267
9-12-66

MASTER

ANNUAL REPORT OF DIVISION ANALYTICAL BRANCH FOR 1965

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

Ralph C. Shank & Staff

**PHILLIPS
PETROLEUM
COMPANY**

ATOMIC ENERGY DIVISION

**NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PRINTED IN USA. PRICE \$6.00. AVAILABLE FROM THE CLEARINGHOUSE FOR FEDERAL
SCIENTIFIC AND TECHNICAL INFORMATION, NATIONAL BUREAU OF STANDARDS,
U. S. DEPARTMENT OF COMMERCE, SPRINGFIELD, VIRGINIA 22151

LEGAL NOTICE

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

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

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

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

IDO-14679
AEC Research & Development Report
Chemistry
TID-4500
Issued: June 1966

ANNUAL REPORT OF DIVISION ANALYTICAL BRANCH FOR 1965

R. C. Shank, Manager

Analytical Development Section

J. E. Rein, Section Chief
G. L. Booman, Assistant

Spectroscopy Section

G. V. Wheeler, Section Chief
R. M. Abernathey - Group Leaders
W. A. Ryder

Chemical Analysis Section

G. A. Huff, Section Chief
M. A. Wade - Group Leaders
J. G. Scott

PHILLIPS
PETROLEUM
COMPANY

Atomic Energy Division
Contract AT(10-1)-205
Idaho Operations Office
U. S. ATOMIC ENERGY COMMISSION

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ANNUAL REPORT OF DIVISION ANALYTICAL BRANCH FOR 1965

SUMMARY - J. M. Crawford

This report presents a general survey of the significant work performed by the Analytical Branch during 1965. Research concerning the development and improvement of the methods and equipment used in various fields of analytical chemistry are described and all new and revised methods that have been established for regular use during the year are reported in detail in appropriate appendixes. Special analytical work in support of specific AEC-sponsored projects is reported, as well as continuing development work in maintaining standards and quality control.

The following paragraphs of this summary are grouped according to the various analytical disciplines represented, and may be considered as brief abstracts of the years accomplishments.

Analytical Development

The recently modified plant zirconium fuel processing headend requires the addition of boric acid for criticality control in the dissolver solution. The accurate determination of total acidity and an acid material balance on the zirconium headend streams is, therefore, of paramount importance. Extensive studies of the methods used in analyzing these streams resulted in a modified method of improved accuracy. This method determines the sum of nitric acid and hydrofluoric acid in process samples with no reaction between boric acid and fluoride, and eliminates problems encountered in the previous method.

Reinvestigation of the spectrophotometric curcumin procedure for microgram amounts of boron was studied as replacement for other procedures; however, interference by various ions was noted and because of other priority work, this investigation was suspended.

A new titrimetric procedure for low-carbon samples is described, but observed values using this method have been low by as much as 15%. These low values, in part, have been traced to incomplete absorption of carbon dioxide, and improvements are being studied.

Modification of the apparatus used for colorimetric determination of micro quantities of fluoride is described in Appendix B.

A procedure is described for the separation of lithium prior to mass isotopic analysis. Isolations of 2- to 20- μ g amounts of lithium after the dissolution have been achieved, along with > 90% recovery of the lithium.

In order to monitor the release of mercury from the Waste Calcination Facility, sagebrush from the vicinity of the calciner off-gas stack was analyzed for mercury by colorimetric procedures.

Mercury determination by spectrophotometric dithizone method was investigated because of erratic results experienced during routine use. Contamination was shown to be the principal cause of erratic results. Concurrently, a study of the same method was undertaken to establish its applicability to samples with very low concentration of mercury. The method has two procedures, each one a correction for various metal ion interference. The method was modified to improve versatility, but its sensitivity proved unsatisfactory with the change of oxidation reagents for samples containing less than 25 μg of mercury.

A procedure for separation of plutonium for mass spectroscopic analysis was developed and is based on high selectivity of a strong basic anion exchange resin for the nitrate complexes of the +4 metal ions in strong nitric acid.

Determination of uranium by the pellet fluorophotometric method was studied by evaluation of two different extraction methods. A hexone extraction procedure proved more desirable than the method using 1% tributylphosphate in hexane.

To calibrate the fuel element gamma scanner, complete ETR fuel plates were dissolved and analyzed for total and isotopic uranium. The methods used were titrimetry, mass spectrometry, and rapid spectrophotometry.

