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ANALYTICAL CHEMISTRY DIVISION

QUARTERLY PROGRESS REPORT

FOR PERIOD ENDING JUNE 26, 1951

AEC RESEARCH AND DEVELOPMENT REPORT

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ANALYTICAL CHEMISTRY DIVISION

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

QUARTERLY PROGRESS REPORT

for Period Ending June 26, 1951

Date Issued

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TABLE OF CONTENTS

	Page
PUBLICATIONS	xiv
ABSTRACT	1
ANALYTICAL CHEMISTRY DIVISION — X-10 SITE	
1. IONIC ANALYSES — RESEARCH AND DEVELOPMENT	6
Microcoulometric Titrations	6
Colorimetric Determination of Nickel in HRE Solutions	9
Determination of Uranium in the HRE Soup	10
Method 1. Changing the potential of the Fe(II)-Fe(III) system	11
Method 2. Removal of iron from uranium solutions using a mercury cathode	12
Isolation of Uranium(VI) by Filter Paper Partition Chromatography and Its Quantitative Determination	13
Separation of U(VI) from Fe(III), Ni(II), and Cr(III) by Filter Paper Partition Chromatography	15
Polarographic Investigation of Irradiated Potassium Bromate	16
Polarographic Determination of Small Quantities of Tungsten in Titanium Metal	17
Determination of Excess Barium Hydroxide in a Barium Sulfide Solution	18
Polarographic Behavior of Technetium	18
Indirect Polarographic Determination of Potassium	18
Analysis of Sodium Fluoride—Potassium Fluoride—Uranium Fluoride Eutectic for Chromium, Nickel, and Iron	19
Ultramicro Determination of Nitrogen as Ammonia	20
Determination of Citrate by Iodate Oxidation	20
Manual of Analytical Procedures for the U^{235} Recovery Process	20
Master Manual of Analytical Test Methods	21
2. RADIOCHEMICAL ANALYSES — RESEARCH AND DEVELOPMENT	22
Nuclear Properties	22

[redacted]

[redacted]

[redacted] FOR PERIOD ENDING JUNE 30

TABLE OF CONTENTS (continued)

	Page
Cyclotron-produced cobalt	22
Decay of Cr^{51}	22
Fast-neutron flux in the ORNL graphite reactor	23
Measurement of Radioactivity	23
The 4π beta proportional counter	23
Plates for gross activity determination	25
Assay of low-level beta activity in liquid wastes	26
Analysis of Radioisotopes	30
Bureau of Standards P^{32}	30
Determination of Fe^{55} in the presence of Fe^{59}	31
Impurities in manganese product	31
4π counting of I^{131}	32
Analysis for Heavy Elements	33
Plutonium polymer	33
Plutonium in Chalk River dissolver solution	34
Identification of Radioelements	34
Miscellaneous Activities	34
Gaseous waste	34
Purification of rubidium	36
Preparation of accelerator targets	36
Training of personnel for other sites	36
3. ACTIVATION ANALYSES — RESEARCH AND DEVELOPMENT	37
New Analytical Procedures	37
Sodium	37
Potassium	38
Barium	40
Strontium	41
Gallium	42
Procedures for other substances	43
Analysis of Titanium for Chlorine and Tungsten	43
New Applications of Activation Analysis	45

[redacted]

[redacted]

TABLE OF CONTENTS (continued)

	Page
4. SPECTROCHEMICAL ANALYSES — RESEARCH AND DEVELOPMENT	46
5. SERVICE ANALYSES	47
Ionic Analyses — Development Group	47
Radiochemical Analyses — Development Group	47
Activation Analyses	47
General Radiochemical Analyses	47
Water Analysis Laboratory	49
Laboratory and Semi-Works Control	50
Pilot Plant Control	51
Modified lanthanum fluoride procedure for plutonium	51
TTA extraction of plutonium	51
Fluorophotometric determination of uranium	52
Radioisotope Analyses	52
New analytical procedure for Tc^{99}	52
New analytical procedure for Nb^{95}	52
Improved analytical procedure for rare earths	52
Improved analytical procedure for C^{14}	52
6. INORGANIC PREPARATIONS	53
Phosphors	53
7. ANALYTICAL CHEMICAL CONTROL OF THE HOMOGENEOUS REACTOR SOLUTION	54
Electromagnetic Densitometer	54
Q measurements	55
Radiation-resistant glasses	56
8. OPTICAL AND ELECTRON MICROSCOPY	57
Effect of Surface Conditions of Test Bombs on Formation of Oxide Layers on 347 Stainless Steel During Pretreatment with 1% HNO_3 at 250°C	57
Extent of Radiation Damage to Painted Surfaces	58
Radioautography of CWS Filters and Other Current Work	59

[redacted]

[redacted]

TABLE OF CONTENTS (continued)

ANALYTICAL CHEMISTRY DIVISION — Y-12 SITE

	Page
9. RESEARCH AND DEVELOPMENT	60
Oxygen and Nitrogen in Lithium	60
Metallic Corrosion Products in Sodium Metal	60
Elements of High-Neutron-Capture Cross-Section in Sodium Metal	60
Oxygen in Sodium	62
Recovery of known amounts of oxygen	62
Comparison of methods	62
Application to samples contained in metal tubes	64
Potassium, Lithium, and Cesium in Sodium Metal	65
Oxygen in Helium and Argon	66
Reaction of Metallic Sodium with Sodium Tetraborate at Elevated Temperatures	67
Determination of Carbon in Lithium	68
Metallic Corrosion Products in Reactor Fuels	69
Removal of eutectic	69
Preparation of sample for spectrographic analysis	69
Development of colorimetric methods	70
Detection of Organic Binder in a Graphite Bearing	72
Investigation of a Synthetic Smoke Mixture	72
Analysis of Uranyl Sulfate Solutions	73
Uranium(IV)	73
Total uranium	75
Oxygen	75
Chromium	76
Cadmium	77
Nickel	77
Iron	78
Recovery of Trace Elements in Extraction of Uranium from Uranyl Solutions	79

[redacted]

[redacted]

TABLE OF CONTENTS (continued)

	Page
Analytical Problems in the Precipitation of Zirconium as Zirconyl Phthalate	80
Evidence of amide or imide formation	81
Identification of the product of the reaction between phthalic anhydride and ammonia	82
Identification of the zirconyl precipitation product	84
Study of the optimum *p*H of precipitation	85
Conclusions	86
Identification of White Solid Residue from Chlorination of Zirconium	86
Determination of Aluminum in Zirconium	87
Quality Control	89
Ionic analysis laboratory	89
Spectrographic laboratory	90
HRE laboratory	90
X-10 laboratories	91
10. CHEMICAL ANALYSIS	93
Analytical Services for the ANP Project	93
Experimental engineering	93
Reactor chemistry	94
Analytical Services for NEPA	94
Analysis of Samples for General Electric Company	95
Analytical Services for the HRE Project	97
Raw Materials	97
Insoluble residues	97
Determination of iron in presence of phosphoric acid	97
Complete analyses	97
Shaker for solvent extraction	98
Marysvale ore	98
Determination of Phosphate in Ores	98
Effect of Temperature on Fluorescence	99
Miscellaneous Colorimetric Analyses	100

[redacted]

[redacted]

TABLE OF CONTENTS (continued)

	Page
Cadmium in uranyl sulfate solutions	100
Reactor fuels	101
11. SUMMARY OF SERVICE ANALYSES	102

[redacted]

[redacted]

LIST OF TABLES

		Page
1.1	Coulometric Titration of Standard Ferrous Sulfate Solution	8
1.2	Nickel in Uranyl Sulfate Solutions	10
1.3	Potentiometric Titration of Uranyl Sulfate Solutions	13
1.4	R_f Values for the U^{233}(VI) Ion	14
1.5	R_f Values for $Fe^{55,59}$(III) and U^{233}(VI)	16
1.6	Data from Indirect Polarographic Determination of Potassium	19
2.1	Comparison of 4π Disintegration Rates with Those Determined by Various Other Methods	24
2.2	Effect of Counter Gas Pressure on Apparent Disintegration Rate of Co^{60}	24
2.3	Composition of Mixed Fission Product Sample 3	26
2.4	Results on Check Samples of Low-Level Beta Activity	27
2.5	Determination of Mixed Fission Product Activity with End-Window and Proportional Counters	28
2.6	Activities of P^{32} Check Samples from National Bureau of Standards	31
2.7	I^{131} Disintegration Rates	33
2.8	Fission Products Leached from Filters	35
2.9	Leaching of Iodine from Filters	35
2.10	Heat-Induced Elimination of Iodine from Filters	36
3.1	Comparison of Activation and Spectrographic Methods for Determining Sodium	38
3.2	Separation of Rubidium and Cesium from Potassium Using 20% 9-Phosphomolybdic Acid	39
3.3	Decontamination Experiments with Barium Procedure Using Radioactive "Spikes"	41
3.4	Decontamination Experiments with Strontium Procedure Using Radioactive "Spikes"	42
3.5	Comparison of Activation and Spectrographic Methods for Determining Strontium	42

[redacted]

[redacted]

LIST OF TABLES (continued)

		Page
3.6	Comparison of Activation and Spectrographic Methods for Determining Gallium	43
3.7	Activation Sensitivities	44
3.8	Chlorine and Tungsten Results	45
5.1	Summary of Analytical Service Work for Period March 27 Through June 26, 1951	48
6.1	Phosphors Prepared for the Physics Division	53
8.1	Properties of Oxide Films Formed on 347 Stainless Steel During Pretreatment with 1% HNO_3	58
9.1	Recovery of Known Amounts of Oxygen in Sodium	62
9.2	Comparison of Results of Determinations of Oxygen in Sodium by the *n*-Butyl Bromide and the Pepkowitz and Judd Methods on Duplicate Samples	63
9.3	Oxygen in Helium After Passage Through NaK at 0.77 cu ft/min	66
9.4	Oxygen in Unpurified Argon	67
9.5	Reaction of 1 g of Borax with 0.1 g of Sodium	68
9.6	Influence of Time of Heating on Oxidation of Chromium to Cr(VI) by 72% Perchloric Acid	71
9.7	Comparison of Results by the Modified Thiocyanate and the Polarographic Methods for the Determination of Uranium	74
9.8	Extraction Made on UO_2SO_4 Solution Containing Traces of Nickel, Chromium, and Iron with Tributyl Phosphate (75%) in Benzene	80
9.9	Recovery of Nickel Following Extraction of $UO_2(ClO_4)_2$ with Tributyl Phosphate	81
9.10	Extinction Coefficients of Phthalic Anhydride and Potassium Biphthalate at Two Chosen Wavelengths	83
9.11	Optical Densities at 276 mμ of the Filtrates from Zirconyl Phthalate Precipitations at Various *p*H Values	86
9.12	Results of Identification Test on Residue from Zirconium Chlorination	87

[redacted]

LIST OF TABLES (continued)

		Page
9.13	Determination of Aluminum in Zirconium	89
9.14	Control Determinations Performed During the Quarter Ending June 22, 1951	90
9.15	Statistical Values Based on Test Results for the Determination of Uranium in the X-10 Laboratories During April, May, and June, 1951	92
10.1	Oxygen Content of Sodium Samples	93
10.2	Effect of $HClO_4$-HF Digestion on Accuracy of Phosphate Determination	99
10.3	Effect of Temperature on Fluorescene of Flux Disks	100
11.1	Sample Types and Components Determined in Service Analyses	102
11.2	Sample Status of Service Analyses	104
11.3	Classification of Determinations by Components	105

[redacted]

LIST OF FIGURES

		Page
Fig. 1.1	Microcoulometric Titration Apparatus and Circuit Diagram	7
Fig. 1.2	Microcoulometric Titration of 1.1 μg of Fe(II)	8
Fig. 1.3	Amperometric Indication of Ferrous Ion	9
Fig. 1.4	Radioautographs of U^{233}(VI) and $Fe^{55,59}$(III) (Filter Paper Chromatogram)	15
Fig. 2.1	Self-Absorption, End-Window Geiger-Mueller Counter	28
Fig. 2.2	Self-Absorption, Proportional Counter	28
Fig. 2.3	Anticoincidence Circuit Diagram	30
Fig. 2.4	Beta and Gamma Decay Curves for CWS Filter	35
Fig. 3.1	Activation Sensitivities	45
Fig. 9.1	Standard Curve for Fluorimetric Determination of Aluminum	88

[redacted]

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April - June, 1951

"Radioactive Hg^{203} and Hg^{205}," W. S. Lyon, *Phys. Rev.* **82**, 276 (1951).

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Y-B31-251. *The n-Butyl Bromide Method for the Determination of Sodium Monoxide in Sodium*, Robert Rowan, Jr., and J. C. White (Apr. 24, 1951).

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Y-B31-258. *Statistical Quality Control Report, April, 1951*, C. D. Susano, Robert Rowan, Jr., and R. L. McCutchen (May 17, 1951).

Y-B31-262. *Conference of March 22, 1951 on the Analysis of Zirconium*, W. K. Miller (June 6, 1951).

Y-B31-264. *Quality Control Report - The Determination of Uranium at the X-10 Laboratories for Period February 1 Through March 31, 1951*, C. D. Susano, Robert Rowan, Jr., and R. L. McCutchen (June 7, 1951).

Y-B31-267. *Statistical Quality Control Report, May, 1951*, C. D. Susano, Robert Rowan, Jr., and R. L. McCutchen (June 25, 1951).

Y-764. *Preparation of Highly Purified Zirconium Oxide*, C. D. Susano and H. P. House (May 25, 1951).

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ABSTRACT

ANALYTICAL CHEMISTRY DIVISION — X-10 SITE

Ionic Analyses — Research and Development. For possible use in analyzing HRE solutions a microcoulometric apparatus was set up and several titrations of ferrous sulfate were completed. The titration of uranium(IV) is now planned. A revised dimethylglyoxime procedure was successfully adapted to the analysis of HRE solutions for nickel. The determination of the total uranium content of HRE soup by potentiometric titration with ceric sulfate after reduction of the uranium(VI) to uranium(IV) was studied. It was found that orthophenanthroline complexed ferrous ion so that uranium(IV) could be titrated with ceric sulfate without interference by iron. The method was found to be about 1% accurate or poorer, depending upon the concentrations of iron and nickel impurities.

The study of the technique of filter paper partition chromatography for the separation and isolation of microgram and submicrogram quantities of uranium(VI) was continued. Optimum conditions for obtaining maximum sharpness of the uranium(VI) band, with 2-methyltetrahydrofuran as the eluent, were established, and a representative average R_f value for the U^{233}(VI) ion under these conditions was found to be 0.86. The procedures for quantitative estimation of the isolated uranium by activation analysis or by extraction and subsequent polarographic determination are under study. The application of this technique to the complete separation of iron, nickel, uranium, and chromium, using an elution with 2,4,6-collidine—0.4 *M* HNO_3 (1:1) following the 2-methyltetrahydrofuran elution, is under study. This separation is of interest in the analysis of HRE solutions containing stainless steel corrosion products.

Irradiated potassium bromate was examined polarographically for reduction products. The polarographic analysis of titanium metal for small quantities (less than 1%) of tungsten was attempted without success, likely because of insufficient separation of half-wave potentials of titanium and tungsten in the 6 *N* HCl required to dissolve the metal. An indirect polarographic determination of potassium was developed based on the polarographic estimation of cobalt in a potassium cobaltinitrite precipitate.

In relation to the ANP Materials Chemistry Division's study of the sodium fluoride—potassium fluoride—uranium fluoride eutectic, work has been undertaken to determine the apparatus required in a hot cell for the analysis of the irradiated eutectic.

A procedure for the determination of citrate by iodate oxidation in the presence of sulfuric acid was evaluated for the Chemistry Division. It gave an accuracy better than ±0.3% in routine use.

Editorial work on the *Manual of Analytical Procedures for the U^{235} Recovery Process*, ORNL-983, was completed and the manual has gone to press.

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Radiochemical Analyses — Research and Development. Investigations of decay schemes and analytical methods for cyclotron-produced cobalt isotopes are in progress. The studies of Cr^{51} with the crystal spectrometer indicated that a suggested modification should be made to the decay scheme previously proposed. The study of the fast-neutron flux in the ORNL graphite reactor is continuing. Further information on the applicability of the 4π proportional counter to radioisotope assay work is reported. A special technique for the preparation of sample mounts is described. A study of the determination of low-level beta activity has begun, and results are reported showing correlation of "check sample" determinations at several AEC sites. Tentative methods for determining several radioisotopes, including Fe^{55} in the presence of Fe^{59}, Ce^{141} in Ce^{141}-Ce^{144} mixtures, and I^{131}, are presented. Methods of plutonium determination in Chalk River material are discussed, including the Pu^{240} measurement. Identification and determination of fission product activities in stack gases are reported.

Activation Analyses — Research and Development. New analytical procedures in which the method of activation analysis is applied to the determinations of sodium, potassium, barium, strontium, and gallium are described. Also, outlines are given of procedures for chlorine and tungsten in titanium by activation analysis. A figure showing the sensitivities of neutron activation analyses for most of the elements is presented.

Spectrochemical Analyses — Research and Development. Spectrographic working curves were established for determining the following metals by the porous cup method: aluminum, barium, bismuth, cobalt, iron, manganese, and scandium. The concentration ranges and matrix solutions are indicated.

Service Analyses. The method of activation analysis for barium, strontium, sodium, and potassium and that for chlorine and tungsten in titanium have been established for routine use. New procedures for determining Tc^{99} and Nb^{95}, improved procedures for plutonium by lanthanum fluoride precipitation and by TTA extraction, and improved procedures for C^{14} and for the rare earths were suggested. The Metallurgy Division's studies of high-temperature alloys, thorium-breeder alloys, and liquid-solid metal interaction were sources of numerous requests for service work, and the demands of the homogeneous reactor project continued to be heavy. A total of 64,817 analyses was made during the quarter.

Inorganic Preparations. Thirty-nine new phosphors of interest to the Physics Division were prepared.

Analytical Chemical Control of the Homogeneous Reactor Solution. The Princo Densitrol instruments, which are being considered for measuring soup density under HRE conditions, are being assembled by the manufacturer. Receipt of one of the low-temperature units is expected by July 1, 1951. Several compromises with regard to construction materials have been agreed upon in order that the preliminary testing of the instruments may be accelerated. It is believed that satisfactory substitutions may be made at a later date for those materials whose resistance to radiation is doubtful.

The feasibility testing of a high-pressure—high-temperature electromagnetic densitometer has been completed. The results showed that it should be possible to detect changes of 0.0001 g/ml in the density of static HRE solutions using apparatus capable of withstanding the conditions of temperature and pressure found in the circulating system of the homogeneous reactor.

Irradiation of cadmium borofluosilicate glasses in the X-10 graphite reactor is continuing. Penberthy Instrument Co. of Seattle, Wash., is developing another type of radiation-resistant glass, one for which the transmission of neutron radiation is relatively increased and which offers low stopping power to gamma radiation.

A bomb designed for testing the mechanical strength and performance of various *Q* coils and insulators at HRE temperatures and equilibrium steam pressures has been utilized.

Optical and Electron Microscopy. A study is reported of the effect of surface conditions of test bombs on the formation of oxide layers on stainless steel during pretreatment with 1% nitric acid. The results are of interest in the corrosion problems of the HRE.

ANALYTICAL CHEMISTRY DIVISION — Y-12 SITE

Research and Development. The analysis of sodium metal is of particular importance to the ANP Experimental Engineering Group. Accordingly, attention has been given to establishing procedures for the determination of certain extraneous substances in sodium. Chemical methods of analysis are being set up for the determination of corrosion products (iron, chromium, cobalt, nickel) in the metal. No difficulty is anticipated in applying available colorimetric methods since their sensitivity and selectivity appear to be adequate. The *n*-butyl bromide method for the determination of oxygen in sodium is now being used routinely. Further indication of the suitability of the method is given by the results of analyses of sodium samples containing known, added amounts of sodium monoxide. Special procedures are discussed for preparing sodium samples, taken in stainless steel tubes, for oxygen determination by the *n*-butyl bromide method. A plan of work is presented for developing procedures for elements of high neutron cross-section which may be contained in sodium. The possibility of separation of the sodium by ion exchange and determination of the potassium with the flame spectrophotometer or by activation analysis is being studied. A similar approach is planned for the lithium and cesium determinations.

In connection with the ANP liquid-metals program the determination of carbon in lithium is of interest. A preliminary evaluation has been made of the simultaneous determination of carbide and carbonate. It is proposed to then determine graphitic carbon by wet combustion of the residue from this determination. The use of *n*-butyl chloride for the determination of oxygen and nitrogen in lithium was found to be unsatisfactory because of the long time required for completion of the reaction between the alkyl chloride and lithium. The applicability of iodobenzene as a reagent for

this determination is being investigated.

Because of the contemplated use of decrepitated borax as a shielding material for the ARE reactor, and the possibility of contact of the sodium at 1500°F with the borax through leakage, the reaction of the two substances was studied in the laboratory up to a maximum temperature of 745°C. There was evidence of the formation of boron and Na_2O but the reaction was not violent under the conditions tried.

The studies of corrosion and of solution stability in HRE test loops necessitated the determination of uranium(IV), total uranium, oxygen, chromium, cadmium, nickel, and iron in uranyl sulfate solutions. A procedure for uranium(IV) is described whereby uranium(IV) in microgram quantities can be separated from uranyl ions by precipitation as UF_4, then oxidized to the hexavalent state and determined colorimetrically or polarographically. Test results are compared for the polarographic and the colorimetric (thiocyanate) method. Two volumetric methods are being studied for the determination of total uranium in an effort to improve the accuracy and output attainable by the currently used potentiometric titration with ferric sulfate, following reduction with chromous sulfate solution. The results are not yet conclusive. For determining the concentration of free oxygen in HRE reactor solutions, polarographic and micro gasometric methods have been adopted. The polarographic method is especially suitable for the lower ranges of oxygen concentration where the precision of the gasometric method is poor. The latter is more rapid at higher concentrations. A colorimetric procedure for chromium in solutions from the HRE test loops has been developed, employing a perchloric acid oxidation and diphenylcarbazide as the chromogenic reagent. The precision of the method is reported to be of the order of 10%. Modified colorimetric (dimethylglyoxime) and polarographic procedures are described for determining nickel. The study of the polarographic determination of cadmium is incomplete. After a comparison of the 2,2′-bipyridyl and 1,10-phenanthroline procedures for determining iron in HRE solutions, the former was adopted for routine use because it was found to be less sensitive to variations in uranyl ion concentration. A study was made of the recovery of trace elements in the extraction of uranium from uranyl solutions with tributyl phosphate. Preliminary results indicate that a tributyl phosphate extraction of the major portion of the uranium may facilitate the determination of trace elements.

The analysis of two eutectic reactor fuels for corrosion products is discussed, consideration being given to the technique of sampling the material, preparing the sample for spectrographic analysis, and development of suitable colorimetric methods for the determination of corrosion products.

In relation to the zirconium refining process, a thorough investigation has been made of the possibility of phthalamidate or phthalimide formation and its effect on the refining process and on the determination of phthalate in recycle liquor. It was established experimentally that zirconium is being precipitated in the

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refining process by a solution of ammonium phthalamidate rather than one of ammonium phthalate. However, the precipitate was found to be zirconyl phthalate. It is recommended that the zirconium precipitation be carried out at approximately *p*H 2 in hot solution in order to obtain maximum zirconium recovery.

In the chlorination of zirconium the by-product gases are led from the zirconium tetrachloride condensers through scrubber lines into absorbing media, in which process a white coating is formed in the scrubber lines. This deposit was identified as hexachloroethane.

A report is made of the investigation of a preparation to be used in the generation of a smoke, desired by the ANP Experimental Engineering Group for use in certain engineering studies. A composition for this preparation is recommended. An apparatus suitable for determining low concentrations of oxygen in helium and argon has been placed in operation.

Service Analyses. Analytical work for the ANP project, which consists principally in the analysis of sodium for oxygen and corrosion products and the analysis of eutectic fuel mixtures and of miscellaneous metals, is reviewed. Difficulties encountered are noted.

A separate laboratory was established for the analysis of samples from the HRE project. Certain of the methods used are briefly outlined. During this period the backlog of HRE samples has been significantly reduced.

Studies of the effect of methods of dissolution of uranium ores and leached residues on the accuracy of the uranium determination are presented. Low temperature (-70°C) was found to have a negligible effect on the intensity of the fluorescence of uranium in fluoride flux disks.

A summary of service analyses (exclusive of HRE work) reveals that samples received exceeded samples reported by 17%, thus effecting a significant increase in the backlog.

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ANALYTICAL CHEMISTRY DIVISION – X-10 SITE

1. IONIC ANALYSES — RESEARCH AND DEVELOPMENT

MICROCOULOMETRIC TITRATIONS

P. F. Thomason and M. T. Kelley

The work of Cooke *et al.*[1] suggested the possibility of using a microcoulometric titration for the determination of micro amounts of uranium in highly radioactive solutions. This method would be particularly useful for the analysis of HRE solutions.

The method has been demonstrated[1] to work in the range of 1 to 10 μg of iron, and some results are reported for as little as 0.001 μg of material. Several systems were studied. Titrations of permanganate, vanadate, and ferrous ion were carried out by electrolytically generated ferrous ion in the first two instances and by electrolytically generated ceric ion in the last case. Accuracies of a few parts per thousand for 10 μg of material are reported.

The apparatus for this method was similar to that recommended by Furman[2] with the exception that a high-sensitivity recording polarograph was substituted for the Ayrton shunt and galvanometer indicating device used by Furman for the amperometric type end point. The circuit of the apparatus is shown in Fig. 1.1. The generating circuit consists of B batteries (90 volts) discharging through a 10-megohm resistance to give a constant current source of approximately 10 μa through the electrolytic cell. The current is measured by determining the voltage drop over a standard 100,000-ohm resistor that forms part of the resistance circuit. The measurement of this voltage drop can be conveniently done with a *p*H meter. The generating electrode consists of platinum foil approximately 1 sq cm in area. The other electrode is a platinum wire dipped in 0.05 *N* sulfuric acid contained in a glass tube that has a sintered glass end below an ammonium sulfate—agar plug to prevent loss of the 0.05 *N* sulfuric acid. A synchronous-motor clock is connected through the double-throw switch so that it is switched on simultaneously with the generator circuit. The indicating system has a platinum indicating electrode approximately 2 sq cm in area. The reference electrode is a saturated lead amalgam electrode in contact with about 0.05 *N* sulfuric acid. It is connected to the reaction vessel by means of an ammonium sulfate—agar bridge. For the ceric-ferrous system the indicator electrodes have impressed on them an emf of 1.0 volt from the recording polarograph, the platinum indicating electrode being the anode. For the generation of ceric ion for oxidation type titrations a saturated solution (approximately 12%) of cerous sulfate is made up in 2 to 3 *N* sulfuric acid. One volume of this stock solution is mixed with 2 volumes of distilled water. A 5-ml volume of this is pipetted into the titration cell.

(1) W. D. Cooke, C. H. Reilley, and N. H. Furman, *A Sensitive End Point Procedure for Microcoulometric Titrations*, paper presented at 119th meeting of American Chemical Society, Boston, Mass., April 3, 1951.

(2) N. H. Furman, personal letter to M. T. Kelley, Apr. 23, 1951.

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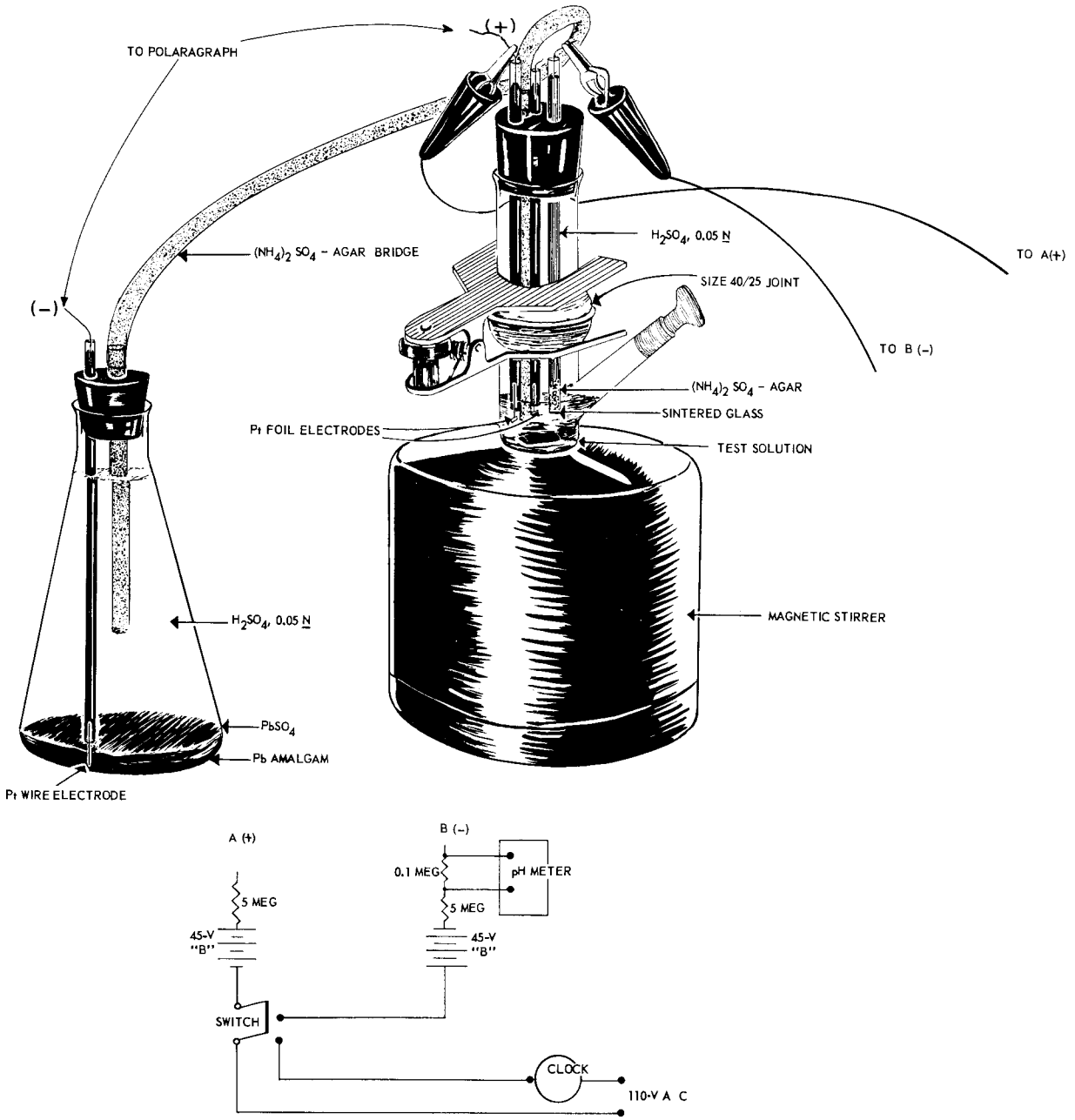

Fig. 1.1 - Microcoulometric Titration Apparatus and Circuit Diagram

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It is deaerated with nitrogen for 10 min and the current is measured with the polarograph. An anodic current is usually obtained, showing that the cerous sulfate solution is relatively more reducing than the end point mixture, for which the end point is usually chosen at zero current. The anodic current is titrated electrically until the cerous sulfate solution shows zero current with the polarograph set at the sensitivity scale required for the amount of material to be titrated. A sensitivity of 0.2 μa for full scale of the polarograph is required for 1 μg of iron. When the ferrous solution is measured into the titration cell and the magnetic stirring is started, an anodic diffusion current for the ferrous ion is observed. The generating current is started and read, and the polarograph proceeds slowly to zero current, which is the end point. A typical titration curve is shown in Fig. 1.2. The coulombs of electricity required for the titration is calculated from the time of titration and the current. One millicoulomb is equivalent to 0.579 μg of ferrous ion. The results obtained when aliquots of a standard ferrous sulfate solution containing 1.1 μg of Fe(II) were titrated in this manner. The results are shown in Table 1.1. One aliquot was titrated, then other aliquots were immediately introduced into the cell in rapid succession and titrated.

The data in Table 1.1 show that, although the results are somewhat low, this equipment is capable of giving results comparable to those of Cooke. However, it was noticed that following a titration there was a decided drift to a more anodic current value if the sample had been allowed to stand.

