Method" (translated), *Zhur. Anal. Khim.* 14, 41 (1959).

It was thought desirable for this work to prepare standards in which the trace elements were incorporated into the crystal lattice of the matrix material rather than existing as separate granules or as a surface coating deposited on matrix granules by evaporation. This was done so that the volatilization of trace elements into the arc from standard mixtures would simulate the release process in samples. A synthetic tissue ash was prepared by fusing appropriate trace-element compounds with potassium pyrosulfate, $K_2S_2O_7$, and adding the trace elements in this form to the other main components of the synthetic ash (KPO_3, NaCl, $CaCO_3$, MgO, and Fe_2O_3). One part by weight of a sample or standard was mixed with one part sodium bromide and one part graphite, and the mixture was burned in a $^3/_{16}$-in.-dia electrode at 8 amp.

A commercially available Stallwood jet was found to give good signal stability when used with a mixture of 2 liters of oxygen and 8 liters of helium per minute.

Progress was made in the control of odors during tissue ashing. Two systems proved effective; both involved combustion of the organic vapors. In one arrangement, the vapors were conducted through an electric tube furnace. In the other, they were conducted through a quartz precombustion coil located over a Meeker burner and were then introduced into the gas-air supply of the burner itself. In both cases, a current of air was introduced into the vapor stream in a downstream direction as it left the muffle. The slight reduction in air pressure thus created in the muffle served to prevent escape of odors from the muffle through cracks or openings other than the vent. An air velocity of 4 liters/min was found sufficient for this purpose. This method of introducing air also provided the additional oxygen needed for complete combustion of the vapors without danger of vapor explosions or localized combustion (glowing) of samples in the muffle.

X-Ray Absorption and Fluorescence – Extension of Wavelength Range (X-10)

H. W. Dunn C. Feldman

In order to facilitate absorption measurements with the General Electric XRD-5 x-ray unit at long wavelengths, a helium chamber was designed (see Fig. 28). Complete freedom of motion of the goniometer parts was obtained by making the chamber in three separate sections with Mylar windows at all the points that are penetrated by the x-ray beam except the entrance and exit slits. To permit insertion of absorption cells of various thicknesses (0.2 to 2.0 cm) into the white radiation beam without unduly prolonging the air path, cylindrical walls having different radii of curvature were fabricated for the crystal housing. Appropriate slots were cut in the crystal housing to permit the wall of smaller radius to be used with thicker sample cells and the wall of larger radius with thinner sample cells.

To permit excitation of higher energy levels, the high-voltage transformer was rewound to give 75 kv. Preliminary tests indicated that the unit could withstand this voltage for hours at a time but that the x-ray tube had to be protected against strike-over between cathode and tube housing by means of a jacket containing transformer oil.

X-Ray Absorption-Edge Analysis (X-10)

H. W. Dunn

The pronounced interelement effects encountered in x-ray fluorescence analysis limit its applicability to nonroutine analysis. The absorption-edge method, however, is essentially free from such effects.[116,117] In this method, the sample (usually in solution) is placed in the collimated, white radiation beam. The intensity of the transmitted x-ray beam is measured immediately above and immediately below a critical absorption edge for the element being determined (e.g., the K_α edge of zirconium). For an instrument of infinite resolving power, the ratio of the two intensities depends only on the concentration of the element being determined. Variations in the concentration or nature of other solutes may change the bulk absorption coefficient of the solution but do not affect this ratio except in very rare cases of interference. In practice, a correction must be made for the structure of the absorption edge.

After an empirical calibration with pure zirconium solutions, the recoveries shown in Table 7 were obtained. The results for solutions that

[116] W. F. Peed and H. W. Dunn, ORNL-1265 (Apr. 1952) (classified).

[117] W. B. Wright and R. E. Barringer, *Uranium Analysis by Monochromatic X-Ray Absorption*, Y-1095 (Aug. 26, 1955).

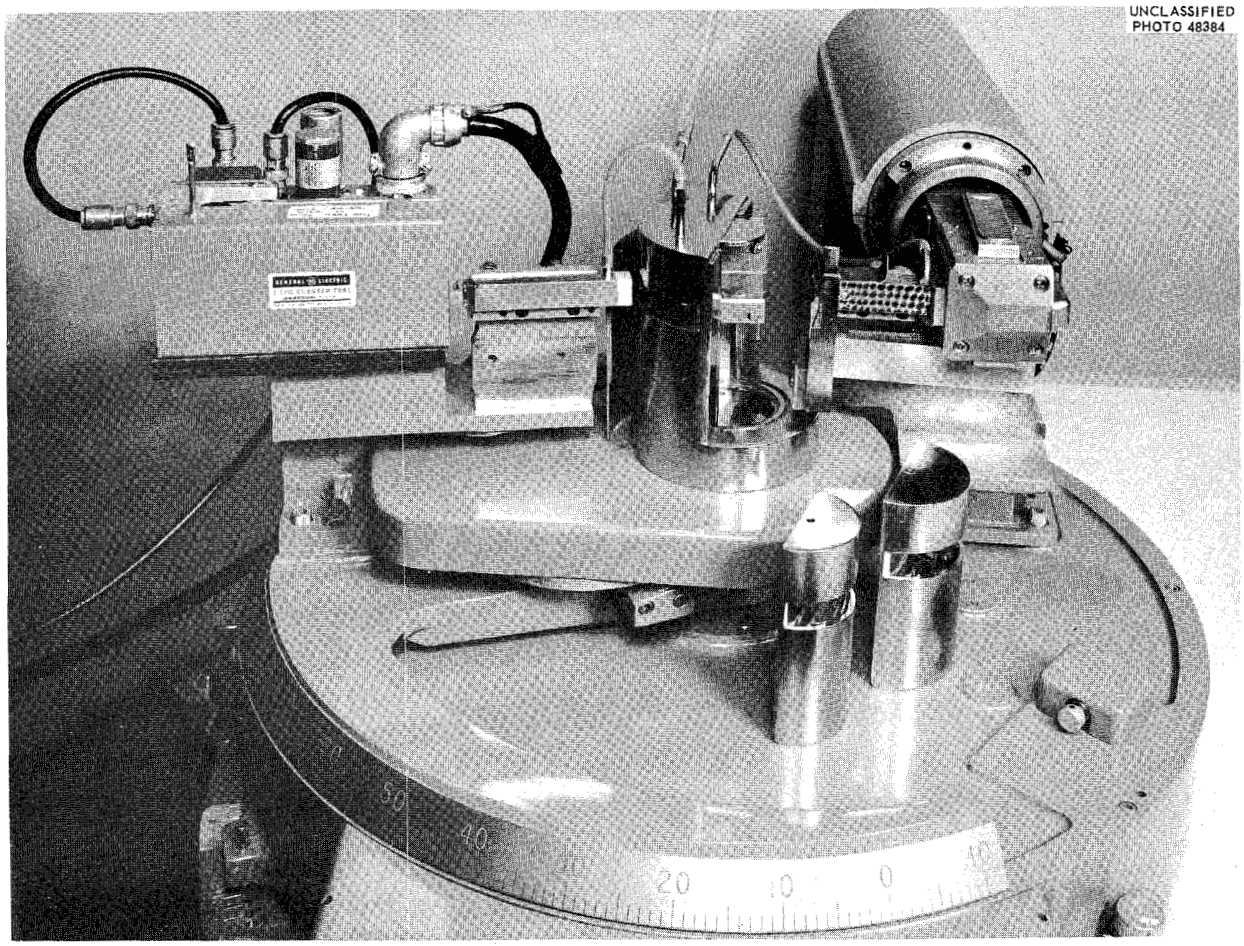

Fig. 28. Helium Chamber for Performing X-Ray Absorption-Edge Analysis on the General Electric XRD-5.

Table 7. Recovery of Zirconium from Solutions in the Absence and Presence of Impurities by X-Ray Absorption-Edge Analysis

Actual Zr Concentration (mg/ml)	Impurities (mg/ml)	Observed Zr Concentration (mg/ml)	Error (%)
0.200		0.203	1.5
1.001		1.009	0.8
5.007		5.006	0.0
25.04		25.04	0.0
0.200	Al, 20.0	0.201	0.5
2.003	Y, 1.00	2.008	0.2
2.003	U, 3.01	2.017	0.7
2.003	Stainless steel, 4.40	2.011	0.4

contained other cations in addition to zirconium were calculated by means of the same parameters and procedures that were used for the pure zirconium solutions. It is evident from the data of Table 7 that the presence of impurities had no measurable effect on the accuracy of the zirconium determination.

The absorption-edge method was applied successfully to the determination of zirconium in zirconium-niobium and zirconium-hafnium alloys in fused-salt reactor fuels and in solutions and residues from the reprocessing of nonradioactive fuel elements. Procedures are now being developed for other elements; a special cell has been prepared for use with alpha-active species.

Electronic Background-Compensating System for Photoelectric Spectrometer (Y-12)

J. A. Norris O. B. Rudolph[118]

Equipment has been designed and built for applying a background correction to measurements made with the photoelectric spectrometer. The wiring diagram is shown schematically in Fig. 29. The multiplier phototube used for measuring the background is placed on the focal curve at 4401 Å. The current from this multiplier phototube charges a 0.1-μf capacitor during a regular analytical exposure. The resulting voltage is monitored by a Keithley electrometer with a voltage output proportional to the capacitor voltage. This electrometer voltage is compared with an externally generated voltage as shown in Fig. 29. The voltage thus established by the balancing system is fed into individual capacitors in each recording channel of a Baird direct reader through variable precision resistors. During the "read" cycle of the electronic system, the background capacitor is connected in series with the regular analytical capacitor, and the reading amplifier triggers at

[118] Physics Division.

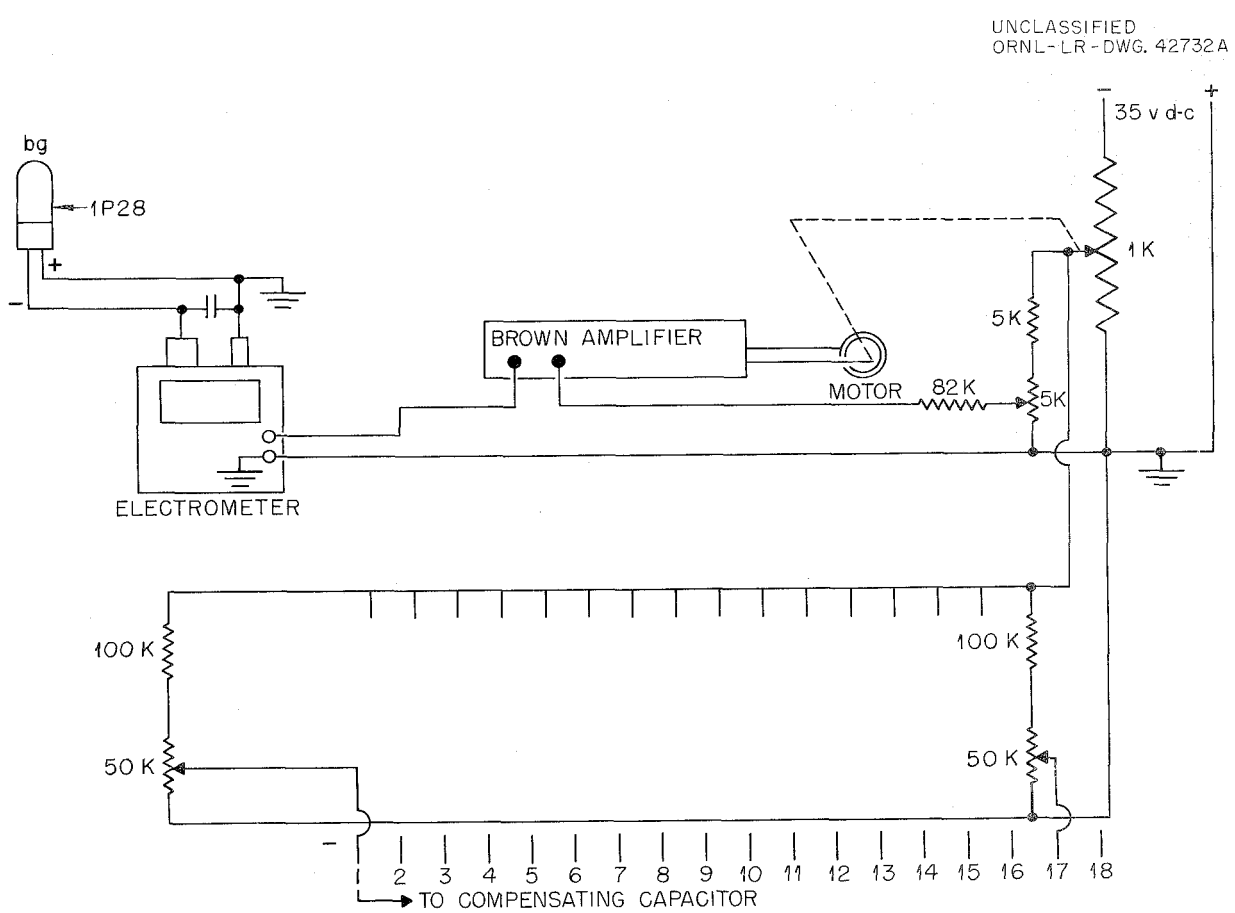

Fig. 29. Schematic Diagram for Electronic Background-Compensating System.

the reduced voltage in the regular manner. Analytical curves for samarium oxide, Sm_2O_3, with and without background compensation are shown in Fig. 30. The corrected curve closely approaches the theoretical background-free curve; this is expected when intensity is linearly related to concentration. The proper background correction is made by exposing a solution of the internal standard only and adjusting the variable resistor to balance out the voltage on the analytical capacitor. The same procedure can be used in work with solid samples by making the background correction when a pure sample of base material is exposed. The internal standard can also be corrected for its associated background.

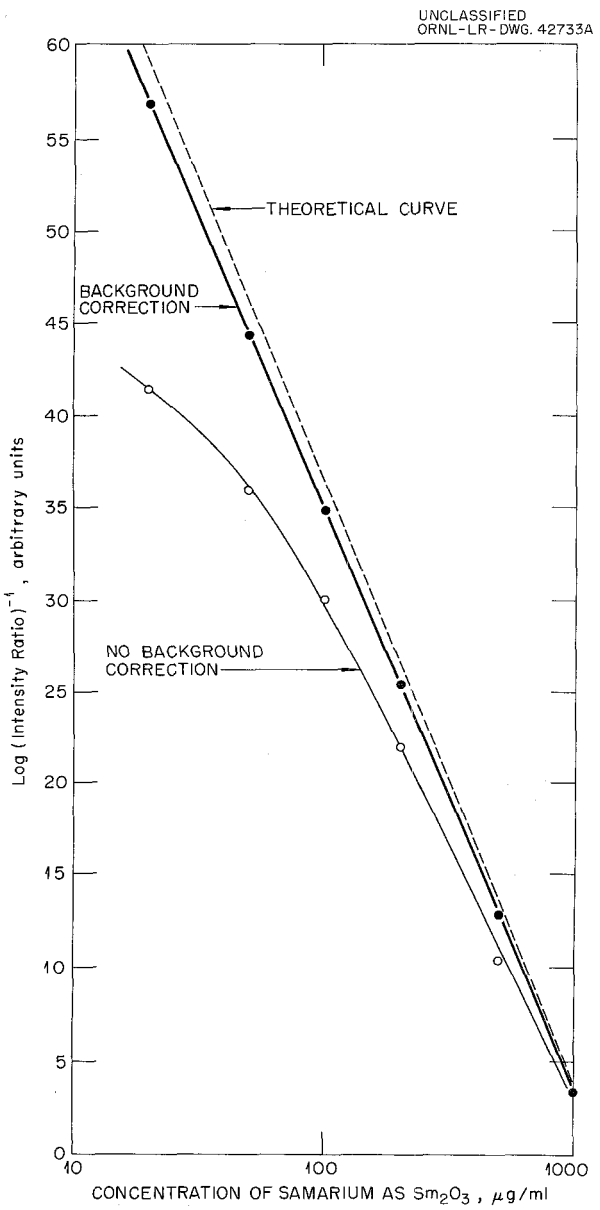

Fig. 30. Analytical Curve for Samarium.

Investigation of Porous-Cup and Revolving-Disk Electrodes by Use of a Photoelectric Spectrometer (Y-12)

J. A. Norris

The investigation of variables associated with the use of porous-cup electrodes in spectrographic analysis has been continued; the operating conditions previously reported[119] were used. The variation of exposure time for multiple exposures of 11 types of porous-cup electrodes and one revolving type, along with the relative dispersion as calculated from variance analyses of each system, is given in Fig. 31. As expected, the relative dispersion is least when the variation of exposure time is minimum. The variation between different lots of electrodes of the same type and from the same manufacturer is greater than can be tolerated for precise analyses. Considerable work has been carried out on the application of the revolving-disk technique. Conditions for making precise analyses are being determined. From preliminary work, it is indicated that results are most reproducible when a disk speed of 40 rpm is used.