The method for extraction-spectrophotometric determination of milligram amounts of uranium was reinvestigated. The range and versatility of the method have been improved by increasing sample size, modifying of salting solution, and using 5-cm absorption cells.

Table III-2 lists recommended methods selected by experimental evaluation of visual titrimetric EDTA analyses.

A procedure was developed using citrate-EDTA masking for the selective determination of iron with 1,10-phenanthroline and the details are presented in Appendix B.

A procedure was developed for the radiometric determination of Am-241 in CPP Final Product samples. Details of procedure are given in Appendix C.

A procedure was developed for radiometric determination of Ce-143 in the presence of large amounts of Np-239. Details of procedure are given in Appendix C.

Separation of the lanthanides from irradiated plutonium was completed for decay scheme studies and the separation was adapted to remote operations. Figure III-2 shows the extraction apparatus used for separation.

The separation of Lu-172 and Tm-172 from adjacent lanthanides was completed by cation exchange chromatography for a study of their decay schemes.

A summary of separation procedures for short-lived, neutron deficient isotopes formed by cyclotron irradiations at Boulder, Colorado is presented in Table III-3.

Recommendations were made for improving the reliability of results obtained when using gravimetric yield determinations for radiochemical analytical methods. Preparation and standardization of carrier solutions and stoichiometry of the precipitate received special attention.

A project is underway to develop a fundamental understanding of the electrochemistry of various species based on mathematical analyses of electrode responses during measurements. These methods have been applied specifically to the interpretation of step-functional controlled-potential measurements of second-order homogeneous reactions. Also mathematical relationships have been derived to correct electrode response data for various changes of current.

A controlled-potential electrochemical method using a step-potential pulse was used for the investigation of uranium(V) disproportionation reaction in perchloric acid. Experimental data were collected during the past year and the precision proved excellent. The interpretation of the data involves the numerical solution to the second-order differential equation describing the disproportionation of uranium(V).

Additional work was done on the new coulometric determination of uranium to determine the effect of diverse ions. Time required is approximately the same as the method used previously, but the elimination of certain steps of the procedure may prove advantageous. Further development has been postponed because priority of other work.

Developments in instrument design include: (1) a digital timer and waveform generator for flexible control of input signal waveforms and output signals. Measurement techniques of various spectra have been speeded up, and the quality and precision of data has greatly improved; (2) rapid evaluation for the performance of operational amplifier instrumentation in controlled-potential electrolysis experiments by a simplified transfer analysis; (3) modification of the electroanalytical potentiostat has been evaluated under experimental conditions. A passive electrical network was used to represent the electrochemical cell impedance.

A series of evaluation of the gas-particulate sampler has been initiated in support of the LOFT program. Controlled experiments are underway to verify the predicted sorption properties of various components of the cartridge for iodine species and for krypton-xenon under LOFT-simulated conditions. The results of temperature stability tests of particulate filter materials are summarized in Table III-4. Iodine activity retained by the particulate filter should be as particles or on the particles. Tests were made in a helium as well as steam-air atmosphere to determine iodine vapor retention of those filters that were thermally stable. The results are summarized in Table III-5.

Boron nitride was studied as a specific sorbing medium for krypton, xenon, and iodine. For krypton and xenon sorption tests, a gas chromatographic column containing 1.1 g boron nitride was used and the results indicated neither krypton and xenon were sorbed to any significant extent by boron nitride. Measurement of iodine adsorption required a 1-in. long cartridge containing 4 g of boron nitride. Iodine sorption in excess of 97% was measured in three different atmospheres, indicating that boron nitride is superior to activated charcoal for specific sorption of iodine, if its relatively high cost can be tolerated. Methods were developed for determination of fission products in LOFT samples, including: (1) separation of tellurium and iodine from other fission products in containment samples, and (2) sequential, fractional separation of multiple fission products from plateout samples and decontamination media. Details of the latter method are given in Appendix C.

Many methods for the dissolution of LOFT melt-down fuel were tested, and the results are summarized in Table III-6. The following three methods show the best results: dissolution with hydrofluoric acid, fusion with potassium pyrosulfate, and fusion with ammonium bifluoride. Because the actual LOFT fuel is expected to be highly refractory when received, the dissolution procedure must provide complete dissolution and quantitative recovery of all fission products; it must be adaptable to Remote manipulation; and must produce a final product that can be tested by radiochemical analysis. The results of dissolution of a simulated LOFT fuel pin using hydrofluoric acid are described in Table III-6.