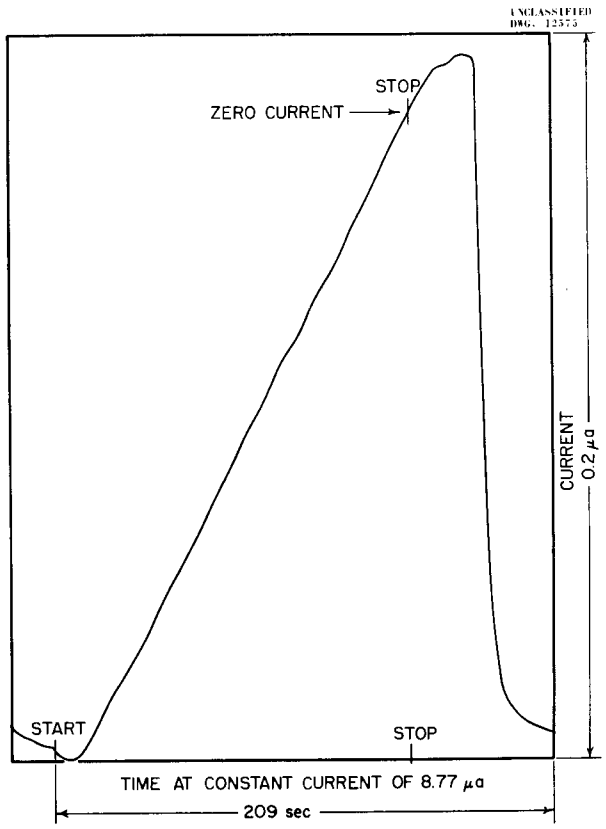

Fig. 1.2 - Microcoulometric Titration of 1.1 μg of Fe(II)

TABLE 1.1

Coulometric Titration of Standard Ferrous Sulfate Solution

1.1 μg of Fe(II); theoretical time for 8.77 μa = 215 sec

ALIQUOT	TIME REQUIRED (sec)
1	204
2	203
3	209
4	206
5	205
6	205

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This was easily seen on a more sensitive polarograph setting (0.05 μa for full scale). If the drift was ignored and another titration was attempted after 10 min, the results were high if the end point was again taken at zero current. This leads to the belief that the results would be inherently high because this unknown, slow reduction would have to be titrated simultaneously with the ferrous ion. It was decided to increase the amount of the ferrous ion to 10 μg and also the generating current to 100 μa to see if this would affect the drift previously noted. The results of these titrations showed that the drift was approximately the same; however, it was, of course, not so noticeable since the 1.0-μa scale was used in order to record the anodic diffusion current of 10 μg of ferrous ion. The cause of this drift will have to be eliminated before extremely accurate titrations can be made.

It was also noticed that a shift to a more anodic current on the recorder occurred when the generating system was switched on. Correspondingly, a jump to the cathodic side occurred when the generating current was turned off, which made it difficult to locate the zero current of the titration. Balancing the generating circuit by placing the switch between the two 45-volt B batteries and placing a 5-megohm resistor on the other terminal of each battery eliminated this difficulty.

The polarograph seems to be equally as good as a sensitive galvonometer in giving the amperometric type end point. The indications consist of two linear branches interacting at zero current as shown in Fig. 1.3.

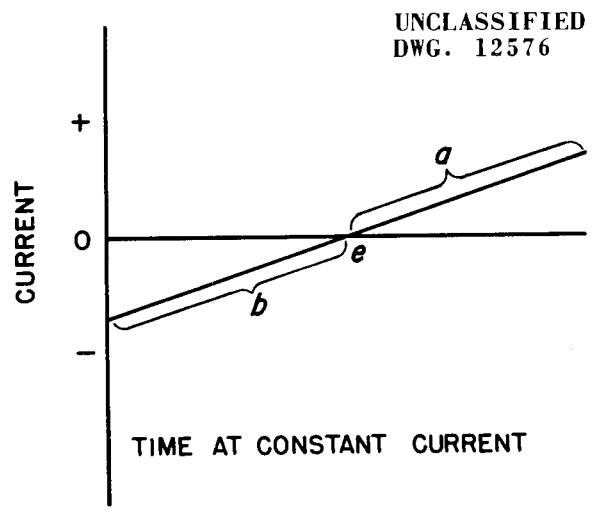

Fig. 1.3 - Amperometric Indication of Ferrous Ion. *a*, Cathodic Current Caused by Generation of Excess Ce(IV); *b*, Anodic Current Caused by Fe(II); *e*, End Point.

It is planned to try the titration of uranium, although the amperometric titration of U(IV) with electrolytically generated Ce(IV) will present more problems than in the case of Fe(II). Uranyl sulfate solutions of the HRE will have to be reduced to U(IV) before a titration can be attempted, and a titration involving the reduction of U(VI) to U(IV) with an electrolytically generated reagent probably would be preferable. The electrolytic generation of Cr(II) from an acid solution of potassium chromium sulfate will be tried, using a mercury pool cathode as the generating electrode.

COLORIMETRIC DETERMINATION OF NICKEL IN HRE SOLUTIONS

A. D. Horton

The usual procedure for determination of nickel gave low results

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when used with HRE solutions on which stainless steel corrosion studies had been made. This procedure consists in oxidizing the nickel with bromine water, removing excess bromine with ammonium hydroxide, and adding 1% dimethylglyoxime in 95% ethyl alcohol. A series of samples is then compared with a single blank which contains all the reagents except dimethylglyoxime.

A procedure developed by Bassett[3] for the determination of nickel in uranium oxides was adapted to the determination of nickel in uranyl sulfate solutions.

A uranyl sulfate solution was prepared which contained, per milliliter, 30 mg of U(VI) and 10 μg of Ni(II). Aliquots of 0.5, 1.0, and 2.0 ml of this solution were pipetted into 50-ml volumetric flasks. Duplicate aliquots were pipetted into another set of flasks to be used as blanks, i.e., analyzed without addition of dimethylglyoxime reagent.

To each flask was added 2 ml of bromine water, 10 ml of 10% citric acid, and 5 ml of 28% ammonium hydroxide. To the sample flasks only, 1 ml of 1% dimethylglyoxime in 95% ethyl alcohol was added, and the solutions were diluted to volume. These were compared with the blanks by use of the Beckman model DU quartz spectrophotometer at 525 mμ.

The percent transmittancy values for these standard solutions plotted on semilog paper produced a straight line beginning at the origin.

[3] L. G. Bassett, "Determination of Nickel in Brown and Orange Oxides," *Manual of Analytical Methods*, A-2912, Vol. III, Part 2, p. 172, (January, 1946).

Three samples containing 30 mg of U(VI) and 5.7, 11.4, and 22.8 μg of Ni(II) per milliliter, which had been analyzed for nickel with low results by the usual method described above, were submitted for analysis. The results of the colorimetric determination of the nickel by the revised dimethylglyoxime procedure of Bassett are given in Table 1.2.

TABLE 1.2

Nickel in Uranyl Sulfate Solutions

U(VI) concentration, 30 mg/ml; test aliquot, 1 ml

SAMPLE	NICKEL (μg)	
	PRESENT*	FOUND
1	5.7	6.0
2	11.4	11.5
3	22.8	23.2

*Estimates of nickel content based on polarographic analysis of standard nickel solution from which the samples were prepared.

The method of Bassett[3] is indicated to be satisfactory for determining nickel in HRE solutions. Other corrosion products of stainless steel, i.e., iron, chromium, and molybdenum, do not interfere.

DETERMINATION OF URANIUM IN THE HRE SOUP

R. B. Hahn

In the operation of the homogeneous reactor it will be necessary to analyze the soup for total uranium content. Since all analyses must be carried out by remote control, a potentiometric

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titration of a small sample is regarded as one of the best methods. After consideration of many methods it was decided that it would be best to reduce the U(VI) to U(IV) with chromous sulfate, then titrate the sample potentiometrically with a standard oxidant, ceric sulfate.

Procedures have been worked out for the analysis of pure uranyl sulfate solutions.[4] However, the HRE soup may contain corrosion products (iron, nickel, chromium) from the stainless steel. The chromium and nickel do not interfere in the potentiometric titration of U(IV), but iron is reduced to Fe(II) and is titrated along with the U(IV). The problem then is to devise a method of titrating U(IV) in the presence of iron impurity.

Two lines of approach were used to this problem: (1) the potential of the Fe(II)-Fe(III) system might be changed by complexing the Fe(II) so that the U(IV) could be titrated without interference by the iron system; (2) the iron might be removed from the uranium prior to titration by the use of a mercury cathode. Both methods were investigated; the results are given in the following discussion.

Method 1. Changing the Potential of the Fe(II)-Fe(III) System. Two substances were investigated as complexing agents for Fe(II), orthophenanthroline[5] and phytic acid.[6] The phytic acid proved unsatisfactory. It did not change the potential of the Fe(II)-Fe(III) system in the right direction, and it formed a precipitate with the ferric ion. Experiments with orthophenanthroline showed a change of potential in the correct direction, and hence a separation of the Fe(II)-Fe(III) and U(IV)-U(VI) breaks was achieved. The detailed procedure is discussed below.

Reagents. (*a*) Standard uranyl sulfate. A known weight of pure U_3O_8 was dissolved in nitric acid. This was fumed with sulfuric acid to eliminate the nitrate and then diluted to volume. The concentration was checked by a gravimetric determination of uranium.

(*b*) Orthophenanthroline (250 mg/ml). 2.5 g of G. F. Smith Company's orthophenanthroline was suspended in 10 ml of water. Sulfuric acid was added dropwise with stirring until the reagent was completely dissolved.

(*c*) Chromous sulfate. This reagent must be prepared freshly each day from potassium chromic sulfate. Approximately 5 g of reagent grade potassium chromic sulfate was dissolved in 50 ml of water, and the solution was run slowly through a Jones reductor filled with amalgamated zinc. The resulting chromous sulfate was stored under a CO_2 atmosphere. (Note: Most procedures call for the addition of sulfuric acid to the potassium chromic sulfate solution, but it was found that the chromous sulfate prepared from the nonacid solution keeps better and gives

(4) C. J. Rodden, *Analytical Chemistry of the Manhattan Project*, pp. 69-76, McGraw-Hill, New York, 1950.

(5) G. F. Smith and F. P. Richter, *Phenanthroline and Substituted Phenanthroline Indicators*, G. F. Smith Co., Columbus, Ohio, 1944.

(6) J. R. Foy and J. B. Thompson "Rapid Iodometric Determination of Iron in Iron Phytate," *Ind. Eng. Chem., Anal. Ed.* 15, 747 (1943).

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better titration curves than that prepared from the acid solution.)

(*d*) Standard ceric sulfate (0.1 *N*). This was prepared by dissolving G. F. Smith Company's ceric sulfate in dilute sulfuric acid and standardizing against arsenious oxide.

Apparatus. (*a*) Titration vessel. A tube 15 cm high and 2 cm in diameter fitted with a sidearm to admit CO_2 gas was used.

(*b*) Titrator. A Precision Scientific Company automatic potentiometric titrator modified for semimicro titrations was used.

(*c*) Electrodes. The reference electrode was a platinum wire sealed into the buret containing the standard ceric sulfate. The indicator electrode consisted of a gold wire dipped into the solution which was being titrated. A gold indicator electrode is preferred to platinum, and for best results the electrode should be cleaned by dipping into chromic acid—sulfuric acid cleaning solution after each titration.

Procedure. The solution to be titrated was placed in the titration vessel, 1 drop of concentrated sulfuric acid was added, and the volume was adjusted to about 2 to 4 ml. A current of CO_2 gas was maintained over the sample, and the solution was stirred with a magnetic stirrer during the entire titration. Chromous sulfate was added slowly until the potential indicated complete reduction. A slight excess is needed, but *a large excess of chromous sulfate should be avoided* since a large excess results in poor end points and drifting potentials.

The feed was turned on and the titration was continued until the Cr(II)-Cr(III) break was complete. At this point 25 mg (100 λ of the above solution) of orthophenanthroline was added for each 0.1 mg of iron present, and the titration was continued until a second break was obtained. The amount of uranium was then determined by the distance between the Cr(II)-Cr(III) break and the U(IV)-U(VI) break. If the titration is continued a small break will be obtained for the Fe(II)-Fe(III) system. The amount of iron can be roughly estimated by the distance between the U(IV)-U(VI) break and the final Fe(II)-Fe(III) break. Table 1.3 shows the results obtained in the titrations of various uranyl sulfate solutions.

A precision and accuracy of about 1% can be obtained in samples containing less than 0.25 mg of iron and less than 0.5 mg of nickel impurity. As the amount of impurity increases, the precision and accuracy of the uranium determination falls off. However, it is thought that the impurities in the HRE soup will be much less than these values.

Method 2. Removal of Iron from Uranium Solutions Using a Mercury Cathode. Since a conventional mercury cathode is unsuitable for remote-control manipulation, investigations were made using cathodes of various metals coated with liquid mercury. Complete removal of iron from uranium solutions was achieved with these electrodes. As this investigation is still in progress, a complete report will be made later.

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TABLE 1.3

Potentiometric Titrations of Uranyl Sulfate Solutions

SAMPLE	IMPURITY ADDED (mg)		ORTHOPHENANTHROLINE ADDED (mg)	URANIUM (mg)	
	IRON	NICKEL		TAKEN	FOUND
1				2.53	2.53
2	0.125		25	2.53	2.51
3	0.250		25	2.53	2.54
4	0.375		25	2.53	2.56
5	0.500		25	2.53	2.62
6		5.0		2.53	2.54
7	0.125	1.0	25	2.53	2.51
8	0.250	1.0	25	2.53	2.83
9	0.250	0.5	25	2.53	2.68
10	0.250	0.5	63	2.53	2.53
11	1.00		63	2.53	2.61
12	1.00		125	2.53	2.58

ISOLATION OF URANIUM(VI) BY FILTER PAPER PARTITION CHROMATOGRAPHY AND ITS QUANTITATIVE DETERMINATION

H. P. Raaen

The need for a method of separating and estimating microgram and submicrogram quantities of uranium(VI) and the potentialities of the technique of filter paper partition chromatography were discussed previously.[7]

Continued study of the technique, in which water-saturated 2-methyltetrahydrofuran containing 2.5% HNO_3 was used as the eluting solvent, has shown that 1.75 hr is the minimum time required for obtaining maximum sharpness of the uranium(VI) band at 25 ± 1°C.

The R_f value of the uranium(VI) ion has been measured from chromatograms obtained under the optimum conditions described, but the method of measurement is subject to variation and requires some explanation. The U(VI) solution was applied to the paper strip along a penciled line ruled across the paper. The distance moved by the U(VI) was considered to be the distance between this line and the center of the band formed by the uranium (always coincident with the

[7] H. P. Raaen, "Isolation of Uranium(VI) by Filter Paper Partition Chromatography and Detection of the Uranium(VI) Locus," *Analytical Chemistry Division Quarterly Progress Report for Period Ending March 26, 1951*, ORNL-1088, p. 21 (in press).

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TABLE 1.4

R_f Values for the U^{233}(VI) Ion

Eluting solvent, 2-methyltetrahydrofuran containing 2.5% HNO_3; temperature, 25 ± 1°C

ELUTION TIME (hr)	OTHER CATIONS PRESENT	DISTANCE MOVED (cm)		R_f
		DRY SOLVENT FRONT	U(VI) BAND	
1.5		19.60	16.75	0.85
1.75		21.75	18.40	0.85
1.75	Ni^{63}(II)	25.55	22.86	0.89
1.75	Cr^{51}(III)	20.08	17.85	0.89
1.75	Ni^{63}(II), Cr^{51}(III)	19.65	17.10	0.87
1.75	$Fe^{55,59}$(III), Ni^{63}(II), Cr^{51}(III)	20.20	18.03	0.89
2.00		23.00	19.50	0.85
2.00		22.79	18.87	0.83
2.25		25.72	21.15	0.82
2.50		22.28	23.10	0.85
				0.86 (avg.)

wet solvent front). This was compared with the movement of the dry solvent front measured from the same line. Thus:

$$R_f = \frac{\text{distance moved by U(VI) band (cm)}}{\text{distance moved by dry solvent front (cm)}} .$$

Representative R_f values are presented in Table 1.4. The data indicate that a representative average for the R_f value is 0.86 and this is independent of reasonable variation in elution time and of the presence of $Fe^{55,59}$(III), Cr^{51}(III), and Ni^{63}(II).

The quantitative estimation of the chromatographically isolated uranium(VI), either in situ by activation analysis or polarographically after extraction from the paper chromatogram, is under study. A series of U^{238}(VI) chromatograms, prepared at conditions optimum for obtaining a sharp U^{233}(VI) band, are currently being activated in the ORNL graphite reactor prior to analysis by the technique of carrier chemistry.[8] Since activation analysis is a time-consuming procedure, the possibility

[8] G. W. Leddicotte and S. A. Reynolds, "Activation Analysis with the Oak Ridge Reactor," *Nucleonics* 8, No. 3, 62 (1951).

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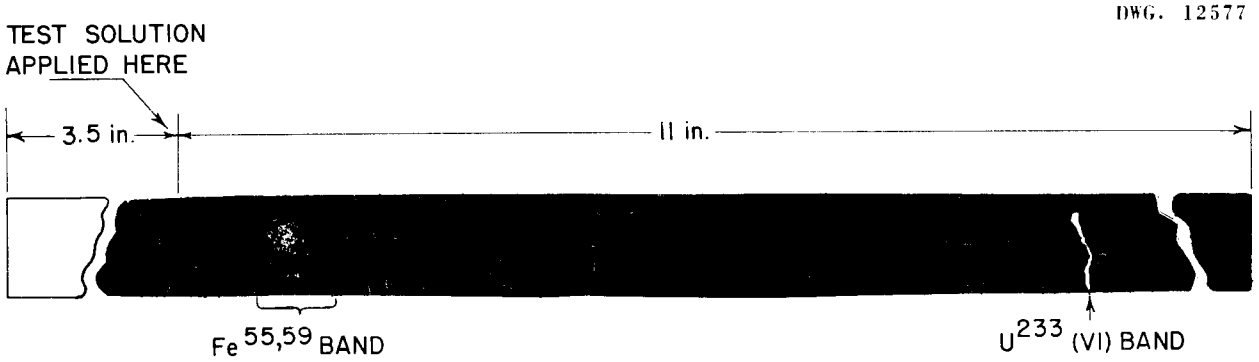

Fig. 1.4 - Radioautographs of U^{233}(VI) and $Fe^{55,59}$(III) (Filter Paper Chromatogram). Eluting Solvent, H_2O-Saturated 2-Methyltetrahydrofuran Containing 2.5% HNO_3 (V/V); Elution Time, 1.75 hr; Temperature, 25 ± 1°C

is being studied of extracting the uranium(VI) from the chromatogram directly into a microelectrolysis cell by use of a modified Soxhlet apparatus and determining the extracted U(VI) polarographically using the "curve follower" instrument.[9] A comparison is being made of the effectiveness of 2-methyltetrahydrofuran and diethyl ether for extracting the U(VI). The radioisotope U^{233} is being used in the study, thus permitting estimate of the rate of removal of the U(VI) from the chromatogram by alpha count measurements. No conclusive results have yet been obtained.

SEPARATION OF U(VI) FROM Fe(III), Ni(II), AND Cr(III) BY FILTER PAPER PARTITION CHROMATOGRAPHY

H. P. Raaen

Because of the possibility of corrosion of the stainless steel reactors used in the HRE program, the separation and determination of U(VI), Fe(III), Ni(II), and Cr(III) is of interest. The successful isolation of U(VI) by paper chromatography under the conditions already described suggested the application of this technique to the separation mentioned.

The separation of U^{233}(VI) and $Fe^{55,59}$(III) by paper chromatography in an exploratory experiment using water-saturated 2-methyltetrahydrofuran as eluting solvent was discussed previously.[7] The experiment was rerun at conditions optimum for the isolation of the U^{233}(VI) band, and a more efficient separation was obtained. This is shown by the radioautograph of Fig. 1.4 and the data of Table 1.5. In Fig. 1.4 it may be seen that the $Fe^{55,59}$(III) band, although isolated, is quite diffuse, covering about 0.75 in. of the chromatogram.

U^{233}(VI) was effectively separated from Ni^{63}(II) and Cr^{51}(III) under the same conditions as were used for the $Fe^{55,59}$(III)-U^{233}(VI) separation.

(9) H. P. Raaen, "Polarographic Determination of Uranium at Uranium(VI) Concentrations of 0.5 and 1.0 γ/ml," ORNL-1088, *op. cit.*, p. 30.

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TABLE 1.5

R_f Values for $Fe^{55,59}$(III) and U^{233}(VI)

Eluting solvent, 2-methyltetrahydrofuran containing 2.5% HNO_3; temperature, 25 ± 1°C; elution time, 1.75 hr

CHROMATOGRAM NO.	DISTANCE MOVED (cm)			R_f VALUE	
	DRY SOLVENT FRONT	U(VI) BAND	Fe(III) BAND	U(VI)	Fe(III)
1	21.45	18.15	2.85	0.85	0.13
2	21.62	18.50	3.05	0.86	0.14
3	22.53	19.15	2.87	0.85	0.13
4	21.70	19.61	2.70	0.86	0.12

The Ni^{63}(II) and Cr^{51}(III) did not move from the locus of application of the test solution.

The chromatographic separation of Cr(III) and Ni(II) on filter paper by the use of the mixed solvent 2,4,6-collidine—0.4 *M* HNO_3 (1:1) has been reported by Pollard *et al.*,[10] the R_f values of Ni(II) and Cr(III) with this solvent mixture being 0.76 and 0, respectively. This suggested that complete separation of the four ions might be effected if the Fe(III)-U(VI) separation was followed by elution of the chromatogram with the collidine—nitric acid mixture.

Preliminary experiments have shown that the R_f values of U^{233}(VI) and and Cr^{51}(III) in this solvent system are 0. The R_f values obtained for Ni^{63}(II) range from 0.68 to 0.77. Radioautographs of the chromatograms reveal high residual concentrations of Ni^{63}(II) at the locus of the test solution and much trailing. These effects, however, may be the result of overloading the chromatogram. The movement of the mixed collidine—nitric acid solvent is slow, being from 12 to 16 cm in 6.75 hr. It is planned to continue the experimentation.

[10] F. H. Pollard, J. F. W. McOmie, and I. I. M. Elbeih, "Analysis of Inorganic Compounds by Paper Chromatography. Part I. Movement of Cations with Complex-forming Solvent Mixtures," *J. Chem. Soc. London* 1951, 466 (1951).

POLAROGRAPHIC INVESTIGATION OF IRRADIATED POTASSIUM BROMATE

H. H. Miller

In his study of irradiated potassium bromate, J. W. Cobble of the Chemistry Division expressed interest in determining possible decomposition products of the bromate. Specifically, it was desired to detect bromine and hypobromite in a solution containing relatively large amounts of bromate and bromide. The polarographic method was selected because of its rapidity and simplicity.

The bromate solutions were analyzed as follows: Approximately 5 g of the

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salt was dissolved in 15 ml of 0.1 *M* KNO_3, and oxidation and reduction curves were obtained with a micro stationary platinum electrode, using the technique developed by Rogers *et al.*,[11] and also with a dropping mercury electrode. The potential range covered by the dropping mercury electrode was +0.4 to -1.2 volts, and that covered by the stationary platinum electrode was +0.6 to -0.7 volt.

Only one wave was obtained that was reproducible, and its appearance was ascribed to the oxidation of Br^- which has a half-wave potential of approximately +0.1 volt vs. SCE. Other waves were obtained, but these were poorly defined and not reproducible. No specific reactions could be attributed to these waves, and thus nothing was learned about the composition of the irradiated bromate solution.

POLAROGRAPHIC DETERMINATION OF SMALL QUANTITIES OF TUNGSTEN IN TITANIUM METAL

H. H. Miller

For analyzing titanium metal for microgram quantities of elements that are difficult to determine by ordinary chemical methods, the method of activation analysis may be applied. It is believed that tungsten may be determined rather accurately by this method because of its relatively large neutron cross-section. S. A. Reynolds wished to check the activation analysis procedure against a reference method and chose the polarographic method because the instrument sensitivity is sufficient to determine micro quantities of metals.

Kolthoff and Lingane[12] state that in a 0.1 *N* HCl solution the half-wave potential of titanium(IV) is approximately -0.8 volt whereas the half-wave potential of tungsten is -0.4 volt in the same background solution. Thus it appeared that it should be possible to determine tungsten in a titanium solution in 0.1 *M* HCl in a straightforward manner since the half-wave potentials of the two metals are sufficiently well separated. Because fluoride interferes with the behavior or the polarographic mercury electrode, it was necessary to dissolve the metal in hot 6 *N* HCl rather than in hydrofluoric acid which is ordinarily used. It was difficult to keep large amounts of titanium in solution in 0.1 *N* HCl, and the polarograms were therefore run instead in 6 *N* HCl. Instead of the small tungsten wave appearing at -0.4 volt, a large wave occurred in that region, evidently caused by the reduction of Ti(IV). It was later learned that previous polarographic work by Nelson[13] had indicated that the half-wave potential of Ti(IV) is dependent on the acidity of the solution and is shifted to the more positive values as the acidity increases. Evidently in 6 *N* HCl there is not sufficient separation of the half-wave potentials of titanium and tungsten to permit the determination of tungsten in large amounts of titanium.

Several chemical separations were tried without success because of the

(11) L. B. Rogers, H. H. Miller, R. B. Goodrich, and A. F. Stehney, "Automatic Recording of Polarographic Data Obtained with Platinum Electrodes," *Anal. Chem.* 21, 777 (1949).

(12) I. M. Kolthoff and J. J. Lingane, *Polarography*, pp. 294-296, Interscience, New York, 1946.

(13) F. Nelson, private communication, June 12, 1951.

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small amount of tungsten present (less than 1%).

DETERMINATION OF EXCESS BARIUM HYDROXIDE IN A BARIUM SULFIDE SOLUTION

H. H. Miller

A solution of barium sulfide containing barium hydroxide was submitted by the Operations Division for the determination of excess $Ba(OH)_2$ in the solution. A barium hydroxide solution had been used to collect the $S^{35}(II)$ in the production of the radioisotope, and it was necessary to determine the amount of free barium hydroxide remaining in the solution.

A 500-λ aliquot was taken from the sample, without exposing the solution to the air, and titrated in a 100-ml suction flask, under an atmosphere of nitrogen, with 0.01 *N* HCl, using methyl red as an indicator. Because of the hydrolysis of the sulfide the titration actually gave total base present; it was therefore necessary to correct for the contribution to the titration made by the sulfide. The sulfide concentration was successfully determined polarographically by the indirect cadmium method.[14]

POLAROGRAPHIC BEHAVIOR OF TECHNETIUM

H. H. Miller

Experiments are being designed for a systematic study of the polarographic behavior of technetium. The approach that Geyer[15] used to study rhenium will probably be taken. Part of the work will be done in collaboration with J. W. Cobble of the Chemistry Division.

INDIRECT POLAROGRAPHIC DETERMINATION OF POTASSIUM

A. D. Horton P. F. Thomason
M. T. Kelley

A procedure has been developed for the indirect polarographic determination of potassium in the range of 5 to 50 μg by precipitation as potassium cobaltinitrite and polarographic determination of the cobalt.

Potassium is precipitated in a 15-ml centrifuge cone by either of two methods,[16,17] using sodium cobaltinitrite as a reagent. After the precipitation, the sample is placed in the refrigerator for 3 hr and then centrifuged. The precipitate is washed three times with 70% ethyl alcohol and then dissolved in 50 λ of 4 *M* hydrochloric acid with heat. The *p*H of the solution is adjusted to 6 to 7 with ammonium hydroxide, and 50 λ of 0.4 *M* pyridine is added. This solution is diluted to 2 ml, and the cobalt is determined polarographically at a half-wave potential of approximately -1.07 volts vs. SCE. Potassium is calculated from the cobalt result. Typical data are presented in Table 1.6.

A formal analytical procedure has been written and will be available soon.

(14) A. D. Horton and P. F. Thomason, *Polarographic Determination of Sulfates*, ORNL-755 (in press).

(15) R. Geyer, "Zur polarographischen Reduktion des Rheniums," *Z. anorg. Chem.* 263, 47 (1950).

(16) C. P. Sideris, "Colorimetric Microdetermination of Cobalt and Potassium," *Ind. Eng. Chem., Anal. Ed.* 9, 145 (1937).

(17) F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, 3 ed, Vol. II, p. 555, Van Nostrand, New York, 1949.

[redacted]

TABLE 1.6

Data from Indirect Polarographic Determination of Potassium

SAMPLE	AMOUNT TAKEN (μg)	AMOUNT FOUND (μg)		RECOVERY (%)
		BLANK	SAMPLE (CORRECTED)	
1	5	0.1	5.0	100.0
2	5	0.7	4.8	96.0
3	10	0.9	10.5	105.0
4	10	0.9	9.7	97.0
5	10	0.7	10.1	101.0
6	10	0.9	10.5	105.0
7	20	0.7	19.6	98.0
8	20	0.7	20.8	104.0
9	50	0.1	52.6	105.2

In the course of this work an improved electrolyte for low concentrations of cobalt was developed. The reduction of the pyridinium ion at the dropping mercury electrode gives a wave immediately following the cobalt wave which results in a poorly defined limiting current for cobalt; therefore a 0.1 *M* pyridine—0.1 *M* pyridinium chloride electrolyte gives poor results in low concentrations of cobalt (below 10^{-3} *M*). It was found that a mixture of 0.1 *M* ammonium chloride and 0.01 *M* pyridine gives an excellent wave, even for as little as 1 ppm of cobalt.

ANALYSIS OF SODIUM FLUORIDE—POTASSIUM FLUORIDE—URANIUM FLUORIDE EUTECTIC FOR CHROMIUM, NICKEL, AND IRON

A. D. Horton

The effect of radiation on the corrosion properties of stainless steel in contact with a sodium fluoride-potassium fluoride-uranium fluoride eutectic will be studied by G. W. Keilholtz of the ANP Materials Chemistry Division. The work of the Y-12 Analytical Chemistry Division (p. 69 ff) has shown that the colorimetric methods for the determination of corrosion products in the nonirradiated eutectic have been satisfactory. The work reported here was undertaken to determine the necessary equipment that will be required in the hot cell for the analysis of the irradiated eutectic. About 1 g of eutectic will be weld-sealed in pencil-sized inconel tubes approximately 2 in. long, and the tubes will be irradiated in the ORNL graphite reactor. The analytical problem involves removing the sample from the tube without contaminating it with metal chips or filings and dissolving the sample and diluting to volume (probably 100 ml). These operations will have to be done by remote control because of the very high radiation levels.

Preliminary work has been done on analysis of the sample. One gram of the nonradioactive eutectic was dissolved in a mixture of nitric and boric acids; a very small amount of silica residue was obtained. Iron, chromium, and nickel were added in concentrations of 1000 ppm each, with respect to the solid sample, and the whole was diluted to 100 ml.

A synthetic sample was prepared for the purpose of obtaining spectrophotometric curves. Uranyl sulfate, ferrous chloride, potassium dichromate, and nickel chloride solutions were mixed in the same proportions as in the sample. Chromium and nickel were determined by use of diphenylcarbazide and dimethylglyoxime,

[redacted]

respectively, and standard calibration curves were obtained with the Beckman model DU quartz spectrophotometer.

Aliquots of the spiked eutectic were analyzed semiquantitatively by the same procedures. These exploratory experiments indicate that spectrophotometric methods are likely to be suitable for determining chromium and nickel in the irradiated eutectic. Iron had not been determined at the time this report was being written.

The possibility of a polarographic determination of all the corrosion products in a single aliquot of sample is also being studied.

ULTRAMICRO DETERMINATION OF NITROGEN AS AMMONIA

H. P. Raaen

It was of interest to W. L. Marshall and H. O. Day to confirm the presence of ammonia in uranyl sulfate prepared at the Y-12 site. This necessitated a method for the determination of ultramicro quantities of ammonia in uranyl sulfate solutions. The procedure of Tompkins and Kirk[18] was adapted for the analyses. The ultramicro amounts of ammonia were separated as gas by the addition of excess alkali, collected in boric acid, and determined by titration with standard HCl. The transfer of the ammonia to the boric acid absorbent was effected by isothermal distillation, using the Tompkins-Kirk diffusion cell, the diffusion being performed under vacuum.

The procedure is applicable to the determination of approximately 0.5 to 20 μg of nitrogen. Duplicate analyses of a sample of ammonium sulfate were made with a recovery of 96.5%; however, the attainable accuracy is reported to exceed 1%. A method for the determination has been written.

DETERMINATION OF CITRATE BY IODATE OXIDATION

H. P. Raaen

In his study of the distribution coefficient of alkali earth ions between Dowex-50 resin and the citrate-containing feed solutions, R. E. Blanco wished to know whether a change occurred in the citrate concentration of the feed solution during equilibration with the resin. The estimated citrate concentration of the solutions ranged from 0.1 to 0.5 *M*. A modification of the procedure of Unger and Haynes[19] was found to be applicable. By their method citrate is determined by iodate oxidation in the presence of sulfuric acid. An excess of potassium iodate is added to the test solution and the excess is determined by the addition of potassium iodide which has a reducing action in the system. An equivalent amount of iodine is formed and is determined iodometrically by titration with standard sodium thiosulfate solution. The accuracy of the procedure is better than ±0.3%, the error usually being positive. The method has been recorded in detail.