Improvements in Equipment for the Spectrometric Determination of Oxygen in Metals (Y-12)

R. E. Weekley

An analog computer has been designed, constructed, and tested and is ready for use with the apparatus for determining gases in metals. This instrument accepts multiplier-phototube currents of millimicroampere magnitude, amplifies the currents, and records either individual spectral line intensities, the ratio of any two spectral line intensities, the ratio of any two intensity-time integrals, or an intensity ratio-time integral. The precision and the accuracy of the computer are unaffected by long-term drift, random thermal

[119] Z. Combs *et al.*, "Investigation of Porous-Cup Electrodes by Use of the Photoelectric Spectrometer," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 74.

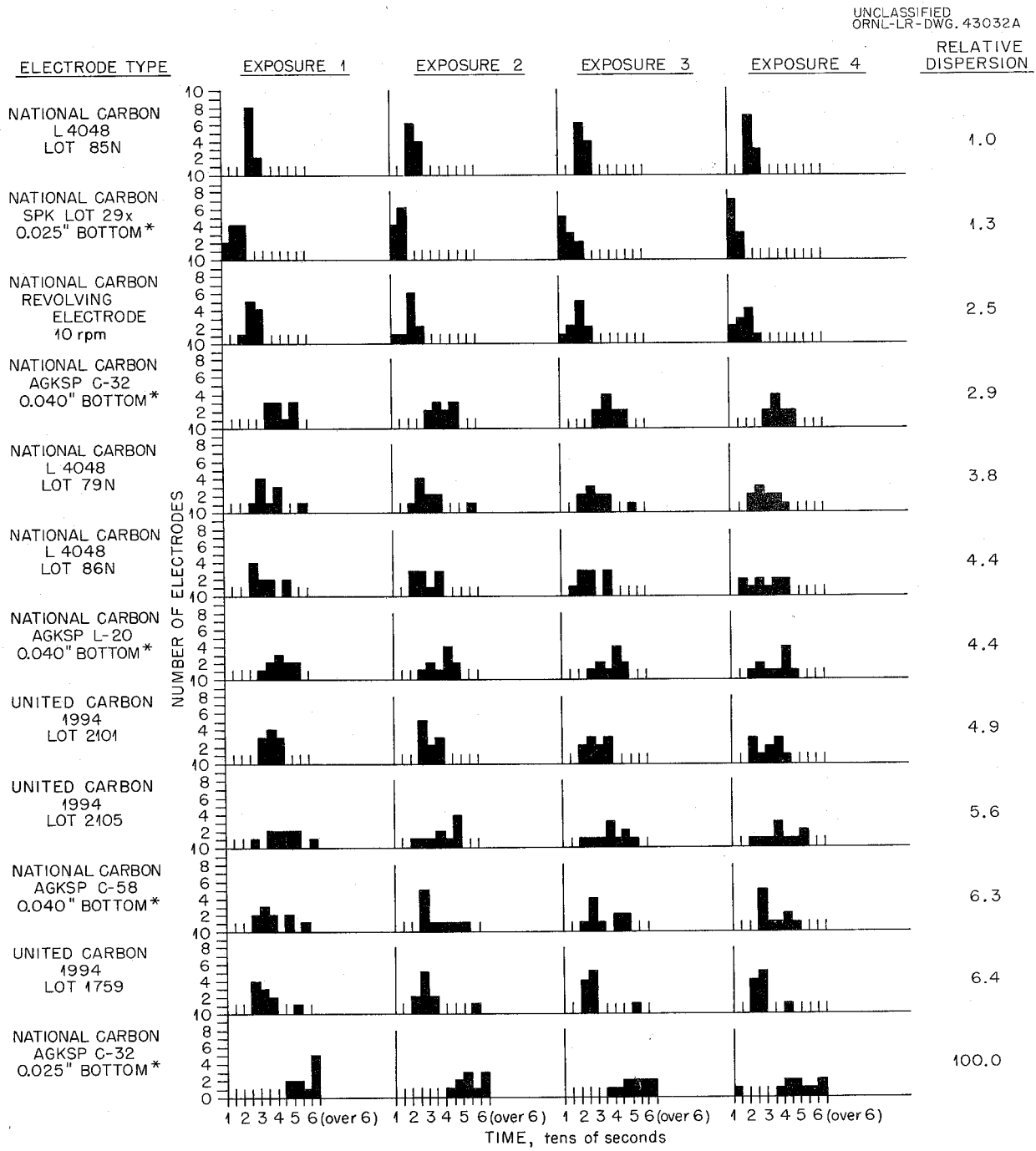

Fig. 31. Variation of Exposure Time for Eleven Types of Porous-Cup Electrodes and One Revolving-Disk Electrode.

noise, and d-c dark currents originating in the multiplier phototubes, and also are insensitive to stray inductive and capacitive effects. This instrument was constructed with commercially available components and a conventional, servo electromechanical current-dividing device. The substitution of photoelectronic detection methods for photographic methods will greatly reduce the analytical time required per sample.

A new control-atmosphere excitation chamber for use in the spectrographic determination of oxygen, nitrogen, and hydrogen in metals is under construction. This two-piece chamber, which is being fabricated of gold-plated copper, is provided with a single quick-release O-ring vacuum seal, water cooling, and a null-balance bridge-type servo system for easily and accurately positioning successive samples with respect to the stationary counter electrode. By eliminating most of the experimental and manipulative difficulties (such as the release of oxide contaminants from the interior surface, the cracking of separators, slow and tedious positioning of samples, and low sample capacity), this new excitation chamber will permit improvements in the precision and accuracy of the analytical method. In addition, it will facilitate both the extension of the basic method to other gas-metal systems and fundamental studies of the mechanism of the evolution of gases from metals in the d-c carbon arc.

THERMAL BREEDER REACTOR PROJECTS ANALYTICAL CHEMISTRY LABORATORY (Y-12)

O. Menis

Flame-Photometric Determination of Palladium in Thorium Oxide

T. C. Rains

A flame-photometric method has been developed for the determination of palladium in slurries of thorium oxide. Palladium is separated from interferences by extracting it as the palladium–α-furildioxime complex[120] from a hydrochloric acid solution into hexone after which the palladium is determined flame photometrically by measurement of its radiant intensity at a wavelength of 363 mμ. Of the minor components commonly present in slurries of thorium oxide, only chromium(VI) interferes; this interference can, however, be eliminated by reducing the chromium(VI) to chromium(III). By the use of a hexone rather than an aqueous solution of the palladium complex, the radiant intensity is increased tenfold. The lower limit of qualitative detection is 0.04 μg of palladium per milliliter of hexone solution aspirated; for this concentration, the response of the 10-mv Brown strip-chart recorder to the radiant intensity is 0.1 mv (i.e., one scale division). In the range of 1 to 6 μg/ml, the relative standard deviation of the method is 3%.

Pyrolytic Separation of Fluoride from Nitrate- and Sulfate-Containing Solutions

T. C. Rains N. M. Ferguson

A study was continued of the evaluation of fission-pyrolysis[121] as a method of separating microgram quantities of fluoride from solutions containing large concentrations of nitric acid and aluminum nitrate and from hydrogen peroxide–containing solution of various sulfates prior to the titration of the fluoride with a solution of thorium nitrate. Interferences with the fluoride titration were encountered when a conventional tungstate flux[121] was used in the pyrolysis of the samples. It was established, however, that when a nitrate-containing sample is made basic and evaporated to dryness and the residue is baked under an infrared lamp to destroy nitrates and then pyrolyzed at 1000°C with uranium trioxide, U_3O_8, as the flux, the fluoride can be volatilized, absorbed in a solution of sodium hydroxide, and titrated without interference. A similar procedure is applicable for sulfate-containing samples except that potassium dichromate is used as the flux and the pyrolysis is carried out at 650°C. For microgram quantities of fluoride, the relative standard deviation is 5% or less.

Flame-Photometric Determination of Iron

T. C. Rains

A study was continued of an extraction procedure for the separation of iron[122] from slurries of

[120] O. Menis and T. C. Rains, "Colorimetric Determination of Palladium with Alpha-Furildioxime," *Anal. Chem.* 27, 1932 (1955).

[121] R. H. Powell, "Separation of Fluoride and Chloride by Fusion Pyrolysis," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 26.

[122] T. C. Rains, "Determination of Iron in Solutions of Uranyl Sulfate and in Other Solutions," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 19.

thorium oxide and from solutions that contained complexing agents, such as fluoride, phosphate, and Versenol, prior to the flame-photometric determination of the iron. It was established that of a number of solvents tested as reagents for the removal of iron from an aqueous solution of hydrochloric acid hexone is best because of its selectivity and its enhancement of the radiant intensity of iron in the flame-photometric determination. Emulsification during the extraction can be prevented by mixing the phases very slowly (i.e., at a rate of about 30 inversions of the separatory funnel per minute). Many interfering elements can be eliminated by backwashing the extract with 6 *M* hydrochloric acid. In order to remove the last trace of thorium from samples that contain this element, the hydrochloric acid solutions used to backwash the extract should also be 0.1 *M* in hydrofluoric acid.[123] The flame-photometric measurement is made on the hexone extraction at 372 mμ. The lower limit of qualitative detection is 0.03 μg of iron per milliliter of hexone solution aspirated; for this concentration, the response of the 10-mv Brown strip-chart recorder to the radiant intensity is 0.1 mv (i.e., one scale division). Over the iron concentration range of 1 to 50 μg/ml, the calibration curve is linear, and the relative standard deviation is 4%.

Potentiometric Determination of Rare-Earth Elements

T. C. Rains

A potentiometric titration method was applied to the determination of microgram quantities of the rare-earth elements. In this procedure the rare-earth element is titrated with a standard solution of disodium dihydrogen ethylenediaminetetraacetate. The end point is established potentiometrically by means of the Dow Precision Recordomatic Titrometer; an amalgamated gold electrode[124] is used as the indicator electrode, and the medium is an aqueous solution that contains 1 drop of 0.01 *M* mercury(II)–disodium dihydrogen ethylenediaminetetraacetate indicator solution. It was established that 50 μg of lanthanum or samarium can be titrated satisfactorily by this means in a 0.05 *M* acetate medium of pH 4.6. With increasing acetate concentration, the potential break becomes less defined. If the solution is heated to 75°C, however, the end point is satisfactory even in 0.5 *M* acetate. From 50 to 250 μg of lanthanum or samarium can be titrated by means of a 0.0001 *M* solution of disodium dihydrogen ethylenediaminetetraacetate with a relative standard deviation of 5%.

Evaluation of Flame Photometry for the Determination of Rare-Earth Elements

T. C. Rains

An investigation was made of the applicability of flame photometry to the estimation of rare-earth elements alone or in mixtures thereof. The hexone (4-methyl-2-pentanone) extract of the 2-thenoyltrifluoroacetone chelate of each of the rare-earth elements was aspirated directly into an oxygen-hydrogen flame, and the emission spectra (see Fig. 32) were recorded over the wavelength range from 380 to 800 mμ by means of an ORNL model Q-1457A single-beam flame photometer. The wavelengths of band crests and lines were fixed from spectra data recorded photographically with a prism spectrograph. These wavelengths, the relative spectral intensity of all lines and bands, and also the widths of all bands have been tabulated.[125] The tabulated data can be used as a guide in establishing necessary separation procedures prior to the flame-photometric determination of specific rare-earth elements. By judicious selection of the wavelength, it is possible to estimate many of the rare-earth elements without encountering serious interference from others of the group. Furthermore, if fractional group separations are made by means of selective solvent extraction, the effects of interfering elements can often be reduced to tolerable limits. A paper that describes this work in detail has been accepted for publication in *Analytica Chimica Acta.*

[123] T. C. Rains and O. Menis, *Flame Photometric Determination of Iron, Parts I, II, III and IV,* ORNL CF-59-5-48 (May 6, 1959).

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

[125] T. C. Rains, H. P. House, and O. Menis, *Evaluation of Flame Photometry for the Determination of Elements of the Rare-Earth Group,* ORNL CF-59-8-141 (Aug. 27, 1959).

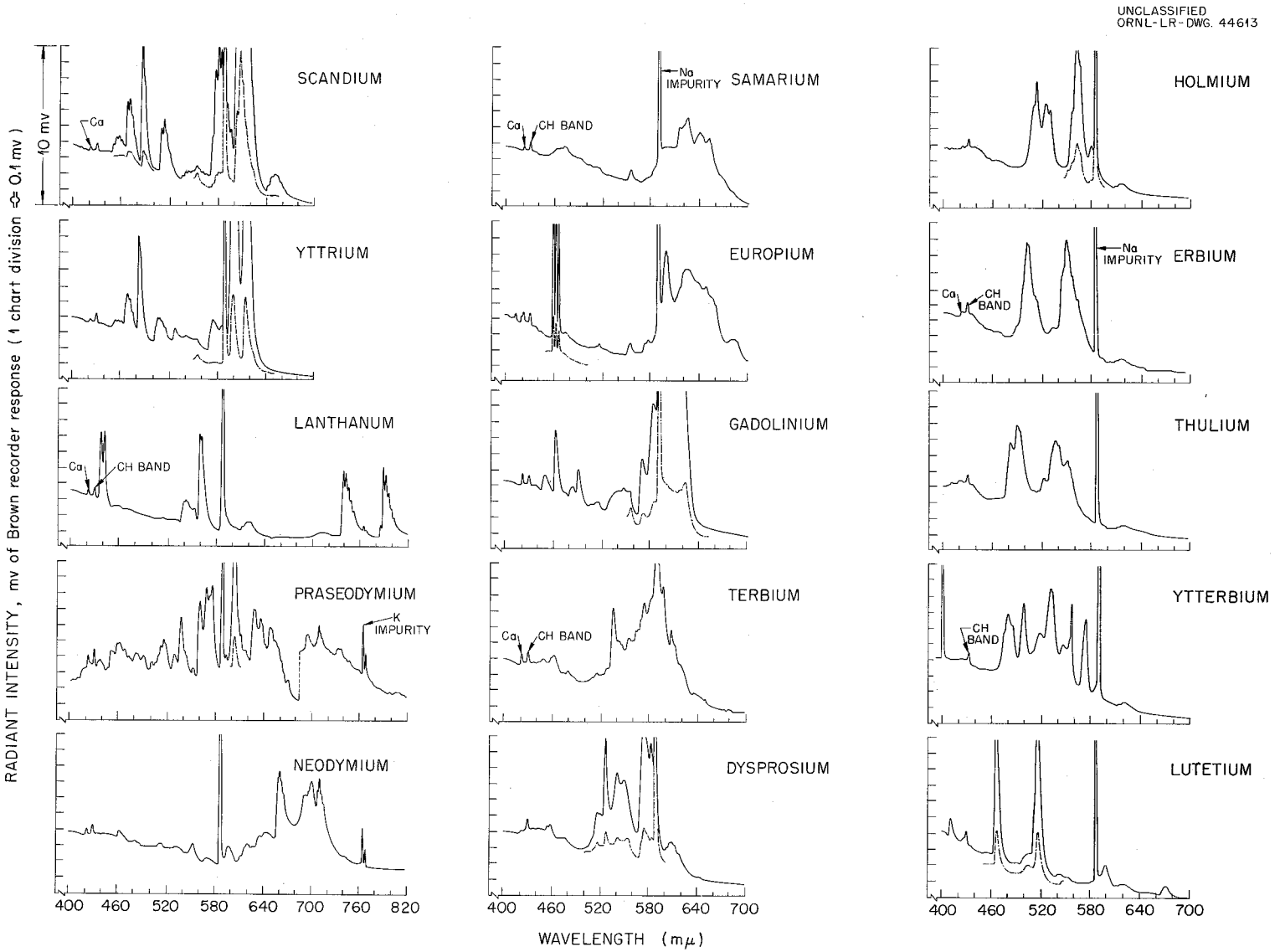

Fig. 32. Flame Emission Spectra of the Rare-Earth Elements.

High-Frequency Titration of Sulfate and Free Acid in Solutions of Uranyl Sulfate

D. L. Manning

A high-frequency method of titration[126] was used for the direct determination of sulfate and free acid in solutions of uranyl sulfate. Sulfate was titrated with a standard solution of barium chloride, and the end point of the titration was established by high-frequency oscillometry. Uranium must be masked with citrate or fluoride; otherwise, the high-frequency titration curve is a continuous straight line rather than two segments of different slope. For the titration of 40 to 70 mg of sulfate, the relative standard deviation is about 2%. Free acid can be determined in a similar manner by using a standard solution of sodium hydroxide as the titrant. Milligram quantities of uranium do not interfere. By continuing the acid titration to a second break (abrupt change in slope), an approximate value of the uranium content of the solution can also be established. This method, however, is not recommended for the accurate determination of uranium because of the nonstoichiometric nature of the reaction between uranium(VI) and sodium hydroxide.[127] For the determination of approximately 0.2 meq of free acid, the relative standard deviation is about 2%.