Certain projects for the improvement of analytical facilities were completed during the year, and others are underway or awaiting approval. Remotely operated equipment in Cell X Cave was equipped with shield assemblies to cut down radioactive background. Approval for construction of the "Analytical Alpha Facility" has been given by AEC, but accomplishment of this project is being delayed by slow delivery of a shielded cave. Another proposal, awaiting action by the AEC, is to convert part of the Remote Analytical Facility into a hot cell for nonroutine work. This hot cell will provide an area for special dissolution and processing of samples that are presently difficult to perform.

The project for the development of methods for accurate determination of the burnup of nuclear fuel is summarized.

Spectroscopy

Iridium in aluminum was studied to determine whether direct excitation was preferable over dissolution. The results indicated a coefficient of variation of 3.5% with a correction for bias of the matrix. This procedure confirmed the direct method.

Boron in thorium was analyzed and preliminary study showed interference by the thorium. Three different concentrations of thorium were used to compensate for interference, and the coefficient of variation for five samples was 4.5%.

The process streams flowing into the CPP waste tanks were analyzed for 90-yr Sm-151 to determine the amount present and evaluate a separation process. Measurement was by isotope dilution mass spectrometry.

Installation of vacuum ion pumps on two single filament surface ionization mass spectrometers has improved performance, peak shape, resolution, and reduced cost because liquid nitrogen is not required for the cold traps.

A Jarrell-Ash microfocus X-ray diffraction unit was installed and can analyze areas down to 10- μ diameter.

A Perkin-Elmer Model 213B Hydrocarbon Detector was purchased for detection of organic concentrations in the LOFT containmant building atmospheres. EBR-II was surveyed and the organic material detected was less than 2 ppm.

Installation of an exhaust vacuum pump, which uses polyphenyl ether on the CEC mass spectrometer, provides higher and more uniform pumping speed and eliminates the dry ice trap.

A Bausch and Lomb dual-grating spectrograph located at TAN was used for the SNAP Destruct Test. The spectrograph was restored to operating condition, checked out, and calibrated for analysis of beryllium filters and fall-out plates.

A new loading procedure and modified sample holder were completed for X-ray diffraction analysis of deliquescent and pyrophoric samples, where sample contact with room atmosphere can not be tolerated.

A silver-spark rotating platform technique was adapted for analysis of rare earth elements directly, either as solution or as solids. The use of silver appears to have certain advantages over copper as an electrode material.

A nuclide vacuum lock has been installed in place of the bolted flange ion source on the Tandem Mass Spectrometer TDD-1. Time required to change samples has been reduced, output doubled, and overall operation improved.

Chemical Analysis

Table V-1 shows time required for different analyses used in the Chemical Analysis Section.

Selenium on polystyrene filters was determined colorimetrically for the Health and Safety Branch and details of this procedure are found in Appendix B.

A special dissolution study was performed on unirradiated power Burst Facility ternary fuel containing oxides of calcium, uranium, and zirconium. A mixed acid dissolution was used on two 4 g samples and complete dissolution was accomplished.

Irradiated thorium and aluminum-clad thorium samples were dissolved in the Multicurie Cell and Remote Analytical Facility and analyzed for aluminum, thorium, uranium, and Cs-137.

Copper and aluminum were determined chelometrically from acid dissolution of copper-aluminum alloy samples containing 6- to 40-% copper.

Iodine was determined colorimetrically from aqueous samples containing iodide which was oxidized and extracted into carbon tetrachloride.

Interference of stainless steel components for radiochemical strontium determination was corrected by precipitating strontium as the oxalate from a weak acid solution.

A method was developed for measuring Xe-133m and Xe-135 without waiting for decay of the Xe-135. The concentrations can be obtained by setting up decay equations for two areas and solving the simultaneous equations.

Tests were made to determine iodine loss in polypropylene dissolvers. These tests indicated radioactive iodine is retained by the dissolvers unless a carrier addition is made prior to dissolution.

Changes in the Kjeldahl procedure for nitrate and ammonia permitting direct titration have improved the accuracy of the method. The previous procedure which used back-titration and a different indicator was unreliable.

Highly radioactive samples for gamma scan analysis require reducing the activity at the detector for measurement, and studies made during the year indicated that increasing the distance from source to detector gives better results than the use of absorbers.

A 3-ft column packed with Raschig rings was found to be satisfactory for routine laboratory mercury purification.

Metal cans are being used for the removal of solid wastes from the Remote Analytical Facility (RAF). Radiation exposure and contamination have been reduced by this technique.