MANUAL OF ANALYTICAL PROCEDURES FOR THE U^{235} RECOVERY PROCESS

H. P. Raaen

Editorial work on the *Manual of Analytical Procedures for the* U^{235}

(18) E. R. Tompkins and P. L. Kirk, "Quantitative Drop Analysis. XVI. An Improved Diffusion Method for Total Nitrogen," *J. Biol. Chem.* 142, 477 (1942).

(19) P. Unger and H. G. Haynes, "Determination of Citrate and Tartrate," *Analyst* 71, 141 (1946).

[redacted]

Recovery Process, ORNL-983, done in collaboration with L. T. Corbin, was completed. The manual has gone to press.

MASTER MANUAL OF ANALYTICAL TEST METHODS

H. P. Raaen

It is believed desirable to establish a master manual of analytical test methods used in the Analytical Chemistry Division laboratories at X-10 and to maintain it as a reference and file of new methods which may be developed. As a first step toward its organization, classified lists of the analytical methods of interest have been submitted by the coordinators and group leaders of the Analytical Chemistry Division at X-10.

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2. RADIOCHEMICAL ANALYSES — RESEARCH AND DEVELOPMENT

NUCLEAR PROPERTIES

Cyclotron-Produced Cobalt (W. S. Lyon and F. L. Moore). Recent preparation by the Operations Division of what was presumed to be Co^{57} has led to a radiochemical investigation of Co^{56}, Co^{57}, and Co^{58}.

The most reliable values for radiations in the active cobalt region are:[1]

72-day Co^{56}:	1.50-Mev β^+ and gammas of 0.85, 1.26, 1.74, 2.01, 2.55, and 3.25 Mev
270-day Co^{57}:	0.26-Mev β^+ and gammas of 0.014, 0.119, and 0.131 Mev
72-day Co^{58}:	85% K, 15% 0.47-Mev β^+, and a 0.81-Mev gamma

The material prepared by the Operations Division by the reaction

$$Fe^{56}(d,n)Co^{57}$$

should be mostly Co^{57}. Exhaustive separations indicate no activities other than cobalt to be associated with the sample. Absorption data in aluminum obtained on a helium-filled tube reveal the presence of two β^+ emitters (identified as to sign by magnetic deflection) with half-thicknesses corresponding to the 1.50-Mev β^+ of Co^{56} and the 0.26-Mev β^+ of Co^{57}. These appear to be present in about equal amounts. Surprisingly enough, however, X-ray counting indicates a tremendous amount of X-ray emission, presumably from Co^{58}. Specific chemical separations for iron and zinc (possible K-capturing contaminants) show that neither is present.

It appears, therefore, that either the mass assignments in this region are in error, or the cross-section for production of Co^{57} by (d,n) reaction is extremely small in comparison to production of the Co^{56} and Co^{58} since Fe^{56} is approximately 92% abundant while Fe^{57} is about 2%, and Co^{56} can be prepared only by the $(d,2n)$ reaction. As stated above, the amounts of Co^{56} and Co^{57} produced were roughly equal (3.40×10^{-3} mc/ml of Co^{56}, 3.32×10^{-3} mc/ml of Co^{57}), but the Co^{58} as determined by X-ray counting and compared with a Fe^{55} standard is 250×10^{-3} mc/ml. These results are puzzling, and it is hoped that additional time and material will be available later for a thorough study of this region of nuclides.

Decay of Cr^{51} (W. S. Lyon). Through the kindness of A. R. Brosi of the Chemistry Division the crystal spectrometer has been used to examine a sample of Cr^{51}, in an effort to determine the number of gamma rays unconverted. Only one was found, this being the 0.330-Mev gamma ray. It is now believed that the apparent second lower energy gamma ray reported previously[2] was an error and was caused by the oblique passage of the 0.330-Mev gamma through the cylindrical lead absorbers used to

(1) K. Way, L. Fano, M. R. Scott, and K. Thew, *Nuclear Data*, NBS Circular 499 (Sept. 1, 1950).

(2) W. S. Lyon, "Disintegration of Cr^{51}," *Analytical Chemistry Division Quarterly Progress Report for Period Ending March 26, 1951*, ORNL-1056, p. 43 (in press).

[redacted]

measure the half-thicknesses of the gamma. Dr. Brosi states that the experimental set-up used would probably result in the appearance of an apparent second weaker energy gamma ray.

The decay scheme previously proposed must now be modified, and it is believed that the decay is approximately 92% K-capture directly to the ground state and about 8% K-capture through the 0.330-Mev gamma excited state.

Fast-Neutron Flux in the ORNL Graphite Reactor (W. S. Lyon and J. M. Larue*). A program is underway to determine fast-neutron flux in various sections of the ORNL graphite reactor. Fast-neutron flux determinations will be made for the reactions

$$P^{31}(n,p)Si^{31} \qquad Al^{27}(n,p)Mg^{27}$$

$$Mg^{24}(n,p)Na^{24} \qquad S^{32}(n,p)P^{32}$$

the target materials being cadmium-shielded. A preliminary run has been made with activity measurements being carried out by ion chamber and absolute β counting.

MEASUREMENT OF RADIOACTIVITY

The 4π Beta Proportional Counter (T. H. Handley). An investigation has been made of the applicability of the 4π proportional counter to radioisotope assay work.[3,4]

A special technique was used to mount sources for this counter. The source mount was a circular stainless steel disk with a 0.5-in.-diameter film-covered hole in the center. At the beginning of this work a thin formvar-polystyrene film was placed over this hole, and both sides of the film were covered with gold or another metal by vacuum evaporation of the metal onto the film to make the complete source mount conducting. Results obtained using such a mount for a Co^{60} source were 20 to 25% lower than those determined by the other counting methods indicated in Table 2.1. The two halves of the counter did not count the same when connected separately, indicating that absorption by the backing was a source of error.

It was decided that a nonconducting mount might be used. A mount was made by covering the hole with a very thin formvar film prepared to have a thickness equivalent to 10 $\mu g/cm^2$, onto which the activity was evaporated. This very thin film had several disadvantages, among them being delicacy and nonresistance to acids. Solutions containing the source to be counted had to be of high specific activity and diluted with distilled water by a large factor to eliminate self-absorption and to prevent the film from breaking because of the action of acids on it. This mount gave results much closer to those obtained by other methods than did the conducting formvar-polystyrene mount.

The two halves of the chamber counted exactly the same for a source of Co^{60} mounted on thin formvar film.

*Oak Ridge School of Reactor Technology.

(3) T. H. Handley, "4π Proportional Counter," *Analytical Chemistry Division Quarterly Progress Report for Period Ending October 10, 1950*, ORNL-867, p. 39 (Dec. 28, 1950).

(4) T. H. Handley, "4π Beta Proportional Counter," *Analytical Chemistry Division Quarterly Progress Report for Period Ending January 10, 1951*, ORNL-955, p. 30 (Mar. 28, 1951).

[redacted]

TABLE 2.1

Comparison of 4π Disintegration Rates with Those Determined by Various Other Methods

NUCLIDE	COMPARISON METHOD	DIFFERENCE (%)
P^{32}	End-window Geiger-Mueller counter[5]	-1.0
Na^{24}	Coincidence counting[6]	-1.0
Co^{60}	Coincidence counting	-2.0
I^{131}[a]	Coincidence counting	-10
Na^{22}	100% gamma ionization chamber[7,8]	-1.3
Nb^{95}	Coincidence counting	-16

[a] In the case of I^{131} the coincidence counting rate was obtained by using the 4π chamber as the beta tube.

This indicated that absorption by the backing was negligible and that for sources emitting more energetic beta rays than those from Co^{60} absorption would also have been negligible. The area of the nonconducting portion of the mount was also reduced by placing adapters over the larger hole, reducing it to 0.25 in. in diameter. No significant change in the counting rate was observed. Absorption effects by the metal or conducting film were much greater than any effects which might have been caused by the nonconduction property of the thin formvar film. Since results obtained for the thin formvar film were much closer to those obtained by other counting methods than those for a metal film, it was decided to use the formvar in the standard method.

Three different kinds of counter gas have been tried in the chamber. In the beginning a 10% methane—90% argon mixture was used at atmospheric pressure. Results were lower than by other counting methods. Methane alone was tried and gave results approximately 3% higher for Co^{60} and 7% higher for Nb^{95} than the methane-argon mixture. A 10% methane-90% helium mixture was also tried but a plateau could not be obtained. The results of an experiment in which various counter gas pressures were used are given in Table 2.2. These data show that the pressure of the counter gas is not significant. A change in position of the plateau was observed for various pressures,

TABLE 2.2

Effect of Counter Gas Pressure on Apparent Disintegration Rate of Co^{60}

COUNTER GAS PRESSURE (cm Hg)	APPARENT DISINTEGRATION RATE (10^5 cpm)
10	2.21
20	2.21
40	2.22
76	2.21

(5) L. R. Zumwalt, *Absolute Beta Counting Using End Window Geiger-Mueller Counters and Experimental Data on Beta-Particle Scattering Effects*, AECU-567 (no date on document).

(6) J. W. Jones and R. T. Overman, *The Use and Calibration of a 100% Geometry Ion Chamber*, MonC-399 (Mar. 20, 1948).

(7) J. W. Cobble, *Calibration of the 4π High-Pressure Ion Chamber*, private communication, June 7, 1950.

(8) G. Friedlander and J. W. Kennedy, *Introduction to Radiochemistry*, pp. 227-228, Wiley, New York, 1949.

[redacted]

but when the voltage was adjusted for this change the observed counting rate was the same.

The chamber has been used as the beta tube or beta detector in a coincidence-counting circuit. The sample is mounted and placed in the chamber as usual with methane at 40 cm Hg pressure as the counter gas. It is then connected to the beta scaler of the coincidence circuit with a preamplifier between the chamber and the circuit. One end of the chamber is placed directly against the gamma detector, usually a scintillation counter, except when additional absorbers are placed between the chamber and the gamma detector to eliminate energetic beta rays. The count is then taken in the usual manner. This arrangement has the advantage over the usual beta detector of eliminating interference from secondary electrons and X rays. It also eliminates the necessity of running an absorption curve when more than one beta ray is emitted by the nuclide being studied and of extrapolating to zero absorber, which extrapolation is difficult to reproduce and is doubtful in the case of very complex decay schemes. Use of the chamber in this manner is based on the theory that, regardless of the complexity of a decay scheme, one pulse only will be generated by each decaying atom, provided there is no excited state and that it decays to a stable daughter. Results obtained may be reproduced with greater precision than when it is necessary to extrapolate to zero absorber. Less counting time is required because of the increased counting efficiency of the chamber over the usual end-window tube. Comparison of this method with other methods has been difficult because of the unreliability of other methods for very complex schemes. However, the 4π chamber does have potential value when used in this manner, and further investigations are planned.

In summary, it may be said that the 4π chamber gives results lower than coincidence-counting methods for beta rays of low maximum energy such as those from Nb^{95}. However, it has potential use as a beta tube in a coincidence circuit. It must be emphasized that great care has to be used in the preparation of the samples and mounts. The sample aliquot must be essentially solid-free and acid-free, and a small volume (5 to 10 λ) must be used to avoid breaking the film. It is very difficult to make such mounts quantitatively. These thin films require special techniques of preparation and care in handling, and extra precautions must be taken in order not to contaminate the inside of the chamber.

Plates for Gross Activity Determination (W. S. Lyon and W. A. Brooksbank). This is a continuation of work reported earlier.[9] Copper and aluminum plates with riffled bottoms have been tested for suitability as counting plates by evaporating solutions containing sodium chloride, 0.5 mg/ml, with very unsatisfactory results, i.e., spattering and nonuniform deposition. A third type of plate, approximately 1.0 cm deep and 1.7 cm in diameter, crisscrossed in the bottom with ridges about 0.01 cm high (forming a checkerboard surface of 0.1-cm squares) has also been tested. The capacity of the plate

[9] T. H. Handley, "Experimental Dishes for Sample Mounting," ORNL-1056, *op. cit.*, p. 47.

[redacted]

was quite low, and, while spreading of the sample was fair, the presence of solids again caused poor results when the solution was evaporated. The consensus is that no metal dish yet suggested would be useful. C. L. Burros believes that the use of a precision-ground watch glass having a cardboard backing might give satisfactory reproducibility. He believes his present watch glasses give reproducibility to several percent, the desired reproducibility being within 1 to 2%.

Assay of Low-Level Beta Activity in Liquid Wastes (W. A. Brooksbank and S. A. Reynolds). Four samples of low-level beta activity were recently sent to a number of AEC sites. These were distributed for two purposes: (1) to check agreement between the organizations when their present methods are used and (2) to demonstrate the applicability of the thallium standard.[10]

It should be emphasized that this was a preliminary survey, that the samples were active enough to be easily measurable, and that only sample 3 was a mixture. Sample 1 was Sr^{89}, sample 2 was Co^{60}, and sample 3 was a fission product mixture. All were made up from known stock solutions of pure radioisotopes, standardized by conventional methods. The composition of sample 3 is shown in Table 2.3. This mixture is perhaps deficient in low-energy beta, compared to normal waste.

The data for these samples reported by the AEC sites are given in Table 2.4. It is apparent that the agreement using the thallium standard is at least as good as that obtained by absolute counting, and the results are much easier to obtain. They will approximate absolute disintegration rates in cases where the average beta energy is not too far from that of thallium. However, this is of slight importance for routine assay work where consistent results and a common basis for reporting are desired, and in which, therefore, the type of beta detector used is relatively unimportant.

TABLE 2.3

Composition of Mixed Fission Product Sample 3

ACTIVITY	% OF TOTAL ACTIVITY
$Ce\text{-}Pr^{144}$	48
$Sr\text{-}Y^{90}$	25
$Zr\text{-}Nb^{95}$	17
Cs^{137}	7
$Ru\text{-}Rh^{106}$	3

Figure 2.1 shows the self-absorption results obtained with a number of radioisotope preparations counted by means of a typical end-window counter. In each case the concentration of activity has been corrected to 1×10^{-3} $\mu c/ml$. Thus the height of the curve is a measure of the efficiency of counting. It is seen that thallium falls near the middle of the range and near the mixed fission products. Figure 2.2 shows the same type of data for a flow type proportional counter. It was planned to correlate

(10) W. A. Brooksbank and S. A. Reynolds, "Low-Level Waste Activity," ORNL-1056, *op. cit.*, p. 45.

[redacted]

TABLE 2.4

Results on Check Samples of Low-Level Beta Activity

SITE	INSTRUMENT	BETA ACTIVITY (10^{-3} $\mu c/cc$) SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 3*	THALLIUM
Los Alamos Scientific Laboratory	End-window Geiger-Mueller counter	0.75*	1.1*		0.94	
Hanford Engineer Works	End-window Geiger-Mueller counter	0.65	0.9	0.88	1.2	
Knolls Atomic Power Laboratory						
Chem. and Chem. Eng. Div.	Windowless proportional counter	0.62*	1.65*		0.83	
Health Physics Div.	End-window Geiger-Mueller counter	0.56	1.3	0.78		0.91
Brookhaven National Laboratory	End-window Geiger-Mueller counter	0.43	2.1		1.3	
Mound Laboratory	Windowless proportional counter	0.56	1.57	0.85	0.97	0.90
Argonne National Laboratory						
Engineering	Windowless proportional counter	0.50	1.34	0.64		1.04
Biology	Windowless proportional counter	0.64	1.70	0.93	0.98	0.95
Oak Ridge National Laboratory						
Analytical Chem. Div.	End-window Geiger-Mueller counter, windowless proportional counter	0.55	1.68	0.92	1.04	1.02
Health Physics Div.	End-window Geiger-Mueller counter,	0.54	1.57	0.80	0.98	
National Bureau of Standards	4π	0.62	1.62	0.99	1.00	1.00
Average		0.58	1.50	0.85	1.03	0.97

*Based on thallium.

[redacted]

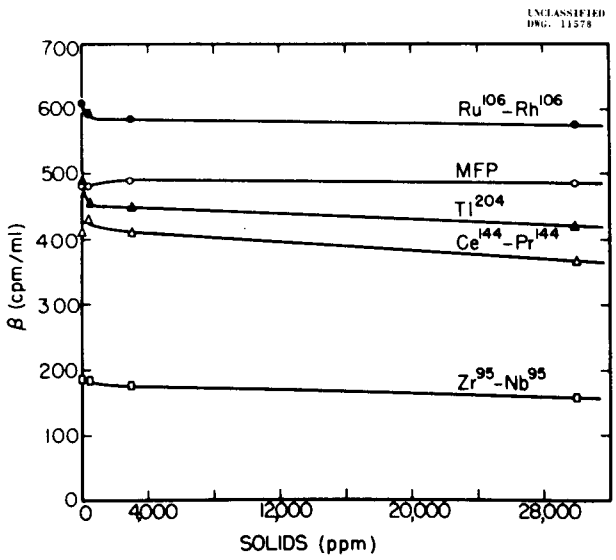

Fig. 2.1 - Self-Absorption, End-Window Geiger-Mueller Counter

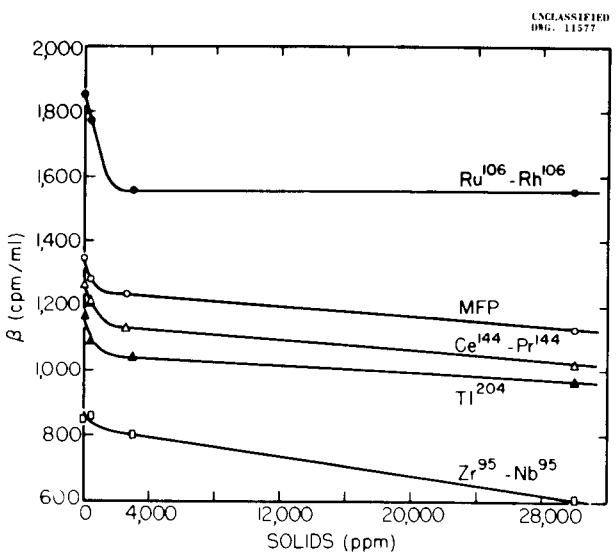

Fig. 2.2 - Self-Absorption, Proportional Counter

results on a variety of counters, but a Bradley PC-1 was not available soon enough, nor were tubes for the Anton anticoincidence device, a low-background beta counter.

Comparison of thallium and fission product activities, done at the 10^{-5} $\mu c/ml$ level, is shown in Table 2.5. The results agree within counting error.

TABLE 2.5

Determination of Mixed Fission Product Activity with End-Window and Proportional Counters

(Thallium as Standard)

Knownmixed fission product activity = 0.92×10^{-5} $\mu c/cc$

Thallium activity = 1.02×10^{-5} $\mu c/cc$

SOLIDS ADDED	MIXED FISSION PRODUCT ACTIVITY (10^{-5} $\mu c/cc$)	
	END-WINDOW COUNTER	PROPORTIONAL COUNTER
400	0.93	1.02
3,000	0.7	0.96
30,000	1.07	0.99

The accuracy of the method of boiling down large sample volumes and then transferring solids to a counting dish is subject to serious doubt. In neutral solution many activities are lost by hydrolysis and by deposition on the walls of containers. The procedure used by Emmons *et al.*[11] in which successive aliquots are dried in the counting dish seems desirable.

Actually, it must be admitted that any method of running gross beta

(11) A. H. Emmons and R. Lauderdale, personal communication, June, 1951.

[redacted]

activity on very dilute waste solutions containing varying amounts of solids will be only approximate. Better data can be obtained by a specific radiochemical scheme in which the purified activity is contained in a definite amount of solids, and thus the technique may be made to give absolute results by appropriate standardization. Carrier is added to a large volume, and separations effected with known losses in boiling down, precipitation, etc. In this way a rather precise value can be obtained for a biologically hazardous material such as strontium, while for gross activity a rough figure might suffice. General concentration techniques such as the ion-exchange method of Emmons and Lauderdale[11] and the aluminum floc technique for rainwater analysis[12] are worthy of consideration.

The limitation in counting low-level beta activity under ideal conditions of solids, etc. is the statistical variation in the background and also in the sample counting rates. The lower limit of valid counts, therefore, can be made lower by use of an efficient anticoincidence device or by arrangement of shielding, either of which will lower the background count at no loss of counter sensitivity. The effectiveness of the counter shielding may be increased or counter tubes may be used in anticoincidence.

For the purpose of studying the anticoincidence arrangement of the counter tubes, the shielding was a standard pig, i.e., 0.25 in. of steel, 2 in. of lead, and 0.25 in. of aluminum. The Geiger-Mueller tubes used were supplied by Anton Electronics Laboratory (Brooklyn, N. Y.). They are 3 in. in diameter and 0.5 in. deep and have mica windows within the thickness limits of 1.4 to 6 mg/cm^2. They are designated as types 1001 H or 1001 T. Their use was recommended by R. Friedman[13] of the Electron Optics Section of the Physics Division, Naval Research Laboratory, who obtained an adequately low background of 5 to 6 cpm per pair of similar tubes when they were used face-to-face with the sample mounted between. In this study an identical tube arrangement was used (mica windows facing each other). The pulses from these tubes were fed into an anticoincidence unit, which had been designed and built by J. T. DeLorenzo and P. W. Hill of the ORNL Instrument Department. The anticoincidence circuit diagram is shown in Fig. 2.3. Any pulse originating in counting tube *A* will be counted by a standard 64-scaler, but any pulse originating in counting tube *B* will not be counted. If a pulse occurs in both tubes *A* and *B* at the same time, it will be canceled in the 6AS6 mixer tube or will be reduced in pulse height sufficiently so as not to trip the scaling circuit. Since the same high-voltage supply is used for both counter tubes, line fluctuations are also canceled.

When this unit was tested with a radioactive source, tube *B* was disconnected, and the pulse from tube *A* was fed to both legs of the circuit, i.e., to the counting section and also to the anticoincidence section. No counts were ever recorded, showing

(12) W. A. Brooksbank, Jr., A. H. Emmons, J. W. Gost, and S. A. Reynolds, *A Preliminary Survey of Radioactive Constituents in Rainwater at ORNL*, ORNL-816 (Dec. 4, 1950).

(13) R. Friedman, private communication, April, 1951.

[redacted]

[redacted]

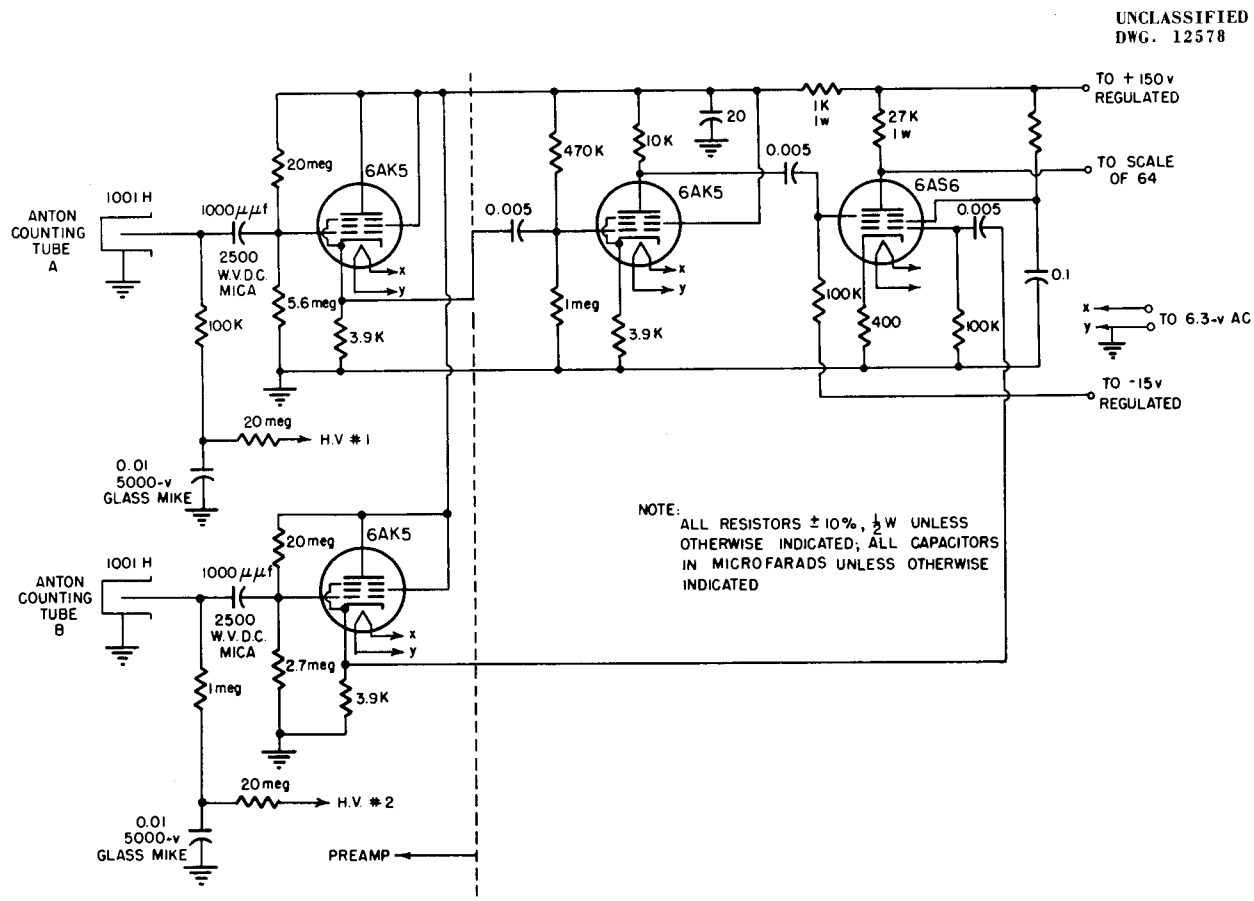

Fig. 2.3 - Anticoincidence Circuit Diagram

100% cancellation if both legs of the circuit are actuated at the same time.

Background at ORNL with "standard" shielding is between 19 to 26 cpm. With the anticoincidence unit it is consistently 16% less. This shows that background in the location tested is not caused primarily by cosmic fluctuations but results from horizonta gamma radiation from the ORNL graphite reactor or high-level chemical operation and sources.

It is planned in the near future to use 7 in. of lead shielding and the anticoincidence circuit with two methane flow type proportional beta counters in the further investigation of the background problem for low-level counting. Of necessity, these tests must be conducted at a greater distance from hot operations.

ANALYSIS OF RADIOISOTOPES

Bureau of Standards P^{32} (W. S. Lyon). Four P^{32} check samples from the National Bureau of Standards were received this quarter. Listed in Table 2.6 are the results of the

[redacted]

[redacted]

TABLE 2.6

Activities of P^{32} Check Samples from National Bureau of Standards

SAMPLE	P^{32} ACTIVITY (dps/cc)		
	RADIOCHEMICAL RESEARCH AND DEVELOPMENT GROUP*	RADIOISOTOPE PRODUCTION GROUP*	NBS**
1		6.32	6.33
2	6.29	6.20	6.33
3	6.36	6.36	6.33
4	186	185	186

*Likely error, ±3%.

**Accurate to ±3%.

P^{32} activities obtained. The results from the Radioisotope Production Group were determined by use of their routine P^{32} method. The Radiochemical Research and Development Group results were obtained using absolute beta counting techniques. The NBS value was obtained by 4π counting in Washington.

Determination of Fe^{55} in the Presence of Fe^{59} (W. S. Lyon). A somewhat perplexing problem in radioisotope assay is the determination of small amounts of 2.94-year Fe^{55} (K-capture) in the presence of large amounts of Fe^{59}. Radioactive iron produced by the Operations Division is now of this nature, and, since medical use requires that the percentage of Fe^{55} be known accurately, X-ray absorption curve methods of determination are of little value because the Fe^{59} gamma rays mask the small amount of X rays. Critical absorption measurements have been tried, and the method appears to be the most practical available. Vanadium is the critical absorber for manganese X rays (produced by K-capture in iron) and the method consists in counting a sample with and without a vanadium absorber, the beta particles being absorbed by a beryllium absorber placed directly below the counter window. The difference in counting rate is ascribed to the Fe^{55} X ray. A known standard is then counted in an identical manner, and the disintegration rate of the sample is determined from the equation

$$\text{dpm} = \frac{\text{cpm sample} \times \text{dpm standard}}{\text{cpm standard}}$$

Unfortunately, no reliable Fe^{55} standard is available. Since Fe^{55} is a pure X-ray emitter, the absolute activity of a sample is difficult to determine. At present a krypton-methane tube is being calibrated for various X-ray-emitting nuclides within the region of iron, and it is hoped that an absolute standard can be prepared using this as a counter. Samples are now in the Hanford graphite reactor, which, when available, will enable known mixtures of Fe^{55} and Fe^{59} to be prepared, and the method to be more closely evaluated. The values of the cross-section for production of Fe^{55} and Fe^{59} are also uncertain, and the redetermination of these constants is to be a secondary part of this program.

Impurities in Manganese Product (W. S. Lyon). A rapid and simple solvent-extraction method for vanadium impurity in manganese products has been used based upon work reported by

[redacted]

Irvine,[14] and has been found satisfactory. The solution to be analyzed is made 1 *M* in KCNS, and the *p*H is adjusted to 3 ± 0.2. The solution is then extracted with 0.1% 8-hydroxyquinoline in hexone. Vanadium is carried into the organic phase.

The KCNS concentration of the aqueous phase is next raised to 8 *M*, and the manganese is extracted at *p*H 6 to 7 into the organic phase. The manganese can be removed from the hexone by washing with 1 *M* KCNS and 8-hydroxyquinoline. Using the above procedure it has been possible to prepare pure Mn^{54} activity for X-ray counter calibration. V^{48} appears to be a common contaminant in Mn^{54} product.

4π Counting of I^{131} (W. S. Lyon and T. H. Handley). Previous data indicate that disintegration rates obtained by 4π counting are consistently lower than those obtained from coincidence counting when low-energy (less than 0.350-Mev) beta emitters are counted. It was thought, therefore, that an experiment in which a 4π counter would serve as the beta detector in a beta-gamma coincidence set-up would be useful in simultaneously comparing disintegration rates measured by both 4π and coincidence counting. In such an experiment the observed beta-counting rate in the 4π counter when corrected for a small (about 1% per 100,000 cpm) dead time loss should equal the calculated counts-per-minute rate from the usual coincidence calculation; i.e.,

$$\text{cpm} = \frac{C_\beta C_\gamma}{C_{\beta\gamma}} .$$

(14) J. W. Irvine, Jr., private communication, January, 1951.

The apparatus used was that described on p. 23 of this report. A voltage plateau was run on the 4π counter in the usual manner, and the resolving time of the system was determined by counting two separate samples by the standard method. A sample of high specific activity, Na^{24} (1.4-Mev beta), was first counted in the assembly, and the observed counting rate in the 4π counter was found to agree with the calculated disintegration rate from coincidence measurement within 1%, indicating that the equipment was performing satisfactorily.

A most difficult problem in counting I^{131} is the preparation of an essentially solids-free sample. The following modification of a standard-radiochemical method was finally developed. The samples so prepared appeared to contain virtually no solids.

Preparation of High-Specific-Activity I^{131} Sources. Ten to twenty times the amount of sample having the desired final counting rate was placed in a 25-ml separatory funnel with 20 μg of iodine carrier. A few drops of NaClO was added, and then HNO_3 was added until the solution was acid. The solution was thoroughly stirred. The sample was reduced with hydroxylamine and extracted with 2 ml of CCl_4. The CCl_4 was washed twice with water, iodine was removed by washing the CCl_4 with 1 ml of sulfurous acid. About 40 μg of Ag (as $AgNO_3$) was added, and the solution was heated for 10 to 15 min. The material was centrifuged 20 min, and all but the last 50 λ of solution was decanted. H_2O was added, and the mixture was stirred and then centrifuged for 20 min.

Several sources of I^{131} were prepared in this manner, and, after they were evaporated on very thin polystyrene films, determinations of the disintegration rates were made as outlined above. Table 2.7 summarizes the data.

TABLE 2.7

I^{131} Disintegration Rates

RUN	I^{131} DISINTEGRATION RATE (10^5 dpm)		DIFFERENCE (%)
	4π COUNTER*	COINCIDENCE COUNTER	
1	1.64	1.75	6.3
2	3.96	4.44	10.8
3	3.39	3.75	9.6

*Counter gas, methane at 30 cm Hg. Data corrected for 1% per 100,000 cpm loss.

From Table 2.7 it is apparent that the 4π counting rate is approximately 10% below the disintegration rate determined by coincidence counting. The sample from run 2 above was determined by coincidence counting, removed from the 4π chamber, and, using the standard beta proportional tube in the beta side of the coincidence counter, an aluminum absorption curve was determined and the disintegration rate was calculated by extrapolation of beta and coincidence counts to zero absorber. The rate so measured agreed with the value obtained by coincidence counting with the 4π chamber within 2%.