Polarographic Determination of Molybdenum

R. G. Ball D. L. Manning

A derivative polarographic method was developed for the determination of low concentrations of molybdenum in impure slurry mixtures of thorium oxide and UO_x. The method is based on the reduction waves of molybdenum, whose half-wave potentials are −0.48 v and −0.64 v vs the S.C.E. in a 0.15 *M* aqueous solution of nitrilotriacetic acid of pH 3. By use of the −0.64 v wave and the standard-addition technique, molybdenum in the concentration range of 20 to 200 μg/ml can be estimated with a relative standard deviation of approximately 5%. Uranium(VI) and chromium(VI) can be tolerated in concentrations up to about ten times that of the molybdenum. The interferences from iron(III) and nickel(II) are more severe. Iron(III) can be present in a concentration approximately seven times that of the molybdenum, whereas the tolerance limit for nickel is a concentration only one-tenth that of the molybdenum.

Spectrophotometric Determination of Osmium

G. Goldstein D. L. Manning

Spectrophotometric methods were developed for the determination of either microgram or milligram quantities of osmium.[128] For milligram quantities, the osmium is oxidized to osmium(VIII) and selectively extracted into chloroform; the absorbancy of the chloroform extract is measured in the ultraviolet region of the spectrum. Of the ions tested, only chloride and ruthenium(VIII) interfere. For 0.4 to 3 mg of osmium per 25-ml final volume, the relative standard deviation is 3%.

For smaller quantities of osmium, a more sensitive method consists in reacting the chloroform extract that contains osmium(VIII) with diphenylcarbazide and, after 2 hr, measuring at 560 mμ the absorbancy of the complex formed. Interferences are the same as for the preceding method. Over the range of 30 to 100 μg of osmium per 25-ml final volume, Beer's law is obeyed, and the relative standard deviation is about 4%.

Still greater sensitivity can be achieved by developing the osmium-diphenylcarbazide complex in an aqueous solution at 65°C, extracting the complex into chloroform, and measuring the absorbancy of the extract. Under these conditions, osmium in the final solution in the concentration range from 0.2 to 1.0 μg/ml can be determined with a relative standard deviation of about 6%. This procedure is less susceptible to interferences than those previously outlined.[129] Iron(III), copper(II), ruthenium(III), and gold(III) interfere seriously, whereas chromium(VI), nickel(II), molybdenum(VI), iridium(III), and chloride interfere only when present in high concentrations.

---

[126] D. L. Manning, "Determination of Thorium," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 22.

[127] C. J. Rodden, *Analytical Chemistry of the Manhattan Project*, p 74, McGraw-Hill, New York, 1950.

[128] G. Goldstein, *A Study of Spectrophotometric Methods for the Determination of Osmium*, M. S. Thesis, University of Tennessee, Aug. 1959.

[129] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3d ed., p 699, Interscience, New York, 1959.

Determination of Uranium(IV) in Thorium Oxide

D. L. Manning

In order to establish the uranium(IV)-to-uranium(VI) ratio in refractory ThO_2-UO_x preparations and aqueous slurries thereof, it was necessary to devise a method for the dissolution of the sample in which the air oxidation of the uranium(IV) is avoided. For this purpose, the sample was dissolved under reflux in 7 *M* phosphoric acid solution that contained a trace of hydrofluoric acid and an excess of a standard solution of potassium dichromate. Following the dissolution, the uranium(IV) was determined by the conventional method in which the excess dichromate is titrated with a standard solution of ferrous sulfate.

Spectrophotometric Determination of Uranium(VI)

D. L. Manning

The procedure of Spinner and Miller[130] for the spectrophotometric determination of uranium(VI) with 1-(2-pyridylazo)-2-naphthol was found to be applicable to the determination of uranium(VI) in the parts-per-million concentration range in thorium oxide–uranium oxide mixtures that may contain corrosion products of stainless steel, various additives, and other impurities. The uranium(VI) is reacted with the reagent in a basic solution (pH 10), following which the insoluble uranium(VI)–1-(2-pyridylazo)-2-naphthol complex is solubilized by extracting it into chloroform. Spinner and Miller used chlorobenzene as the extractant and then centrifuged the mixture of solutions in order to separate the phases. By the use of chloroform as the extractant, the procedure was shortened. The red complex in the chloroform phase exhibits maximum absorbancy at 550 mμ and has a molar absorbancy index of 18,000. The reagent is made nearly specific for uranium(VI) when disodium dihydrogen ethylenediaminetetraacetate, acetate, and cyanide are used as masking agents. If a 1-g test portion of mixed thorium oxide–uranium oxide is taken for analysis, as little as 20 ppm of uranium(VI) in the mixture can be determined. When 20 to 120 μg of uranium(VI) is present in 10 ml of the chloroform phase used for the absorbancy measurement, the relative standard deviation is about 5%.

Determination of Uranium(IV)-to-Uranium(VI) Ratio in Thorium Oxide–Uranium Oxide Mixtures

C. M. Boyd

A controlled-potential coulometric titration method has been applied to the determination of the uranium(IV)-to-uranium(VI) ratio in mixtures of thorium oxide and uranium oxide. The samples are dissolved by refluxing them in either concentrated hydrochloric acid or a 7 *M* solution of phosphoric acid under an atmosphere of argon in order to prevent air oxidation of uranium(IV). The uranium(VI) is then determined by coulometric reduction at −0.3 v vs the silver–silver chloride electrode. A second test portion of the solution is fumed with perchloric acid to oxidize the uranium(IV) to uranium(VI), after which the total uranium(VI) is determined by coulometric reduction. The difference in the amount of uranium(VI) found in the original solution and in the oxidized solution is equal to the uranium(IV) in the sample.

Any iron(III) and chromium(VI) will interfere by being reduced along with the uranium(VI). These interferences cannot be prereduced in the hydrochloric acid medium; a correction is therefore made that is based on the amounts of each found to be present by spectrophotometric analysis. When the coulometric titrations are made in a 3 *M* phosphoric acid medium, the interferences of iron(III) and chromium(VI) can be prevented by a prereduction at 0.0 v vs the silver–silver chloride electrode prior to the reduction of uranium(VI) at −0.3 v. The optimum prereduction potential is affected slightly by the phosphoric acid concentration and by the ratios of iron(III) to uranium(VI) and of chromium(VI) to uranium(VI).

The results of the coulometric titration analysis for the uranium(IV)-to-uranium(VI) ratio agree within 5% of those obtained by the method that consists in the dissolution of the sample in phosphoric acid that contains an excess of a standard solution of dichromate and the subsequent titration of the excess dichromate with a standard iron(II) solution. The coulometric titration method has the particular advantage of being applicable to the titration of less than 1 mg of uranium(VI).

---

[130] I. H. Spinner and F. C. Miller, *The Application of the 1-(2-Pyridylazo)-2 Naphthol Method of Uranium Analysis to Thorium Process Solutions*, CRDC-837, AECL-789 (Feb. 1959).

Determination of Uranium(IV) by Direct Coulometric Oxidation

C. M. Boyd

The direct coulometric oxidation of uranium(IV) at a controlled potential was investigated for application to the determination of uranium(IV) in thorium oxide–uranium oxide mixtures. The uranium(IV)-uranium(VI) couple is irreversible, but it was established that uranium(IV) can be titrated coulometrically by oxidizing it to uranium(VI) at a platinum electrode whose potential is +1.4 v vs a silver–silver chloride electrode. In tests carried out with sample solutions that contained 1 and 10 mg of uranium(IV), the relative standard deviation was 10 and 1%, respectively. For the lower quantities of uranium(IV), the poor precision is due to the relatively large correction that must be applied for the decomposition of water. Chromium(III) does not interfere since it is not oxidized at this potential. The interference of iron(II) can be avoided by preoxidizing the iron(II) at a potential of +0.4 v vs a silver–silver chloride electrode.

Spectrophotometric Determination of Cobalt in Aluminum

G. Goldstein D. L. Manning

A method having a relative standard deviation of less than 1% was required for the determination of approximately 0.15% of cobalt in high-purity aluminum. For this purpose, high-absorbancy spectrophotometry[131] by means of the chromogenic reagent 1-(2-pyridylazo)-2-napthol[132] was applied to the determination of cobalt. A reference standard that contained 50 μg of cobalt and sample aliquots were processed and, after color development, the absorbancies of the samples were measured vs the reference standard. When a 1% error in the transmittancy measurement was assumed, the corresponding error in a single measurement of the cobalt concentration of the final test solution was 0.9%. The relative standard deviation for five cobalt determinations was 0.5%.

[131] R. Bastian, "Determination of High Percentages of Copper," *Anal. Chem.* 21, 972 (1949).

[132] G. Goldstein, D. L. Manning, and O. Menis, "Spectrophotometric Determination of Cobalt with 1-(2-Pyridylazo)-2-naphthol," *Anal. Chem.* 31, 192 (1959).

Simultaneous Extraction and Determination of Neodymium and Samarium

H. R. Hunt[133] O. Menis

In the study of the flame-photometric determination of neodymium,[134] it was established that, of the other rare-earth elements, only samarium and europium interfere. Because of the similarity of their distribution ratios, samarium and europium accompany neodymium when it is extracted by means of 2-thenoyltrifluoroacetone in organic solvents. A study was therefore initiated to develop a method for determining both neodymium and samarium in samples that contained both without separating them.

From a knowledge of the distribution ratios of n components and the amounts of each component extracted under n different extraction conditions (e.g., different pH values) the concentration of each component could be calculated by means of simultaneous equations. For the determination of neodymium and samarium in mixtures, the calculation was made as follows:

$$t_1 = C_A + C_B \ ,$$

$$t_2 = F_A C_A + F_B C_B \ ,$$

where

C_A, C_B = micromoles of Nd and Sm in the sample solution, respectively,

F_A, F_B = fraction of Nd and Sm unextracted, respectively,

t_1, t_2 = total micromoles of Nd and Sm in sample and in aqueous phase after extraction, respectively.

Values for F_A and F_B were calculated from the known distribution coefficient, D, for each $[F = (D + 1)/D]$; t_1 and t_2 were determined by a spectrophotometric titration; C_A and C_B were then calculated from the simultaneous equations.

Optimum experimental conditions, including pH range, concentration of chelating agent, equilibration time, and procedure for determining the total rare-earth elements in sample and raffinates

[133] Research participant from Georgia Tech., Atlanta.

[134] I. B. Rubin and T. C. Rains, "Flame Photometric Determination of Neodymium in Solutions of Uranyl Sulfate," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1958*, ORNL-2662, p 18.

were established experimentally. For this purpose, a spectrophotometric titration was used in which disodium dihydrogen ethylenediaminetetraacetate is added in excess, and the excess is determined by titration with zinc acetate.[135] The relative standard deviation is 2%.

Test results for a series of tests with mixtures that contained a total of 6 μmoles of neodymium and samarium in various ratios are presented in Table 8. The relative standard deviation is within limits consistent with the relative standard deviation of the method used for the determination of the total neodymium and samarium in sample and raffinate. It is also consistent with the estimated relative standard deviation based on the product of the relative standard deviation of the titration and the difference between the extraction coefficients. A study in which a more precise method for the determination of total concentration of rare-earth elements is used will be included in future work on this project.

[135] F. J. Welcher, *The Analytical Uses of Ethylenediaminetetraacetic Acid*, p 168, Van Nostrand, New York, 1958.

Complexometric Titration of Thorium by Use of Xylenol Orange as Indicator

F. L. Layton

A complexometric method for the direct titration of various metals by means of the reagent disodium dihydrogen ethylenediaminetetraacetate and the indicator xylenol orange[136] was applied to the determination of thorium in slurries of thorium oxide, many of which also contained uranium(VI) and numerous minor components. A glycine-acetate buffer solution was found to offer distinct advantages over other buffers previously used.[137] It was established that, in the solution titrated, 10 mg of uranium(VI), 30 mg of aluminum(III), 6 mg of chromium(VI), 1 mg of nickel(II), and 1 mg of iron(II) do not interfere. Iron(III), even in submilligram amounts, interferes and must be reduced to iron(II). Over the range of 15 to 70 mg of thorium, the relative standard deviation of the method is 0.2%.

[136] J. Körbl and R. Pribil, "Xylenol Orange: New Indicator for the EDTA Titration," *Chemist Analyst* 45(4), 102 (1956).

[137] F. L. Layton, *The Application of Xylenol Orange Indicator in the Complexometric Titration of Thorium*, ORNL CF-59-9-38 (Sept. 9, 1959).

Table 8. Accuracy and Precision of the Determination of Samarium and Neodymium in Mixtures

Conditions: Acetate, 1 *M*; thenoyltrifluoroacetone, 0.1 *M* in CCl_4
pH, 4.6
Fraction unextracted: F_A, Nd = 0.49
F_B, Sm = 0.30
Equilibration time, 16 hr
Values calculated by means of simultaneous equations

Mixture	Samarium				Neodymium			
	Present (μg/ml)	Found (μg/ml)	Difference (μg/ml)	Recovery (%)	Present (μg/ml)	Found (μg/ml)	Difference (μg/ml)	Recovery (%)
1	40.0	48.2	8.2	121				
2					41.1	39.8	1.3	97
3	29.9	27.5	2.4	92	11.4	13.1	1.7	117
4	20.0	18.8	1.2	94	21.2	22.4	1.2	107
5	20.0	17.6	2.4	88	21.2	23.4	2.2	110
6	9.9	10.4	0.5	105	31.1	30.6	0.5	97

SERVICE ANALYSES

A summary of the service analyses made by the laboratories of the Analytical Chemistry Division is given in Table 9.

GENERAL SERVICES (Y-12)

L. J. Brady

Counting Laboratory

J. M. Peele

The Counting Laboratory processed 3150 samples during the past year and reported 3552 results. The largest group of these samples was from the Chemical Technology Division and consisted of aqueous and organic samples derived from several different projects. These projects include investigations of solvent extraction of the transuranium elements, the extraction of zirconium-niobium tracer with tributyl phosphate, decontamination experiments on synthetic reactor waste solutions, and the selective extraction of strontium from synthetic reactor waste solutions. The majority of the aqueous samples were solutions of nitric acid, and the organic samples consisted of an organophosphorus or organonitrogen extractant in an inert solvent.

Radiochemical methods were used to determine plutonium, neptunium, americium, ruthenium, zirconium, niobium, total rare-earth elements, gross gamma activity, and gross beta activity. Nonradiochemical methods were used for the determination of uranium, iron, aluminum, thorium, sodium, and free acid.

Samples from the Reactor Chemistry Division were counted for gross gamma activity. These samples were mixtures of fluoride salts to which Ce^{144}, Fe^{59}, or Cr^{51} had been added as a radioactive tracer.

Other samples from the Reactor Chemistry Division were derived from an experiment with Cr^{51} tracer made in order to determine the extent of diffusion of chromium from a molten fluoride salt mixture into the walls of a stainless steel test loop. At the completion of the test, a portion of the loop was cut into small sections, each of which was counted directly in the well of the gamma scintillation counter. The Cr^{51} was then removed from the walls of the metallic specimens by an electropolishing method. The extent of penetration of chromium into the stainless steel was determined by counting both the electrolyte solutions and the metal specimens after successive periods of electropolishing.

Miscellaneous Analyses Laboratory

E. C. Lynn

The staff of the Miscellaneous Analyses Laboratory analyzed approximately 4500 samples during the past year. Studies by the Chemistry Division of chemical-exchange methods of isotopic enrichment accounted for almost half the samples.

Specification testing of metals, alloys, oils, soaps and cleaners, plastic tubing, paint, and ink continued; standard ASTM methods were used where possible.

Samples of sintered uranium dioxide derived from studies conducted by the Ceramics Research Group were analyzed for uranium, nitride, fluoride, and iron. Uranium was determined volumetrically by titration with standard ceric sulfate solution. Nitrogen was distilled as ammonia from alkaline solution, and the concentration in the distillate was determined either spectrophotometrically by use of Nessler's reagent or volumetrically, depending on the range of the concentration of ammonia. The fluoride was separated from uranium by pyrohydrolysis and was then determined in the condensate by the spectrophotometric Thoron method. The spectrophotometric *o*-phenanthroline method was used for the determination of the iron content of these samples.

A series of oil samples that had been subjected to radiation for various times was tested to determine the bromine number, viscosity, and acidity.

Samples of yttrium metal and yttrium-magnesium alloys were analyzed for fluoride. The samples were dissolved by the cautious addition of dilute perchloric acid, after which the fluoride was distilled by the Willard and Winter method, and then determined.

For the Ecology Group of the Health Physics Division, samples of pine needles were prepared for spectrographic analysis by wet ashing the samples with nitric and perchloric acids and then making group separations of the cations present.

In addition, a wide variety of samples derived from many different sources have been analyzed by both micro and macro methods.