New bellows were designed for the RAF manipulators. Their installation is expected to improve remote analytical operations and reduce overall costs.

Standards and Quality Control

An Umpire Qualification program has been initiated in cooperation with various laboratories for the impartial settlement of disputes and differences between the AEC and other industries regarding the fissionable material content. The basis of monetary payments or credits is the quantity and quality of the materials involved as established by analysis. A number of materials will be exchanged for analyses. Qualification will be based on results of specially prepared standards. Several phases have been implemented for the program and will serve as guides for qualification. Table VI-1 summarizes the AEC laboratories that are to prepare and analyze the various standards. Projected plans and completion dates for the various phases of the program are summarized in Table VI-2.

The Quality Control Program was continued with various statistics shown for bias and precision data, training and testing, standards and reagents, and variables of liquid storage stability.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ANNUAL REPORT OF DIVISION ANALYTICAL BRANCH FOR 1965

CONTENTS

	<u>Page</u>
SUMMARY	iii
I. INTRODUCTION	1
II. GENERAL INFORMATION	2
✓ III. ANALYTICAL DEVELOPMENT	6
1. WET CHEMISTRY METHODS	6
1.1 Determination of Acidity in Zirconium Fuel Process Samples	6
1.2 Determination of Microgram Amounts of Boron	8
1.3 Determination of Small Amounts of Carbon in Metals	9
1.4 Microdistillation-Colorimetric Fluoride Determination	9
1.5 Separation of Lithium for Mass Isotopic Analysis	10
1.6 Determination of Mercury	11
1.6.1 In Sagebrush	11
1.6.2 By Spectrophotometric Dithizone Methods	11
1.7 Separation of Plutonium for Mass Spectroscopic Analysis	15
1.8 Determination of Uranium	16
1.8.1 Pellet Fluorophotometric Method	16
1.8.2 Total Uranium in an ETR Fuel Element	17
1.8.3 Extraction-Spectrophotometric Determina- tion of Milligram Amounts of Uranium	18
1.9 Evaluation of Titrimetric EDTA Methods of Analysis with Visual Indicator End Points	18

1.10	Use of Citrate-EDTA Masking for the Selective Determination of Iron With 1,10-Phenanthroline. .	18
2.	RADIOCHEMICAL METHODS.	24
2.1	Determination of Am-241 in CPP Final Product . .	24
2.2	Determination of Ce-143 in the Presence of Large Amounts of Np-239	24
2.3	Separation of the Lanthanide Group from Irradiated Plutonium.	25
2.4	Separation of Lu-172 and Tm-172 from Adjacent Lanthanides	27
2.5	Separations of Short-Lived Neutron-Deficient Isotopes.	27
2.6	Investigation of Yields of Some Radiochemical Methods	29
2.7	Revised Methods for the Determination of Beta Activity	30
3.	ELECTROANALYTICAL STUDIES.	30
3.1	Mathematical Analyses of Electrode Responses . .	30
3.1.1	Second Order Reactions	30
3.1.2	Faradaic Current Considerations	31
3.2	Uranium (V) Disproportionation Reaction in Perchloric Acid	31
3.3	Controlled-Potential Coulometric Determination of Uranium	32
3.4	Instrument Design	32
3.4.1	Digital Timer and Waveform Generator . . .	32
3.4.2	Transfer Function Analysis	33
3.4.3	Electroanalytical Potentiostat Modification	33
4.	DEVELOPMENT IN SUPPORT OF LOFT PROGRAM	34
4.1	Gas-Particulate Sampler	34

4.1.1	Thermal Stability of Particulate Filter Materials	34
4.1.2	Iodine Retention of Particulate Filter Materials	36
4.1.3	Sorption of Krypton, Xenon, and Iodine on Boron Nitride	37
4.2	Determination of Fission Products in LOFT Samples	38
4.2.1	Separation of Tellurium and Iodine from Other Fission Products	38
4.2.2	Determination of 10-Day Fission Products	39
4.3	Dissolution of LOFT Fuel	40
5.	REMOTELY OPERATED FACILITIES	42
5.1	Cell X Cave.	42
5.2	CPP Additional Alpha Handling Facility	42
5.3	RAF Hot Cell	42
6.	BURNUP DETERMINATION OF NUCLEAR FUEL	43
6.1	First Quarter	43
6.2	Second Quarter	44
6.3	Third Quarter	44
6.4	Fourth Quarter	46
✓ IV.	SPECTROSCOPY.	47
1.	SPECTROCHEMICAL ANALYSIS	47
1.1	Determination of Iridium in Aluminum	47
1.2	Determination of Boron in Thorium	47
1.3	Separation and Determination of Sm-151 in CPP Feed Solutions	47
2.	IMPROVED EQUIPMENT AND METHODS	48
2.1	Installation of Ion Pumps on MA 30 and MA 31 Mass Spectrometers	48