The assembly used was such that counts on the 4π chamber could be recorded from either the top or the lower hemisphere, or both, of the chamber. Data were taken with the 4π counter as beta detector in the coincidence circuit using first one hemisphere, then the other, and finally both. In every instance the observed counting rate in the 4π counter was lower in the lower hemisphere than in the top. This difference was about 6% and was presumably caused by the absorption of very-low-energy beta particles in the film. However, the coincidence-determined rate was the same for each half and the same as the rate determined when used as a 4π counter.

ANALYSIS FOR HEAVY ELEMENTS

Plutonium Polymer (F. L. Moore). The Chemical Technology Division was interested in knowing whether polymeric plutonium was produced in a system containing UO_2SO_4 at a concentration of 92 mg of uranium per milliliter and 0.1 to 0.5 mg of plutonium per milliliter at a *p*H of about 2. Since it is well known that TTA will not extract polymerized Pu(IV), a logical approach seemed to be to use a TTA extraction to estimate the polymer. First, it was necessary to check the behavior of normal Pu(IV) in the UO_2SO_4 system. Sulfate ion is known to complex Pu(IV) readily, but experiments indicated that the TTA method extracted the normal plutonium quantitatively from the UO_2SO_4 system described above.

When 65% polymeric Pu(IV), prepared in very dilute nitric acid, was introduced into the system, TTA extracted only the unpolymerized part of the Pu(IV). If the UO_2SO_4 solution containing the polymeric Pu(IV) was heated to 90°C for 5 min, the plutonium

was depolymerized quantitatively. Preliminary work thus indicates that a TTA extraction by the routine method may offer a way of estimating polymeric Pu(IV) in UO_2SO_4 solutions.

Since the UO_2SO_4 solutions are heated at 250°C, it is possible that plutonium polymer may not form in the process.

Plutonium in Chalk River Dissolver Solution (F. L. Moore). ORNL will leave the problem of assaying Chalk River dissolver solutions for plutonium for the purpose of determining payment to the Canadian Goverment. A preliminary study of possible methods has been made and is to be reported in detail in ORNL-1101, entitled *Preliminary Investigation of Methods for the Determination of Plutonium in Chalk River Dissolver Solutions.*

The methods being considered for the determination of total plutonium alpha activity are the lanthanum fluoride, TTA, and direct gross alpha methods. The direct gross alpha method is indicated to be the most practical, the TTA method appearing to be a good alternate and the lanthanum fluoride giving the lowest yields of the three.

In addition to a method for total plutonium alpha activity, another method must also be available for the accurate determination of Pu^{239}/Pu^{240} ratios since the high fluxes now in use at Chalk River will cause a considerable production of Pu^{240}. Five possible methods for the determination of Pu^{239}/Pu^{240} ratios are suggested: (1) pulse analysis, (2) specific activity determination, (3) fission counting, (4) activation analysis, and (5) mass spectrometric determination. Of these the mass spectrometric method appears to be the most practical.

IDENTIFICATION OF RADIOELEMENTS

F. L. Moore and W. S. Lyon

Analyses for impurities in radioisotopes have been done as requested. The scheme of Handley[15] has been employed routinely.

Of interest is the isolation and identification of Am^{241} and Np^{237} in the II-AW streams of the Purex process (Hanford material, 400-g/T level).

MISCELLANEOUS ACTIVITIES

Gaseous Waste (D. J. Coombe and S. A. Reynolds). In order to determine the efficiency of the Cottrell precipitator installed in the off-gas lines from Building 3026 and from the isotope production area, a series of tests and chemical analyses were made on samples submitted by J. C. Suddath.

The samples were in the form of CWS filters 9 in. in diameter, which had been placed at certain positions in the off-gas system to collect gas and particles being blown through the system. For convenience the filters were labeled A, B, and C to designate their position in the system. Filter A was taken before the precipitator, B after the precipitator, and C downstream from the filter house.

The first series of samples submitted covered the period from March 7, 1951 to May 1, 1951. Presumably the

[15] T. H. Handley, "Qualitative Analysis Scheme," *Analytical Chemistry Division Quarterly Progress Report for Period Ending January 10, 1951*, ORNL-955, pp. 47-51 (Mar. 28, 1951).

[redacted]

areas using the off-gas lines in question were operating under normal conditions. Beta and gamma decay studies were followed on samples A, B, and C from several runs. A typical set of beta and gamma decay curves is shown in Fig. 2.4. To further identify the activity on the filters, a leaching procedure was devised which consisted in mechanically tumbling the filters in about 200 ml of 6 *N* HNO_3 until they were well broken up. They were then digested for half an hour on a hot plate, and the mixture was cooled and filtered. The filtrate was analyzed for fission products.

Data from a typical HNO_3 leach are shown in Table 2.8.

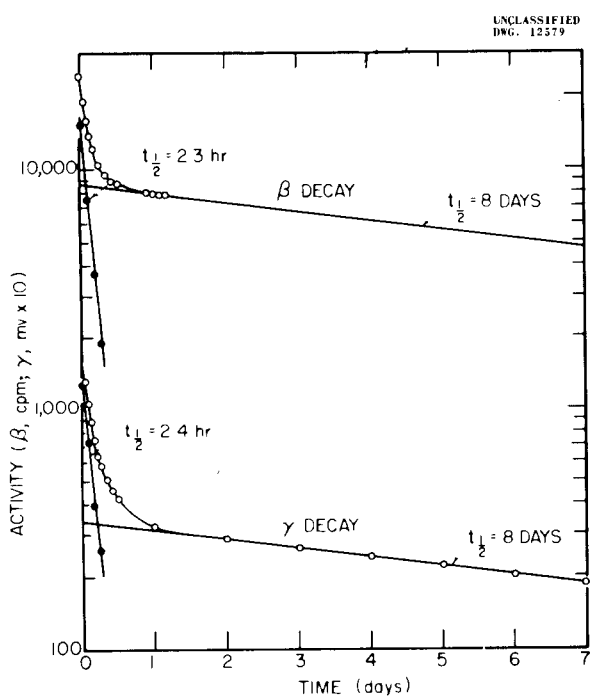

Fig. 2.4 - Beta and Gamma Decay Curves for CWS Filter

TABLE 2.8

Fission Products Leached from Filters

FILTER	GROSS BETA (cpm/ml)	BARIUM (cpm/ml)	TOTAL RARE EARTHS (cpm/ml)	RUTHENIUM (cpm/ml)
A	2.6×10^4	4	52	None detected
B	5.7×10^4	13	9	None detected
C	1.8×10^4	2	None detected	None detected

Data from the decay studies and fission product analyses indicated that over 99% of the activity on or in the filters was iodine.

In order to determine the chemical nature of the iodine activity several filters were leached with distilled water, carbon tetrachloride, and acetone. Results of these experiments are shown in Table 2.9 below.

TABLE 2.9

Leaching of Iodine from Filters

LEACH	ACTIVITY LEACHED (%)		
	FILTER A	FILTER B	FILTER C
Water	68		
CCl_4	16	7	5
Acetone	9	10	11

A number of volatility tests were made by inserting strips of the filters in glass tubes partially immersed in an oil bath. The tubes

[redacted]

were stoppered with rubber stoppers fitted with two glass tubes, which enabled a stream of dried air to be pulled into and out of the system by vacuum. The oil bath was heated to the desired temperature and kept fairly constant for 3 hr. At the end of this time the tubes were removed from the oil bath, and the activities of the strips and of control strips from each filter were measured by the gamma ionization chamber. Results are given in Table 2.10.

TABLE 2.10

Heat-Induced Elimination of Iodine from Filters

Time = 3 hr

FILTER	TEMPERATURE (°C)	LOSS (%)
A	90	None detected
B	90	None detected
A	180	None detected
B	180	None detected
A	240	50
B	240	45
A	300	64
B	300	66

There was little or no activity loss until a temperature was reached at which the filter began to char and a brown liquid began to distill over into a trap. This seems to indicate that the iodine had reacted with chemicals in the filter, presumably organic.

Radioautographs were made of several runs. Many particles were found on A filters, few or none on B, and few on C.

Another series of filters was submitted for gross gamma count, radioautographs, and fission product analysis. These filters represented samples taken during the recent RaLa run. The data from this series of filters are incomplete and will be reported later in a separate report with Messrs. Watson and Suddath of Chemical Technology.

Purification of Rubidium (W. A. Brooksbank). A target material of $Rb_2{}^{86}CO_3$ was purified of Cr^{134} for F. Pleasonton of the ORNL Physics Division by the method given previously.[16]

Preparation of Accelerator Targets (R. A. Bolomey). A progress report on the preparation of targets to be bombarded by positively charged particles will be issued soon. This will include the making of thick and thin targets of aluminum, B^{10}, B^{11}, deuterium, tritium, and nitrogen. Most of the discussion will concern tritium, including the stability of tritium targets.

Training of Personnel for Other Sites (S. A. Reynolds, W. S. Lyon, and F. L. Moore). Courses based on Friedlander and Kennedy's *Introduction to Radiochemistry* and training in practical radiochemical laboratory operations have been given personnel of the Du Pont, Phillips Petroleum, and American Cyanamid companies.

(16) W. A. Brooksbank, "Alkali Metals Separations," ORNL-867, *op. cit.*, p. 52.

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3. ACTIVATION ANALYSES — RESEARCH AND DEVELOPMENT

NEW ANALYTICAL PROCEDURES

G. W. Leddicotte

Sodium (R. Hahn and G. W. Leddicotte). As described earlier,[1] the procedure for the determination of trace amounts of sodium by radioactivation analysis, in which the radioisotope Na^{24} ($t_{½}$ = 14.8 hr) is carried on an isotopic carrier of sodium and precipitated as sodium zinc uranyl acetate, had certain limitations as a good analytical procedure. The unfavorable factors of a large molecule resulting from the uranyl acetate reagent, thus increasing the possibility for self-absorption, and the growth of the UX_1^{234} beta activity in the separated sodium zinc uranyl acetate precipitate appeared significant enough to warrant further study on another procedure for separating sodium in another weighable form.

Dr. H. H. Willard suggested that the general type of procedure desirable for a determination of this kind is one in which a sodium salt may be dissolved in the least quantity of water, followed by the precipitation of sodium as NaCl upon addition of an organic solvent or mixture of solvents in which the precipitated NaCl is but slightly soluble. The procedure ultimately decided upon was an adaptation of a method used by Willard and Smith[2] for the separation and determination of sodium and lithium by precipitation with an *n*-butanol solution of hydrogen chloride.

In this procedure the reagent is prepared according to the procedure of Willard and Smith by treating butanol with hydrogen chloride generated by the action of concentrated sulfuric acid added dropwise to solid NaCl. The gas is absorbed in reagent grade *n*-butanol, being passed into the alcohol until the density of the reagent is 0.87 g/ml (12% HCl).

Sodium is precipitated, after separation from other elements, as outlined in reference 1. The precipitate of sodium zinc uranyl acetate, after being washed with zinc uranyl acetate solution, 95% ethanol, and ethyl ether, is treated with 12% butanol-HCl reagent. The resulting mixture is stirred thoroughly while being held at a temperature of -15 to -20°C. After standing 5 to 10 min, the mixture is centrifuged and the supernatant discarded. The precipitate is then washed with a mixture of 10 ml of ethyl ether and 10 ml of butanol-HCl reagent. The mixture is again centrifuged and the supernatant discarded. By use of 10 ml of ethyl ether the precipitate is transferred to a tared filter paper (Whatman No. 1) and washed with small portions of ethyl ether. It is then dried at 110°C for 10 min, cooled, weighed as NaCl, mounted, and counted. No interference from zinc or uranyl ions was experienced.

(1) W. A. Brooksbank, G. W. Leddicotte, T. H. Handley, N. D. Lee, and C. W. Keenan, "Activation Analyses, Sodium," *Analytical Chemistry Division Quarterly Progress Report for Period Ending October 10, 1950*, ORNL-867, p. 37 (Dec. 28, 1950).

(2) H. H. Willard and G. F. Smith, "The Separation and Determination of Sodium and Lithium by Precipitation from Alcoholic Perchlorate Solution," *J. Am. Chem. Soc.* 44, 2816 (1922).

[redacted]

In Table 3.1 are compared the results obtained on a series of metal foils by activation analysis by the method outlined above with those obtained by the manufacturer's spectrographic analysis of the same samples.

TABLE 3.1

Comparison of Activation and Spectrographic Methods for Determining Sodium

SAMPLE	SODIUM IN SAMPLE (%)	
	BY ACTIVATION ANALYSIS	BY SPECTROGRAPHIC ANALYSIS
1	0.0008	0.0007
2	0.0006	0.0006
3	0.0008	0.0009
4	0.0015	0.0013
5	0.0010	0.0009

Potassium (G. W. Leddicotte). *In the Presence of Magnesium Metal and Lithium Salts.* The determination of potassium in magnesium metal and lithium salts, in which the potassium, as K^{42} ($t_{½}$ = 12.4 hr), is carried on an isotopic carrier of potassium and precipitated as potassium chloroplatinate, has been described previously.[3] A modification of this procedure has since been developed in the manner of O'Leary and Papish[4] in which K_2PtCl_6 is precipitated directly in a solution containing 60 to 70% ethanol by volume. Such a modification has been found more satisfactory than the former method of evaporating the chloride (or nitrate) solution and leaching out the soluble salts (chloroplatinates, etc.) from the residue with 95% ethanol. It has the obvious advantage of being more rapid and eliminates the possibility of error resulting from some occlusion of the soluble alkali chloroplatinates on the insoluble K_2PtCl_6 precipitate.

In this procedure the heavy metals, added as holdback carriers to the solution of the irradiated sample, are separated by H_2S or NH_4OH precipitation, followed by the precipitation of the alkaline earths (such as barium or strontium) with ammonium carbonate. The filtrate is evaporated to a volume of approximately 1 ml, and the solution is then made acid with a minimum quantity of HCl (or HNO_3) and sufficient chloroplatinic acid (containing 1 g of platinum in each 10 ml of solution) is added to convert all the chlorides (or nitrates) present into the corresponding chloroplatinates. Absolute ethanol is added until the solution contains 60 to 70% alcohol by volume. A few milliliter of ethyl ether is then added to the solution, and the precipitate is allowed to settle while cooling in an ice bath. The K_2PtCl_6 may be further purified by dissolving the precipitate in a minimum amount of warm water, adding ethanol and ether to reprecipitate the potassium chloroplatinate. The K_2PtCl_6 is then transferred to a tared filter paper (Whatman No. 1) by use of small portions of ethanol and washed several times with ethanol until the liquid becomes colorless. The precipitate is then dried at 110°C, cooled, weighed, mounted, and counted.

(3) W. A. Brooksbank, G. W. Leddicotte, T. H. Handley, N. D. Lee, and C. W. Keenan, "Activation Analyses, Potassium," ORNL-867 *op. cit.*, p. 38.

(4) W. J. O'Leary and J. Papish, "Analytical Reactions of Rubidium and Caesium," *Ind. Eng. Chem., Anal. Ed.*, 6, 107, esp. p. 110 (1934).

[redacted]

In the Presence of Rubidium and Cesium. Sodium, lithium, magnesium, calcium, and strontium do not interfere in the above procedure since their chloroplatinates are readily soluble in strong alcohol. However, rubidium and cesium interfere. Because of this and the desirability of quantitatively determining trace amounts of potassium in solid Rb_2CO_3, as well as in other rubidium and cesium compounds, some work has been done on developing another procedure for determination of potassium.

In a 16-hr bombardment at normal pile flux (suitable activation conditions for use in most potassium determinations) rubidium and cesium are capable of producing large amounts of radioactivity as the radioisotopes, i.e., Rb^{87} ($t_{½}$ = 17.5 min), Rb^{86} ($t_{½}$ = 19.5 days), and Cs^{134m} ($t_{½}$ = 3.15 hr). Thus it is necessary to find a procedure which will permit the determination of potassium (as the radioisotope K^{42}, $t_{½}$ = 12.4 hr) with minimum contamination from these radioisotopes of rubidium and cesium during the course of the analysis.

Preliminary work has indicated that an adaptation of a procedure used by O'Leary and Papish[4] for the separation of rubidium and cesium from potassium seems feasible. The values given in Table 3.2 are indicative of the decontamination possible when rubidium and cesium are added individually as radioactive "spikes" to a solution of a known amount of inactive potassium ions. The potassium ions plus the radioactive "spike" are then carried through a procedure in which rubidium (or cesium) holdback (10 mg) is added and is precipitated as $Rb_6PO_4 \cdot 9MoO_3$ from a nitric acid solution by the addition of 20% 9-phosphomolybdic acid. After a second scavenge with rubidium (or

TABLE 3.2

Separation of Rubidium and Cesium from Potassium Using 20% 9-Phosphomolybdic Acid

Rubidium and cesium added as radioactive "spikes" to inactive potassium

EXPT.	TOTAL ACTIVITY ADDED (cpm)		TOTAL ACTIVITY RECOVERED ON $KClO_4$ (cpm)		DECONTAMINATION (%)
	AS Rb	AS Cs	AS Rb	AS Cs	
1	3.7×10^6		482		>99.98
2	2.4×10^6		352		>99.98
3	4.1×10^5		332		99.92
4		2.3×10^7		327	>99.99
5		3.4×10^7		290	>99.99

[redacted]

[redacted]

cesium) carrier, followed by filtration, the excess molybdate ion is removed by precipitation as Ag_2MoO_4. A scavenge of excess silver is made by the addition of HCl. The resulting solution, after filtration, is treated with 70% perchloric acid, and the potassium is precipitated as $KClO_4$ from alcoholic solution.

The adaptability of this procedure to the determination of milligram amounts of potassium (added as isotopic carrier for the radioactive K^{42}) in samples of Rb_2CO_3 whose weight is many times that of the potassium added is being studied. O'Leary and Papish showed that as much as 30 mg of rubidium was quantitatively precipitated by the 9-phosphomolybdic acid. Our studies are over the range of 30 to 150 mg of rubidium (40 to 200 mg of Rb_2CO_3) which is a reasonable amount of sample for activation analysis. This work has not been completed, but we have been able to show that 80 mg of rubidium will precipitate under conditions similar to those outlined in the above procedure.

Although the decontamination of rubidium and cesium (Table 3.2) seems reasonable, the proposed procedure has the disadvantages of being one which is not too rapid and of giving a quantitative yield (not greater than 40%) which is much lower than is usual for most radiochemical separations. Both these factors are being considered in the work now started, and it is hoped that some progress will be made in clearing up these points.

Barium (G. W. Leddicotte). Additional work has been done in adapting the method of activation analysis for barium to further applications. The procedure first set forth by Glendenin[5] has been modified for a rapid separation of barium as the radioisotope Ba^{139} ($t_{1/2}$ = 84 min). These modifications to the procedure consisted chiefly in the addition of specific holdback, or scavenging, carriers. It was shown by decontamination experiments that the addition of copper, iron, or sodium holdback carriers was sufficient to inhibit the coprecipitation of short-lived contaminating activities of groups other than the alkaline earths when barium was finally precipitated as barium chloride. The alkaline earth contaminants, usually as the short-lived Sr^{87m} ($t_{1/2}$ = 2.7 hr), were removed by separating barium from strontium as the chromate in a buffered acetic acid solution in which strontium is soluble. A second scavenging with strontium was made, and the barium was weighed as $BaCrO_4$ or precipitated and weighed as $BaCl_2 \cdot H_2O$ from HCl-ether solution.

In carrying out the procedure known amounts of standardized barium carrier and strontium, copper, iron, and sodium holdback carriers are added to a solution of the irradiated sample. (Strontium may be determined on the same sample by the addition of a known amount of standardized strontium carrier which is separated as described in the procedure outlined in the next section.) The barium and strontium are precipitated as nitrates by the addition of fuming HNO_3. The precipitate is dissolved in H_2O, additional copper, iron, and sodium carriers are added, and a second

[5] L. E. Glendenin, "Determination of Ba and Sr Activities in Process Solutions," *Development of Methods for the Determination of Fission Product Activities in Plant Process Solutions*, Chicago report CN-1312, p. 10 (May 15, 1945).

[redacted]

[redacted]

fuming HNO_3 precipitation is made. The solution of the nitrates is then neutralized, acetic acid and acetate buffer are added, and the barium is precipitated as $BaCrO_4$ when Na_2CrO_4 is added to the solution. The solution is then filtered (the filtrate may be discarded or saved for strontium determination), and the $BaCrO_4$ is washed with hot water and dissolved in HCl. Additional strontium holdback carrier is added to a solution of the $BaCrO_4$, and $BaCrO_4$ is reprecipitated. This may be weighed as such or dissolved and precipitated as $BaCl_2 \cdot H_2O$ from HCl-ether solution. Either form must be dried, weighed, mounted, and counted. Representative results are shown in Table 3.3.

The same procedure was applied to a series of samples of magnesium metal. No comparison of results is made. since results by another method are not available.

Strontium (G. W. Leddicotte). Strontium may also be determined in a manner similar to that outlined for barium. The filtrate from the $BaCrO_4$ precipitation is heated, additional barium holdback carrier is added, and the $BaCrO_4$ is filtered off. The filtrate is made basic with NH_4OH and heated, and ammonium oxalate is added. The precipitate of $SrC_2O_4 \cdot H_2O$ is washed with NH_4OH, H_2O, C_2H_5OH, and ether. It is then weighed, mounted, and counted. Table 3.4 shows the decontamination effects of using radioactive "spikes" of sodium, copper, and barium in this procedure.

The same procedure was applied to a series of samples of magnesium

TABLE 3.3

Decontamination Experiments with Barium Procedure Using Radioactive "Spikes"*

RADIOACTIVE "SPIKE"	TOTAL ACTIVITY ADDED (10^7 cpm)	TOTAL ACTIVITY RECOVERED ON BARIUM PRECIPITATE (cpm)	DECONTAMINATION (%)
Na	4.00	6	>99.99
Na	3.00	10	>99.99
Cu	1.30	24	>99.99
Cu	1.57	21	>99.99
Sr	2.50	23	>99.99
Sr	8.70	60	>99.99

*Analysis made by two different analysts; duplicate or quadruplicate samples used.

[redacted]

TABLE 3.4

Decontamination Experiments with Strontium Procedure Using Radioactive "Spikes"

RADIOACTIVE "SPIKE"	TOTAL ACTIVITY ADDED (10^7 cpm)	TOTAL ACTIVITY FOUND ON BARIUM PRECIPITATE (cpm)	DECONTAMINATION (%)
Na	4.00	37	>99.99
Cu	1.30	40	>99.99
Ba	0.13	10	>99.99

metal. Table 3.5 gives a comparison of a few of these results obtained by activation analysis with those obtained by the manufacturer using spectrographic methods.

TABLE 3.5

Comparison of Activation and Spectrographic Methods for Determining Strontium

SAMPLE	STRONTIUM CONTENT (%)	
	BY ACTIVATION ANALYSIS	BY SPECTROGRAPHIC ANALYSIS
1	0.0001	0.0001
2	0.0003	<0.0010
3	0.0008	<0.0010

Gallium (G. W. Leddicotte). Trace amounts of gallium in metal ingots and foils have been determined by neutron activation analysis. Gallium has two stable isotopes,[6] Ga^{69} (60.2%) and Ga^{71} (39.8%). The more abundant isotope forms 20-min Ga^{70} by neutron capture; the less abundant isotope captures a neutron to form 14.1-hr Ga^{72}:

$$Ga^{69} + n \longrightarrow Ga^{70} + \beta^- \qquad (Ga^{70}\ t_{1/2} = 20\ \text{min})$$

$$Ga^{71} + n \longrightarrow Ga^{72} + \beta^- \qquad (Ga^{72}\ t_{1/2} = 14.1\ \text{hr})$$

Both radioisotopes can be used for activation analysis; however, because of its longer half-life, Ga^{72} has been the choice for gallium determination by radioactivation. It is possible to achieve a sensitivity of detection of 10^{-3} μg in a 16-hr bombardment at normal pile flux since the "atomic" cross-section for the reaction $Ga^{71}(n, \gamma)Ga^{72}$ is 1.35 barns (10^{-24} cm^2).[7]

Gallium is ether extractable as the chloride[8] and can be determined gravimetrically as the 8-hydroxyquinolate, $Ga(C_9H_6OH)_3$.[9] This combination of chemical properties permitted the

(6) M. G. Inghram and D. C. Hess, Jr., "On the Isotopic Composition of Meteoritic and Terrestrial Gallium," *Phys. Rev.* 74, 343 (1948).

(7) G. W. Leddicotte and S. A. Reynolds, "Activation Analysis with the Oak Ridge Reactor," *Nucleonics* 8, No. 3, 62 (1951).

(8) G. E. F. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis*, p. 96, Wiley, New York, 1938.

(9) F. J. Welcher, *Organic Analytical Reagents*, vol. 1, p. 293, Van Nostrand, New York, 1947.

[redacted]

development of an analytical procedure which apparently frees gallium activity from other interfering activities.

In this procedure a known amount of standardized gallium carrier is added to a solution of the bombarded sample. Concentrated HBr is then added and the solution is evaporated to dryness. The addition of HBr and evaporation is repeated at least twice more. The residue is then taken up in 6 *N* HCl and extracted three times with equal volumes of diethyl ether. The combined extracts are washed with 6 *N* HCl and the gallium is re-extracted into an equal volume of H_2O. After boiling out traces of the ether, the solution is made 0.3 *N* in HCl, and copper, iron, barium, and sodium holdback carriers are added. Copper is removed from the solution by saturation with H_2S. Two more scavengings are made by the addition of more copper carrier. The H_2S is boiled out and iron and barium are removed by precipitation with NaOH and Na_2CO_3. The scavenging is repeated twice more by adding additional iron and barium carriers. After the filtration the solution is again made 6 *N* in HCl and extracted with diethyl ether. The gallium is re-extracted into H_2O. The water layer is further diluted and heated to near boiling, a few milliliters of 8-hydroxyquinoline solution (50 g per liter in 2 *M* acetic acid) is added, and gallium 8-hydroxyquinolate is precipitated by the dropwise addition of 6 *M* ammonium acetate. The mixture is filtered through a tared filter paper (Whatman No. 1), and the precipitate is washed with warm and cold H_2O. After being dried for 15 min at 110°C, the precipitate is weighed, mounted, and counted.

In Table 3.6 the activation analysis results on the above-mentioned samples are compared with results obtained spectrographically by the manufacturer.

TABLE 3.6

Comparison of Activation and Spectrographic Methods for Determining Gallium

SAMPLE	GALLIUM IN SAMPLE (%)	
	BY ACTIVATION ANALYSIS	BY SPECTROGRAPHIC ANALYSIS
1	0.014	0.013
2	0.012	0.013
3	0.010	0.012
4	0.012	0.014
5	0.013	0.013

Procedures for Other Substances. Development and decontamination studies are being run on procedures for the following:

- Molybdenum in zirconium oxide
- Lead in ion-exchange resins
- Magnesium in metals
- Sulfur and phosphorus in oil shales limestone
- Cadmium and antimony in metals
- Cesium in rubidium carbonate
- A qualitative analysis scheme

ANALYSIS OF TITANIUM FOR CHLORINE AND TUNGSTEN

S. A. Reynolds

Titanium is quite suitable for activation analysis because of its low

[redacted]

cross-section and the short half-life of the activity produced (6 min). Table 3.7 shows the sensitivities of the analysis for certain elements whose concentrations in titanium are of interest.

Methods for determination of two of these, chlorine and tungsten, have been investigated to some extent at Oak Ridge National Laboratory, and methods for the others are known. Outlines of the methods used for chlorine and tungsten are given below.

Chlorine Determination. The following steps are used in the determination of chlorine:

1. Dissolution of titanium in HNO_3-HF.
2. Addition of carrier (HCl); precipitation of AgCl.
3. Dissolving in NH_4OH; "scavenging" with iron.
4. Reprecipitation of AgCl with HNO_3.
5. Filtration, drying (alcohol, ether), weighing, counting.

Tungsten Determination. The following steps are used in the determination of tungsten:

1. Dissolution of titanium in HNO_3-HF.
2. Addition of carrier (Na_2WO_4); precipitation by boiling with HCl (H_3BO_3 added).
3. Dissolving in NH_4OH; precipitation with HNO_3.
4. Dissolving in NH_4OH + small amount of HF.
5. Repeated ether extraction of solution made 6 *f* in HCl.
6. Precipitation by heating HCl solution after adding H_3BO_3.

TABLE 3.7

Activation Sensitivities

ELEMENT	PRODUCT	$t_{1/2}$	RADIATION TYPE	SENSITIVITY[7] (μg)
Cl	38	38 min	β, γ	0.03
Cr	51	26 days	K, γ, *e*	0.2
Mn	56	2.6 hr	β, γ	0.006
Fe	59	47 days	β, γ	9
Co	60	5 years	β, γ	0.02
Ni	65	2.6 hr	β, γ	0.03
Cu	64	13 hr	K, β, γ	0.007
Nb	94m	6.6 min	I.T., *e*	10 - 100
Mo	99	67 hr	β, γ	0.1
Ta	182	117 days	β, γ	0.007
W	187	1 day	β, γ	0.003

7. Dissolving in NH_4OH; addition of $(NH_4)_2S$ + Fe [$Fe(OH)_3$ precipitates].

8. Precipitation of W with H_2SO_4; oxidation with aqua regia.

9. Dissolving in NH_4OH; "scavenging" with Fe.

10. Precipitation by cinchonine from slightly acid solution.

11. Ignition, weighing, counting.

Preliminary results obtained in analysis of titanium by these methods are given in Table 3.8.

A figure (Fig. 3.1) showing at a glance the sensitivities of neutron activation analyses for most of the elements has been prepared.

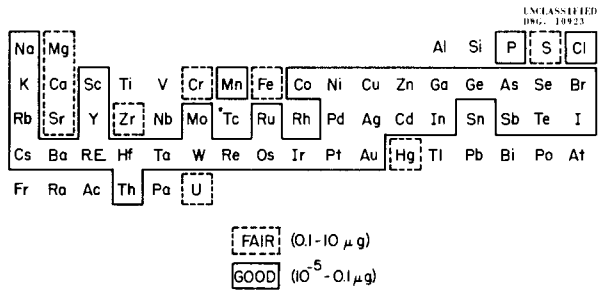

Fig. 3.1 - Activation Sensitivities

NEW APPLICATIONS OF ACTIVATION ANALYSIS

G. W. Leddicotte

Further inquiries have been made regarding the use of the method of activation analysis for determining trace amounts of chlorine in organic vegetable matter and for sulfur and phosphorus in oil shales and limestone. A group of the latter samples has been received for experimental work.

TABLE 3.8

Chlorine and Tungsten Results

SAMPLE	CHLORINE (ppm) BY ACTIVATION ANALYSIS	CHLORINE (ppm) BY POTENTIOMETRIC ANALYSIS*	TUNGSTEN (ppm)
H	19 to 22	≤35	7-14
L	3 to 6	≤10	146-157
M	17	≤35	6-10
Z**	26	≤25	82, 131, 178

*Potentiometric titration using silver-calomel system, automatic titrator. Data furnished by P. F. Thomason, Ionic Analysis Research and Development Group.

**Turnings (probably nonuniform).

4. SPECTROCHEMICAL ANALYSES — RESEARCH AND DEVELOPMENT

A. Estepp
C. Feldman
J. Gillespie
M. Murray

Working curves were established for determination of the following metals by the porous cup method:

METAL	CONCENTRATION RANGE (ppm)	MATRIX SOLUTION
Al	1 - 20	Na, 1%
Ba	3 - 50	$HClO_4$, dilute
Bi	125 - 1000	H_2SO_4, 10%
Co	3 - 50	Al, 0.2% (in 10% H_2SO_4)
Fe	2 - 40	Co, 0.2% (in 10% H_2SO_4)
Mn	1.5 - 25	Al, 0.2% (in 10% H_2SO_4)
Sc	0.2 - 3.0	H_2SO_4, 10%

A paper entitled "The Cooperative Standardization of Spectrographic Emulsion Contrast Factors" was prepared for submission to the *Journal of the Society for Applied Spectroscopy*. Also, a revised and enlarged version of the chapter "Photographic Photometry," was written for inclusion in the forthcoming ASTM (Committee E-2) book *Suggested Methods in Spectrographic Analysis*.

Instruction and training has been given to W. F. Morris, Jr., of the Arco Project in the following phases of spectrochemical analysis: spectrograph illumination, emulsion calibration, solution techniques, photometric measurements, and qualitative analysis.

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5. SERVICE ANALYSES

IONIC ANALYSES — DEVELOPMENT GROUP

P. F. Thomason

The demand by the HRE Group for analytical service work continued to be rather heavy. Most of the requested uranium and sulfate analyses required gravitometry in order to obtain the necessary accuracy. This type of analysis is time-consuming, and the number of analyses was comparatively large for this quarter.