Table 9. Summary of Analytical Service Work

Group Making Analyses	Number of Persons		Number of Results Reported																									
			For ORNL																		For Others							
	Scientists	Technicians	Analytical Chemistry	Biology	Chemical Technology	Chemistry	Director's	Electronuclear Research	Health Physics	Instrumentation and Controls	Isotopes	Metallurgy	Neutron Physics	Operations	Physics	Reactor Chemistry	Reactor Experimental Engineering	Reactor Projects	Solid State	Thermonuclear Experimental (Sherwood Project)	Armour Research Foundation	K-25	Miscellaneous	North Carolina State College	Paducah	University of Tennessee	Y-12	Total
General Services (Y-12)	1																											
Counting Laboratory	1	1			2,934											604		13									1	3,552
Miscellaneous Analyses Laboratory and Raw Materials Laboratory*	2	10	1010		16,794	2986	45		40		55	215	6			236	540	369	5			6	10				309	22,626
Ionic Analyses* (X-10)	12	0	26		620	116			234		8	260	50		166	683	123	76										2,362
Low-Radiation-Level Radiochemical Analytical Laboratory (X-10)	2	1			73				1,620		6		2				3									174		1,878
Mass Spectrometric Analyses* (Y-12)	10	6	2381	164	249	1047					3,085	2,554	23		56	4,410	164	14,324	187				106				6596	35,346
Nuclear Analyses* (X-10)	6	6	76		1,051	43	1518		34	5	8	1,102	1	5,396	52	63	677	516	427	2								10,971
Optical and Electron Microscopy* (X-10)	3	3	44	1784	468	80	56	4	72	112		356			24		308	28					88					3,424
Process Analyses (X-10)	1																											
High-Alpha Analytical Laboratory	2	3			11,545	29		256				10	242			65			2								22	12,171
Pilot Plant Control Laboratory	8	11			40,615	10			4		4,813	20	590	3,012			27	1,084	17						2			50,194
Process-Development Analytical Laboratory	3	6	44		21,844	31			134		4	123	5	128			63											22,376
Radioisotopes-Radiochemistry Laboratory	3	18			3,725	1519	526		2,916		25,000	77	725	534			117	463	233				183				1012	37,030
Reactor Analyses Laboratory	5	7			280	1			25		12		1			128	11,434				19			39				11,939
Special Analyses Laboratory	10	8		10	15,527	25			2,242		1,167	8,858	307	1,127	11	3,550	826		15									33,665
Radiochemical Analyses* (X-10)	5	1	16		560	5	40		1,365		213		131	122	20		365	6	302			4	12			66		3,227
Reactor Projects Laboratory* (Y-12)	11	5														11,917		2,551					1188					15,656
Spectrochemical and X-Ray Analyses* (X-10)	8	2	10	3	1,716	276	45		186	13	118	1,171	206	276	118	269	2,384	1,029	17	10								7,847
Spectrochemistry Laboratory* (Y-12)	4	1	2529		3,466	80	36	75	1,230		9,400	2,613	35		248	2,630	1,786	650		58							1289	26,125
Thermal Breeder Reactor Projects Analytical Chemistry Laboratory* (Y-12)	8	8			1,600	41	20		49			326					75,835	14									115	78,000
Total	105	97	6136	1961	123,067	6289	2286	335	10,151	130	43,889	17,685	2324	10,595	695	24,555	94,652	21,123	1205	70	19	10	1587	39	2	240	9344	378,389

*These groups also do research and development work.

Raw Materials Laboratory

J. R. Lund E. C. Lynn

During the past year, the staff of the Raw Materials Analytical Laboratory reported approximately 17,200 results on nearly 6400 samples. Most of these samples were derived from studies of solvent-extraction processes in which organophosphorus compounds, high-molecular-weight amines, or quaternary ammonium compounds were used as extractants. The media from which the extractions were made consisted principally of sulfuric acid leach liquors, such as leach liquors of monazite sand and Blind River leach liquor; approximately neutral solutions of high ionic strength, principally 0.5 to 5 *M* solutions of sodium sulfate; and very basic solutions of sodium hydroxide and/or sodium carbonate and ammonium carbonate.

Some of the methods commonly used for the various determinations are summarized below.

Method	Constituent
Spectrophotometric	U, Th, Mo, Fe, V
Fluorometric	U
Gravimetric	SO_4^{2-}, CO_3^{2-}
Volumetric	NH_3, U, Th, Fe, V

The constituent for which the most analyses were made was uranium, followed in order by thorium, iron, molybdenum, vanadium, ammonia, sulfate, and carbonate. The organic extractants, organophosphorus compounds, amines, and quaternary ammonium compounds, and the aqueous leach solutions were generally analyzed for one or more of the following metals: uranium, thorium, iron, vanadium, or molybdenum. In addition to the above-mentioned constituents, analyses for ammonia, carbonate, and sulfate were made on many of the aqueous solutions.

The wide diversity of the work can perhaps best be visualized when it is considered that only constituents for which more than 300 analyses were made during the year are included in the above table and that only approximately 40% of the reported analyses are represented by these constituents. Thus, about 60% of the work consisted in analyses for constituents that were determined less frequently than once per day. These less-frequent tests included such physical measurements as specific gravity, refractive index, viscosity, interfacial tension, and the coulometric determination of traces of water in organic media.

IONIC ANALYSES (X-10)

P. F. Thomason

Ionic service analyses were related to the Reactor Chemistry Division's research in HR fuels and the Chemical Technology Division's studies of the reprocessing of fuels from power reactors. Analyses relative to the studies of disposal of purex wastes in salt mines were made for the Health Physics Division. Analyses for the Metallurgy Division were related to their development of alloy-type fuel elements.

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

C. L. Burros

The Low-Radiation-Level Radiochemical Analytical Laboratory was completed and occupied in February. Since the primary purpose of the laboratory is to analyze and count samples of low levels of radioactivity, maximum precautions were taken in the location and design of the building in order to ensure the lowest possible background radiation. The floor plan is shown in Fig. 33.

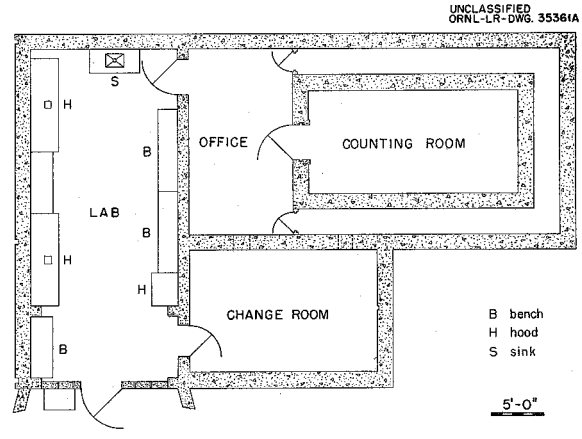

Fig. 33. Floor Plan of Low-Radiation-Level Radiochemical Analytical Laboratory.

The following instruments (Fig. 34) have been put into operation in the laboratory: alpha-range analyzer, a low-background beta counter, a 200-channel gamma scintillation spectrometer, gamma scintillation counters, and G-M counters.

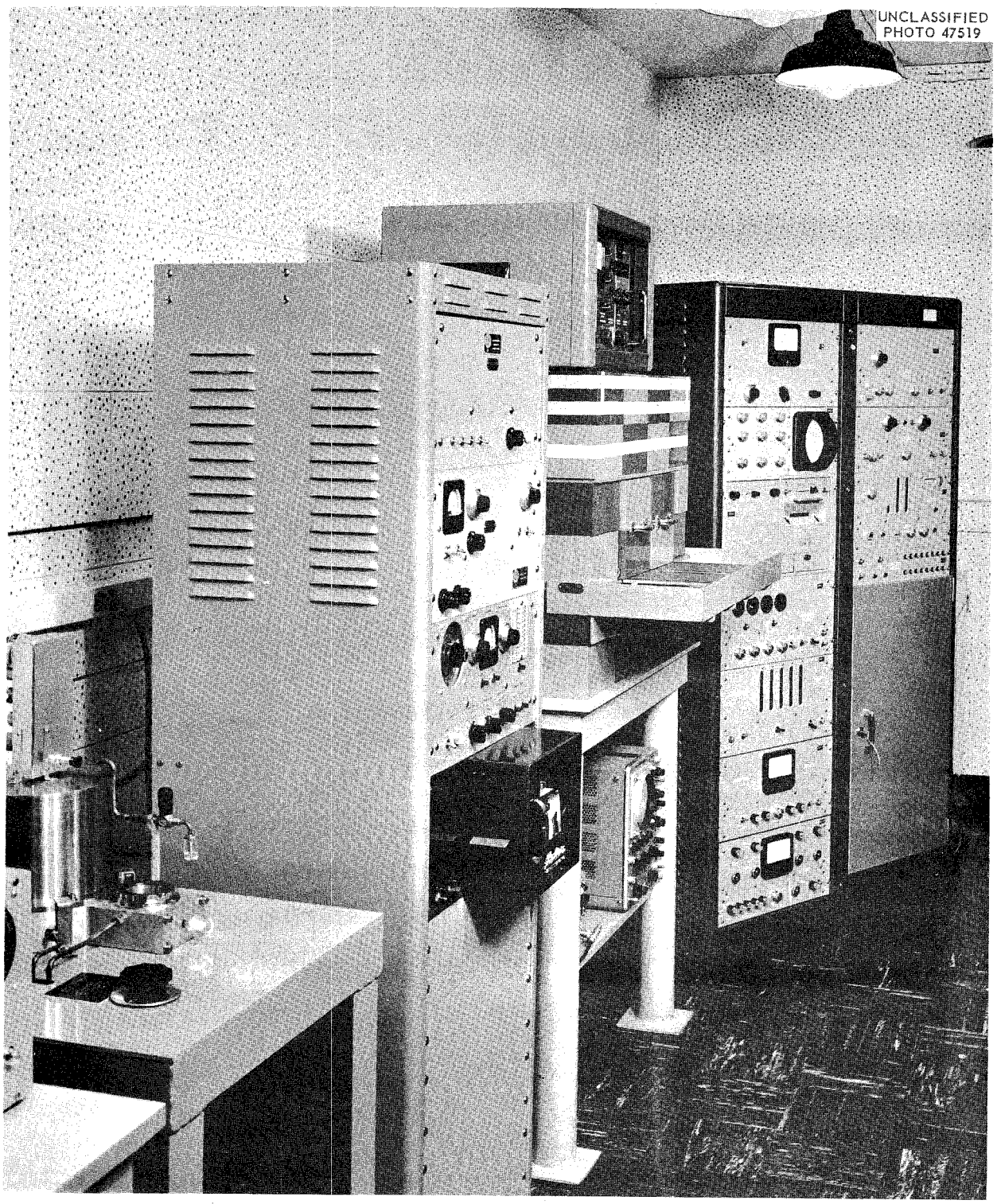

Fig. 34. Counting Equipment in the Low-Radiation-Level Radiochemical Analytical Laboratory.

Most of the analyses done to date have been for the Health Physics Division in connection with their ecological, waste-disposal, and area-monitoring programs.

Special Equipment

Removable Sink Covers (J. H. Moneyhun, C. L. Burros). – Each of the 9-ft-long hoods in the laboratory contains a sink used only for discarding waste solutions. The sinks were converted to cup sinks, and each was provided with a cover plate into which a funnel was set. The usable work space within the hoods was thereby increased. When water flows continuously from the faucet into the funnels, the sinks serve both as receptacles for waste solutions and as traps for fumes from acids or organic solvents.

Sample Holders for Use with the Low-Background Beta Counter (D. K. Smith, C. L. Burros). – The low-background beta counter is equipped with two independent counting chambers, and samples can be inserted into the chambers by means of sample-holder slides. The sample holders furnished by the manufacturer are not adaptable to present sample-mounting technique because the mounted samples cannot be interchanged between the low-background beta counter and the G-M counters.

Since the magnitude of the radioactivity of a sample is often not known, it must first be checked on a G-M counter in order to determine whether the activity level will be suitable for the low-background beta counter. In order to eliminate the remounting of the sample, which would possibly cause spread of contamination and yield loss, holders were designed and fabricated of Lucite that would accommodate samples mounted in the same manner as for a G-M counter. This new holder is "universal" since it will accommodate a small Cl^{36} standard and also a $2 \times \frac{1}{2}$ in. Pyrex dish.

Dolly for the Scintillation Counter Shields (J. H. Moneyhun). – An aluminum dolly was designed and built for transporting and supporting the two lead shields for the scintillation counters. Each shield is 18 in. tall by 10 in. in diameter and weighs 450 lb. To facilitate the positioning of samples in the counting well of the rear shield, the rear half of the dolly platform was raised 3 in.

Vacuum Trap (C. L. Burros, G. F. Strawn[1]). – A trap was designed and fabricated to prevent corrosive agents and organic solvents from contaminating the oil in the vacuum pump for the laboratory vacuum system. The charging chamber is $2\frac{1}{2}$-in.-dia sched-40 pipe, 17 in. long, fitted with a 9-in.-dia flange at the top and a $2\frac{1}{2}$-in.-dia disk welded in at the base. The outer chamber is made from 4-in.-dia, sched-40 pipe and is 19 in. long. The flange has a circular groove which retains an O-ring sealing gasket. The base of the outer chamber is cupped and is fitted with a draw-off valve. Type 347 stainless steel was used in the fabrication of the trap. Fumes in the vacuum line are condensed and frozen on the outside surface of the inner chamber, which is charged with dry ice and acetone. Collected condensate is drawn off by means of a valve at the bottom of the outer chamber.

Vacuum System for the Alpha-Range Analyzer (C. L. Burros). – In order to keep the noise and fumes from the vacuum pump used with the alpha-range analyzer out of the counting room, the pump was mounted in the corridor adjacent to the counting room. The corridor is a 30-in.-wide passageway that surrounds the counting room. The pump is mounted approximately 8 ft above the floor in order to prevent its obstructing the passageway. The switch to the pump is mounted in the counting room near the analyzer.

Counter Tables (C. L. Burros). – Separate tables were designed and constructed to support the detection chamber of an alpha-range analyzer and an anticoincidence beta counter. The table for the anticoincidence counter will support a load of 5000 lb. The detection chamber of the alpha-range analyzer contains a Frisch grid, which is microphonic. In order to reduce vibration to the grid, the chamber rests on a rubber pad and is held in position by rubber-lined Z clamps. Tubings for gas and vacuum lines are mounted beneath the table. The selector to the gas-vacuum valve is mounted on the surface of the table. Designs for both tables have been adopted by the Instrument Department for use with similar counters.

---

[1] Engineering and Mechanical Division.

Spectrometer Standards for Leaf Samples

J. H. Moneyhun

A series of leaf samples were received for gamma spectrometric analysis. In attempting to prepare a suitable standard a simple yet satisfactory standard was developed.

The standards were prepared in round plastic boxes, identical with those used for the leaf samples, by cutting a cellulose sponge to fit the box and pipetting an aliquot of the standard solution of radioactive material onto the sponge. To approximate the weight of the leaf samples, which were ~50% water, the standard solution was diluted to such an extent that the weight of the aliquot added would approximate the weight of the sample.

For one series of samples, only ½ in. thick, the standard solution was added directly to the sponge. On a series of thicker samples, the standard solution was added in two aliquots; one was deposited in the plastic box, the sponge was placed in the box, and the second aliquot was placed on the top of the sponge. Checks were made in both cases to determine that the distribution of the standard solution was even. It is felt that these standards were satisfactory from the standpoints of both density and geometry. An advantage of considerable significance is that upon the accidental spillage of such a standard the major portion of the activity would be retained in the sponge.

MASS SPECTROMETRIC ANALYSES (Y-12)

J. R. Sites

During 1959 the Analytical Mass Spectrometry Group reported 70% more analyses from 63% more samples than in 1958 (33,346 analyses from 4423 samples).

Two gaseous-sample and three solid-sample mass spectrometers are in full-time use. An increasing number of isotopic analyses are being made of various enrichments of uranium, and the isotopic composition of very small amounts of fission-product xenon and krypton is being determined.

During the past two years over 20,000 mass spectrometric analyses have been reported to the Reactor Projects Division relative to their experiments on graphite outgassing and the effects of the contaminants evolved on proposed materials of construction.[2] A typical set of curves of impurity concentration as a function of time and temperature is shown in Fig. 35. When different graphites, construction materials, and temperatures are used in the tests, the characteristics of the corresponding sets of curves show the impurity variations.

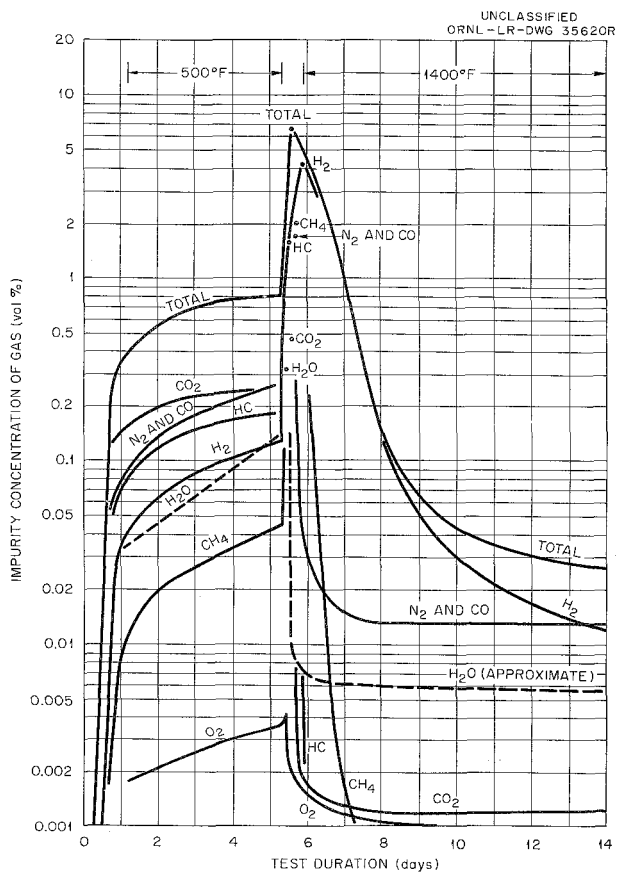

Fig. 35. Typical Outgassing Data for Type TSF Graphite at 500 and 1400°F.