In addition to the uranyl sulfate solutions analyzed for the HRE Group, some preliminary analyses of uranyl phosphate solutions being studied by that group were also made.

Work for the Isotope Development Department included ionic analyses for Ru, W, Co, $SO_4^{=}$, and Ba.

Several volumetric determinations of plutonium for the Chemical Technology Division were completed this quarter.

RADIOCHEMICAL ANALYSES — DEVELOPMENT GROUP

S. A. Reynolds

For the Chemical Technology Division analyses were made of liquid and gaseous waste samples, actual and simulated, and for plutonium in other samples. Isotope products were assayed and tested for purity for the Operations Division. Activation analyses were made for chlorine and tungsten in titanium.

ACTIVATION ANALYSES

G. W. Leddicotte

At the present time most of the analytical work done by the Activation Analyses Group is in a developmental stage for application to service analyses. However, procedures for the determination of barium, strontium, sodium, and potassium can now be accepted as routine methods. Thus the following analyses (already shown in the service report Table 5.1) made during the quarter may be considered to have been routine: 20 analyses for barium for the Operations Division, and 14 analyses for sodium and 14 for potassium for Reynolds Metals Co., Sheffield, Alabama.

GENERAL RADIOCHEMICAL ANALYSES

C. L. Burros

Of the total work for this quarter, 59% was done for the Pilot Plant Control Group, 90% of the work of the last month being for this group. The remainder of the work consisted in determining active constituents for the following programs:

1. Rate of fission product removal from Hanford dissolver solution by electrochemical means (H. L. Peeler).
2. Removal of alpha and beta activity, along with uranium, from the organic solvent used in the Purex process, specifications being <200 beta cpm/ml and <5 alpha cpm/ml; a 0.5-in. pulse column is being used. It is hoped to make the process

[redacted]

TABLE 5.1

Summary of Analytical Service Work for Period March 27 Through June 26, 1951

Group Making Analyses	NO. OF PERSONNEL		ORNL DIVISIONS REQUESTING ANALYSES									OTHERS REQUESTING ANALYSES							TOTAL
	Tech.	Non-Tech.	Anal. Chem.	Chem.	Chem. Tech.	Engr. Maint.	Health Physics	Metal-lurgy	Opera-tions	Physics	Reactor Tech.	ANP	ANL	AEC Idaho Op.	K-25	Phillips Pet. Co. (training)	Reynolds Metals Co.	Matl. Chem. Y-12	
Activation Analyses	1	2	160	25					36	22		4		16			82	20	365
Radiochemical Development	5	0	43		364		2		43	2						4			458
Ionic Development	6	1		702	78				8										788
Spectrochemical	4	0	15	72	63	1	10	219	31	13	8		2	9					443
General Radiochemical	4	6			9,043		38												9,081
Water Analysis	2	6		93	1,609	46	32	863	91	57	3		48						2,842
Laboratory and Semi-Works Control	3	11		147	15,917			10	122										16,196
Optical and Electron Microscopy	3	1		122	341		16				60		11		27				577
Pilot Plant	9	18			21,705														21,705
Radioisotope Production Control	5	17		343	5,174		20		6,825										12,362
Total	43	62	218	1,504	54,294	47	118	1,092	7,156	94	71	4	61	25	27	4	82	20	64,817

continuous rather than batch (C. V. Ellison).

3. Decontamination studies on laboratory furniture (C. D. Watson).

4. Decontamination studies on homogeneous reactor fuel (I. R. Higgins).

WATER ANALYSIS LABORATORY

J. H. Edgerton

The determination of citrate in three groups of samples submitted by R. E. Blanco was made by the iodate oxidation procedure described on p. 20 of this report. The excellent reproducibility of the test results and their agreement with the anticipated values indicated that the procedure is accurate to within ±0.1% in routine use.

Polarographic techniques were used to analyze for lead, tin, zinc, and cadmium in samples submitted by the Physics Division in their bulk shielding studies. Also, cobalt and nickel were determined together in a medium of 0.1 *N* KCl and 0.1 *M* pyridine containing 100 μg of thymol per milliliter for the Chemical Technology Division.

The Naval Reactor Division of Argonne National Laboratory submitted aqueous and solid samples from their high-temperature corrosion studies for determination of corrosion products.

Thorium breeder salts containing thorium, silica, fluoride, chloride, and phosphorus were submitted by the Chemistry Division for analysis. Thorium, fluoride, chloride, and phosphorus were determined as described in previous quarterly reports. The silica was determined by fusing the sample containing thorium, silica, and fluoride with sodium hydroxide. The fused sample was leached with water, and the thorium was filtered out. The silica in the filtrate was then determined colorimetrically by measuring the intensity of the blue silicomolybdate produced by the action of ammonium molybdate and stannous chloride on dissolved silica.

Liquid samples from tests for corrosion attack by bath metals of lithium, lead, and sodium on stainless steels and other high-temperature alloys were analyzed for the Metallurgy Division. The substances determined were silica, iron, chromium, nickel, molybdenum, niobium, thorium, uranium, titanium, sodium, and lithium.

The Metallurgy Division requested analyses for thorium, beryllium, silicon, carbon, sodium, and iron in the thorium-beryllium alloys. The samples were dissolved in nitric and hydrochloric acids, the thorium was precipitated with ammonium hydroxide, and the beryllium was determined on the filtrate in an acetate—acetic acid buffer solution at a *p*H of 5.5 using aurintricarboxylate (aluminon) as the color reagent. Silicon, carbon, sodium, and iron were determined as described in previous quarterly reports.

The Metallurgy Division is making studies of liquid-solid metal interaction for the ANP program. Copper-bismuth alloys which contained from 0.2 to 21% copper were analyzed for bismuth and copper. After solution of the samples in nitric acid, separation of the bismuth and copper was

accomplished by adding ammonium hydroxide to complex the copper. When a *p*H of 7.0 was reached, hydrochloric acid and hot water were added to precipitate the bismuth as bismuth oxychloride (BiOCl). Copper was determined on the filtrate by the colorimetric method using sodium diethyldithiocarbamate.

Alloys from the Metallurgy Division which contained less than 0.1% sulfur were analyzed by the hydrogen sulfide evolution method. The samples were dissolved with hydrochloric and hydrofluoric acids. The evolved hydrogen sulfide was absorbed in an ammoniacal solution of zinc. When the evolution was complete the solution was acidified with hydrochloric acid and titrated with a standard solution of potassium iodate containing potassium iodide.

The Metallurgy Division submitted alloys for boron determination. The boron was separated from interfering elements by distillation as methyl borate from a solution containing methyl alcohol and phosphoric acid. Boric acid forms a strong monobasic acid with mannitol when the methyl borate is hydrolyzed by sodium hydroxide. The boric acid is liberated by adding acid until the solution is neutral to *p*-nitrophenol. Mannitol is added to form the complex acid which is titrated to the phenolphthalein end point.

New apparatus for the determination of boron, arsenic, bismuth, antimony, sulfur, tin, nickel, and cobalt is being tested.

Other chemical analyses were performed as indicated in Table 5.1.

LABORATORY AND SEMI-WORKS CONTROL

L. T. Corbin

The Chemical Technology Division's study of the Purex process required the analysis of samples from various countercurrent runs for uranium, plutonium, nitric acid, gross beta, and gross gamma. Also, samples from the second plutonium cycle from two Hanford level runs were analyzed. Plutonium was determined by direct mounting and counting. The reducing normality of hydroxylamine sulfate was determined by the method of standardizing hydroxylamine hydrochloride.[1]

The Homogeneous Reactor Group submitted several samples for determination of uranium, ammonia, and nitrate. The ammonia and nitrate were determined by the Kjeldahl method.

Vanadium analyses were done for the Volatility Process Group of the Chemical Technology Division by the ferrous sulfate—persulfate method.[2]

The evaluation of the induction heater for fusion of fluorophotometric plates has progressed slowly this quarter because of changes being made on the Model No. Q-1165 fluorophotometer by the Development Group of the Instrument Division. Gold plates are being used rather than platinum plates. The relatively low melting point of gold necessitates the use of some flux other than sodium fluoride. Fluxes of the following

(1) J. Rosin, *Reagent Chemicals and Standards*, p. 205, Van Nostrand, New York, 1946.

(2) W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, p. 360, Wiley, New York, 1929.

[redacted]

compositions were tested: 80% Na_2CO_3 + 20% NaF, and 60% Na_2CO_3 + 40% NaF. A standard fluorophotometric curve for uranium was prepared for each flux and standard uranium samples were analyzed. The results for aqueous samples were satisfactory. However, if tributyl phosphate extraction was necessary to remove quenching materials or fission products, spattering occurred during the fusion. This difficulty was eliminated by use of aluminum nitrate instead of nitric acid as the salting agent in the extraction. Further study is needed before the fluorophotometric uranium procedure can be revised to specify the use of gold plates and induction fusion.

A Beckman model K automatic titrator has been set up for use in making acid-base and oxidation-reduction titrations.

The *Manual of Analytical Procedures for the U^{235} Recovery Process*, ORNL-983, prepared in collaboration with the Ionic Analyses Group for use at Arco by American Cyanamid Company personnel is being printed.

Miscellaneous analyses requested by other groups are summarized in Table 5.1.

PILOT PLANT CONTROL

E. J. Frederick

No changes have been made in the routine control procedures during this quarter. The procedures described below are under investigation.

Modified Lanthanum Fluoride Procedure for Plutonium. A modification has been proposed in the determination of plutonium in I-EU streams by the lanthanum fluoride method. Because of the small amounts of plutonium present and the interferences caused by the occlusion of very minute traces of alpha-emitting uranium daughter, a metastasis step has been inserted after the carrying of the plutonium on the lanthanum fluoride precipitate. By this step, the LaF_3 precipitate is reacted with a 30% KOH solution and the $La(OH)_3$ formed is dissolved in HNO_3. The LaF_3 is reprecipitated and the procedure is then run in the normal manner. Limited data on analysis of plutonium standards by both the modified and standard methods show good agreement. Decontamination of a plutonium-free uranyl nitrate solution by the modified procedure was excellent, giving a background alpha activity of approximately 20 cpm/ml. This work is being continued.

TTA Extraction of Plutonium. The follow-through of zirconium in the TTA extraction of plutonium, together with the build-up of activity in the Purex process, has caused a radiation hazard from the plutonium plates brought into the counting room.

Investigation has been started on the extraction of zirconium from the plutonium by TTA under oxidizing conditions. According to the procedure under study the organic phase is discarded and the plutonium in the aqueous phase is reduced to the tetravalent state and extracted as usual. Analysis of a series of plutonium standards by this method has shown recovery to be greater than 90%, but as yet no decontamination studies have been made. If separation and decontamination are both

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achieved the suitability of the procedure for the determination of plutonium in Arco feed solutions will be investigated.

Fluorophotometric Determination of Uranium. The model 475 fluorophotometer has been altered to operate similarly to the new model Q-1165. Instrument factors have been checked and agree with the calculated values. Further testing is necessary before the accuracy and precision of measurements made with the remodeled instrument are known.

RADIOISOTOPE ANALYSES

E. I. Wyatt

New Analytical Procedure for Tc^{99}. A method has been developed for the determination of Tc^{99} when present in, or as a complex of, tetraphenylarsonium chloride. The separation of technetium from ruthenium is almost quantitative when an ammoniacal solution of tetraphenylarsonium chloride containing a small amount of hydrogen peroxide is extracted with an equal volume of chloroform. The technetium can then be stripped from the chloroform with 1 *N* HCl. The chloroform extraction requires no more than 15 sec shaking time in a separatory funnel. The effects of varying the volume, temperature, and concentration of reagents have not been thoroughly investigated. A comparison of this procedure with the distillation procedure submitted in the last quarterly report (ORNL-1088, p. 68) has been made and the results agree favorably.

New Analytical Procedure for Nb^{95}. A new analytical procedure for Nb^{95} has been developed which will shorten the analysis time required by the present method.[3] The method involves precipitating the niobium in acetone with ammonium hydroxide, dissolving the precipitate in oxalic acid, reprecipitating with tetraphenylarsonium chloride, dissolving this second precipitate in acetone, reprecipitating with ammonium hydroxide, and, finally, igniting to the oxide for counting. The formulas of the precipitates are not known.

Improved Analytical Procedure for Rare Earths. The extraction of rare earths into TTA-xylene has been investigated as an analytical method of shortening the rare earth procedure currently used.[4] The extractions are made at a *p*H of 5.0 to 5.5. The rare earths are stripped with 3 *N* HCl containing the carrier for trivalent rare earths, and the zirconium is left in the organic phase. Rare earths may then be precipitated as the oxalates for weighing and counting purposes.

Improved Analytical Procedure for C^{14}. Aqueous solutions of the sodium salts of Versene have been used to sequester the barium in solid $BaC^{14}O_3$ samples and yield homogeneous solutions from which $C^{14}O_2$ may be evolved. This procedure eliminates the need for a preliminary evolution of gas and its subsequent trapping in caustic.

[3] D. N. Hume, N. E. Ballou, and L. E. Glendenin, *A Manual of the Radiochemical Determination of Fission Product Activities*, Chicago report CN-2815, p. 31 (June 30, 1945).

[4] *Ibid.*, p. 48.

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6. INORGANIC PREPARATIONS

PHOSPHORS

R. H. Sampley

The preparation of phosphors of interest to the Physics Division was continued. Further study of some of the lithium stannates necessitated the duplication of previously reported preparations. A list of the compounds prepared and showing the activators added is given in Table 6.1. Unless otherwise shown, the amount of each preparation was 0.1 mole, and 1% activator was added.

TABLE 6.1

Phosphors Prepared for the Physics Division

PHOSPHOR	ACTIVATOR	PHOSPHOR	ACTIVATOR
LiI (impure)		Li_2SnO_3	Cu
$LiNO_3$ (~400 g)		Li_2SnO_3	Mn
Li_3PO_4	Ce(III)	Li_2SnO_3	Pb
$LiBePO_4$	Ce(III)	Li_2SnO_3 (0.2 mole)	Sb
$LiBePO_4$	Sn	Li_2SnO_3	Ta
$LiBePO_4$	Tl	Li_2SnO_3	Ti (0.1%)
$LiCaPO_4$	Sn	Li_2SnO_3	Ti (0.1%)
$LiCaPO_4$	Tl	Li_2SnO_3	Ti (10%)
$LiMgPO_4$	Sn	Li_2SnO_3	Tl
$LiMgPO_4$	Tl	Li_2SnO_3	Zr
$LiZnPO_4$	Sn	$Li_4SnTi_2O_8$	
$LiZnPO_4$	Tl	$Li_6Sn_2Ti_2O_{11}$	
Li_2BaSiO_4	Ce(III)	Li_2TiO_3	Ce(III)
Li_2BeSiO_4	Ce(III)	$Li_2Ti_2O_5$	Ce(III)
Li_2MgSiO_4	Ce(III)	$Li_2Ti_2Si_2O_5$	Ce(III)
Li_2SrSiO_4 (0.2 mole)	Ce(III)	Li_2WO_4	
Li_2ZnSiO_4	Ce(III)	Li_4WO_5	
Li_2SnO_3		SnO_2	Ti
Li_2SnO_3 (0.2 mole)	Ce(III)	SnO_2	Tl

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7. ANALYTICAL CHEMICAL CONTROL OF THE HOMOGENEOUS REACTOR SOLUTION

W. H. Davenport and R. H. Powell

Full details of recent analytical work on the continuous control of the HRE soup solution appeared in ORNL-1057.[1]

ELECTROMAGNETIC DENSITOMETER

The design and operation of the densitometer are described in ORNL-1057.[1] The bomb was tested for performance and calibrated, using distilled water, according to the following procedure: After pretreatment of the float and bomb chamber with 1% nitric acid, the chamber was filled with distilled water. The instrument was then calibrated for coil current vs. density of water over a temperature range from 25°C to the temperature at which the float sank. The water was taken as a standard, and its density was determined from temperature-density tables for water after first correcting the observed temperature for the temperature gradient in the bomb.

Four calibrating runs were made in which the temperature was increased at a fairly constant rate, 2 to 3°C per minute. The coil current was increased until the float sank, the temperature and current readings were noted, and the current was returned to zero. This procedure was repeated at intervals, each interval corresponding to about a 5°C rise in temperature. The results showed poor reproducibility between runs, as would be expected, since temperature and current were recorded while both were changing. The average reproducibility error, i.e., the average deviation of any point from a smooth curve through all the points, was ±0.001 g/cc over the density range 0.864 to 0.924 g/cc.

Two more runs were made in which the current was held at a point slightly less than would be required to move the float, and the temperature was slowly increased until the float sank. The average reproducibility error of the points obtained in this manner was ±0.0004 g/cc over the same range.

The relation of coil current to the density of liquid and float has been expressed by Richards[2] as

$$\rho = Ri^2 + P$$

where ρ = density of solution (g/cc)

R = a constant = a function of the configuration of the system, depending on size and shape of magnet, susceptibility of armature, etc.

i = coil current (amp)

P = float density (g/cc)

Over a small current range R should be a constant in a system whose geometry is fixed.

(1) W. H. Davenport and R. H. Powell, "Analytical Chemical Control of the Homogeneous Reactor Solution," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending May 15, 1951*, ORNL-1057 (in press).

(2) A. R. Richards, "An Electromagnetic Densitometer," *Ind. Eng. Chem., Anal. Ed.* 14, 595 (1942).

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The value of R was determined at different current settings for the electromagnetic densitometer by substituting the appropriate numbers into Richard's expression. The density of water was determined from the corrected temperature, and the density of the float was corrected for thermal expansion. Since the current range was relatively large (0.0 to 0.5 amp), R became a variable constant, being slightly lower at higher currents.

Several experimental runs were made using uranyl sulfate solutions (30.915 mg of uranium per milliliter) instead of water. The data were plotted as temperature vs. coil current. The density of uranyl sulfate at any temperature on the curve could then be determined by substituting into Richard's equation the value for current taken from the curve and the values for R and P derived from the water runs. After application of the required corrections, the density of the uranyl sulfate was found to average 0.0421 g/cc higher than the density of water at the corresponding temperatures over the range 183 to 232.5°C. The density of another aliquot of the same uranyl sulfate solution had been determined previously at 25°C, using a pycnometer, and found to be 0.0421 g/cc higher than that of water.

The apparatus has several disadvantages in its present design. It is difficult to thermostat evenly since the principle on which it is based requires that the large magnet be placed immediately below the sample chamber. In addition, the chamber has a small reservoir at the base, into which the iron core of the float extends. It would be impossible to drain the liquid from this trap or to get satisfactory circulation into this section. Another difficulty may be encountered when the iron cores of the electromagnet and the float are placed in a radiation field. Changes in permeability of the cores due to radiation would change the calibration of the instrument.

It may be possible, although time-consuming, to calibrate the instrument for sinking temperatures of the float at different concentrations of uranyl sulfate when no current is applied. This method, which would be quite sensitive and would eliminate the objections accompanying the use of the electromagnet, will be tried.

Q **Measurements.** A bomb of special design[1] having four gold O rings has been used to test the behavior of glazed ceramics during the gasketing of ceramic insulators for use in a high-pressure system. The ceramic insulators, which encase a copper coil, are made of Lava grade 1137 which has been powdered, compressed, and fired. Both the glaze received from the American Lava Corp. and that from E. Cantrell of the ORNL Research Shops have cracked during gasketing at room temperature. For this reason no experiments have been made to determine the effect of temperature on the system or on the Q measurement.

The effect of the bomb construction and of the position of the gold gaskets on the Q value of the Q coils was determined. The Q value of a coil measured in air at 20 megacycles was 62 when the coil was outside the bomb and 52 with the coil inside the bomb.

No gasketing tests were made on a third Q coil since its collar had unfavorable dimensions for gasketing.

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Previous information on the rupture strength of a similar grade A Lava (powdered, compressed, and fired) ceramic indicated a rupture strength of 3600 psi whereas the rupture strength of the natural, fired grade A Lava was over 9000 psi. These ceramics failed in their first testing because an irregular surface, which was not machined after glazing, resulted in an unevenly distributed load on the ceramic. These ceramics, however, were not eliminated from possible use. The rupture strength of the ceramic can be increased three times by using a natural grade 1137 Lava for the collar of the *Q* coil, into which collar is machined a plug hole for the thimble of the existing *Q* coils. The glazes of the collar and thimble might be used as agents for bonding them. By such a combination of materials it should be possible to secure maximum strength of the collar under gasketing conditions and also a smooth polish of the glaze on the collar. Pyrex glass[3] has been observed to increase slightly in tensile and impact strengths in both slow- and fast-neutron fields although the color of the pyrex darkens. This suggests that pyrex should be studied for possible insulating use in lieu of ceramics in the construction of the *Q* coil. Accordingly two pyrex disks, 53 mm diameter x 6.5 mm thickness, neither fire-polished nor strain-relieved, were fastened into the *Q* coil bomb with gold *Q* rings and tested for strength during gasketing. Both pyrex disks cracked during the test. It is believed that cracking occurred at approximately 565 psi steam pressure and 250°C. The gold gasket at the thermowell end of the bomb began leaking at 880 psi, and the test was discontinued. The rate of temperature rise was about 2°C per minute. In spite of the cracked disks there was no leaking of the bomb solution into the volume below the *Q* coil housing.

The test on gasketing pyrex will be repeated using fire-polished strain-relieved disks of the same dimensions.

Radiation-Resistant Glasses. The neutron-absorbing glasses obtained from A. Silverman, as described in ORNL-925,[4] are still in the ORNL graphite reactor. Upon discharge each glass specimen will be tested for changes in its optical spectrum.

As a new approach to the problem of obtaining a suitable glass for HRE use, the possibility of a glass relatively transparent to gamma and neutron radiation is being considered in cooperation with the Penberthy Instrument Co., Seattle, Wash. They will attempt to develop a glass having such a property by using components of suitable low atomic number and low-cross-section neutron capture. This approach is opposite to that of using neutron- and gamma-absorbing glass.

(3) J. C. Horsman, *Summary of NRX Pile Irradiations*, NP-1922, p. 6 (Dec. 8, 1950).

(4) W. H. Davenport, Jr., and R. H. Powell, "Analytical Control of the Homogeneous Reactor Solution," *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending November 30, 1950*, ORNL-925 (Jan. 30, 1951).

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8. OPTICAL AND ELECTRON MICROSCOPY

T. E. Willmarth F. D. McNeer
B. I. Gary

Since the work of this section is devoted to providing optical and electron microscopy and radioautographic service to ORNL, associated plants, and the A.E.C., most of its studies are best reported by the individual or group for whom the work was done. Only studies of general interest are included here.

EFFECT OF SURFACE CONDITIONS OF TEST BOMBS ON FORMATION OF OXIDE LAYERS ON 347 STAINLESS STEEL DURING PRETREATMENT WITH 1% HNO_3 AT 250°C

In connection with the HRE project additional optical and electron microscope studies have been made of oxide films or layers formed on stainless steel 347 during passivation. Although the bulk of this material will be covered in separate reports, the observations made from one group of samples are included here.

Samples of 347 stainless steel were passivated with 1% HNO_3 at 250°C for 1, 4, 8, and 24 hr in two bombs. One bomb had been used repeatedly for corrosion tests without chemical or mechanical cleaning of the internal surfaces; the other was a freshly machined and cleaned stainless steel bomb. All steel samples were prepared for the test by degreasing, abrading with Nos. 80 and 120 paper, degreasing again in acetone, and rinsing with ethanol. Oxide films formed during the test were stripped from these samples by the hydrobromic acid—methanol method and then studied by optical and electron microscopy and by electron and X-ray diffraction. The results of this study are shown in Table 8.1.

With the exception of the 1-hr sample taken from the new bomb, all the oxide films were too thick for transmission studies with the electron microscope or by electron diffraction using the same instrument. Identification of the major constituents was made by R. M. Steele of the Metallurgy Division using the X-ray spectrometer. α Fe_2O_3 was believed to be the major constituent, although the possibility exists that it was Cr_2O_3. The two oxides are difficult to differentiate by X-ray methods.

It should be noted that the thickness of the oxide film built up in 1 hr in the old bomb was identical with that found on the 24-hr sample from the new bomb. The layer formed in 24 hr in the old bomb was of approximately the same thickness as that formed on the 4- and 8-hr samples in the same bomb. This may indicate that, under these conditions of pretreatment, after a certain layer thickness is attained, an equilibrium condition tends to exist between the walls of the bomb and the surface of the sample. Microscopic examination indicated that this heavy layer differs somewhat in composition from the film found next to the metal. The substrate film appears almost structureless, whereas the upper layer contains fairly large, uniform-sized crystallites of about 0.5 to 1.0 μ particle size. This layer appeared not to be well bonded to the substrate film, as was indicated by the sloughing off of areas of it, thus exposing the underlying film.

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TABLE 8.1

Properties of Oxide Films Formed on 347 Stainless Steel During Pretreatment with 1% HNO_3

Temperature, 250 °C

PRETREATMENT TIME (hr)	PROPERTIES OF OXIDE FILM*		
	COLOR	SURFACE PROPERTIES	APPROXIMATE THICKNESS (μ)
Pretreated in New Stainless Steel Bomb			
1	Colorless to straw-yellow	Nonuniform thickness	<0.1 to 0.25
4	Straw-yellow to orange	Nonuniform properties	<0.2 to 0.3
8	Straw-yellow to blue-green	Nonuniform properties	<0.25 to 0.3
24	Red to red-black	Uniform coat of microcrystallites	1.0
Pretreated in Used Stainless Steel Bomb**			
1	Orange to gray	Nonuniform properties	1.0
4	Red to gray	Uniform coat of microcrystallites	2.0
8	Red to black	Uniform coat of microcrystallites	3.0
24	Red to black	Disappearance of much of crystalline layer appearing in 4- and 8-hr samples	3.0

*α Fe_2O_3 or Cr_2O_3 believed to be the major constituent of the film.

**Repeatedly used for corrosion tests.

Other current work on films formed on stainless steels under different conditions includes a study of the composition and physical characteristics of the film formed on 347 stainless steel during pretreatment in 1% HNO_3 for 24 hr at 150, 200, and 250°C and the study of films formed on stainless steel types 347, 347 S-6, 17-7, 410, 420, 440, and 446 pretreated in 1% HNO_3 at 250°C for 12 hr and then exposed for two weeks to water in a thermal loop at 500°F and at a flow rate of 5.5 gpm. Early observations on one sample, type 446, indicated the major constituent of the film to be Fe_3O_4.

EXTENT OF RADIATION DAMAGE TO PAINTED SURFACES

A study of the extent of radiation damage to painted surfaces is being

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made for the Unit Operations Group of the Chemical Technology Division. Selected areas of a number of concrete samples coated with paints produced by various manufacturers were photographed and then exposed to radiation. The painted surfaces exposed to 10^4 and 10^5 r of gamma radiation showed no radiation damage. Exposures will be increased stepwise to a maximum of 10^9 r of gamma radiation to complete the experiment.

RADIOAUTOGRAPHY OF CWS FILTERS AND OTHER CURRENT WORK

Extensive radioautography and photomicrography was done for the Unit Operations Group in connection with the recent RaLa run. Approximately 240 radioautographs were taken of CWS filters, particles were counted, and backgrounds were studied. The details of this work are reported elsewhere.

Current work includes particle-size studies of dispersed methylene blue, of oxides of uranium dispersed in bentonite, and of exchange resins; an investigation of the homogeneity of exchange resins; a study of welded 347 stainless steel to check for the presence of intergranular corrosion; and a structural study of a large number of zirconium samples to which micro amounts of other elements have been added.

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ANALYTICAL CHEMISTRY DIVISION – Y-12 SITE

9. RESEARCH AND DEVELOPMENT

R. Rowan, Jr.

OXYGEN AND NITROGEN IN LITHIUM

J. C. White

In a previous progress report[1] the importance of the determination of oxygen and nitrogen in lithium was noted. That report discussed the application of alkyl halides to this determination and mentioned the possibility of using *n*-butyl chloride as a reagent. Further work has shown that the reaction between the alkyl chloride and lithium requires at least 36 hr for completion so that this reagent does not appear to be very promising.

The applicability of iodobenzene as a reagent for these determinations was studied. Although the reaction proceeds satisfactorily, the end products are not amenable to separation by water extraction; no distinct water—organic solvent phases are formed when hexane, ethyl ether, acetone, or benzene is added. It was hoped that a sharp separation, such as is obtained in the *n*-butyl bromide method[2] for oxygen in sodium, would be possible. The sample weight could then be determined by titration of the water layer. Diphenyl, the organic end product, is sparingly soluble in most solvents. Further work will be conducted on this phase of the problem.

Attention has recently been centered on stearic acid, $CH_3(CH_2)_{16}COOH$, as a possible reagent. An alcoholic solution containing 1 g of stearic acid per milliliter can be prepared at 50°C. This concentration is sufficient for ready reaction with lithium, and preliminary tests indicate that the oxide and nitride are insoluble in this solution. Lithium stearate is slightly soluble in alcohol so that, upon cooling, a mixture of lithium stearate, excess stearic acid, and lithium oxide and nitride separates. Ethyl ether readily dissolves the excess stearic acid, but further separation is more complicated. Addition of water to lithium stearate produces an insoluble "lithium soap" which foams and forms a gelatinous, difficult-to-handle precipitate. This phase of the problem is also being considered for further study.

METALLIC CORROSION PRODUCTS IN SODIUM METAL

J. C. White and L. J. Brady

In accordance with a request of the ANP Experimental Engineering Group, chemical methods of analysis are being set up for the determination of corrosion products (iron, chromium, cobalt, nickel) in sodium metal. No great difficulties are anticipated since the colorimetric methods available for these elements are of great sensitivity and selectivity.

ELEMENTS OF HIGH-NEUTRON-CAPTURE CROSS-SECTION IN SODIUM METAL

J. C. White

Methods are being considered for the determination of elements of high-

(1) J. C. White, "Oxygen and Nitrogen in Lithium," *Monthly Progress Report of the Analytical Chemistry Division (Y-12 Site)*, ORNL Y-12 Area, report Y-B31-248, p. 1 (April 12, 1951).

(2) J. C. White and R. Rowan, Jr., *The n-Butyl Bromide Method for the Determination of Sodium Monoxide in Sodium*, ORNL Y-12 Area, report Y-B31-251 (April 24, 1951).

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neutron-capture cross-section in sodium metal, in accordance with a request of the ANP Experimental Engineering Group. Previous investigation at Knolls Atomic Power Laboratory has shown that the concentration of such elements is usually of the order of 10 ppm or less. In the following paragraphs the desired element is named and the accepted method or a proposed method is noted. Actual developmental work in this laboratory has not yet been started on many of the following, which are listed in decreasing order of the urgency of the need for a method of quantitative determination.

1. *Rare earths.* No method has been published for this determination. Considerable work has been done at the Knolls Laboratory and it is understood that a report of these methods will be issued in the near future. The use of ion-exchange resins for separation and concentration appears to hold the greatest promise of success. This work will be a cooperative venture with the Radiochemical Section of the Analytical Chemistry Division.

2. *Boron.* The use of curcumin for this determination has been described,[3] but it has been suggested that 1,1′-dianthrimide is a more efficient and sensitive reagent. The latter will be investigated soon.

3. *Cadmium.* A polarographic method has reportedly been used successfully. The determination appears to be straightforward and should require little developmental work. Activation methods will also be tried.

4. *Chlorine.* A micro Mohr titration method is contemplated.

5. *Lithium.* This determination is discussed on p. 65.

6. *Carbon.* A study must first be made to determine whether all the carbon is present as carbide or partly as graphitic carbon. This determination is of particular importance in the analysis of lithium metal.

7. *Calcium.* The method, which is based on the precipitation of calcium oxinate, is reported in the literature.[4]

8. *Cesium.* This determination is discussed on p. 65.

9. *Fluorine.* A modification of one of the methods generally used for the determination of trace amounts of fluorine in water may be applicable.

10. *Potassium.* This determination is discussed on p. 65.

11. *Manganese.* The usual method, involving the oxidation of the element to permanganate, has been tried with some success.

12. *Copper.* A polarographic method has been applied successfully.

13. *Mercury.* No suitable methods are available, although KAPL is experimenting with a spectrographic technique.

(3) J. Rynasiewicz, M. P. Sleeper, and J. W. Ryan, *Boron in Sodium Metal. Determination of Microgram Amounts by Alcohol Extractions,* KAPL-405 (Sept. 21, 1950).

(4) J. Rynasiewicz and M. E. Polley, "Calcium in High-Purity Sodium Salts. Determination of Microgram Amounts by the Oxine-Oxalate Method," *Anal. Chem.* 21, 1398 (1949).