PROCESS ANALYSES (X-10)

L. T. Corbin

High-Alpha Analytical Laboratory

J. H. Cooper

Most of the analyses performed by the High-Alpha Analytical Laboratory were for the Chemical Technology Division relative to the reprocessing

[2] A. M. Smith and J. H. DeVan, *Effects of Contaminants Outgassed from Graphite on Structural Materials in High Temperature Gas*, ORNL CF-59-9-48 (Sept. 15, 1959).

of power-reactor fuel. The end-product solutions of plutonium, depleted uranium, and U^{233} were submitted to this group for accountability assay. Over 600 neutron-threshold detectors[3] were made.

In its study of the chemistry of the transuranium elements, the Chemical Technology Division required analyses for Am^{241} in the presence of high concentrations of lithium salts. Since the high salt content interfered with a gross-alpha count and since the conventional methods for americium[4,5] were too time-consuming, a method of gross-gamma counting was adopted. Experiments with pure solutions showed that Am^{241} counted 1.52×10^6 counts·min^{-1}·μg^{-1} through 1.1-g/cm^2 aluminum on a well-type scintillation counter.

The High-Alpha Analytical Laboratory obtained a controlled-potential coulometer for the determination of plutonium in product solutions. The time required for a plutonium determination by this method is about one-third that required by the previously used ceric sulfate potentiometric titration.[6] Preliminary investigations show that the coulometric method has a relative standard deviation of ~0.3%, whereas that of the potentiometric method is ~0.7%. Neither method shows a bias.

The High-Alpha Analytical Laboratory is cooperating with the Chemical Technology Division in designing facilities for processing transuranium elements. The laboratory has presented a layout for the analytical laboratories and has ordered 21 glove boxes of various types to be used in the handling of all alpha-emitting radioactive materials.

High-Radiation-Level Analytical Facility (HRLAF)

J. E. Morton

During 1959, minor modifications and repairs were made to the HRLAF and to the equipment used in it. A pressure-sensing device was located in the exhaust system to activate an alarm when the exhaust vacuum falls below a safe minimum. Aluminum channels were installed beneath each work-cell window in order to prevent zinc bromide solution from small window leaks from dropping down onto instruments on the instrument chase. An ultrasonic cleaner was purchased and installed in the work area for use in the decontamination of apparatus. Almost all the Teflon packings of the remotely controlled sampling pipets were replaced during the year, and a supply of these and other spare parts for the pipets was established.

Efforts to shorten manipulator down time and to increase manipulator efficiency were continued. The preventive maintenance schedule was continued, and eight more manipulators were completely overhauled. Down time was decreased, and contamination of the operating area was prevented by increased use of disposal boots and sleeves. The manipulator power packs were modified to supply more voltage to the canting motors. The $\frac{1}{32}$-in.-dia innerfinger cables were replaced by more pliable $\frac{1}{16}$-in.-dia (7-strand, 21-ply) cables. All manipulators were equipped with ambidextrous fingers.

Pilot-Plant Control Laboratory

C. E. Lamb

Approximately 80% of the analyses made by the Pilot-Plant Control Laboratory were for the Chemical Technology Division. Groups within the division requesting the majority of the analyses were the following: Power Reactor Fuel Reprocessing Plant Operation – Buildings 3019 and 3505; Power Reactor Fuel Reprocessing – Chemical Development; Transuranic Studies – Chemical Development; HR Thorium Oxide Production – Pilot Production; and Volatility Studies – Chemical Development. Other analyses were made for the Isotopes, Operations, Reactor Projects, and Neutron Physics Divisions.

At the request of the Power Reactor Fuel Reprocessing Pilot Plant, a coulometer and related equipment was set up in the High-Radiation-Level Analytical Facility for the determination of uranium in solutions of reactor fuels. The method is more satisfactory than the ammonium thiocyanate spectrophotometric method used previously because it is more rapid and the results are more precise.

---

[3] L. T. Corbin and J. H. Cooper, "Isolation Analyses," *Anal. Chem. Ann. Prog. Rep. Dec. 31, 1957*, ORNL-2453, p 52.

[4] G. W. Smith, "Americium-241," Method No. 2 31030 (5-18-54), *ORNL Master Analytical Manual;* TID-7015, sec 2.

[5] F. L. Moore, "Total Americium and Curium, Lanthanum Fluoride Method," Method Nos. 2 31031, 2 31241, 9 008031, 9 008241 (8-29-55), *ORNL Master Analytical Manual;* TID-7015, secs 2 and 9.

[6] J. H. Cooper, "Plutonium, Potentiometric Ceric Sulfate Method," Method No. 9 0432620 (8-7-53), *ORNL Master Analytical Manual;* TID-7015, sec 9.

A monitor for the continuous measurement of background radioactivity has been installed in each room of the Pilot-Plant Control Laboratory. Each one is set to alarm audibly for personnel evacuation when the background radioactivity reaches a predetermined limit.

Process-Development Service Laboratory

G. R. Wilson

The Chemical Technology Division has requested the determination of thorium in low concentrations in the presence of sulfuric acid and stainless steel and of aqua regia and stainless steel in connection with their work in decladding stainless steel fuel elements. It was found that the triisooctylamine-in-xylene extraction procedure used by Shults *et al.*[7] to extract uranium from Darex and Sulfex dissolver solutions would also extract thorium. The stripping agent was changed from 0.05 *M* $HClO_4$–1 *N* H_2SO_4 to 0.05 *M* $HClO_4$–1 *N* HNO_3 because sulfuric acid interferes in the spectrophotometric determination of thorium.[8] A study is being made in order to determine the limitations of the extraction. All tests were made using 500 μl of standard solutions that contained 83 μg of thorium per milliliter and various concentrations of different acids. Thorium can be quantitatively extracted from acids and mixtures of acids at least as concentrated as the following: 14 *N* HNO_3, 12 *N* HCl, 6 *N* HCl–6 *N* HNO_3, 5 *N* H_3PO_4 (containing sufficient HNO_3 to keep the thorium in solution), and 10 *N* H_2SO_4. Thorium can be extracted from higher concentrations of sulfuric acid if the aluminum salting agent is adjusted so that the aqueous phase before extraction is neutral or acid-deficient. Further work will be done on the method.

Radioisotopes-Radiochemistry Laboratory

E. I. Wyatt

R. R. Rickard H. A. Parker

About 70% of the work of the Radioisotopes-Radiochemistry Laboratory for the past year has been for the Isotopes Division. Half the work was done on products for shipment and half for process control, mainly in connection with the Fission Products Pilot Plant. The possibility of using a liquid scintillation counter for C^{14} and S^{35} work has been explored, and it will be used in the future. A 20-channel gamma scintillation spectrometer has been put into service.

A radiochemical procedure for the determination of Pm^{147} was developed and is being used routinely. The method takes advantage of the difference between the solubility of neodymium iodate, $Nd(IO_3)_3$ (used to carry Pm^{147}) and that of yttrium iodate, $Y(IO_3)_3$, in 0.3 *M* HCl.

Several new techniques are being used in the determination of Tc^{99}. For highly radioactive samples, shielding must be provided until most of the fission products can be removed. This can be accomplished by scavenging with ferric hydroxide, by remote handling equipment, by using a shielded cation-resin column to hold up the fission products, or by using a polarograph with a shielded cell.

In the past year a great many requests for the determination of Tc^{99} in samples of UO_3, UO_2, UF_4, etc., have been received. The sample is dissolved by digestion with potassium carbonate and hydrogen peroxide, and technetium is extracted from this solution into methyl ethyl ketone. In all the chemical separations used, Tc^{99} is finally coprecipitated with tetraphenylarsonium perrhenate for final weighing and counting.

Reactor Analyses Laboratory

U. Koskela

The HRT, its associated chemical plant, and other HR programs continued to supply most of the samples that were analyzed during the past year. The coulometric[9] determination of uranium and copper in a single aliquot has been extended to include the determination of nickel.[10,11] A new method for the determination of free acid has been

[7] W. D. Shults *et al.*, *Progress Report on the Analysis of Dissolver Solutions by Controlled-Potential Coulometric Titration*, ORNL-2776, p 9 (Sept. 14, 1959).

[8] G. R. Wilson, "Thorium, Spectrophotometric Thoron Method," Method Nos. 1 218710 and 9 00718710 (3-26-54), *ORNL Master Analytical Manual;* TID-7015, sec 1.

[9] L. G. Farrar, P. F. Thomason, and M. T. Kelley, "Controlled Potential Coulometric Determination of Uranium and Copper in Homogeneous Reactor Fuels," *Anal. Chem.* 30, 1511 (1958).

[10] O. Menis *et al.*, "Coulometric Determination of Nickel in Homogeneous Reactor Fuel," *HRP Quar. Prog. Rep. Apr. 30 and July 31, 1958*, ORNL-2561, p 331.

[11] A. D. Horton *et al.*, "The Coulometric Titration of HRT Fuel in the High-Radiation-Level Analytical Facility, Determination of Copper, Uranium, and Nickel," *Proceedings, Second Conference, Analytical Chemistry in Nuclear Reactor Technology*, TID-7568 (Pt. 2), p 96 (Apr. 1959).

introduced. The evaluation of these methods has been reported.[12]

Special Analyses Laboratory

W. R. Laing

Several new methods have been put into use and a number of existing methods adapted for new types of samples. Additional laboratory equipment has been obtained, and the control program has been expanded.

Among the new methods were the determination of the oxygen-to-uranium ratio and nitrogen in UO_2 compacts. Polarography was used for the oxygen-to-uranium ratio and the sodium phenate method for nitrogen. The rare-earth elements were determined by complexometric titration using a recording potentiometric titrator. Small pieces of lead capillary were analyzed for silver and nickel, and the weight of extremely thin gold foils was determined by dissolution of the foils and analysis of the solutions for gold.

Some of the existing methods were modified in order to analyze for acid in stainless steel solutions that contained dichromate; to titrate zirconium complexometrically; and to analyze $UO_2 \cdot ThO_2 \cdot Al_2O_3$, $UO_2 \cdot ThO_2 \cdot SiO_2$, and $ThO_2 \cdot PdO$ powders.

New equipment and instruments included a Leco conductometric carbon analyzer, controlled-potential coulometric titrators, and two hot cells provided with 4-in.-thick lead walls and "wiggle tong" manipulators. The equipment required for the measurement of the surface area of radioactive samples by the continuous-flow method has been installed in one of the cells.

Gases in niobium and its alloys and boron in alloys and solutions have been determined.

In other work, highly precise determinations of uranium were performed as part of the "eta" project. Samples of barytes concrete and magnetite ore were analyzed for major and minor constituents. Irradiated stainless steels that contained boron were analyzed for B^{10} burnup.

The X-10 control program was expanded to include more complex synthetic samples. Seven simulated power-reactor fuel-reprocessing feeds, four synthetic HRT blanket samples, three controls for HRP Chemistry fuel solutions, and one standard solution for the Spectrographic Laboratory were prepared. These solutions contained two to nine compounds.

The total number of results reported for the past year was 33,665.

RADIOCHEMICAL ANALYSES (X-10)

S. A. Reynolds

Over 80% of the service analyses made by the Radiochemical Analyses Group were performed for four ORNL divisions. For the Health Physics Division many gamma spectrometric determinations of fission products and other activities were made in various materials including water, soil, airborne particles, and gases trapped in charcoal. Work for the Chemical Technology Division included special analyses for transuranic elements and gamma spectrometric identifications and determinations of fission products. For the Reactor Experimental Engineering Division and the Solid State Division, many analyses for fission gases and their daughters, as well as other radionuclides, were performed.

REACTOR PROJECTS LABORATORY (Y-12)

J. C. White W. F. Vaughan

A total of 7738 samples was analyzed by the Reactor Projects Laboratory. Most of these samples were fused fluoride salts, that is, either single salts or mixtures of two or more of the fluorides of uranium, sodium, lithium, potassium, zirconium, rubidium, yttrium, beryllium, chromium, nickel, iron, and magnesium. Analyses were made primarily for the following corrosion products: nickel, chromium, iron, molybdenum, titanium, and copper. Approximately 25% of the salts were analyzed for the major constituents in order to determine their exact compositions. In those for which the determinations of not all the constituents were requested, at least beryllium determinations were required. For the above determinations, gravimetric, volumetric, and spectrophotometric methods were used.

Of the samples received by the laboratory, 14% were millings from graphite rods that had been impregnated with fused salts, either $LiF\text{-}BeF_2\text{-}UF_4$ or $LiF\text{-}BeF_2\text{-}ThF_4\text{-}UF_4$. The millings were analyzed to determine the depth of penetration of the fluoride salt into the graphite rods. A new graphite-dissolution procedure was developed which requires

[12] O. Menis *et al.*, "Analytical Chemistry," *HRP Prog. Rep. May 1 Through Oct. 31, 1959*, ORNL-2879, p 247–50 (in press).

only half the time of the nitric acid–perchloric acid procedure (see "Dissolution of Graphite," this report). Uranium was determined by means of the spectrophotometric dibenzoylmethane method; beryllium by the spectrophotometric *p*-nitrobenzeneazo-orcinol method; thorium by the Thoron spectrophotometric method or, if present in high concentrations, by the volumetric titration with disodium dihydrogen ethylenediaminetetraacetate; and lithium by the flame photometric method.

THERMAL BREEDER REACTOR PROJECTS ANALYTICAL CHEMISTRY LABORATORY (Y-12)

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

During 1959 the staff of the Thermal Breeder Reactor Projects Analytical Chemistry Laboratory reported 78,000 results on 9958 samples, about 95% of which were submitted by the Reactor Experimental Engineering Division. Concomitant with a reduction of activity in this division, approximately 30% fewer samples were analyzed than during the previous year. The samples consisted principally of solutions of uranyl sulfate (many of which contained copper sulfate), slurries of thorium oxide, and mixtures of thorium oxide with smaller amounts of uranium oxides. Analyses were made less frequently on a wide variety of materials, including solutions of HNO_3, H_3PO_4, HF, and H_2O_2 and water samples. Methods of analysis included gravimetric; volumetric, including potentiometric and spectrophotometric titrations; spectrophotometric; flame photometric; fluorometric; polarographic; coulometric; gasometric; and thermogravimetric. Among the physical measurements that were also made on many samples were pH, specific gravity, particle-size distribution, conductivity, and zeta potential.

The uranyl sulfate solutions were most frequently analyzed for uranium, copper, sulfate, nickel, and free acid and occasionally for a number of other ions, the most common of which was chloride, and for the corrosion products of stainless steel in addition to nickel. The dissolved oxygen, carbon dioxide, and hydrogen in the uranyl sulfate solutions were also frequently determined.

Thorium oxide and mixtures of thorium oxides with other oxides, notably those of uranium and aluminum, were analyzed for thorium, additives, including molybdenum and palladium, and corrosion or erosion products. In many samples containing uranium, the uranium(IV)-to-uranium(VI) ratio was established. The oxygen, carbon dioxide, and hydrogen contained in slurries of thorium oxide were also determined, and the zeta potential of thorium oxide slurries was measured. The particle-size distribution of thorium oxide was determined in a large number of slurries and also of aluminum oxide and zirconium oxide in a limited number of samples. A revised method was adopted for the estimation of thorium in which the thorium is titrated directly with a solution of disodium dihydrogen ethylenediaminetetraacetate by means of xylenol orange as the indicator and a glycine–acetic acid buffer to control the pH of the solution.

Iron, nickel, chromium, and free acid were determined in nitric and phosphoric acid solutions. Occasionally these solutions were analyzed for other corrosion products of stainless steel. Similar analyses and also pH and conductance measurements were made on water samples. Other work included the determination of fluoride and free acid in solutions of hydrofluoric acid, the establishment of the concentration of solutions of hyrdogen peroxide, and the evaluation of the chloride content of a variety of materials used in corrosion-erosion and hydrodynamic tests. Fusion pyrolysis was used to separate chloride and fluoride prior to their determinations. Thermogravimetric analyses were also made on a number of solid samples, principally inorganic compounds, and also on mixtures of thorium oxide with other metallic oxides.

PRESENTATIONS OF RESEARCH RESULTS

The Analytical Chemistry Division sponsored a Third Conference on Analytical Chemistry in Nuclear Reactor Technology at Gatlinburg, Tennessee, on October 26–29, 1959. The committee consisted of C. D. Susano (Chairman), J. H. Cooper, G. W. Leddicotte, J. A. Norris, R. W. Stelzner, and J. P. Young. Forty-one papers were presented, augmented by panel discussions.

There were 215 registrants: 90 from Oak Ridge, 6 from other AEC installations, 105 from industrial plants and laboratories, 6 from universities and colleges, and 8 foreign guests. Many of those in attendance from industrial plants, commercial laboratories, and universities are also engaged in AEC-related projects.

In order to make the information presented at this conference generally available, the proceedings will be published, as were the proceedings of the first conference (TID-7555) and the second conference (TID-7568, Parts 1, 2, and 3).

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

PUBLICATIONS

Books

Author(s)	Title	Publisher
Kelley, M. T. (ed.)	*Progress in Nuclear Energy, Analytical Chemistry* (vol 1)	Pergamon, London, 1959

Articles

Author(s)	Title	Publication
Bate, L. C., G. W. Leddicotte	"An Evaluation of the Particle-Size Distribution in Multicomponent Systems"	*Proceedings, Second Conference, Analytical Chemistry in Reactor Technology; Particle-Size Analysis*, TID-7568 (Part 3), p 43 (April 1959)
Berg, R. H.,[1] L. C. Bate, G. W. Leddicotte	"Particle-Size Distribution of Thorium Oxide by Electronic Sizing"	*Ibid.*, p 83
Blanchard, R. L.,[2] G. W. Leddicotte, D. W. Moeller[3]	"Water Analysis by Neutron Activation"	*J. Am. Water Works Assoc.* 51, 967 (1959)
Eshelman, H. C.,[4] J. A. Dean,[5] O. Menis	"Extraction and Flame Spectrophotometric Determination of Aluminum"	*Anal. Chem.* 31, 183 (1959)
Goldstein, G.	"A Study of Spectrophotometric Methods for the Determination of Osmium"	M. S. Thesis, University of Tennessee, August 1959

[1]Coulter Industrial Sales Co., Elmhurst, Ill.

[2]Now associated with U. S. Public Health Service, Salt Lake City, Utah.

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

[4]Southwest Louisiana Institute, Lafayette.

[5]University of Tennessee, Knoxville.

Author(s)	Title	Publication
Goldstein, G., D. L. Manning, O. Menis	"Determination of Aluminum in Thorium Oxide and a Separation Scheme for Interfering Ions"	*Talanta* 2, 52 (1959)
	"Spectrophotometric Determination of Cobalt with 1-(2-Pyridylazo)-2-naphthol. Separation from Interfering Ions"	*Anal. Chem.* 31, 192 (1959)
Halperin, J., J. H. Oliver,* H. S. Pomerance	"The Thermal Neutron Absorption Cross-Section of ^{240}Pu"	*J. Inorg. & Nuclear Chem.* 9(1), 1 (1959)
Handley, T. H., C. L. Burros	"Determination of Radioactive Cesium"	*Anal. Chem.* 31, 332 (1959)
Harmatz, B., T. H. Handley, J. W. Mihelich[6]	"Nuclear Spectroscopy of Odd-Mass (161-173) Nuclides Produced by Proton Irradiation of Er and Yb"	*Phys. Rev.* 114, 1082 (1959)
Kahn, B.,[7] D. W. Moeller,[3] T. H. Handley, S. A. Reynolds	"Analysis for Radionuclides in Aqueous Wastes from an 'Atomic' Plant"	*Am. Soc. Testing Materials Spec. Tech. Publ. No. 235* (1959)
Kelley, M. T., D. J. Fisher, R. W. Stelzner, W. L. Maddox, H. C. Jones	"Instrumentation for Chemical Analyses"	*Proceedings, Second Conference, Analytical Chemistry in Nuclear Reactor Technology; Instrumentation, Remote Control Techniques, and Nucleonics,* TID-7568 (Part 2), p 3–12 (April 1959)
Kelley, M. T., H. L. Hemphill, D. J. Fisher	"Servo-Controlled Pipetter for Precise Delivery of Microliter Drops"	*Ibid.*, p 98
Kelley, M. T., H. C. Jones, D. J. Fisher	"Controlled-Potential and Derivative Polarograph"	*Anal. Chem.* 31, 1475 (1959)
	"Electronic Controlled-Potential Coulometric Titrator"	*Ibid.*, pp 488, 956
	"High-Sensitivity, Recording, Scanning Flame Spectrophotometer"	*Ibid.*, p 178
Kelley, M. T., R. W. Stelzner, D. J. Fisher	"Instrumentation for the Remote Determination of Density by the Falling-Drop Method"	*Proceedings, Second Conference, Analytical Chemistry in Nuclear Reactor Technology; Instrumentation, Remote Control Techniques, and Nucleonics,* TID-7568 (Part 2), p 106 (April 1959)
Kelley, M. T., R. W. Stelzner, W. R. Laing, D. J. Fisher	"Automatic Coulometric Titrator for Karl Fischer Determination of Water"	*Anal. Chem.* 31, 220 (1959)

[6]University of Notre Dame, Notre Dame, Ind.

[7]Massachusetts Institute of Technology, Graduate House No. 518A, Cambridge.

Author(s)	Title	Publication
Koskela, U., L. G. Farrar, J. E. Attrill, J. L. Mottern[8]	"Analytical Service for the HRT"	*Proceedings, Second Conference, Analytical Chemistry in Nuclear Reactor Technology; Instrumentation, Remote Control Techniques, and Nucleonics*, TID-7568 (Part 2), p 125 (April 1959)
	"Analytical Service for the Homogeneous Reactor Test"	*Proceedings, Seventh Hot Laboratories and Equipment Conference*, p 439, Engineers Joint Council, New York, 1959
Kubota, H., J. G. Surak[9]	"Determination of Fluoride by Conductometric Titration"	*Anal. Chem.* 31, 283 (1959)
Leddicotte, G. W., W. S. Lyon	"Special Radiochemical Analysis in the Operation of ORNL Reactors"	*Proceedings, Second Conference, Analytical Chemistry in Nuclear Reactor Technology; Instrumentation, Remote Control Techniques, and Nucleonics*, TID-7568 (Part 2), p 145 (April 1959)
Leddicotte, G. W.,* W. T. Mullins,* L. C. Bate,* J. F. Emery,* R. E. Druschel, W. A. Brooksbank[10]	"The Use of Neutron Activation Analysis in Analytical Chemistry"	*Progress in Nuclear Energy, Analytical Chemistry*, M. T. Kelley (ed.), vol I, p 123–37, Pergamon, London, 1959
Lyon, W. S.	"Isotopic Analysis: Cerium-141 and Cerium-144"	*Nuclear Sci. and Eng.* 4, 709 (1958)
Lyon, W. S., R. L. Macklin	"Neutron Activation at 195 kev"	*Phys. Rev.* 114, 1619 (1959)
Maddox, W. L., M. T. Kelley	"A Gamma Absorptiometer for Laboratory Analysis of the Heavy Elements"	*Talanta* 3, 172 (1959)
McDowell, B. L., A. S. Meyer, Jr., R. E. Feathers, Jr.,[11] J. C. White	"Spectrophotometric Determination of Traces of Nickel with 4-Isopropyl-1,2-cyclohexanedionedioxime"	*Anal. Chem.* 31, 931 (1959)
Menis, O., T. C. Rains, J. A. Dean[5]	"Extraction and Flame Spectrophotometric Determination of Lanthanum"	*Ibid.*, p 187
Menis, O., T. C. Rains, D. L. Manning, G. Goldstein, I. B. Rubin	"Determination of Aluminum, Zirconium, Molybdenum, Uranium, and Titanium in Thorium Oxide Slurries"	*Proceedings, Second Conference, Analytical Chemistry in Nuclear Reactor Technology; Specific Applications of Diverse Methods of Chemical Analysis*, TID-7568 (Part 1), p 157 (April 1959)

[8]Davison Chemical Co., Erwin, Tenn.

[9]Temporary summer employee from Marquette University, Milwaukee.

[10]Now associated with Structures and Mechanical Laboratory, Army Ballistic Missile Agency, Redstone Arsenal, Ala.

[11]Union Carbide Corporation, New York Office, New York.

Author(s)	Title	Publication
Meyer, A. S., Jr., C. M. Boyd	"Determination of Water by Titration with Coulometrically Generated Karl Fischer Reagent"	*Anal. Chem.* 31, 215 (1959)
Miller, F. J., P. F. Thomason	"Direct Thermometric Titration of Boric Acid"	*Talanta* 2, 109 (1959)
	"Thermometric Titration of Acids in Presence of Hydrolyzable Cations"	*Anal. Chem.* 31, 1498 (1959)
	"Thermometric Titration of Uranium(IV) with Potassium Dichromate"	*Anal. Chim. Acta* 21, 112 (1959)
Moeller, D. W.,[3] G. W. Leddicotte, S. A. Reynolds	"Radionuclides in Reactor Cooling Water"	*J. Sanit. Eng. Div. (Proc. Am. Soc. Civil Engrs.)* 85, No. SA2 (Part 1) (1959)
Moore, F. L., W. D. Fairman,[12] J. G. Ganchoff,[13] J. G. Surak[9]	"Selective Liquid-Liquid Extraction of Iron with 2-Thenoyltrifluoroacetone-Xylene. Application to Homogeneous Reactor Solutions"	*Anal. Chem.* 31, 1148 (1959)
Moore, F. L., S. A. Reynolds	"Radiochemical Determinations of Uranium-237"	*Ibid.*, p 1080
Rickard, R. R., E. I. Wyatt	"Radiochemical Determination of Fission Ruthenium in Aqueous Solutions"	*Ibid.*, p 50
Ross, W. J., J. C. White	"Extraction and Determination of Thorium from Sulfate and Phosphate Solutions with Tri-*n*-octylphosphine Oxide"	*Ibid.*, p 1847
Shults, W. D.	"Controlled-Potential Coulometric Determination of Europium"	*Ibid.*, p 1095
Shults, W. D., P. F. Thomason	"Controlled-Potential Coulometric Determination of Copper and Uranium"	*Ibid.*, p 492
Young, J. P., J. C. White	"A High-Temperature Cell Assembly for Spectrophotometric Studies of Molten Fluoride Salts"	*Ibid.*, p 1892
	"Extraction of Titanium Thiocyanate with Tri-*n*-octylphosphine Oxide. Direct Colorimetric Determination in the Organic Phase"	*Ibid.*, p 393
Zittel, H. E., F. J. Miller, P. F. Thomason	"Amperometric Titration of Barium"	*Ibid.*, p 1351

[12] Argonne National Laboratory, Lemont, Ill.

[13] U. S. Army.

Reports

Author(s)	Title	Report No.
Ball, R. G.	"Spectrophotometric Determination of Copper in Yttrium Metal with Neocuproine"	ORNL CF-59-4-106 (Apr. 21, 1959)
	"Use of a 2^4 Factorial Experiment to Investigate the Effect of Certain Factors on the Reliability of Iron Values Obtained by the Volumetric, Dichromate Method"	ORNL CF-59-3-107 (Mar. 20, 1959)
	"Ultraviolet Spectrophotometric Determination of Osmium Tetroxide in $CHCl_3$"	ORNL CF-59-6-43 (June 9, 1959)
Ball, R. G., D. L. Manning, O. Menis	"The Determination of Mercury, Copper, and Zinc by Derivative Polarography – Application to Solutions of Uranyl Sulfate Containing Corrosion Products"	ORNL-2717 (May 7, 1959)
Bate, L. C., G. W. Leddicotte	"Study of Dispersant Agents for Thorium Oxide"	ORNL CF-59-8-43 (Aug. 7, 1959)
Biggers, R. E.	"Measurements of Small Amounts of H_2O in D_2O by Near-Infrared Absorption Spectroscopy"	ORNL CF-58-12-143 (Dec. 8, 1958)
	"Reports and Information Concerning Work on Plutonium Chemistry Carried Out During the Past Two Years for the Analytical Chemistry and Chemical Technology Divisions"	ORNL CF-59-2-59 (Feb. 19, 1959)
	"Stability of Fused Quartz and Sapphire Optical Window Materials to Radiation Levels Comparable to Those Present in a Loop of the HRT Fuel Solution Circulating System"	ORNL CF-58-11-113 (Nov. 26, 1958)
Biggers, R. E.,* J. M. Chilton	"Review and Bibliography on: Design and Use of Windows for Optical Measurements at Elevated Temperatures and Pressures (1881–1959)"	ORNL-2738 (May 27, 1959)
	"Proposed Program for Elevated Pressure and Temperature Investigations Using the Cary Spectrophotometer Now Located in Building 3508 at ORNL: Feb. 1, 1959 to July 15, 1960"	ORNL CF-59-2-17 (Feb. 5, 1959)
	"Specifications No. CTD-2 for the Design and Construction of a High Temperature-Pressure Recording Spectrophotometer," preceded by: "Invitation for Subcontract to Design and Construct a High Temperature-Pressure Absorption Cell System for a Model 14PM Cary Recording Spectrophotometer"	Specifications No. CTD-2 Jan. 19, 1959, Revision No. 2, Dec. 16, 1959 (Chemical Technology Division)

Authors(s)	Title	Report No.
Biggers, R. E.,* J. M. Chilton	"Trip to Applied Physics Corporation Regarding Contract to Build High Temperature Spectrophotometer"	ORNL CF-59-3-9 (Mar. 3, 1959)
Blanchard, R. L.,[2] G. W. Leddicotte	"The Determination of Trace Elements in Water by Neutron Activation Analysis"	ORNL-2620 (July 24, 1959)
Blevins, E. L.	"Hexone Extraction-Coulometric Titration of Uranium"	ORNL CF-59-6-82 (June 22, 1959)
Boyd, C. M., H. P. House, O. Menis	"Micro-Electrophoretic Determination of the Zeta Potential of Thorium Oxide"	ORNL-2836 (Nov. 10, 1959)
Brady, L. J.	"Resistance of Tygon and Duroflex Plastic Tubing to Certain Chemical Reagents"	ORNL CF-59-4-59 (Apr. 16, 1959)
Emery, J. F., L. C. Bate	"Determination of Niobium in Thermocouple Wire and Stainless Steel 347L"	ORNL CF-59-7-105 (July 21, 1959)
Ferguson, R. L., G. W. Leddicotte	"Surface-exchange Method for Determination of Surface Area of UO_2 Powder"	ORNL CF-59-8-62 (Aug. 6, 1959)
Goldstein, G.	"High-Precision Determinations by Means of High-Absorbancy Spectrophotometric Method. Application to the Determination of Cobalt in Aluminum"	ORNL CF-59-4-71 (Apr. 13, 1959)
	"Spectrophotometric Determination of Microgram Quantities of Osmium with Diphenylcarbazide"	ORNL CF-59-7-16 (June 2, 1959)
Holsopple, H. L.	"Survey of Anodizing Processes for Aluminum"	ORNL CF-59-8-132 (Aug. 27, 1959)
Holsopple, H. L., Jr.	"An Attempt to Duplicate a Direct Spectrophotometric Method for Thorium Proposed by Gurupada Banerjee"	ORNL CF-59-8-144 (Aug. 13, 1959)
Holsopple, H. L., C. D. Susano	"Analysis of White, Toilet, Cake Soap"	ORNL CF-59-6-23 (June 4, 1959)
Layton, F. L.	"Application of Xylenol Orange Indicator in the Complexometric Titration of Thorium"	ORNL CF-59-9-38 (Sept. 9, 1959)
Leddicotte, G. W., S. A. Reynolds	"Neutron Activation Analysis"	ORNL CF-56-7-106, 5th Issue (July 9, 1959)
McCutchen, R. L.	"Comparison of Two Colorimetric Methods for Uranium"	ORNL CF-59-3-108 (Mar. 25, 1959)
	"Evaluation of a Graphical Method for the Comparison of Interlaboratory Tests"	ORNL CF-59-6-66 (June 15, 1959)
McDowell, B. L.	"Gas Chromatographic Determination of Nitrogen and Carbon Monoxide"	ORNL CF-59-3-73 (Mar. 18, 1959)
Manning, D. L.	"Determination of Tetravalent Uranium in Thorium Oxide–Uranium Oxide Mixtures. Parts I, II and III"	ORNL CF-59-4-40 (Apr. 4, 1959)
	"High-Frequency Titration as Applied to the Determination of Thorium, Uranium, Sulfate and Free Acid. Parts I Through V"	ORNL CF-59-5-72 (May 11, 1959)

Authors(s)	Title	Report No.
Menis, O.	"The Removal of Corrosion Scale from Heat Exchanger by Chemical Treatments"	ORNL CF-59-4-107 (Apr. 15, 1959)
Miller, C. E.[14]	"Comparison of Beta with Gamma Counting for the Measurement of 2.56 h Nickel-65"	ORNL CF-58-12-26 (Dec. 10, 1958)
	"Neutron Activation Analysis Methods for the Group VIII Elements"	ORNL-2715 (May 5, 1959)
Miller, F. J.	"The Determination of Technetium in Uranium Trioxide"	ORNL CF-59-10-27 (Oct. 9, 1959)
Norris, J. A.	"Background Correction for Photoelectric Spectrophotometer"	ORNL CF-59-7-145 (July 24, 1959)
Peele, J. M.	"The Effect of Acid Concentration and of Digestion Time on the Fluoride Precipitation of Rare-Earth Elements"	ORNL CF-59-5-102 (May 20, 1959)
Rains, T. C.	"Flame Photometric Determination of Iron: Separation by Extraction from HCl Medium with Hexone"	ORNL CF-59-3-106 (Mar. 24, 1959)
Rains, T. C., H. P. House, O. Menis	"Evaluation of Flame Photometry for the Determination of Elements of the Rare-Earth Group"	ORNL CF-59-8-141 (Aug. 27, 1959)
Rains, T. C., O. Menis	"Flame Photometric Determination of Iron, Parts I, II, III and IV"	ORNL CF-59-5-48 (May 6, 1959)
Reynolds, S. A.	"Measurement of the 'Active Deposit' of Thoron"	ORNL CF-59-8-68 (Aug. 17, 1959)
Ross, W. J.	"Direct Spectrophotometric Determination of Uranium in Cyclohexane Solutions of Tri-*n*-octylphosphine Oxide"	ORNL CF-59-4-100 (Apr. 21, 1959)
Rubin, I. B.	"Abstracts of Papers Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Mar. 2–6, 1959"	ORNL CF-59-4-51 (Apr. 10, 1959)
Shults, W. D., B. B. Hobbs, E. L. Blevins, P. F. Thomason	"Progress Report on the Analysis of Dissolver Solutions by Controlled-Potential Coulometric Titration"	ORNL-2776 (Sept. 14, 1959)
Susano, C. D.	"Partial Analysis of a Liquid Germicidal Disinfectant"	ORNL CF-59-4-93 (Apr. 23, 1959)
Susano, C. D., H. P. House, M. A. Marler (eds.)	"Proceedings, Second Conference, Analytical Chemistry in Nuclear Reactor Technology"	TID-7568, Parts 1, 2, and 3 (April 1959)
White, J. C.	"Determination of Thickness of Oxide Film on Phosphor Bronze"	ORNL CF-59-5-77 (May 19, 1959)
		ORNL CF-59-2-31 (Feb. 6, 1959) (classified)

[14] Armour Research Foundation, Chicago, Ill.