[redacted]

14. *Hydrogen.* An elaborate apparatus for this determination, which involves the preferential diffusion of hydrogen through an iron vessel into a vacuum, is described in the literature.[5]

OXYGEN IN SODIUM

J. C. White and W. J. Ross

Recovery of Known Amounts of Oxygen. The determination of oxygen in sodium has been discussed in previous reports.[2,6] In connection with the further investigation of the *n*-butyl bromide method, which has been developed for this determination, the preparation of sodium samples containing known, added amounts of oxygen as sodium monoxide has been studied. The method of preparation consists in reacting high-purity sodium peroxide and sodium[7] at 300 to 400°C to form sodium monoxide quantitatively:

$$Na_2O_2 + 2Na \xrightarrow{300 \text{ to } 400^\circ C} 2Na_2O$$

Because of this reaction oxygen is not believed to be present in sodium except in the form of sodium monoxide. If the temperature is allowed to rise rapidly, the reaction proceeds with explosive violence. The temperature is, however, easily controlled by the use of a sand bath for heating the reaction vessel. A high ratio of sodium to sodium peroxide (100 to 1) also decreases the possibility of an explosion. The reaction is carried out under mineral oil, and the temperature is maintained at 400°C for 30 min. The completeness of the reaction under such conditions has been found to be dependent upon intimate contact of the peroxide and sodium. The presence of the mineral oil tends to prevent such contact; however, if the peroxide is embedded in the sodium, the reaction will proceed satisfactorily. Incomplete reactions are readily detected because of the yellow color of the peroxide. The recovery of known amounts of oxygen is shown in Table 9.1.

TABLE 9.1

Recovery of Known Amounts of Oxygen in Sodium

OXYGEN (%)				
ADDED AS Na_2O_2	BLANK*	TOTAL, BLANK + ADDED	FOUND	DIFFERENCE
0.224	0.054	0.278	0.285	+0.007
0.101	0.054	0.155	0.158	+0.003
0.110	0.054	0.164	0.161	-0.003
0.218	0.054	0.272	0.282	+0.010
0.145	0.054	0.199	0.210	+0.011
				0.007 (avg.)

*Average of three determinations.

Comparison of Methods. A comparison of results obtained on duplicate samples by this method and by the method of

(5) L. P. Pepkowitz and E. R. Proud, "Determination of Hydrogen. Universal Gasometric Micromethod," *Anal. Chem.* 21, 1000 (1949).

(6) J. C. White and W. J. Ross, "Determination of Oxygen in Sodium," *Analytical Chemistry—ANP Program Quarterly Progress Report,* ORNL Y-12 Area, report Y-B31-237, p. 2 (March 7, 1951).

(7) C. E. Weber and L. F. Epstein, *Problem in the Use of Molten Sodium as a Heat Transfer Fluid,* KAPL-139; *J. Metallurgy Ceramics,* Issue No. 3, TID-67, p. 103 (May, 1949).

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TABLE 9.2

Comparison of Results of Determinations of Oxygen in Sodium by the *n*-Butyl Bromide and the Pepkowitz and Judd Methods on Duplicate Samples

SAMPLE	OXYGEN (%)			100(*A* - *B*)/*A*
	A *n*-BUTYL BROMIDE	*B* PEPKOWITZ AND JUDD	DIFFERENCE *A* - *B*	
1	0.043	0.034	0.009	21
2	0.012	0.011	0.001	8
3	0.019	0.025	-0.006	-32
4	0.047	0.043	0.004	8
5	0.022	0.038	-0.016	-73
6	0.024	0.010	0.014	58
7	0.017	0.022	-0.005	-29
8	0.028	0.018	0.010	36
9	0.020	0.025	-0.005	-25
10	0.029	0.018	0.011	38
11	0.027	0.026	0.001	4
12	0.038, 0.036, 0.037 } 0.037	0.069, 0.037, 0.049 } 0.052	-0.015	-41
13	0.042, 0.032, 0.030 } 0.035	0.029, 0.038, 0.062 } 0.043	-0.009	-26
14	0.025, 0.031, 0.018, 0.025, 0.021 } 0.024	0.010, 0.018, 0.021 } 0.016	0.007	29

Pepkowitz and Judd[8] is shown in Table 9.2.

[8] L. P. Pepkowitz and W. C. Judd, "Determination of Sodium Monoxide in Sodium," *Anal. Chem.* 22, 1283 (1950).

There is no indication that either method gives consistently higher or lower results than the other, although more data are required to resolve this question definitely. In general, the agreement between the two methods

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is satisfactory. The results for samples 12, 13, and 14 indicate that the *n*-butyl bromide method gives better precision, which is in agreement with previous observations.

The bromide method is now being used in the routine laboratory work.

Application to Samples Contained in Metal Tubes. The use of stainless steel tubes instead of glass for sampling sodium for oxygen determinations has necessitated the development of a different technique in preparing the sample for analysis by the *n*-butyl bromide procedure. Glass ampoules or tubes containing sodium can be crushed beneath the surface of the reagent, but this technique is obviously impossible in the case of steel tubes. Three procedures are possible with steel tubes: (1) reaction of the sodium in the tube with concentrated *n*-butyl bromide reagent; (2) removal of the sodium by extrusion with a mechanical press; and (3) removal of the sodium by melting in a high-boiling liquid which does not react with sodium.

It was experimentally demonstrated that the first of these procedures is unsatisfactory because the rate of reaction of sodium and *n*-butyl bromide is a function of the surface exposed. The amount of surface area exposed at the ends of the 0.75-in. tubing is so small that an intolerably long reaction time is required. In addition, it is extremely difficult to remove the sodium bromide crust on the ends of the tube in order to expose a fresh surface for reaction. For example, 12 to 15 hr of constant boiling and agitation was required for complete reaction of the sodium in two 1-in. tubes of sodium in pure *n*-butyl bromide. This drastic treatment was found to cause partial decomposition of the reagent with the formation of hydrobromic acid by virtue of the catalytic effect of the steel tubes. In an experiment to test the catalytic effect of steel tubes on the decomposition of the reagent, approximately 0.2% titratable bromide ion was found in *n*-butyl bromide which had been refluxed for 2 hr in the presence of the steel sample tubes.

Extruding the sodium from the steel sample tubes with the aid of a mechanical press has the disadvantage of leaving a layer of sodium on the walls of the tube. This layer may well contain a larger proportion of sodium monoxide than the bulk of the sample. The operation must, of course, be performed beneath the surface of a dry liquid which is inert to sodium.

The third method of removal of the sample, that of melting the sample out under an inert solvent, is currently being investigated. Hexane is an ideal solvent for use in the *n*-butyl bromide method because it can be obtained in relatively pure form, is practically free from water, and shows little tendency to absorb moisture. However, its boiling point (69.0°C) is lower than the melting point of sodium (97.5°C). Higher-boiling paraffins, which should be suitable for this purpose, are unobtainable in quantity at present. Aromatics such as toluene (b.p. 110°C) and xylene (b.p. 141°C) were therefore investigated. It was demonstrated that these compounds can be purified and dried but that they show a pronounced tendency to absorb moisture from the air. It is not to be implied that toluene and xylene cannot be obtained free from water, but, on a

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routine basis, maintaining these liquids in a water-free state appears to be impractical.

In further attempts to find a suitable solvent, white gasoline and ordinary kerosene were passed through silica gel columns to remove sulfur- and oxygen-containing compounds as well as a portion of the aromatics. The gasoline was distilled and the 100 to 140°C fraction was used as a covering liquid in which to melt sodium. This solvent proved to be unsatisfactory since it evidently contained some constituent which was reactive toward sodium. In the case of the kerosene, however, it was indicated that reactive constituents, including water, were present in smaller concentrations than in any other solvent tested except hexane. These conclusions are based upon qualitative observations of the length of time a fresh sodium surface retained its brightness in the solvent. Drying tests are underway in which quantitative determinations of water will be made on the solvents by the Karl Fischer method.

So far, the most promising liquid in which to melt sodium from metal sample tubes appears to be kerosene. Other solvents, including decahydronaphthalene, will be investigated.

POTASSIUM, LITHIUM, AND CESIUM IN SODIUM METAL

J. C. White

In connection with the development of methods for the determination of elements of high-neutron-capture cross-section in sodium metal, the determination of potassium in sodium is currently being studied. This program, which was requested by the ANP Experimental Engineering Group, will shortly be extended to the determination of lithium and cesium in sodium metal.

It is generally agreed that the concentration of these alkali metals in sodium will be of the order of 10 to 100 ppm, which low concentration range suggests the use of the flame spectrophotometer. However, the marked interference of sodium in such determinations is well known. In the present investigation it is planned to separate as much sodium as possible from the other alkali metals so that sodium interference will be minimized.

This separation appears possible only by the use of ion-exchange resins. The work of Beukenkamp and Rieman[9] who successfully separated sodium from potassium with Dowex-50, starting with a mixture having a mole ratio of 365 of sodium to 1 of potassium, has been studied for possible adaptation. A column of Dowex-50, a strong sulfonic acid type cation-exchange resin, was prepared in accordance with the recommendations of Beukenkamp and Rieman after being converted from the sodium salt to the acid form by treatment with 10% hydrochloric acid. Initial tests were made by passing a mixture of 1 g of sodium and 1 mg of potassium as chlorides through the column and eluting with 0.70 *M* HCl. The concentration—vs.—volume eluted curve did not agree with that obtained by Beukenkamp and Rieman. Sodium was eluted throughout the washings, but the concentration gradually decreased to such an extent that, at the elution

[9] J. Beukenkamp and W. Rieman III, "Determination of Sodium and Potassium, Employing Ion-Exchange Separation," *Anal. Chem.* 22, 582 (1950).

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volume of highest potassium concentration, the mole ratio of sodium to potassium was 6.4 to 1. Since this ratio lies well within the reported limits of separation, a complete separation appears possible by passing the eluted volume of high potassium content through a second column.

To ensure a more efficient initial separation, refinement of the apparatus is planned in order to permit extremely slow flow rates, of approximately 0.2 ml/min/sq cm. It is hoped that conditions may be found which will provide a satisfactory separation in one pass, although it is likely that such a separation will require a column of impractical height.

The same general plan is contemplated for the separation of lithium and cesium from sodium.

Plans are currently underway to apply the method of activation analysis instead of flame photometry to this determination. The work will be done in cooperation with the Radiochemical Section of the Analytical Chemistry Division.

OXYGEN IN HELIUM AND ARGON

J. C. White and W. J. Ross

As reported recently,[10] an apparatus suitable for determining low concentrations of oxygen in helium and argon by the method of Brady[11] has been placed in operation. The apparatus has since been moved to the ANP Experimental Engineering Group site, Building 9201-3, where analyses are being performed with the objective of testing the efficiency of the gas-purification train in use at that location.

Tests were made to determine the level to which the oxygen content of helium can be reduced by passage through a column of sodium-potassium alloy (NaK). The results for oxygen determinations in helium which had been so treated are set forth in Table 9.3.

TABLE 9.3

Oxygen in Helium After Passage Through NaK at 0.77 cu ft/min

Helium tank No. 95032

TEST	OXYGEN (ppm)
1	41
	19
2	30
	28
3	33
	25
	18

The first sample of test No. 1 was taken without first flushing the cylinder outlet line, in order to determine the effect of this procedure on the oxygen content of the sample. The high value found emphasizes the necessity of flushing the line before withdrawing samples for analysis.

Samples of argon from five different tanks, none of which had undergone purification, were analyzed for

(10) J. C. White and J. R. Lund, "Determination of Oxygen in Argon and Helium," Y-B31-237, *op. cit.*, p. 6.

(11) L. J. Brady, "Determination of Small Amounts of Oxygen in Gases," *Anal. Chem.* 20, 1033 (1948).

oxygen. In two cases multiple determinations were made on samples from the same tank in order to test the precision of the analytical method. The test results are given in Table 9.4.

TABLE 9.4

Oxygen in Unpurified Argon

TANK NO.	OXYGEN (ppm)		
	SINGLE DETERMINATION	AVERAGE	STANDARD DEVIATION
T 10999	32		
	32		
	34		
	24		
	19		
	29	28.3	5.7
T 4499	40		
	39		
T 14375	46		
T 1676	33		
T 6679	31		
T 7240	40		

REACTION OF METALLIC SODIUM WITH SODIUM TETRABORATE AT ELEVATED TEMPERATURES

J. C. White

The ANP Experimental Engineering Group is contemplating the use of decrepitated borax, $Na_2B_4O_7$, as a shielding material for the ARE reactor. The proposed physical arrangement is such that a leak in the primary coolant system, which will contain sodium at 1500°F, would result in contact between the borax and the sodium. The present investigation was made for the purpose of determining what takes place when these two materials are brought in contact at elevated temperatures.

The first experiment consisted in mixing 1.0 g of dehydrated borax and 0.1 g of sodium in a quartz tube and heating the mixture in an atmosphere of dry argon. In the first trial the temperature was gradually increased to 500°C over a period of 3 hr. The sodium showed no evidence of having reacted with the borax and was still intact except for a crust of white borax.

In the second experiment the same conditions were maintained except that the temperature was gradually increased over a period of 2 hr to 660°C. At this temperature dark fumes, which condensed at the wall of the tube, were noticed, and a black crust appeared over the sodium. The sodium globule was noticeably smaller than the original size, and the borax had changed from a white to a yellowish-black powder. The black crust was scraped from the sodium, washed with alcohol and water, and identified as elemental boron by the following tests: It was unattacked by boiling concentrated HCl but could be fused with sodium carbonate; the melt gave a positive boron test with turmeric paper; X-ray-diffraction examination showed that the material was principally elemental boron.

A third experiment was conducted by rapidly heating 1.0 g of borax in contact with 0.1 g of sodium to the melting point of borax, 741°C (1366°F). The entire mixture turned black, as did the walls of the tube. The sodium had completely reacted, as was evidenced by the absence of a violent evolution of hydrogen when the black mass was crushed and washed with

alcohol. Hydrogen was evolved when the material was washed with water. Chemical identification again indicated that metallic boron was present and that the wash water was quite basic. These results indicate that the following reaction probably took place:

$$Na_2B_4O_7 + 12Na \longrightarrow 4B + 7Na_2O$$

It has been requested that another experiment be made in order to simulate the actual conditions of a leak in a system employing sodium as a coolant and borax as a shielding material. Molten sodium at 1500°F will be dropped into molten borax to determine how violent the reaction is under these conditions. It is significant that the reaction was not violent under the conditions of the experiments so far tried.

A summary of the results is given in Table 9.5.

TABLE 9.5

Reaction of 1 g of Borax with 0.1 g of Sodium

MAXIMUM TEMPERATURE (°C)	TIME (min)		RESULTS
	TOTAL	AT MAXIMUM TEMPERATURE	
500	180	25	No evidence of reaction
660	120	25	Black crust on unreacted sodium; borax turned yellow-black
745	20	5	Mixture entirely black; evidence of boron and Na_2O

DETERMINATION OF CARBON IN LITHIUM

W. K. Miller J. C. White
D. L. Manning

In connection with the ANP liquid metals coolant program, work is being carried out on the development of a method for the determination of carbon in lithium. It is generally agreed that most of the carbon in lithium is present as lithium carbide, Li_2C_2, which decomposes upon contact with water to form acetylene, C_2H_2. Some carbon probably exists as carbonate, and there is a possibility that graphitic carbon may be present.

A feasible method for the simultaneous determination of carbide and carbonate has been set up and tested, although incompletely. Graphitic carbon can be determined by wet combustion of the residue from the carbide and carbonate determination. By dissolving a sample containing lithium carbonate and carbide in dilute acid, carbon dioxide and acetylene are evolved. Carbon dioxide can be absorbed in ascarite and weighed.

A promising method for the determination of acetylene which was reported by Hanna and Siggia[12] depends on the reaction of the gas with an alkaline solution of potassium iodomercurate, K_2HgI_4, according to the following reaction:

$$2HC{\equiv}CH + K_2HgI_4 + 2KOH \longrightarrow (HC{\equiv}C)_2Hg + 4KI + 2H_2O$$

An excess of standard base is added to the iodomercurate solution before the reaction, and the unreacted portion is titrated at the completion. The method was tested by analyzing

(12) J. G. Hanna and S. Siggia, "Determination of Acetylene and Monosubstituted Acetylenes," *Anal. Chem.* 21, 1469 (1949).

[redacted]

samples of calcium carbide of unknown purity. Upon solution of the carbide directly into the reagent, about half the available gas escaped into the atmosphere. Solution of the carbide, followed by sweeping the generated acetylene into a solution of the reagent with carbon dioxide—free argon, was not an improvement. However, by bubbling the gases through two solutions of the reagent, it was possible to titrate an almost theoretical yield of acetylene. The final train consisted of an argon tank, an ascarite tube, a generating flask, a drying tube, a micro absorption tube for determining carbon dioxide, two absorption towers containing alkaline solutions of potassium iodomercurate, and an ascarite guard tube. The acetylene and CO_2 were generated by adding dilute acid through a dropping funnel to the sample in the generating flask, and the gases were swept into the absorption media by means of a slow stream of argon. Duplicate determinations of the carbide content of impure calcium carbide indicated that a precision of about 5% was attained. However, it is believed that this precision can be improved. Only a negligible quantity of carbonate was found in the calcium carbide.

METALLIC CORROSION PRODUCTS IN REACTOR FUELS

J. C. White W. J. Ross
L. J. Brady

Methods and techniques are being developed for the determination of metallic corrosion products in two reactor fuels, one a eutectic of $KF-NaF-UF_4$ in the amounts of 26.0, 46.5, and 27.5 mole %, respectively, and the other a eutectic of $BeF_2-NaF-UF_4$ in the amounts of 12, 76, and 12 mole %, respectively. These products contain iron, nickel, chromium, and possibly molybdenum in widely varying concentrations.

The overall problem can be divided into three phases:

1. Removal of the eutectic from the metal container and subsequent sampling.
2. Preparation of the sample for spectrographic analysis.
3. Development of suitable colorimetric methods for the determination of iron, nickel, chromium, and molybdenum.

Removal of Eutectic. The following procedure has proved satisfactory for removal of the eutectic from the metal tube in which it has been heat-treated: The tube is cut into several sections (1 to 1.5 in. long), placed in a graphite holder, and heated in an argon atmosphere in a quartz tube at 700°C. The physical arrangement is such that when the eutectic melts it will flow by gravity into a graphite mold. After cooling, the solidified melt is removed and sampled.

Preparation of Sample for Spectrographic Analysis. It was originally planned that spectrographic analyses would be made on the samples in the as-received condition. It is believed that the corrosion products exist in the fused fluoride mixture either in the metallic state or as fluorides. Since the spectrographic procedure is dependent on suitable standards, it would be necessary to prepare the eutectics with the corrosion products present as the elements or as fluorides in concentrations in the range of

[redacted]

4 to 1000 ppm. This does not appear feasible for several reasons, foremost of which is the difficulty of obtaining sufficiently pure standards. Direct spectrographic analysis therefore seems impractical.

The present procedure is to prepare standards with the impurities as oxides in a U_3O_8 matrix. Experience has shown that excellent quantitative results can be obtained on such a mixture. The preparation of samples of the eutectic for spectrographic analysis with the impurities in the oxide form is best accomplished by an ammoniacal precipitation of the uranium and corrosion products and subsequent ignition of the precipitate to the oxides. This treatment also serves to separate sodium and potassium from the other elements. The alkalis, if present, react with U_3O_8 to form diuranates, and these compounds cannot be tolerated from the standpoint of the spectrographic procedure. Iron and chromium are precipitated as hydroxides along with the uranium, which carries nickel hydroxide down with it. This precipitate is ignited at 850°C and is then ready for spectrographic analysis. Molybdenum probably does not precipitate completely under these conditions, but, in any event, MoO_3 would be volatilized at such an ignition temperature. The determination of this particular corrosion product is not of great importance in the present tests.

Development of Colorimetric Methods. Various colorimetric procedures for the determination of low concentrations of iron, nickel, chromium, and molybdenum are available. In the present case, since interference by uranium is proportional to the amount present, standard curves for the determination of each of the metals of interest have been prepared with a solution of the eutectic (melted in a graphite vessel in order to avoid the presence of metallic corrosion products) as the blank. The uranium concentration of this solution was about 7 mg/ml. Solution was effected by mixing the sample with 0.1 to 0.5 g of boric acid (to facilitate fluoride removal as BF_3) and fuming with 72% perchloric acid until all the green-colored salt had disappeared.

Several solvents other than perchloric acid were tested, including sulfuric acid, a mixture of sulfuric and nitric acids, and 85% phosphoric acid. Sulfuric acid alone attacks the eutectic only slightly, but its solvent powers are improved greatly by the addition of nitric acid. Phosphoric acid dissolves the eutectic readily but appears to be of little use in view of the interference of phosphate ion in analytical procedures.

The presence of perchloric acid presents certain difficulties in the determination of chromium by *sym*-diphenylcarbazide by the usual procedure in which an evaporation step in the presence of ethanol is required. In addition, the oxidation to Cr(VI) by permanganate or persulfate has not been satisfactory, very erratic results having been obtained in preliminary tests. These difficulties have resulted in the development of different oxidizing techniques. The use of perchloric acid, a strong oxidizing agent itself, as a solvent for the eutectic suggested its use for oxidizing chromium to the hexavalent state. Considerable work has been done on the effectiveness of perchloric acid as an oxidant.

The effect of time of boiling and fuming was studied by adding 5 ml of 72% perchloric acid to a 5-ml aliquot of the solution and boiling for predetermined periods of time.

The results shown in Table 9.6 indicate that a quantitative oxidation is possible and that the loss of chromium by volatilization was negligible for periods up to 12 min at least. The optimum boiling time appears to be around 8 min under the conditions of the test. This phase of the determination is still under study.

TABLE 9.6

Influence of Time of Heating on Oxidation of Chromium to Cr(VI) by 72% Perchloric Acid

CHROMIUM (μg)		RECOVERY (%)	BOILING TIME* (min)
ADDED	FOUND		
29.0	31.5	109	5
29.0	23.3	80	7
29.0	27.5	95	7
29.0	30.0	103	8
29.0	32.8	113	10
29.0	25.0	86	12
29.0	28.3	98	12
29.0	28.8	99	20
72.5	72.5	100	5
72.5	75.5	104	7
72.5	75.5	104	7
72.5	75.5	104	8
72.5	75.5	104	10
72.5	60.0	83	12
72.5	63.0	87	12

*Samples were taken to fumes under an infrared lamp and then transferred to a hot plate and boiled for the time shown

The effect of time-of-standing on the color complex of Cr(VI) with *sym*-diphenylcarbazide was also investigated. The results clearly indicated that the color development was complete within 7 min after addition of reagent and that it remained stable for at least 50 min.

The *p*H of the solution in which the color is to be developed is maintained between 0 and 1, or around 0.2 *N* with respect to perchloric acid. This is believed to be the optimum acidity for stability of the complex.

No particular difficulties were encountered in determining either iron by the 2,2′-dipyridyl method or nickel by the dimethylglyoxime method. Standard curves were prepared for concentrations as low as 15 ppm (on the basis of the eutectic) of both iron and nickel. A suitable standard curve has also been prepared for the colorimetric determination of chromium by the diphenylcarbazide method. Although curves have been prepared for the colorimetric determination of molybdenum, the method employed may not be entirely satisfactory and further work is being done in this case.

On the basis of the results obtained so far, the range of concentration of chromium in eutectic samples is wide, varying from zero to as much as 4000 ppm, with the majority of the results in excess of 1000 ppm. The iron concentration varies also, but, in general, it is not so high as that of chromium. Concentrations of nickel, for the most part, are less than 50 ppm. No molybdenum has been found, although at present it is impossible to report whether this results from lack of corrosion or loss of molybdenum in preparing the sample for analysis.

DETECTION OF ORGANIC BINDER IN A GRAPHITE BEARING

W. K. Miller

In a recent progress report[13] an outline was given of tests made on a sample of graphite bearing to determine the presence or absence of an organic adhesive. It was concluded that the bearing probably does contain such a binder. Several tests were made, some of which were inconclusive while others indicated the presence of a binder. These latter included (1) determination of weight loss which indicated charring of the sample and an appreciable weight loss when it was subjected to a temperature of 950°C in an inert atmosphere and (2) a hydrogen determination.

It was decided that the validity of the above tests for the presence of organic constituents could be determined by comparing the results of these tests with those obtained when graphite, which was known to be free of organic material, was subjected to a high-temperature treatment in an inert atmosphere. A sample of binder-free graphite was subjected to the test. A weight loss of only 0.3% was obtained by heating at 950°C for 1 hr. This is in sharp contrast to the 3% weight loss of the graphite bearing, also after 1 hr of heating. On the basis of this test and the previous tests, it is concluded that the graphite bearing contained an organic binder.

INVESTIGATION OF A SYNTHETIC SMOKE MIXTURE

W. K. Miller

At the request of the ANP Experimental Engineering Group, a brief investigation has been made of a preparation to be used in the generation of smoke. The smoke is desired for use in certain engineering studies.

A liquid mixture for the preparation of a synthetic fog or smoke is described in U. S. Patent 2,407,384, dated September 10, 1946, an abstract of which appears in *Chemical Abstracts* **41**, 1052 (1947). A copy of the patent is not available at this time, but, according to the abstract, it is claimed that this mixture yields a stable fog and does not clog or corrode the spray equipment. The mixture consists of carbon disulfide, carbon tetrachloride, and titanium tetrachloride to which phosphorus equivalent to 0.1 to 0.2% of the titanium tetrachloride, is added. Since the abstract does not give detailed specifications, it was the purpose of this brief investigation to determine the practical limitations of the recommended constituents for producing a suitable fog. Because of the hazardous nature of CS_2, it was considered important to determine the lowest concentration of this component essential for a satisfactory smoke.

The tests which were made in the laboratory indicate that:

1. The high solubility of phosphorus in CS_2 accounts for the use of this compound and for the fact that the minimum amount necessary to carry the requisite quantity of phosphorus should be used.

2. Practically any ratio of organic solvent (CS_2-CCl_4) to $TiCl_4$ will yield a dense smoke, but the most desirable appears to be one which requires a minimum of solvent.

[13] W. K. Miller and J. R. Lund, "Detection of an Organic Binder in Graphite," *Analytical Chemistry Division Quarterly Progress Report for Period Ending March 26, 1951*, ORNL-1088, p. 93 (in press).

[redacted]

3. The organic constituent CCl_4 apparently has the combined purpose of (*a*) stabilizing the smoke and (*b*) producing a more finely divided residue. The latter property aids in preventing clogging.

4. The most dense smoke is obtained through the use of $TiCl_4$ alone, but this smoke is not the most desirable because of its instability and the clogging properties of the residue which it produces.

For further tests it was recommended that a mixture of the following components be prepared: 0.1 to 0.2 g of P in 1 ml of CS_2, 25 ml of CCl_4, and 75 ml of $TiCl_4$. It was suggested that the ratio of CCl_4 to $TiCl_4$ be altered in either direction in the field tests for the purpose of obtaining the most desirable smoke.

ANALYSIS OF URANYL SULFATE SOLUTIONS

O. Menis C. K. Talbott
F. E. Jenkins

Uranium(IV). In connection with studies of corrosion and solution stability in HRE test loops, a knowledge of the uranium(IV) concentration in the solution is desirable. A method for the determination of tetravalent uranium in uranyl sulfate solutions has therefore been developed.

Soluble uranium(IV) in microgram quantities can be separated from uranyl ions by precipitation of the former as UF_4.[14] After the separation the uranium(IV) can be oxidized to the hexavalent state and determined colorimetrically or polarographically. This procedure appears to be straightforward. It was found that there were, however, a great many difficulties to overcome. On a micro scale tetravalent uranium is very susceptible to air oxidation,[15] and it is necessary to precipitate the trace amounts immediately after collection of the sample. Furthermore, it has been shown that a soluble complex of the type $U(SO_4)_2 \cdot 2HF$ is formed,[16] and this must be decomposed in order to precipitate the uranium quantitatively.

Development work included the following phases of study: (1) stabilization of uranium(IV) in the sample, (2) methods for its complete recovery, and (3) procedures for its quantitative estimation.

Even in the presence of hydroxylamine hydrochloride, an oxidation inhibitor, it was found that uranium(IV) is unstable in uranyl solution. Appreciable loss by air oxidation is best avoided by precipitating the trace amounts immediately after collecting the sample.

The precipitation of uranium tetrafluoride in a solution which was 2 *N* in both hydrofluoric and hydrochloric acids was found not to be quantitative. Only about 50% recovery was obtained by this precipitating mixture. Polarographic analysis of the filtrate and wash solutions accounted for the remaining 50%.

(14) V. G. Lopin and E. K. Gerlin, *Determination of Uranium as Fluoride*, translated in document A-3127 from *J. of Gen. Chem. USSR*, Vol. VI, Issue II.

(15) L. P. Pepkowitz, *Microvolumetric Assay of Uranium*, MDDC-727 (Dec. 3, 1945; decl. Jan. 28, 1947).

(16) G. O. Morris, *The Complex Between $U(SO_4)_2$ and HF. Evidence for Its Existence and Instability*, BR-454A (June 23, 1944).

[redacted]

In order to determine the optimum conditions for quantitative precipitation of uranium(IV) as the fluoride, precipitating reagent mixtures, wash solutions, and experimental conditions were varied. It was found that the use of ammonium chloride, ammonium nitrate, or ammonium acetate as a salting-out agent reduced the solubility of uranium tetrafluoride to a negligible value. Boiling the solution before separation of the precipitate gave low recoveries, but no loss of uranium(IV) was observed when the operation was carried out at room temperature. The use of the salting-out agent in the wash solution also improved the results. Ammonium nitrate was found to be more desirable than ammonium chloride for use in the precipitating and wash solutions because the precipitate could be more easily washed free of this salt. The recovery of uranium(IV) in synthetic standard samples of tetravalent uranium in uranyl solution by precipitation as the fluoride in the presence of 4 *N* NH_4NO_3 was found to be excellent. In one series of synthetic samples of uranyl sulfate containing 3.4, 6.8, and 13.6 μg of uranium(IV) per milliliter, 3.5, 7.0, and 14.5 μg, respectively, were recovered. In another series of synthetic samples containing 13.4, 26.8, and 40.2 μg of uranium(IV) per milliliter the recovery was 13.0, 27.2, and 39.5 μg, respectively.

The last phase of the development work associated with the determination of uranium(IV) in uranyl solution involved a study of methods for the quantitative estimation of uranium after separation by the fluoride precipitation. No agreement could be obtained between results of determinations by the colorimetric thiocyanate method[17] and by the polarographic method.[18] The colorimetric method as described by Sandell[17] gave poor precision and accuracy. A modified thiocyanate method[19] developed by the Argonne National Laboratory proved to be superior. Agreement of the results obtained by the latter method with theoretical and polarographic values was good, as is illustrated in Table 9.7. In the modified thiocyanate method, stannous chloride is replaced by sodium thiosulfate as a reducing agent for iron. Instability of color, blank variations, and deviations from Beer's law can be traced to interference by a strong reducing agent.

TABLE 9.7

Comparison of Results by the Modified Thiocyanate and the Polarographic Methods for the Determination of Uranium

TEST	URANIUM CONCENTRATION (μg/ml)		
	COLORIMETRIC	POLAROGRAPHIC	THEORETICAL
1	16.7	16.2	16.7
2	34.0	33.8	33.4
3	49.4	50.4	50.1

The procedure adopted for the determination of uranium(IV) in uranyl solution involves the precipitation of uranium tetrafluoride with HF using

(17) E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2d rev and enl ed, p. 601, Interscience, New York, 1950.

(18) C. J. Rodden, *Analytical Chemistry of the Manhattan Project*, NNES, Div. VIII, Vol. 1, pp. 606-608, McGraw-Hill, New York, 1950.

(19) Chemical Engineering Division, *Summary Report for October, November, and December, 1950*, ANL-4588 (Mar. 1, 1951).

[redacted]

lanthanum fluoride, introduced as $La(NO_3)_3$, as a carrier in a solution which is 4 *N* in NH_4NO_3 and which contains 1% hydroxylamine sulfate. The precipitate is digested, centrifuged, and washed with solutions containing ammonium nitrate and sodium fluoride. The precipitate is finally dissolved with nitric and boric acids and oxidized to uranium(VI) with permanganate. The excess permanganate is destroyed with hydroxylamine. The uranium is then determined by the modified thiocyanate method.[19] Acceptable results are being obtained routinely by this method.

Total Uranium. The method that has been used routinely for the determination of total uranium in HRE solutions is potentiometric titration with ferric sulfate following reduction with chromous sulfate solution.[20] This procedure, while satisfactory in other respects, requires a relatively large amount of the analyst's time per determination. The introduction of a Precision-Dow automatic titrator improved the output of determinations per man-hour but resulted in a decrease in accuracy. The relative purity of the test solutions (only trace quantities of contaminants are present) suggested that a variety of methods might be applicable, and the need for increasing output led to the investigation of some of the established volumetric procedures.