Author(s)	Title	Report No.
Winchester, J. W.[15]	"A Preliminary Investigation of a Chromatographic Column Separation of Rare Earths Using Di(2-ethylhexyl)phosphoric Acid"	ORNL CF-58-12-43 (Dec. 30, 1958)
Winchester, J. W.,[15] L. C. Bate, G. W. Leddicotte	"Determination of Li^6 in Aqueous Solution by Neutron Activation Analysis"	ORNL CF-59-7-127 (July 10, 1959)
Winchester, J. W.,[15] R. E. Meyer, L. C. Bate,* G. W. Leddicotte*	"Determination of Oxygen in Oxide Films by Neutron Activation Analysis"	ORNL CF-59-7-128 (July 15, 1959)
Young, J. P.	"Status Report – Spectrophotometry of Molten Fluoride Salts"	ORNL CF-59-3-112 (Mar. 25, 1959)

New Methods Issued to ORNL *Master Analytical Manual*

Author(s)	Title	Number(s)	Date
Apple, R. F.	"Magnesium and/or Yttrium, Disodium Dihydrogen Ethylenediaminetetraacetate Potentiometric Titration Method"	1 214720 1 219620 9 00714720 9 00719620	6-29-59
Bate, L. C., G. W. Leddicotte	"Particle-Size Distribution in Thorium Oxide, Neutron Activation–Sedimentation Method"	5 10200 9 082104	7-31-59
Belew, W.	"Spectrometer, Perkin-Elmer Model 12-C, Infrared"[16]	1 003033 9 003033	8-11-59
French, J. R.	"Barium, Flame Photometric Method" (originally used at Y-12)[16]	1 210831 9 00710831	6-7-56
	"Calcium, Flame Photometric Method" (originally used at Y-12)[16]	1 211531 9 00711531	6-8-56
	"Rubidium, Flame Photometric Method" (originally used at Y-12)[16]	1 217231 9 00717231	6-7-56
	"Sodium, Flame Photometric Method" (originally used at Y-12)[16]	1 217931 9 00717931	6-7-56
Goldstein, G.	"Cobalt, Spectrophotometric 1-(2-Pyridylazo)-2-naphthol–Chloroform Method"	1 212211 9 00712211	1-29-59
Jones, H. C.	"Automatic Coulometric Titrator, ORNL Model Q-2005, Electronic, Controlled Potential"	1 003029 9 003029	8-17-59
Kubota, H.	"Uranium Dioxide Stoichiometry, Polarographic Method"	1 220017	8-12-59
Layton, F. L.	"Uranium in Uranyl Sulfate Solution, Density Method"	9 082218	10-10-58
Leddicotte, G. W.	"The Method of Activation Analysis"	5 10100	8-4-59
	"Neutron Activation Analysis at ORNL"	5 10101	8-3-59
	"Calculation of Activation Analysis Data"	5 10123	8-6-59

[15]Massachusetts Institute of Technology, Cambridge.

[16]Record copy only method.

Author(s)	Title	Number(s)	Date
Leddicotte, G. W.	"Antimony, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11040	8-10-59
Lund, J. R.	"Boron, Spectrophotometric Carminic Acid Method"	1 211211 9 00711211	9-14-59
Lund, J. R., R. E. Biggers	"Spectrophotometer, Recording, Warren Spectracord"	1 003032 9 003032	8-5-59
Lynn, E. C.	"Sulfur Dioxide in Organic or Inorganic Absorbants, Iodimetric Titration Method"	1 220016 9 00720016	7-30-59
Manning, D. L.	"Uranium(IV) in Thorium Oxide Uranium Oxide Mixtures, Volumetric Potassium Dichromate Method"	9 082219	7-10-59
	"Zirconium in Thorium Oxide, Thenoyltrifluoroacetone Extraction–Morin Fluorometric Method"	9 082220	7-29-59
	"Zirconium in Thorium Oxide, Spectrophotometric Quercetin Method and Spectrophotometric Morin Method"	9 082221	7-29-59
McDowell, B. L.	"Iron in Organophosphorus Extracts, Spectrophotometric o-Phenanthroline Method"	1 214112 9 00714112	7-13-59
	"Nickel, Spectrophotometric 4-Isopropyl-1,2-cyclohexanedionedioxime Method"	1 215412 9 00715412	7-2-59
Menis, O.	"Automatic Titrator, Dow Recordomatic Titrometer"	1 003021 9 003021	5-7-59
	"Copper, Spectrophotometric Diethyldithiocarbamate Method"	1 212310 9 00712310	5-6-59
	"Uranium, Stannous Chloride–Potassium Dichromate Volumetric Method"	1 219271 9 00719271	5-7-59
	"Zirconium, Spectrophotometric Chloranilic Acid Method"	1 219811 9 00719811	7-27-59
Menis, O., M. L. Druschel	"Fluoride, Chrome Azurol S Spectrophotometric Method"	1 212811 9 00712811	5-7-59
Meyer, H. C.	"Lithium, Flame Photometric Method"	1 214530 9 00714530	5-11-59
	"Sodium, Flame Photometric Method"	1 217930 9 00717930	4-9-59
Miller, F. J.	"Bromine (Bromide), Potentiometric Silver Nitrate Titration Method"	1 211320 9 00711320	5-6-59
	"Chlorine (Chloride), Potentiometric Silver Nitrate Titration Method"	1 212020 9 00712020	1-29-59
	"Iodine (Iodide), Potentiometric Silver Nitrate Titration Method"	1 213920 9 00713920	5-6-59
Mullins, W. T., G. W. Leddicotte	"Nickel, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11540	7-31-59
Peele, J. M.	"Petroleum Distillate in Aqueous Solution, Distillation Method"	1 10010 9 00603	7-30-59

Author(s)	Title	Number(s)	Date
Raaen, H. P.	"Lithium Carbide in Metallic Lithium, Spectrophotometric Acetylene–Silver Perchlorate Method" (cross reference)	9 09211	10-29-58
Rains, T. C.	"Halides, Indirect Flame Photometric Method"[16]	1 220010	1-28-59
Rubin, I. B.	"Titanium, Spectrophotometric 8-Quinolinol Method"[16]	1 219012 9 00719012	2-2-59
	"Tungsten, Spectrophotometric Thiocyanate Method"[16]	1 219110 9 00719110	1-30-59
	"Titanium in Thorium Oxide and Thorium Oxide Slurries, Spectrophotometric Tiron Method"	9 082203	2-12-59
Sherrill, H. S.	"Settling Rate of Slurries, X-Ray Photographic Method"[16]	1 10011 9 00604	8-14-59
Shults, W. D.	"Oxides of Nitrogen, Spectrophotometric Method"	1 220015 9 00720015	7-13-59
Young, J. P.	"Titanium, Spectrophotometric Thiocyanate–Tri-*n*-octylphosphine Oxide (TOPO) Method"	1 219014 9 00719014	2-9-59
	"Zirconium, Tri-*n*-octylphosphine Oxide Extraction–Pyrocatechol Violet Spectrophotometric Method"	1 219813 9 00719813	5-7-59
Zittel, H. E.	"Barium, Polarographic Method"	1 210820 9 00710820	9-26-58
	"Technetium, Polarographic Method"	1 218320 9 00718320	7-24-59
	"Tungsten, Polarographic Method"	1 219120 9 00719120	5-7-59

ORAL PRESENTATIONS

At Meetings of Professional Societies

Author(s)	Title	Presented at
Ball, R. G., D. L. Manning, F. L. Layton[17]	"The Determination of Chloride by Cathodic Stripping Polarography"	Southeastern Regional Meeting, American Chemical Society, Richmond, Va., Nov. 4–7, 1959
Bate, L. C.,[17*] R. E. Druschel, W. J. Hampton*	"The Analysis of Subsieve Particulates of Thorium Oxide by Nuclear Analysis Methods"	3rd Industrial Nuclear Technology Conference, Chicago, Sept. 22–24, 1959
Bate, L. C., G. W. Leddicotte[17]	"Neutron Radioactivation Methods for the Particle-Size Analysis of Subsieve Particulates"	136th Meeting, American Chemical Society, Atlantic City, Sept. 13–18, 1959
Bate, L. C.,[17] G. W. Leddicotte	"The Quantitative Analysis of Complex Mixtures of Radionuclides by Gamma Ray Spectrometry"	Southeastern Regional Meeting, American Chemical Society, Richmond, Va., Nov. 4–7, 1959

[17]Speaker.

Author(s)	Title	Presented at
Cooper, J. H.	"The High-Alpha-Radiation Analytical Facility of the Oak Ridge National Laboratory"	3rd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 26–29, 1959
Dunn, H. W.	"X-Ray Absorption Edge Analysis"	3rd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 26–29, 1959
Emery, J. F.	"Neutron Activation for the Determination of Trace Impurities in Silicon Halides"	Analytical Group Meeting, Semiconductor Analysis Group, New York, June 19, 1959
Emery, J. F.,[17] G. W. Leddicotte	"A Crystal Discriminatory Counter"	3rd Industrial Nuclear Technology Conference, Chicago, Sept. 22–24, 1959
Ferguson, R. L.	"Surface-Exchange Method for the Determination of Surface Area of UO_2 Powder"	Southeastern Regional Meeting, American Chemical Society, Richmond, Va., Nov. 4–7, 1959
Goldberg, G.	"Determination of Oxygen in Fluoride Salts by High-Temperature Fluorination with $KBrF_4$"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Mar. 2–6, 1959
Goldstein, G.,[17] O. Menis, D. L. Manning	"Extraction of Thorium with Thenoyltrifluoroacetone. Effect of Acetic Acid"	136th Meeting, American Chemical Society, Atlantic City, Sept. 13–18, 1959
Hill, F. M.,[17] W. R. Laing	"A Microtitration Method for the Determination of Boron in Stainless Steel"	Southeastern Regional Meeting, American Chemical Society, Richmond, Va., Nov. 4–7, 1959
Kelley, M. T.	"Analytical Instrumentation"	American Chemical Society Local Section, Urbana, Ill., Jan. 8, 1959
Kelley, M. T.,[17] D. J. Fisher, W. D. Cooke,[18] H. C. Jones	"Controlled-Potential and Derivative Polarography"	2nd International Congress of Polarography, Cambridge, England, Aug. 24–29, 1959
Kelley, M. T., H. C. Jones, D. J. Fisher[17]	"Electronic Controlled-Potential Coulometric Titrator for Pu Analysis"	3rd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 26–29, 1959
Kelley, M. T.,[17] G. W. Leddicotte	"Nuclear Methods of Analysis"	Greek Chemical Society, Athens, Oct. 7, 1959
Kelley, M. T.,[17*] E. B. Wagner, D. J. Fisher*	"Automatic Recording, Velocity-Servo, Potentiometric Titrator"	135th Meeting, American Chemical Society, Boston, Apr. 5–10, 1959
Koskela, U.	"Chemical Analyses for the ORNL Aqueous Homogeneous Reactor"	135th Meeting, American Chemical Society, Boston, Apr. 5–10, 1959

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

Author(s)	Title	Presented at
Koskela, U., L. G. Farrar, J. E. Attrill, J. L. Mottern[8]	"Analytical Service for the Homogeneous Reactor Test"	Seventh Hot Laboratories and Euipment Conference, Cleveland, Apr. 7–9, 1959
Kubota, H.	"The Polarographic Determination of Uranium(VI) in Uranium Dioxide"	135th Meeting, American Chemical Society, Boston, Apr. 5–10, 1959
Leddicotte, G. W.	"Activation Analysis at ORNL Pile"	Industrial Radioisotope Training Course, ORINS, Oak Ridge, Apr. 29 and Nov. 13, 1959
	"Activation Analysis for the Determination of Trace Impurities in Group V–VIII and Their Compounds"	Symposium on the Analysis of Semiconductor Materials, Battelle Memorial Institute, Columbus, Feb. 10, 1959
	"Experience in the USA on the Use of Radioactivation Analysis"	International Atomic Energy Agency – Joint Commission on Applied Radioactivity Symposium on Radioactivation Analysis, Vienna, June 1–3, 1959
	"Nucleonics in Analytical Chemistry"	Frontiers in Chemistry, Western Reserve University, Cleveland, Feb. 13, 1959, and 10th Annual Naval Reserve Science, ORINS, Oak Ridge, Dec. 8, 1959
	"Radioactivation Analysis"	Radioisotope Conference, University of Liége, Liége, Belgium, June 15, 1959
Leddicotte, G. W.,[17] W. T. Mullins, J. E. Strain	"Experimental Evaluation of Radiochemical Procedures for Radioactivation Analyses"	136th Meeting, American Chemical Society, Atlantic City, Sept. 13–18, 1959
Leddicotte, G. W.,[17] J. E. Strain, L. C. Bate	"Determination of Lithium Isotopic Ratios by Neutron Radioactivation Analysis"	136th Meeting, American Chemical Society, Atlantic City, Sept. 13–18, 1959
Macklin, R. L., G. DeSaussure, J. D. Kington, W. S. Lyon* (presented by R. C. Block)	"Measurement of η for U^{233}, U^{235}, and Pu^{239} by the Manganese Bath Technique"	American Physical Society, Cleveland, Nov. 27, 1959
Manning, D. L.,[17] O. Menis	"Some Applications of High-Frequency Titrimetry"	3rd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 26–29, 1959
Mihelich, J. W.,[6,17] B. Harmatz, T. H. Handley*	"Nuclear Levels of Odd-A Nuclei for Odd Neutron Numbers 99 to 107"	Meeting of the American Physical Society, Cleveland, Nov. 27, 1959

Author(s)	Title	Presented at
Miller, C. E.,[12,17] G. W. Leddicotte	"Neutron Activation Analysis Methods for the Group VIII Elements"	3rd Industrial Nuclear Technology Conference, Chicago, Sept. 22–24, 1959
Miller, H. H., M. T. Kelley,[17] P. F. Thomason	"Polarographic Studies of the Reduction of Pertechnetate Ion in Aqueous Solutions"	2nd International Congress of Polarography, Cambridge, England, Aug. 24–29, 1959
Moore, F. L.	"Liquid-Liquid Extraction of Uranium and Plutonium from Acetate Solution with Tri(iso-octyl)amine. Separation from Thorium and Fission Products"	136th Meeting, American Chemical Society, Atlantic City, Sept.13–18, 1959
Mullins, W. T.	"The Determination of Trace Elements by Neutron Activation Analysis"	2nd Annual Texas Conference on the Utilization of Atomic Energy, College Station, Nov. 12–13, 1959
Mullins, W. T.,[17] J. H. Oliver, W. A. Brooksbank,[10] G. W. Leddicotte	"The Use of Neutron Radioactivation as a Qualitative or Semiquantitative Analysis Method"	3rd Industrial Nuclear Technology Conference, Chicago, Sept. 22–24, 1959
Norris, J. A.	"The Photoelectric Determination of Hafnium in Zirconium Oxide. The Role of the 'Carrier'"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Mar. 2–6, 1959
Norris, J. A.,[17] Z. Combs	"Matrix Effects in a Graphite Semi-quantitative Procedure"	Southeastern Section of the Society of Applied Spectroscopy, Birmingham, Ala., Sept. 19, 1959
Rains, T. C., H. P. House, O. Menis[17]	"Evaluation of Flame Photometry for the Determination of Elements of the Rare-Earth Group"	3rd Annual Conference, Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 26–29, 1959
	"Flame Photometry in Organic Solvents – Applicability to the Estimation of Rare Earth Elements"	Southeastern Meeting of the Society for Applied Spectroscopy, Birmingham, Ala., Sept. 19, 1959
Rains, T. C.,[17] O. Menis	"Flame Photometric Determination of Iron"	136th Meeting, American Chemical Society, Atlantic City, Sept. 13–18, 1959
Reynolds, S. A.	"Instruments for Radioactivity Measurements"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Mar. 2–6, 1959
	"Analysis for Radionuclides in Homogeneous Reactor Fluids"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Mar. 2–6, 1959
Ross, W. J.,[17] J. C. White	"Extraction of Thorium from Sulfate and Phosphate Solutions with Tri-*n*-octylphosphine Oxide"	135th Meeting, American Chemical Society, Boston, Apr. 5–10, 1959