The methods studied were (1) reduction of the uranyl ion by means of a Jones reductor[21] or silver reductor,[22] followed by titration with ceric sulfate solution using a color indicator (ferroin) and (2) direct titration of the acidity of the uranyl solution with NaOH solution.[23]

The procedure which employs the Jones reductor was adopted, since, on a routine basis, it was found to be less troublesome than the silver reductor method. A considerable increase in output was realized.

Although still under investigation, the sodium hydroxide titration method shows promise of being the most satisfactory of those tried with regard to wide applicability and speed. The latter advantage will be realized to the fullest extent only if the method is used in conjunction with the automatic titrator. By this method uranium can be determined in nitrate and fluoride solution as well as in sulfate solution. A study is being made of the variables affecting the method, including the concentration of free acid.

Differential spectrophotometry is also being investigated as an alternative method for the determination of uranium in relatively pure solutions.

Oxygen. The need for information as to the concentration of free oxygen in HRE reactor solutions has led to the adoption of polarographic and micro gasometric methods for this determination. Synthetic samples were prepared and sampling techniques and efficiency of absorber solutions were investigated. Polarographic readings were calibrated against the oxygen concentration as determined by a micro Winkler method.[24]

(20) Rodden, *op. cit.*, p. 63.

(21) *Ibid.*, pp. 54-57.

(22) *Ibid.*, pp. 59-62.

(23) *Ibid.*, pp. 74-75.

(24) *Standard Methods for the Examination of Water and Sewage*, pp. 105-110, American Public Health Association, New York, 1946.

[redacted]

The procedure is as follows: The liquid sample is collected in a bomb at 1000 psi and 250°C. The sample is then transferred from the bomb into an evacuated vessel equipped with a condenser, and the gases are boiled out of the solution through the condenser into a mercury-filled gas buret. The gas is repeatedly passed through an Orsat type absorbing vessel filled with absolute ethanol (saturated with an electrolyte) until no further absorption occurs. Through an outlet in the absorbing vessel a fraction of the solution is introduced into the cell of the polarograph. Making use of the calibration curve, the oxygen concentration may then be determined from polarographic measurements.[25] A blank determination is also carried out on the residual gas.

In an alternate procedure the gas is absorbed in an alkaline pyrogallol solution and the amount of oxygen present is determined from the volume change. At an oxygen concentration level of 11 ppm, the maximum relative error of results by the polarographic method on a group of eight samples, each analyzed on a different day, was 2%. The relative error of the results for a similar group of four samples analyzed for oxygen by the pyrogallol absorption method was 20%. The polarographic method is especially suitable for the lower ranges of oxygen concentration where the precision of the gasometric method is poor. For higher concentrations the gasometric procedure has the advantage of speed.

Chromium. In connection with the determination of corrosion products in solutions from HRE test loops, a study was made of the determination of microgram quantities of chromium in uranyl sulfate solutions. The diphenylcarbazide method described by Rodden,[26] in which chromium is oxidized to chromate by means of permanganate and the excess permanganate is destroyed with sodium azide, was found to be troublesome.

In the search for a more satisfactory oxidation procedure, periodate, persulfate catalyzed by silver, and perchloric acid were utilized as oxidizing agents. Only perchloric acid oxidation produced a color stable enough to be of analytical use. Consequently, a study was made of the optimum conditions for the determination of chromium colorimetrically by diphenylcarbazide, using perchloric acid as the oxidizing agent. The length of boiling with perchloric acid, the effect of allowing the solution to stand after oxidation both with and without the chromogenic reagent, the effect of nitrate ions, and the final *p*H of the solution, were studied.

A study made of the effect of time of boiling indicated that the best precision was obtained by boiling the perchloric acid solution for 4 min after dense fumes first appeared. The optimum color development was obtained by adding the reagent immediately after oxidation. The intensity of the color developed on adding the reagent after 4 hr of standing was only 33% of that obtained when the color was developed immediately after oxidation of the chromium. After 16 hr no chromium could be detected by the diphenylcarbazide reagent. The color, once developed, was stable for 1.5 hr, after which the optical

(25) I. M. Kolthoff and J. J. Lingane, *Polarography*, p. 311, Interscience, New York, 1941.

(26) C. J. Rodden, *op. cit.*, pp. 447-449.

[redacted]

density gradually diminished with time.

It was found that the use of nitric acid in conjunction with perchloric acid decreased the sensitivity of the method slightly, but, in the interests of safety, nitric acid is used routinely to oxidize any organic material that might be present. The *p*H of the final solution on which the optical density measurements are made is not critical in the strongly acidic region. The use of perchloric acid as an oxidant offers a very rapid method for determining chromium, but the results on control samples indicate that the precision is no better than 10% (relative error). A study of the mechanism of the oxidation of chromium to the hexavalent state may result in an improvement in precision.

Cadmium. In order to test the reproducibility of sampling of HRE test loop solutions, an "inert" ion, cadmium, was introduced into the solution and determined in the samples. For this determination the following procedure was investigated: Cadmium was extracted from uranyl solution with a dithizone—carbon tetrachloride solution, then stripped from the organic layer[27] with dilute acid and determined polarographically by the standard addition method.[28]

When the polarographic procedure was tested alone on synthetic samples both precision and accuracy were good. The results averaged 98.2% of the theoretical on samples containing 8 to 22 μg of cadmium per milliliter. For the extraction procedure, however, the accuracy was poor. While there was a close agreement within a given series of extractions, the recovery was generally in the vicinity of 50 to 60%. A study of the factors affecting recovery of cadmium in the dithizone procedure is planned but has not yet been undertaken.

Nickel. *Colorimetric Method.* Because of difficulties encountered in the determination of nickel colorimetrically by means of dimethylglyoxime in uranyl sulfate solutions, the applicability of this method in the HRE analytical work has been investigated. Much of the trouble has been found to center around the oxidation of nickel to the nickelic state. The *p*H control, range of concentration, wavelength selection, and choice of oxidant were studied.

According to Rodden[29] ammonium persulfate is the best oxidant for use in this determination from the standpoint of stable color formation. Since erratic results in routine determinations were often obtained with the ammonium persulfate used, bromine and potassium periodate were also tried. Bromine oxidation gave a color which was obviously very unstable and no attempt was made to obtain density readings. The periodate oxidation produced a color which faded rapidly with time. In spite of the difficulties encountered in the initial use of this oxidant, ammonium persulfate appears to be the most promising reagent.

The performance of different samples of ammonium persulfate was tested. The results indicated that certain lots of ammonium persulfate gave satisfactory results (complete oxidation of nickel) while others did not.

(27) *Ibid.*, p. 398.

(28) Kolthoff and Lingane, *op. cit.* p. 340.

(29) Rodden, *op. cit.*, pp. 433-435.

[redacted]

It was further found that samples of the unsatisfactory material, when dissolved in water, yielded solutions of low *p*H (approximately 1 or less), while the *p*H of solutions of satisfactory reagent was much higher (approximately 3). This correlation between the *p*H of a water solution of the reagent, as well as its ability to oxidize nickel completely, furnishes a rapid and convenient method of checking the reagent before use in the routine analytical laboratory.

The nickel dimethylglyoxime solution gives a maximum density reading between 500 and 550 mμ. In order to determine the best wavelength for the determination of nickel in the presence of uranium, the absorption measurements were made at 520, 540, and 560 mμ. The results indicate that 520 mμ is the optimum wavelength for the measurement, although Beer's law is obeyed in all cases and the interference of uranium is not serious at any wavelength in the region studied.

It was also necessary to determine the range of nickel concentration in which the determination could be carried out. It was found that when the nickel concentration exceeded 1.5 μg per milliliter of final solution, a precipitate of nickel dimethylglyoxime formed. In order to avoid the necessity of working with low optical density readings, a cell of longer light path was adopted. Finally, the quantity of ammonium hydroxide needed to make the solution slightly alkaline has been determined.

Further study is planned in order to determine the effect of chromium, iron, and manganese and of larger concentrations of uranium on the determination of nickel by this method. The preliminary extraction of nickel dimethylglyoxime with chloroform as an alternative procedure will also be tested.

Polarographic Method. The polarographic determination of nickel in uranyl solutions containing traces of iron and chromium has been studied in order to test the accuracy of the colorimetric method. The uranium and traces of iron and chromium were precipitated by the addition of pyridine, and the nickel pyridine complex was determined polarographically.[30] It was found necessary to resort to an overnight digestion period in order to ensure the complete precipitation of uranium. The addition of ammonium nitrate, followed by digestion of the solution for 30 min in a hot water bath, was not sufficient to accomplish this separation. The minimum time required for complete precipitation of uranium was not established, since overnight digestion was found to be convenient. A stock solution containing nickel, uranium, iron, and chromium in concentrations representative of HRE solutions was analyzed by this method.

The results of this investigation indicate that the polarographic method as described is satisfactory for the determination of nickel in HRE solutions. It is longer and more troublesome than the colorimetric method, however, and it has no advantage over the latter with regard to accuracy and precision. Its principal utility is as an independent method for checking the colorimetric method.

Iron. As a part of the HRE program of analysis of uranyl sulfate solutions

[30] Kolthoff and Lingane, *op. cit.*, p. 334.

[redacted]

for trace elements, an investigation was made of the available colorimetric methods for the determination of iron. The 1,10-phenanthroline and 2,2′-bipyridyl methods, both reported by Rodden,[31] were tested. The 2,2′-bipyridyl complex, absorbing at a higher wavelength than the 1,10-phenanthroline complex, was found to be the least sensitive of the two to variations in uranyl ion concentration. For this reason the 2,2′-bipyridyl method was adopted for routine application.

RECOVERY OF TRACE ELEMENTS IN EXTRACTION OF URANIUM FROM URANYL SOLUTIONS

F. E. Jenkins and O. Menis

In anticipation of the possible use of more highly concentrated uranyl solutions in connection with the HRE program, methods for the determination of metallic corrosion products in solutions with uranium concentration of the order of 400 mg/ml are being investigated.

In colorimetric determinations of trace elements (nickel, chromium, iron, manganese) in uranyl solution, a decrease occurs in the sensitivity with an increase in the concentration of uranium. This interference becomes quite marked with uranium concentrations of the order of 400 mg/ml. A method by which a major fraction of the uranium could be removed would help to eliminate this interference. Bartlett[32] has shown that the relative quantity of uranium sulfate extracted by tributyl phosphate in the presence of large concentrations of foreign ions is high. He has also shown that the distribution coefficients for iron, copper, nickel, and chromium in tributyl phosphate is extremely small. It remained to be determined whether, in the presence of large concentrations of uranium, the distribution coefficients for trace elements remain negligible. Experiments were undertaken to determine the recovery of trace amounts of iron, chromium, and nickel in the aqueous phase after extraction of uranyl sulfate and uranyl fluoride solutions by tributyl phosphate.

The procedure followed was, in general, that of Bartlett.[32] The extraction was made on the uranyl sulfate solution after the addition of an aqueous nitrate salt solution. In the case of the uranyl fluoride solution the uranium was in one case extracted directly from an aqueous nitrate solution, and in the other converted to the perchlorate and then extracted from a perchloric acid—perchlorate salt solution. After extraction, the uranyl salts were stripped from the tributyl phosphate back into the aqueous phase by extraction with a sodium sulfate solution. Uranium was then determined colorimetrically in both aqueous solutions (initial and final) by the thiocyanate method.[17]

The relative amounts (percent) extracted, or the distribution constants for concentrations in the range of 17 to 50 mg of uranium per milliliter of the aqueous phase, were calculated. These values were considerably smaller than those obtained by Bartlett for a lower range of uranium concentration (0.04 to 0.2 mg per milliliter of aqueous phase).

(31) Rodden, *op. cit.*, p. 422.

(32) T. W. Bartlett, *Some Factors Influencing the Use of Tributyl Phosphate for the Extraction of Uranium in Analyses*, Carbide and Carbon K-25 Area, report K-706 (Feb. 27, 1951).

[redacted]

TABLE 9.8

Extraction Made on UO_2SO_4 Solution Containing Traces of Nickel, Chromium, and Iron with Tributyl Phosphate (75%) in Benzene

SALT PRESENT*	URANIUM (mg)	PHASE VOLUME (ml)		DISTRIBUTION OF U, (mg)		K, CONC. U (Org) / CONC. U (Aq)
		ORGANIC	AQUEOUS	ORGANIC	AQUEOUS	
NH_4NO_3	435	15	25	283	133	3.5
	1245	15	25	620	694	1.5
$Al(NO_3)_3$	435	15	25	296	118	4.2
	1245	15	25	590	683	1.4

*10% salt solution in aqueous phase.

Bartlett's distribution constant values were of the order of 100 to 1000, while those found in the present investigation for uranyl sulfate, fluoride, and perchlorate solutions were of the order of 3, 38, and 18, respectively. The fact that these values were so low when compared with those of Bartlett was probably due to the saturation of the tributyl phosphate phase as a consequence of the high uranium concentration.

The recoveries of microgram quantities of iron and nickel in the aqueous phase were, within the limits of analytical accuracy, quantitative. Chromium, however, was in most cases not recovered quantitatively either from the original aqueous phase or the stripped organic phase, chiefly because of analytical difficulties. Some typical data are presented in Tables 9.8 and 9.9.

These preliminary results indicate that a tributyl phosphate extraction of the major portion of the uranium may facilitate the determination of trace elements. The study will be continued, with greater volumes of tributyl phosphate being employed, in order to establish the conditions for which the maximum extraction of uranium occurs under equilibrium conditions. The percent recovery of trace elements in concentrations of 2 to 20 μg per milliliter of original uranyl solution will also be determined.

ANALYTICAL PROBLEMS IN THE PRECIPITATION OF ZIRCONIUM AS ZIRCONYL PHTHALATE

W. K. Miller and N. D. Baxter

In previous progress reports[33,34] details have been given of the development of an ultraviolet absorption method for the determination

(33) W. K. Miller and S. A. McKinnon, "Determination of Phthalate in Recycle Liquors," ORNL-1088, *op. cit.*, p. 102.

(34) W. K. Miller, "Determination of Ammonium Phthalate in Recycle Liquor," *Analytical Chemistry Division Quarterly Progress Report for Period Ending January 10, 1951*, ORNL-955 p. 98 (Mar. 28, 1951).

[redacted]

TABLE 9.9

Recovery of Nickel Following Extraction of $UO_2(ClO_4)_2$ with Tributyl Phosphate

SALTING AGENT*	URANIUM (mg)	NICKEL (μg)	PHASE VOLUME (ml)		NICKEL (μg)		RECOVERY (%)	
			ORGANIC	AQUEOUS	ORGANIC	AQUEOUS	IN AQUEOUS PHASE	TOTAL
$NaClO_4$	1950	100	50	25	0.0	95.0	95.0	95.0
$NaClO_4$	1950	100	50	25	0.0	90.0	90.0	90.0
$NaClO_4$ + $HClO_4$**	1950	100	50	25	0.0	90.0	90.0	90.0
$NaClO_4$ + $HClO_4$**	1950	100	50	25	0.0	97.0	97.0	97.0

*30% salt solution in aqueous phase.

**1.2 *N* with respect to $HClO_4$.

of the phthalate ion in recycle liquors from the zirconium refining process. A comparison has been made of the results of phthalate determinations by this method and by the lead acetate method.[35] In the evaluation of the results it was pointed out that a likely error in the absorption method could be introduced by side reactions between phthalic anhydride and ammonia in the preparation of standard solutions of phthalate by dissolving the anhydride in aqueous ammonia. Since the ammonium phthalate solutions used in the zirconium refining process are prepared in this manner, the standard solutions for the ultraviolet method were prepared by the same procedure. The formation of phthalimide, or, more probably, ammonium phthalamidate, would give rise to either a positive or negative error, depending on the relative absorptions of the phthalate ion and of the side reaction product. During the past quarter considerable effort has been expended in the investigation of phthalamidate or phthalimide formation and its effect on the zirconium refining process and on the determination of phthalate in recycle liquor.

Evidence of Amide or Imide Formation. Because the carbon and zirconium content indicated that the precipitate was zirconyl phthalate, the possibility of amide formation was not seriously considered until it was discovered that the absorption spectra of phthalic anhydride and potassium biphthalate do not agree when each is dissolved in aqueous ammonia. This evidence was tested

(35) L. G. Overholser and W. R. Grimes, *Chemical Determination of Phthalate Ion*, ORNL Y-12 Area, report Y-602 (April 17, 1950).

[redacted]

further by dissolving the two solids in (*a*) 1:5 aqueous ammonia and (*b*) sodium hydroxide, and measuring the respective absorptions of several dilutions of the resulting solutions under both acidic and basic conditions at chosen wavelengths. The results are shown in Table 9.10.

Agreement of the extinction coefficients of the two compounds when dissolved in sodium hydroxide in contrast to the disagreement when dissolved in ammonium hydroxide indicates that a reaction other than the formation of ammonium phthalate had taken place between phthalic anhydride and ammonia, since the spectrophotometric measurements in either solution would be expected to represent the absorption of the phthalate ion if salt formation were the only reaction. The agreement between the absorption of the samples when dissolved in sodium hydroxide rules out the possibility that the observed facts are explained by the presence of an impurity in the phthalic anhydride.

Identification of the Product of the Reaction Between Phthalic Anhydride and Ammonia. It was at first believed that the principal product of the reaction between phthalic anhydride and aqueous ammonia is ammonium phthalate and that the amide or imide forms only as a side reaction product. It was planned to separate the compounds and to determine the type and quantity of side reaction product by precipitating phthalate with an excess of either lead acetate or zirconyl chloride and measuring the ultraviolet absorption spectrum of the filtrate. A difference between the wavelengths of the absorption bands of the filtrate and those of the phthalate solution before precipitation would indicate that the phthalate had been removed by precipitation and that the side reaction product remained in the filtrate. Lead acetate was found to be impractical as a precipitating agent for this study, since the reagent exhibits a strong absorption band in the wavelength region of interest. Although there was no similar interference in the case of zirconyl chloride, no shift of the absorption peak was observed for the filtrate from the precipitation of the solution by this reagent. No apparent separation of phthalate and the suspected phthalamidate was effected.

Since no specific precipitants for phthalate or phthalamidate were known other than those which had been tried, the problem of identifying the proposed side reaction product was approached by synthesizing phthalimide and studying the absorption properties of this compound and its half-hydrolyzed derivative, phthalamidic acid. Phthalimide was prepared by heating phthalic anhydride and aqueous ammonia to 300°C.[36] The melting point and nitrogen content of the synthetic product indicated that the compound was pure. Phthalimide exhibited a strong absorption band with a maximum at 299 mμ, a wavelength at which the solution of phthalic anhydride in ammonia did not absorb. It was thus shown that the latter solution did not contain an appreciable quantity of phthalimide.

The hydrolysis of phthalimide on standing in the presence of 25% aqueous sodium hydroxide in the cold

(36) H. Gilman and A. H. Blatt, *Organic Syntheses*, collected volume I, p. 457, Wiley, New York, 1941.

TABLE 9.10

Extinction Coefficients of Phthalic Anhydride and Potassium Biphthalate at Two Chosen Wavelengths

PHTHALIC ANHYDRIDE					POTASSIUM BIPHTHALATE				
CONCENTRATION (10^{-3} *M*)	276 mμ*		271 mμ**		CONCENTRATION (10^{-3} *M*)	276 mμ*		271 mμ**	
	DENSITY	EXTINCTION (10^3)	DENSITY	EXTINCTION (10^3)		DENSITY	EXTINCTION (10^3)	DENSITY	EXTINCTION (10^3)
Samples Dissolved in Ammonium Hydroxide									
1.082	1.300	1.20	0.920	0.850	0.979	1.300	1.33	0.765	0.781
0.541	0.640	1.18	0.462	0.854	0.490	0.640	1.31	0.385	0.786
0.271	0.320	1.18	0.240	0.886	0.245	0.320	1.31	0.194	0.792
0.108	0.127	1.18	0.095	0.880	0.098	0.127	1.30	0.077	0.786
0.054	0.063	1.18	0.046	0.852	0.049	0.065	1.33	0.039	0.796
Avg.		1.18		0.864			1.32		0.788
Samples Dissolved in Sodium Hydroxide									
1.081	1.400	1.30	0.820	0.759	1.028	1.340	1.30	0.780	0.759
0.540	0.700	1.30	0.412	0.763	0.514	0.670	1.30	0.395	0.768
0.270	0.350	1.30	0.205	0.759	0.257	0.340	1.32	0.195	0.758
0.108	0.140	1.30	0.080	0.740	0.103	0.135	1.31	0.080	0.778
0.054	0.069	1.28	0.039	0.740	0.051	0.068	1.32	0.037	0.725
Avg.		1.30		0.754			1.31		0.757

*Final dilution was made distinctly acid before the measurement at 276 mμ.

**Final dilution was made distinctly basic before the measurement at 271 mμ.

for 1 to 2 hr, followed by acidification, is reported to give the half-hydrolyzed derivative, phthalamidic acid.[37] A solution was prepared by this procedure, and its spectrum was measured in the ultraviolet region. The absorption of the solution was quite similar to that of phthalic anhydride in aqueous ammonia, but, since it was still believed at that time that the chief product of the reaction between phthalic anhydride and ammonia was ammonium phthalate, it was assumed that the hydrolysis had gone to completion and that the phthalate ion had been formed.

A survey of the literature on the subjects of phthalamidic acid and phthalamidates revealed that very little work has been done on the compounds, probably because phthalimide, which, in general, undergoes the same reactions, is more readily prepared in a pure state. However, several general methods for the preparation of phthalamidic acid were found, and the compound was prepared by two of these methods.[38,39] The white solid which was obtained melted sharply at 149°C, resolidified at 165°C, and finally remelted as phthalimide at 231°C. This is the exact behavior reported for phthalamidic acid. A nitrogen analysis confirmed the purity of the compound. The absorption spectrum of this material in solution was found to be identical with that of the solution prepared by dissolving phthalic anhydride in ammonium hydroxide. This suggests that the reaction of phthalic anhydride with ammonia probably results in an almost quantitative yield of ammonium phthalamidate, rather than only a small amount, as a side reaction product. Evaporation, under reduced pressure, of a solution prepared in exactly the same manner as the feed solutions of the zirconium refining process produced a salt which, when acidified, yielded an acid which proved to be phthalamidic acid as evidenced by its melting point and a nitrogen determination. Thus it was shown that zirconium is being precipitated in the refining process by a solution of ammonium phthalamidate rather than one of ammonium phthalate.

Identification of the Zirconyl Precipitation Product. The presence of an amide group in the precipitant suggested that perhaps the precipitate from the refining process is not zirconyl phthalate but a nitrogen-bearing compound. The formation of a nitrogeneous compound which contains the ratio of carbon to zirconium known to be present did not appear likely, but precipitations were made in an effort to prepare, if possible, a zirconium salt containing the amido group. The precipitations were carried out at a *p*H of 2, with digestion for 2 hr on a hot plate before filtering. After being thoroughly washed with aqueous HCl (*p*H 2), the precipitates were dried at 110°C and submitted for nitrogen determinations. Only traces of the element were found. In no case was the nitrogen content high enough to suggest that the element was combined in the zirconyl precipitate.

The absence of a significant amount of nitrogen in the precipitate verified the deduction of the original investigators of the process that the

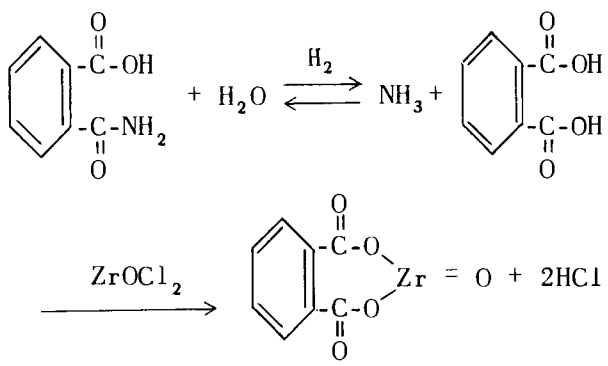
(37) L. F. Fieser and M. Fieser, *Organic Chemistry*, p. 671, Heath, Boston, 1944.

(38) E. Chapman and H. Stephen, "The Preparation of Phthalamic Acids and Their Conversion Into Anthranilic Acid," *J. Chem. Soc.* 127, 1791 (1925).

(39) *Beilsteins Handbuch der organischen Chemie*, Band IX, p. 809, Julius Springer, Berlin, 1926.

[redacted]

precipitate is zirconyl phthalate. Since the feed solution has been shown to consist almost exclusively of ammonium phthalamidate, it must be concluded that the amide is hydrolyzing in the precipitation process. This is not surprising in view of the conditions under which the precipitation is made. A hot acid solution is conducive to hydrolysis of amides. Hydrolysis is probably caused to go to virtual completion, according to the following mechanism:



The precipitation of the hydrolysis product would tend to speed hydrolysis and cause the reaction to go to completion.

Early tests indicated that the precipitation of zirconyl phthalate is completed almost immediately at the boiling temperature, but continues for at least several hours in the cold. This phenomenon was demonstrated by precipitating ammonium phthalamidate with zirconyl chloride at *p*H 2 at the two temperatures and centrifuging the products. The centrifugate of the hot precipitation remained clear, but that of the cold precipitation became cloudy after each centrifugation, possibly because hydrolysis, and consequently precipitation, is a slow process at room temperature.

Study of the Optimum *p*H of Precipitation. Zirconyl phthalate precipitation tests have shown that (1) if the *p*H of precipitation is too strongly acid, the precipitate does not form, and (2) if the *p*H is not sufficiently acid, hydrous zirconium oxide precipitates in preference to zirconyl phthalate. For this reason tests were made to determine the optimum *p*H of precipitation.

By adding an excess of zirconyl chloride to the ammonium phthalamidate under ideal precipitating conditions, filtering the precipitate, and determining phthalate spectrophotometrically on the filtrate, the completeness of precipitation can be tested. Although in the refining process an excess of phthalamidate is added to zirconyl chloride, an excess of zirconyl ion was used for these tests since phthalate is more readily determined in the filtrate than is zirconium. A number of tests were made by adding the zirconyl chloride solution to strongly acidified solutions of ammonium phthalamidate, and slowly adding ammonium hydroxide to the hot solutions until the desired *p*H was reached. It was noted that precipitation began at about *p*H 0.5. Precipitations were made under identical conditions at *p*H's varying from 1 to 7, and optical density measurements were made on the filtrates at 276 mμ. In two series of such determinations, it was found that the optimum *p*H of precipitation (minimum quantity of phthalate in filtrate) was between 2 and 3. The lower limit is recommended because at *p*H 3 there is the danger of precipitation of iron. The results of one of the above series of tests is shown in Table 9.11.

[redacted]

TABLE 9.11

Optical Densities at 276 mμ of the Filtrates* from Zirconyl Phthalate Precipitations at Various *p*H Values

*p*H	OPTICAL DENSITY
0.9	0.415
1.8	0.184
3.3	0.162
4.5	0.248
5.1	0.357
6.3	1.48

*The filtrate was diluted to 250 ml and acidified before the optical density was measured.

Conclusions. On the basis of the experimental evidence obtained during the course of this study, it is recommended that the zirconium precipitation be carried out at approximately *p*H 2 in hot solution in order to obtain maximum zirconium recovery. The present operating temperature of about 85°C with a half-hour digestion of the precipitate is sufficient, but the *p*H of precipitation has previously been more acid than *p*H 2.

IDENTIFICATION OF WHITE SOLID RESIDUE FROM CHLORINATION OF ZIRCONIUM

W. K. Miller

Zirconium tetrachloride is produced at the Y-12 plant by chlorination of the oxide with carbon tetrachloride at approximately 600°C:

$$ZrO_2 + 2CCl_4 \xrightarrow{600°C} ZrCl_4 + 2COCl_2$$

The by-product gases, which consist largely of phosgene, but contain appreciable quantities of carbon monoxide, chlorine, carbon dioxide, and probably a few other gases, are led from the zirconium tetrachloride condensers through scrubber lines into absorbing media. When the units were disassembled a white coating was found to have been formed in the scrubber lines. A sample of the white solid was submitted to this laboratory for identification.

The sample as received appeared moist and had an odor of phosgene. A colorless liquid, boiling at 65 to 75°C and having an odor of carbon tetrachloride, was obtained as a distillate by heating the moist solid in a distilling flask. A dry product with a characteristic organic odor remained as the residue. This dry residue, obtained by heating the sample at 110°C, was used for subsequent tests.

Solubility tests, sublimation and melting point determinations, and a qualitative analysis for elements were made in the preliminary study. Quantitative analyses included determinations of (1) carbon and (2) loss of weight on heating. The results of these tests are given in Table 9.12.

The criterion for solubility was the complete dissolution of an approximately 0.1-g portion of the solid in 5 ml of solvent. A sealed capillary was used in the melting point determination in order to prevent sublimation. The sample was fused with metallic sodium to convert the elements to the ionic state for the qualitative analysis. The melt was dissolved in water and the solution was filtered. A charred residue indicated that the solid was of an organic nature. Tests were

[redacted]

TABLE 9.12

Results of Identification Test on Residue from Zirconium Chlorination

Solubility tests	
In water	Insoluble
In 5% sodium hydroxide	Insoluble
In 5% hydrochloric acid	Insoluble
In concentrated sulfuric acid	Insoluble
In ether	Soluble
Physical constants	
Sublimation point (°C)	185
Melting point (°C)	184 - 187
Qualitative analysis	
Chlorine	Present
Sulfur	Absent
Nitrogen	Absent
Quantitative analysis	
Carbon (%)	10.3
Loss of weight on heating to approximately 300°C (%)	99.8

made for chlorine, sulfur, and nitrogen according to standard procedures.[40]

The insolubility of the solid in polar solvents, its charring on fusion with sodium, and the presence of chlorine indicated a nonpolar, organic chlorine compound, probably a chlorinated hydrocarbon. A study of the reactions of carbon tetrachloride revealed that when heated to high temperatures the compound decomposes, the principal product being hexachloroethane, a white solid, melting at 187°C and subliming at 185°C. The odor, melting point, and sublimation point of the unknown sample were found to be identical with those of a sample of Eastman Kodak Company hexachloroethane. A carbon determination and an X-ray-diffraction analysis, the latter being carried out by the Physics Section of the Stable Isotopes Division, confirmed the identity of the white solid as hexachloroethane.

[40] R. L. Shriner and R. C. Fuson, *Systematic Identification of Organic Compounds*, Wiley, New York, 1940.

DETERMINATION OF ALUMINUM IN ZIRCONIUM

W. K. Miller and N. D. Baxter

In accordance with an agreement reached at the Washington conference on zirconium, March 22, 1951, a sample of zirconium hydride, ZH-6, submitted by E. B. Read, MIT Metallurgical Laboratory, coordinator of the program of cooperative analysis of zirconium, was analyzed chemically and spectrographically for aluminum. It was requested that each of the cooperating laboratories determine aluminum chemically by both the fluorometric method now in use at the New Brunswick laboratory[41] and the Bureau of Mines colorimetric method, the procedure for which was supplied by Mr. Read. However, because of time limitations and because Mr. Read had reported that MIT obtained unsatisfactory results by the colorimetric method, this laboratory attempted only the fluorometric method. A portion of the sample was ignited to the oxide at 800°C and the ignition product was submitted for spectrographic analysis.

The procedure reported by the New Brunswick laboratory[41] was followed

[41] A. R. Eberle, *Fluorimetric Determination of Aluminum in Zirconium Metal and Zirconium Oxide*, USAEC New Brunswick Laboratory, report NYO-2013 (Jan. 22, 1951).

[redacted]

in the chemical determination of aluminum. Briefly, the method consists of the following steps: solution of the sample; precipitation and filtration of the oxides; solution of the oxides and precipitation of zirconium as the salicylate; filtration of the salicylate; evaporation of the filtrate to dryness; ignition of the residue; carbonate fusion of the residue after ignition; solution of the fusion mixture and filtration of the insoluble carbonates; acidification of the filtrate and heating to expel carbon dioxide; addition of the reagent, pontochrome blue black R; adjustment to volume and measurement of fluorescence. Standard samples of aluminum-free zirconium oxide are carried through the same procedure with the addition of known amounts of aluminum before the oxide precipitation.

A preliminary study was made of the fluorescence of the aluminum complex by means of a Klett fluorometer in conjunction with a Rubicon galvanometer. A study of fluorescence vs. concentration of standard aluminum solutions indicated that a suitable working curve can be constructed for low concentrations of aluminum. The fluorescence diminishes if the concentration of aluminum is too high. In zirconium samples of aluminum concentration greater than 50 ppm, smaller aliquots must necessarily be taken for fluorescence measurements.