Author(s)	Title	Presented at
Rubin, I. B.,[17] O. Menis	"The Colorimetric Determination of Titanium in Thorium Oxide by Means of Disodium 4,5-Dihydroxy-*m*-benzenedisulfonate"	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Mar. 2–6, 1959
Strain, J. E.,[17] J. H. Oliver, G. W. Leddicotte	"Preparation, Properties and Uses of Alpha, Gamma, and Neutron Sources Using Americium-241"	3rd Industrial Nuclear Technology Conference, Chicago, Sept. 22–24, 1959
Thomason, P. F.,[17] W. D. Shults, B. B. Hobbs, E. L. Blevins	"Controlled-Potential Coulometric Analysis of Dissolver Solutions of Various Reactor Fuels"	SS Material Management Meeting, Germantown, Md., May 25–28, 1959
Willmarth, T. E.	"Cintel Flying Spot Microscopy"	13th Meeting of AEC Metallography Group, Illinois Institute of Technology, Chicago, Jan. 14–15, 1959
Young, J. P.	"Spectrophotometry of Molten Fluoride Salts"	Gordon Research Conference on Molten Salts, Meriden, N.H., Aug. 31–Sept. 4, 1959
Zittel, H. E., M. T. Kelley,[17] F. L. Conover,[19] G. R. Wilson	"Effects of Phosphate and Other Anions in the Polarography of Uranium in Acid Media"	2nd International Congress of Polarography, Cambridge, England, Aug. 24–29, 1959

Under the ORNL Traveling Lecture Program

Lecturer	Lecture Title	Presented at
Cameron, A. E.	"Geological Age Determination by Isotopic Measurements"	Louisiana State University, Baton Rouge, Jan. 13, 1959
		Tulane University, New Orleans, La., Jan. 14, 1959
		Birmingham-Southern College, Birmingham, Ala., Feb. 17, 1959
		University of Alamana, University, Feb. 18, 1959
		Tuskegee Institute, Tuskegee, Ala., Feb. 19, 1959
		Alabama State College, Montevallo, Feb. 21, 1959
		Bethany College, Bethany, W. Va., Apr. 21, 1959
		Georgian Court College, Lakewood, N.J., Apr. 22, 1959
		Emory University, Atlanta, Ga., Nov. 17, 1959
		Oglethorpe University, Atlanta, Ga., Nov. 17, 1959
Reynolds, S. A.	"Analytical Radiochemistry"	Tuskegee Institute, Tuskegee, Ala., Dec. 3, 1959

[19] Vanderbilt University, Nashville, Tenn.

ANALYTICAL CHEMISTRY DIVISION

M. T. KELLEY, DIRECTOR
K. A. ODOM,* SEC.
C. D. SUSANO, ASSOCIATE DIRECTOR
B. E. YOUNG, SEC.
O. G. STONE, ASSISTANT TO DIRECTOR
K. A. ODOM,* SEC.
H. P. RAAEN,* REPORTS EDITOR
H. E. ZITTEL,* HRP COORDINATOR

O. G. STONE, ASSISTANT TO DIRECTOR
A. L. HARROD, PROCUREMENT
W. H. BYRD, SEC.
M. P. COLEMAN, SEC.
M. L. DOSSETT, SEC.
M. I. SARGENT, SEC.

C. D. SUSANO ASSOCIATE DIRECTOR
C. L. MOORE, PROCUREMENT
E. W. BOGLE, SEC.

RESEARCH AND DEVELOPMENT

RADIOCHEMICAL ANALYSES
S. A. REYNOLDS, GROUP LEADER
J. S. ELDRIDGE
T. H. HANDLEY
W. S. LYON
F. L. MOORE
R. H. RODRIGUEZ**
ANALYST
W. B. TOWNS

NUCLEAR ANALYSES
G. W. LEDDICOTTE, SUPERVISOR
L. C. BATE
J. F. EMERY
R. L. FERGUSON
W. T. MULLINS
J. E. STRAIN
ANALYSTS
L. M. FRAKES
W. J. HAMPTON
R. W. HARVEY
F. S. MCNABB
J. H. OLIVER
N. B. TUCK

IONIC ANALYSES
P. F. THOMASON, GROUP LEADER
E. L. BLEVINS
R. E. BIGGERS
D. A. COSTANZO
B. B. HOBBS
A. D. HORTON
H. KUBOTA
F. J. MILLER
H. P. RAAEN*
W. D. SHULTS, II
C. C. WHITE
H. E. ZITTEL*

SPECTROCHEMICAL AND X-RAY ANALYSES
C. FELDMAN,* SUPERVISOR
H. W. DUNN
P. V. HOFFMAN
S. R. KOIRTYOHANN
W. R. MUSICK
M. M. MURRAY
C. A. PRITCHARD
R. L. SHERMAN
ANALYSTS
A. H. MARSHALL
J. C. MCCOWN

OPTICAL AND ELECTRON MICROSCOPY
T. E. WILLMARTH, GROUP LEADER
T. G. HARMON
H. W. WRIGHT
ANALYSTS
J. S. ACREE
N. P. HUNTSMAN
W. H. SMITH

ANALYTICAL INSTRUMENTATION
D. J. FISHER, GROUP LEADER
H. C. JONES
W. L. MADDOX
R. W. STELZNER

SERVICE

INORGANIC PREPARATIONS
D. E. LAVALLE, SUPERVISOR
C. F. HARRISON

LOW-LEVEL RADIOCHEMICAL LABORATORY
C. L. BURROS, SUPERVISOR
J. H. MONEYHUN
ANALYST
D. K. SMITH

SERVICE (CONT.)

PROCESS ANALYSES
L. T. CORBIN, SECTION CHIEF

HIGH-RADIATION-LEVEL ANALYTICAL LABORATORY
J. E. MORTON, SUPERVISOR

HIGH-ALPHA LABORATORY
J. H. COOPER, SUPERVISOR
G. V. PIERCE
ANALYSTS
C. J. COLBY
W. C. MASSEY
M. V. TURNBILL

PROCESS DEVELOPMENT CONTROL LABORATORY
G. R. WILSON, SUPERVISOR
W. L. BELEW
H. S. SHERRILL
ANALYSTS
G. R. ARCHER
W. E. BAYLESS
G. HICKEY
S. W. HOPKINS
R. L. LEWIS
J. T. WHITE

PILOT PLANT CONTROL LABORATORY
C. E. LAMB, SUPERVISOR
E. C. FEARNOW
C. C. FOUST
M. J. GAITANIS
R. E. JONES
H. D. MCMURRAY
J. C. PRICE
A. F. ROEMER, JR.
ANALYSTS
W. H. AKERS
R. BURNS
B. E. GILL
L. GUINN
F. E. HAGA
R. A. JONES
D. D. PAIR
P. M. ROWAN
H. C. SMITH
A. C. STEWART
E. L. VILES

SPECIAL ANALYSES LABORATORY
W. R. LAING, SUPERVISOR
J. L. BOTTS
H. G. DAVIS
B. J. GINOCCHIO
F. M. HILL
H. C. MEYER
R. B. QUINCY, JR.
R. H. SAMPLEY
G. A. WESTERDAHL
J. S. WIKE
ANALYSTS
E. E. BONIFACIUS
G. S. BROWN
J. D. HILL
K. C. LANNOM
G. OLERICH
B. PHILPOT
S. H. PRESTWOOD
A. D. WILSON
J. V. WINCHESTER

RADIOISOTOPES-RADIOCHEMISTRY LABORATORY
E. I. WYATT, SUPERVISOR
H. A. PARKER
R. R. RICKARD
ANALYSTS
J. H. DAVIDSON
M. L. FREEMAN
C. L. GHANN
P. S. GOUGE
E. C. HENDREN
R. H. HOLLAND
S. H. MCCARLEY
K. J. NORTHCUTT
J. H. OXENDINE
P. W. PAIR
J. D. PENDLETON
F. B. PHILLIPS
G. W. ROBINSON, JR.
T. G. SCOTT
J. SLESSINGER, JR.
K. M. WALLACE
W. R. WARREN

REACTOR ANALYSES LABORATORY
U. KOSKELA, SUPERVISOR
L. G. FARRAR
C. P. BAKER
R. E. CORCORAN
S. R. DINSMORE
ANALYSTS
G. M. CAMPBELL
G. I. GAULT
F. K. HEACKER
M. H. MCCORQUODALE
J. L. SHARP
H. L. WEBB
H. L. WHITTINGTON

MASS SPECTROMETRY
A. E. CAMERON,* SECTION CHIEF
J. F. WILDER, SEC.

REFEREE ANALYSES LABORATORY
A. E. CAMERON,* GROUP LEADER
E. F. BLASE
W. H. CHRISTIE
H. O. FINLEY
A. S. TRUNDLE, III
R. L. WALKER
J. R. WALTON
ANALYSTS
E. G. MILLER
N. WILSON

ANALYTICAL MASS SPECTROMETRY
J. R. SIYES, SUPERVISOR
E. J. SPITZER
ANALYSTS
B. E. DANIELS
H. P. GHANN
M. M. MCMAHAN
C. E. PRATHER

SPECIAL PROBLEMS IN MASS SPECTROMETRY
J. F. BURNS

STAFF
H. P. HOUSE*
M. A. MARLER
R. L. MCCUTCHEN

REACTOR PROJECTS LABORATORY
J. C. WHITE,* SECTION CHIEF
E. M. ZARZECKI, SEC.

RESEARCH
A. S. MEYER, JR., GROUP LEADER
G. GOLDBERG
H. L. HOLSOPPLE
W. J. ROSS
I. B. RUBIN

DEVELOPMENT
J. C. WHITE,* GROUP LEADER
J. E. ATTRILL
C. A. HORTON
J. P. YOUNG

SERVICES
W. F. VAUGHAN, SUPERVISOR
R. F. APPLE
D. E. CARPENTER
ANALYSTS
R. C. BRYANT
L. R. HALL
L. E. IDOM***
A. H. MATTHEWS
D. B. WAGONER
C. M. WILSON

GENERAL SERVICES
L. J. BRADY, SECTION CHIEF

RAW MATERIALS LABORATORY
J. R. LUND, SUPERVISOR
ANALYSTS
B. S. CARMACK
E. E. HENDREN
K. I. PRESSLEY
R. M. RAMSEY

COUNTING LABORATORY
J. M. PEELE, SUPERVISOR
ANALYSTS
C. S. ALLEY
A. E. THOMAS

MISCELLANEOUS ANALYTICAL LABORATORY
E. C. LYNN, SUPERVISOR
ANALYSTS
M. R. CHILDS
J. H. HACKNEY
O. B. HAYNES
W. F. ROGERS
P. Z. WESTERDAHL

SPECTROCHEMICAL ANALYSES
C. FELDMAN,* GROUP LEADER
J. A. NORRIS, SUPERVISOR
Z. COMBS
J. J. MUNDZAK
R. E. WEEKLEY
ANALYST
E. H. WATERS

THERMAL BREEDER REACTOR PROJECTS ANALYTICAL CHEMISTRY LABORATORY
O. MENIS,* SECTION CHIEF
H. P. HOUSE,* ASSISTANT SECTION CHIEF
A. R. HEAGERTY, SEC.

DEVELOPMENT
O. MENIS,* GROUP LEADER
C. M. BOYD

D. L. MANNING, GROUP LEADER
G. GOLDSTEIN

T. C. RAINS, GROUP LEADER
N. M. FERGUSON

SERVICES
C. K. TALBOTT, SUPERVISOR
F. L. LAYTON
ANALYSTS
T. P. BACON
W. D. CLAPP
C. A. CLARK
P. S. GOODWIN
B. D. HICKS
T. G. MILLER
E. ONKST

*DUAL CAPACITY
**ALIEN GUEST
***ON LOAN TO CHEMISTRY

ADMINISTRATIVE AND CLERICAL	13
ANALYST	97
SCIENTISTS	117
TOTAL	227

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4. Reactor Experimental Engineering Library
5-7. Central Research Library
8-27. Laboratory Records Department
28. Laboratory Records, ORNL R.C.
29. A. M. Weinberg
30. L. B. Emlet (K-25)
31. J. P. Murray (Y-12)
32. J. A. Swartout
33. E. D. Shipley
34. M. T. Kelley
35. C. D. Susano
36. M. L. Nelson
37. E. H. Taylor
38. A. H. Snell
39. F. L. Culler
40. M. J. Skinner
41. S. C. Lind
42. W. H. Jordan
43. T. A. Lincoln
44. C. E. Winters
45. A. Hollaender
46. K. Z. Morgan
47. C. P. Keim
48. A. S. Householder
49. H. E. Seagren
50. D. Phillips
51. J. M. Schreyer (Y-12)
52. G. E. Boyd
53. R. B. Briggs
54. G. W. Parker
55. L. J. Brady
56. H. P. House
57. O. Menis
58. C. H. Secoy
59. L. E. Burkhart (Y-12)
60. R. N. Lyon
61. S. A. Reynolds
62. P. F. Thomason
63. J. L. Gabbard
64. D. E. LaValle
65. A. R. Brosi
66. J. A. Norris
67. E. I. Wyatt
68. G. W. Leddicotte
69. C. Feldman
70. T. E. Willmarth
71. E. C. Lynn
72. L. T. Corbin
73. T. C. Rains
74. P. M. Reyling
75. H. P. Raaen
76. J. C. White
77. J. P. Young
78. U. Koskela
79. D. J. Fisher
80. G. C. Williams
81. W. A. Pfeiler (Y-12)
82. R. S. Livingston
83. A. S. Meyer, Jr.
84. R. L. McCutchen
85. J. M. Peele
86. J. A. Lane
87. R. W. Johnson
88. R. A. Charpie
89. J. R. Lund
90. W. F. Vaughan
91. C. L. Burros
92. J. H. Cooper
93. W. R. Laing
94. C. E. Lamb
95. G. R. Wilson
96. C. K. Talbott
97. E. J. Frederick
98. M. A. Marler
99. D. L. Manning
100. A. E. Cameron
101. J. R. Sites
102. W. R. Rathkamp
103. J. F. Burns
104. H. A. Laitinen (consultant)
105. W. W. Meinke (consultant)
106. D. N. Hume (consultant)
107. C. E. Larson (consultant)
108. N. H. Furman (consultant)
109. L. L. Merritt (consultant)
110-111. ORNL – Y-12 Technical Library, Document Reference Section

EXTERNAL DISTRIBUTION

112. Office of Isotope Development, AEC, Washington (H. Miller)
113. Division of Research and Development, AEC, ORO
114. General Electric Company, Richland (R. J. Brouns)
115. duPont Company, Wilmington
116. Bettis Plant
117. National Lead Company, Inc. (Raw Materials Development Laboratory)
118-674. Given distribution as shown in TID-4500 (15th ed.) under Chemistry-General category (75 copies – OTS)

Reports previously issued in this series are as follows:

ORNL-686	Period Ending March 31, 1950
ORNL-788	Period Ending June 30, 1950
ORNL-867	Period Ending October 10, 1950
ORNL-955	Period Ending January 10, 1951
ORNL-1088	Period Ending March 26, 1951
ORNL-1113	Period Ending June 26, 1951
ORNL-1129	Period Ending September 10, 1951
ORNL-1233	Period Ending December 26, 1951
ORNL-1276	Period Ending March 26, 1952
ORNL-1361	Period Ending June 26, 1952
ORNL-1423	Period Ending September 26, 1952
ORNL-1474	Period Ending January 10, 1953
ORNL-1547	Period Ending April 20, 1953
ORNL-1639	Period Ending October 20, 1953
ORNL-1717	Period Ending April 20, 1954
ORNL-1788	Period Ending October 20, 1954
ORNL-1880	Period Ending April 20, 1955
ORNL-1973	Period Ending October 20, 1955
ORNL-2070	Period Ending April 20, 1956
ORNL-2218	Period Ending December 31, 1956
ORNL-2453	Period Ending December 31, 1957
ORNL-2662	Period Ending December 31, 1958