The procedure in this laboratory involved dissolution of 1-g portions of the hydride and 1.35-g portions of the standard, aluminum-free zirconium oxide. These solutions were diluted to 200 ml, and 50-ml aliquots were taken for the determinations. To the 50-ml aliquots of the standard sample, 0.000, 0.005, 0.010, 0.020, 0.030, and 0.050 mg of aluminum were added. From these samples a standard curve (Fig. 9.1) was prepared, and the aluminum content of sample ZH-6 was determined by reference to the curve. It will be noted on the figure that two points on the standard curve do not fall in line.

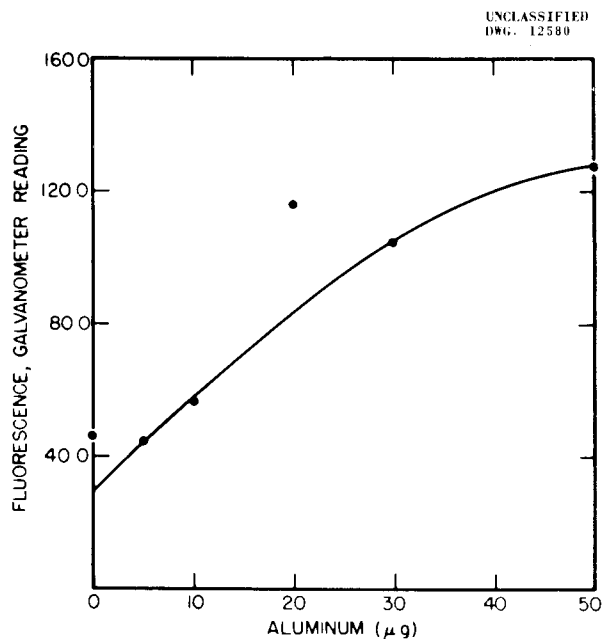


Fig. 9.1 - Standard Curve for Fluorimetric Determination of Aluminum

Triplicate determinations were made on the sample of zirconium hydride, but one of the results was obviously in error since the fluorescence was less than that of the standard sample which contained no aluminum.

Spectrographic determinations of aluminum were made on eight portions of the ignited oxide. Although six of the results are in agreement, the remaining two are unusually high.

[redacted]

The spectrographic laboratory reported that the ignited oxide appeared to be nonhomogeneous, both visually and spectrographically. The iron content was unusually high. Both spectrographic and chemical results are reported in Table 9.13.

TABLE 9.13

Determination of Aluminum in Zirconium

TEST	GALVANOMETER READING	ALUMINUM (ppm)
Chemical Analysis		
1	105	30
2	80	17
3	20	
Spectrographic Analysis		
1		20*
2		20*
3		20*
4		20*
5		20*
6		20*
7		135*
8		200*

*Spectrographic results are converted from oxide to metal.

The results in Table 9.13 are not encouraging. The lack of precision of the chemical method can probably be traced to one or more of the many steps of the procedure prior to formation of the fluorescent complex. Separation by precipitation of a major component away from microgram quantities of the desired constituent is never desirable, although the error involved in this step is minimized by the identical treatment given the standard. The numerous transfers involved in the procedure are likewise conducive to error. The effects of *p*H and other variables were not studied, but these may also contribute to the error. It is not contemplated at present that further study will be made of this method.

QUALITY CONTROL

R. L. McCutchen

During the quarter the quality control activities were considerably broadened, the total number of determinations on standard samples amounting to 1324, which is more than twice the number carried out in the preceding quarter. The distribution with respect to laboratory, type of material, component determined, and method of test, is given in Table 9.14.

Ionic Analysis Laboratory. A brief survey of the control results for this period,[42,43] indicates that:

1. The precision and accuracy of the test results for the fluorimetric determination of uranium have improved significantly.

2. The test results for the colorimetric determination of uranium by the *l*-ascorbic acid method are erratic and some remedial work will be necessary in order to correct this condition.

3. The vanadium control program, which was placed in operation

[42] C. D. Susano, R. Rowan, Jr., and R. L. McCutchen, *Statistical Quality Control Report, April 1951*, ORNL Y-12 Area, report Y-B31-258 (May 17, 1951).

[43] C. D. Susano, R. Rowan, Jr., and R. L. McCutchen, *Statistical Quality Control Report, May 1951*, ORNL Y-12 Area, report Y-B31-267 (June 25, 1951).

[redacted]

[redacted]

TABLE 9.14

Control Determinations Performed During the Quarter Ending June 22, 1951

LABORATORY	TYPE OF MATERIAL	CONSTITUENT DETERMINED	METHOD	NO. OF DETERMINATIONS	TOTAL
Ionic Analysis	Synthetic	Na	Flame photometer	18	
	Synthetic	CO_3	Gas evolution	1	
	Synthetic	V	Colorimetric	63	
	Synthetic	U	Fluorimetric	51	
	Synthetic	U	Colorimetric	31	
	Synthetic	U	Potentiometric	3	
	Marysvale ore	U	Fluorimetric	6	
	Carnotite leach	U	Fluorimetric	22	
	Carnotite ore	U	Fluorimetric	28	
	Carnotite ore	V	Colorimetric	28	
					251
Spectrographic	Synthetic	Fe	Spectrographic	24	
	Synthetic	Ni	Spectrographic	24	
	Synthetic	Cr	Spectrographic	24	
	Synthetic	Mn	Spectrographic	24	
					96
HRE	Synthetic	U	Potentiometric	56	
	Synthetic	U	Volumetric	8	
	Synthetic	Fe	Colorimetric	31	
	Synthetic	Ni	Colorimetric	44	
	Synthetic	Cr	Colorimetric	4	
					143
X-10	Synthetic	U	Fluorimetric	440	
	Synthetic	U	Colorimetric	394	
					834
					1324

during the quarter, reveals that the precision of this determination in the range 0.3 to 4.0 mg/ml is ±10% (99.5% confidence level for the average of duplicate determinations).

4. The sodium, carbonate, and potentiometric uranium programs have been temporarily suspended since these determinations are not being required in any quantity at present.

Spectrographic Laboratory. A comparison of vanadium and platinum as internal standards in the porous cup method for the spectrographic determination of certain trace elements has been completed.[42] The substitution of vanadium for platinum as the internal standard improved the test results for iron, nickel, and chromium significantly, but there was no improvement in the case of manganese.

HRE Laboratory. During the early part of May the facilities for the HRE Control Laboratory were completed and the laboratory was put into full-scale operation. The

[redacted]

[redacted]

work up to the present time has consisted of the determination of total uranium and the corrosion products iron, nickel, and chromium in uranyl sulfate solutions. A control program covering the determination of these elements was initiated for this laboratory on the first of May; the principal conclusions derived from this program are summarized in the following paragraphs.[43]

The uranium test results have been erratic with greater variation than is to be expected for the potentiometric method, except during the latter part of May (22 - 31), during which period the precision and accuracy of the results by the ordinary manual procedure were very good. The introduction of a Precision-Dow automatic titrator on May 15 resulted in an overall reduction in the precision of the test results. There is reason to believe, however, that the automatic titrator is capable of producing results which are fully comparable to those of the manual procedure at its best. The poor accuracy and precision observed may be caused either by faulty functioning of the instrument or by the fact that proper operating conditions have not yet been established.

About the middle of June it was decided to abandon the potentiometric method for uranium(VI) determination in favor of a direct titration with a color indicator, since it was indicated that this change can be made with considerable gain in output without loss of accuracy. It is too early to draw any conclusions as to the precision and accuracy of the test results by this new procedure.

On May 15 the method for the determination of nickel in HRE solutions was modified to eliminate an extraction step. This change in procedure resulted in improvement of both the accuracy and precision of the test results.

The method being used for the determination of iron in HRE solutions appears to be satisfactory, although a 5% positive bias is observed. The precision of the iron test results expressed as the limit of error of one determination (99.5% confidence level) was found to be ±16%. A limit of error of this magnitude is satisfactory, considering the low concentrations of iron present in the samples being analyzed.

Shortly after the quality control program was initiated, it became evident that the test results for chromium were 60 to 80% low. Consequently, a modified method has recently been placed in use. To date, insufficient control data have been accumulated to indicate the accuracy and precision attained with the modified method.

X-10 Laboratories. Although small biases have appeared from time to time in the colorimetric and fluorimetric test results from both X-10 laboratories, the results have, in general, been good.[43] The values given in Table 9.15 for the standard error of the average of duplicate determinations is indicative of the precision of the test results. Since the bias values (relative) for the determinations were almost invariably less than 2%, the standard error values of Table 9.15 also furnish a fairly precise measure of the accuracy of the results from these laboratories during the period.

[redacted]

[redacted]

TABLE 9.15

Statistical Values Based on Test Results for the Determination of Uranium in the X-10 Laboratories During April, May, and June, 1951

LABORATORY	METHOD	URANIUM CONCENTRATION (μg/ml)	STANDARD DEVIATION, S (μg/ml)	STANDARD ERROR OF DUPLICATE DETERMINATIONS (%)	
				99.5% CONFIDENCE LIMIT *	95% CONFIDENCE LIMIT **
3550	Fluorimetric	1.7	0.15	25	17
3019	Fluorimetric	1.7	0.18	30	20
3550	Fluorimetric	4.3	0.24	16	11
3019	Fluorimetric	4.3	0.35	24	16
3550	Fluorimetric	6.8	0.26	11	7
3019	Fluorimetric	6.8	0.41	18	12
3550	Colorimetric	341	4.5	4.0	2.6
3019	(ammonium thiocyanate)	341	6.8	6.0	3.9
3550	Colorimetric	511	5.3	3.1	2.1
3019	(ammonium thiocyanate)	511	9.1	5.1	3.5
3550	Colorimetric	682	6.9	3.0	2.0
3019	(ammonium thiocyanate)	682	10.9	4.7	3.2

* Standard error of duplicate determinations, %, at 99.5% confidence limit = $3S \times 100/\text{avg}$.

** Standard error of duplicate determinations, %, at 95% confidence limit = $2S \times 100/\text{avg}$.

The ratios of the standard deviation values for the results from the two laboratories indicate that the precision of results from Laboratory 3550 is superior by a factor of 1.4 in the case of the fluorimetric method and 1.5 in the case of the colorimetric method.

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10. CHEMICAL ANALYSIS

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

ANALYTICAL SERVICES FOR THE ANP PROJECT

L. J. Brady J. M. Peele
J. A. Norris*

Experimental Engineering. Samples of sodium metal derived from corrosion test experiments comprised a sizable portion of the work for the Experimental Engineering Group during this quarter. Minor metallic impurities in relatively pure sodium were determined spectrographically; the oxygen content was determined by chemical methods.

Recently, larger samples (5 to 10 g) of sodium have been used for trace-metal analysis. Although more time is required and greater care must be exercised in dissolving the larger samples, it will now be possible to report lower minimum values for the concentration of trace elements.

The method developed by White and Rowan[1] is being employed to analyze sodium metal samples for sodium monoxide. The thin-walled glass bulbs used by the Experimental Engineering Group for sampling sodium are well adapted to testing by this method. The glass can be crushed easily, thus exposing a large surface of sodium to the organic halide. The results given in Table 10.1, which were taken at random from the samples reported since the White method has been placed in regular use, give some indication of the precision attained.

TABLE 10.1

Oxygen Content of Sodium Samples

LABORATORY NO.	OXYGEN (%) UPPER BULB, *A*	OXYGEN (%) LOWER BULB, *B*	DIFFERENCE, *A* - *B*
53762	0.039	0.038	0.001
53470	0.032	0.028	0.004
53975	0.045	0.041	0.004
54098	0.030	0.031	-0.001
54261	0.044	0.036	0.008
54267	0.031	0.032	-0.001
54354	0.039	0.031	0.008
54484	0.016	0.016	0.000
			0.003 (avg.)

Samples of sodium metal which were exposed to beryllium oxide for varying periods of time have been tested to determine the concentration of beryllium. The sample is dissolved in ethanol and converted to the chloride by the addition of hydrochloric acid. The solution is then evaporated to dryness and the residue is ground and dried. The beryllium content is determined spectrographically. To date, the beryllium content of all the samples tested has been found to be below the limit of detection (<8 ppm, based on the weight of sodium metal).

In addition to the regular sodium samples, this laboratory has analyzed

*Isotope Analysis Methods Laboratory.

(1) J. C. White and R. Rowan, Jr., *The n-Butyl Bromide Method for the Determination of Sodium Monoxide in Sodium*, ORNL Y-12 Area, report Y-B31-251 (April 24, 1951).

[redacted]

samples of metal residues which were taken from various parts of the corrosion test loops. Both spectrographic and chemical methods were applied in determining the composition. Some of these samples were found to be metal alloys rich in cobalt, chromium, and nickel; others were found to contain large concentrations of lithium nitride.

Preparations are underway to increase the number of corrosion test loops. This will undoubtedly result in an increase in the number of samples to be analyzed during the next quarter.

Reactor Chemistry. A total of 64 samples of reactor fuels was submitted recently for the determination of metallic corrosion products. Of these samples, 43 are portions of a eutectic of BeF_2-NaF-UF_4, and 21 are samples of a KF-NaF-UF_4 eutectic. These materials were allowed to remain in contact with the walls of metal capsules for a number of hours at temperatures well above the melting point of the eutectic. The samples were then cooled, and the capsules were cut into sections approximately 1 in. long and submitted for analysis.

Before the reactor fuels could be analyzed it was necessary to remove the melt from the metal capsules. To accomplish this, the procedure described on p. 69 of this report was used. The eutectic containing BeF_2 was found to be more difficult to melt and did not flow from the metal capsule as readily as did the other mixture. However, this technique has been applied successfully in the preparation of all samples received to date. The graphite used to make the mold is of high purity, so that no appreciable contamination is introduced into the sample during contact with the mold.

The analysis of these samples for chromium, iron, nickel, and molybdenum by colorimetric methods adapted to this use by the Research and Development Group is just getting underway. These methods are discussed in the section of this report entitled "Metallic Corrosion Products in Reactor Fuels, Development of Colorimetric Methods," p. 70.

It is anticipated that samples of this type will be analyzed at the rate of approximately 12 per week during the coming month.

ANALYTICAL SERVICES FOR NEPA

L. J. Brady and J. A. Norris*

All the analytical work for NEPA was completed during this quarter. No samples were submitted after April 23, and the final samples were reported on May 22. On the first of March, 79 samples were on the NEPA backlog, and 67 additional samples were received before the end of April. All these samples were reported by May 23, making a total of 993 samples analyzed for NEPA during the period from March 1, 1950 to May 23, 1951.

Samples analyzed during this quarter consisted of the following types: sodium (86), silicon carbide (22), ferrous and nonferrous metals (19), sodium hydroxide (5), and miscellaneous samples (14). The methods of analysis used were, with a few minor changes, those outlined in previous quarterly progress reports.

*Isotope Analysis Methods Laboratory.

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Significant changes in the procedure for the spectrographic determination of trace metal impurities in sodium by the porous cup technique consist in (1) the use of mercuric ion as a carrier in the separation of the impurities from sodium by precipitation methods and (2) the substitution of vanadium for platinum as an internal standard in solutions to be tested spectrographically. A solution containing approximately 2 mg of mercuric ion is added to each sample and this metal is subsequently precipitated along with the trace metals contained in the sodium. The mercury serves as a carrier and facilitates quantitative separation of the trace metals from the solution containing the sodium.

Since the results of comparative tests with platinum and vanadium as internal spectrographic standards indicate that greater precision is obtained when vanadium is employed,[2] a solution of this metal is now being added to the samples and the use of platinum as a standard has been discontinued.

The method of White and Rowan[1] for determining sodium monoxide in sodium metal was employed for analyzing regular samples during the latter part of this period. The precision obtained by this method appears to be comparable to that claimed by the originator of the method.

Semimicro techniques recommended by White and Ross[3] were used in determining the silicon dioxide, free silicon, and carbon content of silicon carbide. The limitations imposed by the small amounts of samples which were available necessitated the use of such methods.

Ferrous and nonferrous alloys were analyzed by both chemical and spectrographic means. The majority of these tests were made in order to identify the metal or to determine whether the metal conformed to specification requirements with respect to chemical composition.

Miscellaneous samples analyzed during the period include: zirconium hydride, lithium hydride, barium hydride, calcium and sodium oxides, zirconium boride, a ceramic coating frit, uranium carbide, and irradiated phosphoric acid. In order to perform the required determinations on this group of samples, diverse methods, some of which gave rise to considerable development work, were employed.

ANALYSIS OF SAMPLES FOR GENERAL ELECTRIC COMPANY

L. J. Brady and J. M. Peele

During this quarter responsibility for operation of the S-50 installations was transferred from the Fairchild Engine and Airplane Corporation, NEPA Division, to the ANP Division of Air Gas Turbine Department, General Electric Company. Since the transfer a number of samples have been submitted to this laboratory for analysis.

A total of 23 samples was received during this period, 20 of which were sodium metal samples to be analyzed for oxygen. These sodium samples were taken from the sodium test

(2) R. L. McCutchen, "Spectrographic Analysis of Sodium Metal," *Analytical Chemistry—ANP Program Quarterly Progress Report*, ORNL Y-12 Area, report Y-B31-260, p. 19 (May 31, 1951).

(3) J. C. White and W. J. Ross, "Microanalysis of Silicon Carbide," *Analytical Chemistry Division (Y-12 Branch) - Quarterly Progress Report*, ORNL Y-12 Area, report Y-B31-218, p. 8 (Dec. 13, 1950).

[redacted]

loops located at Y-12 which are operated by General Electric Company. The nature of the operation of this equipment makes it necessary to sample the sodium in metal tubes. The sodium is circulated through the 0.25-in.-i.d. sample tubes at the temperature of the molten metal in the test loops for a sufficient time to permit equilibrium to be established between the sodium in the tube and that in the tank of the test equipment. The sample is then isolated from the system by valves and the sodium is allowed to solidify. These samples are next submerged in mineral oil and transferred to the laboratory for analysis. The metal sample tubes are 6 in. long and the walls are scored to a depth of 20 mils at intervals of 1 in.

Initially attempts were made to analyze these samples by an adaptation of the method of White and Rowan. The sample tubes were cut into 1-in. sections under mineral oil, and the sections were placed in *n*-butyl bromide. Hexane, which is mixed with the organic halide in the method outlined by White and Rowan, was eliminated here in order to accelerate the reaction of the sodium and *n*-butyl bromide. The attempts to react the sodium and thus remove it from the sampling tube did not meet with great success. Sodium bromide which was formed during the reaction packed in the ends of the tube and prevented further contact of the organic halide with the unreacted sodium metal. Boiling of the halide did not appreciably increase the rate of the reaction but resulted in partial decomposition of the butyl bromide, probably because of catalytic action of the metal sample tube.

A second attempt to analyze samples of this type was made by extruding the sodium from sections of the sample tube with a mechanical press, then collecting the extruded sample under mineral oil to prevent contact with air, and immediately transferring this material to the hexane—organic halide mixture. Two important objections have prevented further use of this technique: (1) it appears likely that segregation of the oxide in the sample tube may occur during the cooling process, and, since a layer of sodium remains on the walls of the tube after extrusion of the bulk of the sodium in the press, the extruded sodium will not be truly representative of the entire sample; and (2) some air is entrapped in the mineral oil during the manipulation required to extrude the sodium and this may contaminate the sample before it can be transferred to the tube in which it is to be reacted with butyl bromide.

The Research and Development Group is working to develop a method of removing the sodium by melting it under an inert organic solvent which can be made completely anhydrous and which can be employed as a diluent for the butyl bromide in the subsequent analysis. Further attempts to test the samples from the sodium test loops will be made when a suitable method for removing the sodium from the metal sample tubes has been developed.

In addition to the sodium samples submitted by the General Electric Company, one sample of plexiglas and two samples of metal alloy chips were received from the S-50 area. The results of the analysis of the latter three samples have been reported.

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ANALYTICAL SERVICES FOR THE HRE PROJECT

A. F. Roemer, Jr.

A separate laboratory for the analysis of samples from the HRE project was established by the Analytical Chemistry Division on March 1, 1951. To provide added working space, the analytical work was transferred from a restricted area within the corrosion laboratory in Building 9204-1 to a separate laboratory in this building which was rebuilt for this specific purpose. At present seven persons are engaged in this work; further expansion of personnel is planned.

The work consists principally in the analysis of uranyl sulfate solutions which simulate HRE fuel solutions, for total uranium, uranium(IV), nickel, iron, chromium, titanium, and, less commonly, for several other metallic elements. In addition, similar analyses are occasionally performed on 1% nitric acid wash solutions. A potentiometric method is used for the determination of total uranium; other determinations are made by colorimetric methods. Methods of analysis now in use are, for the most part, satisfactory. Difficulty has been encountered in the chromium determination, and work is being done to correct this trouble. This work is reviewed in Sec. 9 of this report.

Between March 1 and June 30, 2897 samples were received, 2217 of which have been reported, leaving a backlog on July 1 of 680 samples. During this period 10,099 determinations were made.

RAW MATERIALS

J. R. Lund S. R. Buxton
E. C. Lynn

Insoluble Residues. In general, samples of residues from leached ores are readily decomposed by the customary treatment with nitric-perchloric-hydrofluoric acids. It was noted, however, that some of the samples of carnotite, after going through such a routine decomposition process, still contained milligram quantities of material that proved to be insoluble in the 20% nitric acid which is normally used as solvent. The insoluble material was collected and portions were treated with H_2SO_4 and HF; a weight loss of approximately 98% of the residue indicated that the insoluble portion was essentially silicon dioxide. Later, spectrographic examination of similar portions confirmed this conclusion. In addition, the uranium content of these residues was found to be of the order of 0.1 to 0.2 ppm based on the original sample weight (0.5 g). Since the total uranium content of the samples was of the order of 100 to 300 ppm, it is obvious that the fraction of the total uranium left in the insoluble residue is insignificant.

Determination of Iron in Presence of Phosphoric Acid. Cupferron separations have been employed to remove the interfering phosphate ion prior to the colorimetric determinations of iron in samples containing up to 40% phosphoric acid.

Complete Analyses. Complete analyses were made on three Marysvale ores, three high-lime ores, and one phosphate rock during the quarter. In addition, complete analyses were

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made on one phosphate and one Marysvale leach solution. Complete metal analyses were made on 18 carnotite leach solutions.

Shaker for Solvent Extraction. A Fischer-Hahn shaker with a modified sample-bottle holder was found to serve quite satisfactorily as a means of agitating samples in applying the TBP-varsol-HNO_3 extraction process. This equipment has notably increased the efficiency of operations. Currently the sample holder accommodates 24 bottles of 25 ml capacity. It is planned, however, to increase the capacity to 48 bottles. Bottles are being designed to meet the requirements both for processing and for subsequently extracting the solutions that are commonly analyzed fluorimetrically.

Marysvale Ore. Difficulty continues to be encountered in obtaining agreement between fluorimetric and colorimetric results for the uranium content of Marysvale ore. Work is continuing on locating the source of this trouble and applying corrective measures.

DETERMINATION OF PHOSPHATE IN ORES

E. C. Lynn J. M. Rogers
S. R. Buxton J. H. Hackney

A treatment with nitric, perchloric, and hydrofluoric acids affords an expedient method for dissolution of phosphate, carnotite, and Marysvale ores. Since it was not known whether phosphate is lost in processing samples by such treatment, tests were conducted to establish the applicability of this method of dissolution to samples on which the phosphate concentration is to be determined. Bureau of Standards samples were employed for the tests.

Weighed samples were transferred to platinum dishes. Ten milliliters of 70% $HClO_4$, 5 ml of concentrated HNO_3, and 20 ml of 48% HF were added to each dish, and the contents were evaporated until light fumes of $HClO_4$ were observed. An additional 20 ml of HF was added, and the samples were again evaporated to fumes of $HClO_4$ and fumed for periods of 10, 20, and 30 min. (Fuming operations were conducted at approximately 280°C.) The samples were cooled and diluted to the proper volume with water, and the phosphate content was determined colorimetrically by the conventional phosphovanadomolybdate method that is generally used in this laboratory. A Beckman model B instrument was used to measure the optical densities of the solutions.

The results of these tests are shown in Table 10.2. Those for sample 120 reveal that phosphorus is not lost when samples of ore are digested with $HClO_4$-HNO_3-HF solutions. The results for the samples fumed for 10 min are somewhat lower than the certified value. However, the remaining results, i.e., for samples fumed 20 and 30 min, are slightly higher. The differences found in these determinations are within the limit of error for the method.

The results shown for sample 1-*a* are in excellent agreement as to precision, but there is a low bias with respect to accuracy. It is quite possible that the bias may be related to the fact that the calibration curve which was used was established by means of readings taken on a different portion of the

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TABLE 10.2

Effect of $HClO_4$-HF Digestion on Accuracy of Phosphate Determination

BUREAU OF STANDARDS NO.	TIME FUMED (min)	PHOSPHORUS PENTOXIDE (%)		DEVIATION FROM BUREAU OF STANDARDS (%)
		BUREAU OF STANDARDS VALUE	FOUND	
120	10	35.3	35.2	-0.3
			35.0	-1
			35.1 (avg.)	-0.5
120	20		35.4	+0.3
			35.3	0
			35.4 (avg.)	+0.3
120	30		35.9	+2
			35.4	+0.3
			35.7 (avg.)	+1
1-*a*	10	0.15	0.14	-7
			0.14	-7
			0.14 (avg.)	-7
1-*a*	20		0.14	-7
			0.14	-7
			0.14 (avg.)	-7
1-*a*	30		0.15	0
			0.14	-7
			0.14 (avg.)	-7

scale of the instrument. Even if it is assumed that the low results are attributable to loss of phosphorus, the loss is not significant at this concentration level.

EFFECT OF TEMPERATURE ON FLUORESCENCE

C. M. Boyd and J. R. Lund

Tests were made to determine what effect the cooling of flux disks containing uranium would have on the intensity of the fluorescence produced when the disks are irradiated with ultraviolet light. The fluorescence of several flux disks was determined after they had been cooled to room temperature and again after they had been cooled to -70°C. The first five samples (or flux disks) were prepared using pure solutions of uranyl nitrate as the source of uranium, while the

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TABLE 10.3

Effect of Temperature on Fluorescence of Flux Disks

SAMPLE	GALVANOMETER DEFLECTION (scale divisions)					INCREASE OF FLUORESCENCE (%)
	FLUX COOLED TO 25°C	FLUX COOLED TO -70°C				
		TEST 1	TEST 2	TEST 3	AVG.	
1	92	100	100	100	100	9
2	91	100	99	101	100	10
3	70	73	77	77	76	9
4	83	88	87	87	87	5
5	93	102	99	102	101	9
6	14	16	16	16	16	14
7	92	101	97	93	97	5
8	10	11	12	13	12	20

remaining three were prepared using purified solutions of the R_2O_3 group of carnotite ore. The quantity of uranium in the fluxes ranged from 1 to 5 μg.

The readings of the galvanometer deflections, which bear a direct relation to fluorescence intensity, are reported in Table 10.3. While the intensity of the fluorescence is increased by a small amount as a result of cooling the disks to -70°C, the increase is insufficient to offer much promise as a way of advancing the limits of detection to any significant extent.

MISCELLANEOUS COLORIMETRIC ANALYSES

S. R. Buxton and J. M. Rogers

Cadmium in Uranyl Sulfate Solutions. A colorimetric method for the determination of cadmium in uranyl solutions was tested.[4] In this method the cadmium is complexed with dithizone and subsequently extracted with chloroform. Erratic and low results were obtained in the first series of tests, but later results established that the method was wholly reliable. It was at first thought that the high sulfate concentration was responsible for incomplete extraction of cadmium. However, such an assumption proved to be false, and the discrepancies are now attributed to the improper techniques that were initially employed. It was found that the procedure given in the foregoing reference must be followed precisely. The analyses of uranyl sulfate solutions bearing 82 ppm of cadmium yielded test results which ranged from 82 to 86 ppm.

[4] C. J. Rodden, *Analytical Chemistry of the Manhattan Project*, p. 396, McGraw-Hill, New York, 1950.

Reactor Fuels. The mercury cathode cell was employed to make preliminary separations of micro quantities of chromium, nickel, iron, and molybdenum from macro quantities of uranium, alkali metals, and beryllium.[5] After the metals were deposited at the cathode, the mercury was removed by distillation, and chromium, iron, and nickel were determined in the residue by conventional colorimetric methods. No molybdenum was found in the residue. Tests made on the electrolyte confirmed that the metals iron, chromium, and nickel had been completely removed.

[5] C. E. Bricker, N. H. Furman, and B. McDuffie, *A Method for the Determination of Traces of Metals,* AECD-2600 (October, 1947; decl. May 25, 1949); AECD-2601 (October, 1947; decl. May 24, 1949).

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11. SUMMARY OF SERVICE ANALYSES

L. J. Brady J. W. Robinson
R. Rowan, Jr.

The service work done during the past quarter is summarized in Table 11.1. Table 11.2 gives information on the status of samples at the end of the quarter, and Table 11.3 gives the classification of determinations by components.

TABLE 11.1

Sample Types and Components Determined in Service Analyses

SAMPLE	NO. OF SAMPLES REPORTED	PRINCIPAL DETERMINATIONS
	RAW MATERIAL	
Leach solutions from:		
Carnotite ore	346	U, V, Fe, Al, PO_4, SO_4
Marysvale ore	159	U, Fe, Al, PO_4, SO_4, F
Phosphate rock	61	U, Fe, Al, PO_4, SO_4
Ores and leached residues from:		
Carnotite ore	103	U, V, Fe, Al, Ca, Mg, SO_4
Marysvale ore	104	U, Fe, Al, Ca, Mg, PO_4, SO_4, F
Phosphate ore	63	U, Fe, Al, Ca, Mg, PO_4, SO_4
Carbonate solutions and residues	206	U, Na, CO_3
Eluates	40	U, Fe, V, SO_4, PO_4
Controls	149	U, V, Na, CO_3
Miscellaneous	67	
	1298	
	HRE MATERIALS	
Uranyl sulfate	2262	U, NH_4, SO_4, NO_3, trace metals
Gas	28	H_2, CO_2, O_2, CO
Ferrous metals	22	C, Si, Fe, Ni, Cr, Mn, S, P
Uranyl fluoride	12	U, F
Iodide solutions	10	I
Uranium trioxide	5	U, UO_4, H_2O
Water	2	Mg
	2341	

[redacted]

TABLE 11.1 *(Continued)*

SAMPLE	NO. OF SAMPLES REPORTED	PRINCIPAL DETERMINATIONS
	ANP MATERIALS	
Gas	7	N, O_2
Corrosion products and residues	10	U, Fe, Cr, Ni, Mo
Lithium metal	10	Spectrographic
Sodium metal	66	O_2, spectrographic
Alkali-uranium solutions	60	U, Na, K, Li
Alcohol	15	H_2O
Beryllium compounds	7	Be, F, H_2O
Uranium fluoride	5	U, F
Alkali—uranium fluoride melts	3	U, Si, Na, Li, F, PO_4
Miscellaneous metal fluorides	3	Al, Pb
Ferrous metal	1	C, Mn, P, S, Si, Cu
	187	
	ISOTOPE SEPARATION	
Transformer	72	Dielectric strength, acidity, H_2O
	72	
	MATERIALS LABORATORY	
Steel	12	C, Mn, P, S, Si, Ni, Cr, Mo, Ti, Zr
	12	
	HEALTH PHYSICS	
Oil	3	Alpha count
Standard solutions	5	
	8	
	ZIRCONIUM PRODUCTION	
Zirconium metal and compounds	30	Zr, Cl, C, H, N
Steel	2	C, P, S, Mn, Si, Cr, Ni, Ma, Ti, Nb
Phthalic acid derivatives	10	C, H, N
	42	

[redacted]

TABLE 11.1 *(Continued)*

SAMPLE	NO. OF SAMPLES REPORTED	PRINCIPAL DETERMINATIONS
	BIOLOGY	
Bone	17	Spectrographic
Water	3	*p*H, total solids, conductivity
Gas	1	O_2
	21	
	MISCELLANEOUS	
Various	46	
	46	
Grand total	4027	

TABLE 11.2

Sample Status of Service Analyses

Backlog as of March 26, 1951	437
Number of samples received, March 26, 1951 to June 22, 1951, inclusive	4943
Total	5380
Number of samples reported, March 26, 1951 to June 22, 1951, inclusive	4027
Backlog as of June 22, 1951	1353

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[redacted]

TABLE 11.3

Classification of Determinations by Components

DETERMINATION	NO. OF DETERMINATIONS
U	8986
Si	146
Fe	2260
Al	218
Ca	80
Mg	62
V	1063
Cr	1252
Ni	2514
Ti	30
Mn	41
Na	201
K	80
SO_4	185
PO_4	256
CO_3	45
F	69
I	40
N, NO_3, NH_4	228
C	123
CO_2	100
O_2	40
H_2	60
H_2O	115
Spectrographic	530
*p*H	680
Miscellaneous	430
Total	19,834

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