2.2	Installation of Microfocus X-ray Diffraction Unit	48
2.3	Detection of Hydrocarbons in Reactor Containment Buildings	49
2.4	Conversion of CEC Vacuum System	49
2.5	Restoration of Spectrograph for SNAP Test . . .	49
2.6	Analysis of Deliquescent and Pyrophoric Samples by X-ray Diffractometry	49
2.7	Silver Spark-Rotating Platform Technique for Spectrochemical Determination of Rare Earths . .	50
2.8	Installation of Vacuum Lock On Tandem Mass Spectrometer	50
✓ V.	CHEMICAL ANALYSIS	51
1.	MANPOWER REQUIREMENTS FOR DIFFERENT ANALYSES	51
2.	ANALYTICAL SERVICES	53
2.1	Health and Safety Branch	53
2.1.1	Analysis of Polystyrene Filters for Selenium	53
2.2	Nuclear Safety Research Branch	53
2.2.1	Dissolution of Ternary Fuels (calcium, uranium, and zirconium oxides)	53
2.3	Nuclear Technology Branch	54
2.3.1	Analysis of Irradiated Thorium Samples .	54
2.4	Reactor Engineering Branch	
2.4.1	Determination of Copper and Aluminum in Copper-Aluminum Alloys	54
3.	IMPROVEMENTS IN METHODS AND EQUIPMENT	54
3.1	Colorimetric Determination of Iodine	54
3.2	Determination of Strontium in Stainless Steel .	55
3.3	Simultaneous Determination of Xe-133m and Xe-135	55

3.4	Iodine Loss in Polypropylene Dissolvers	56
3.5	Determination of Inorganic Nitrate and Ammonia. .	57
3.6	High Activity Gamma Spectrometry.	57
3.7	Purification of Mercury	58
3.8	Improvements in the Waste Disposal System (Remote Analytical Facility).	58
3.9	New Design of Castle Manipulators Bellows	59
✓ VI.	STANDARDS AND QUALITY CONTROL.	60
1.	UMPIRE QUALIFICATION PROGRAM	60
1.1	Umpire Service Needed	60
1.2	Implementation of Program	60
1.3	Status of Program	61
1.4	Future Plans.	62
2.	QUALITY CONTROL.	63
2.1	Bias and Precision Data	63
2.2	Training and Testing Program.	64
2.3	Standards and Reagents.	64
	APPENDIX A - PUBLICATIONS AND OTHER ACTIVITIES	71
1.	U. S. ATOMIC ENERGY COMMISSION REPORTS	73
2.	JOURNAL ARTICLES	73
3.	PAPERS	74
✓	APPENDIX B - METHODS ADDED TO ANALYTICAL MANUAL IN 1965. . . .	75
1.	TITRIMETRIC DETERMINATION OF ACIDITY OF HYDROLYZABLE ION SOLUTIONS	77
2.	MICRODISTILLATION-COLORIMETRIC FLUORIDE DETERMINATION	91
3.	EXTRACTION-FLUOROPHOTOMETRIC DETERMINATION OF URANIUM	101

4.	DETERMINATION OF MILLIGRAM AMOUNTS OF URANIUM BY AN EXTRACTION-SPECTROPHOTOMETRIC MEASUREMENT METHOD . . .	109
5.	COLORIMETRIC DETERMINATION OF SELENIUM	125
6.	TITRIMETRIC DETERMINATION OF THORIUM (AND ALUMINUM) IN THORIUM METAL AND THORIUM METAL SLUG CLAD WITH ALUMINUM	129
7.	COLORIMETRIC DETERMINATION OF IODINE	139
8.	DETERMINATION OF INORGANIC NITRATE AND AMMONIA	145
9.	SPECTROPHOTOMETRIC DETERMINATION OF MILLIGRAM LEVELS OF PHOSPHOROUS AS MOLYBDIVANADOPHOSPHORIC ACID	151
10.	VOLUMETRIC DETERMINATION OF CHROMIUM(VI)	161
11.	TITRIMETRIC DETERMINATION OF PEROXIDE	167
12.	COLORIMETRIC DETERMINATION OF IRON WITH 1,10- PHENANTHROLINE	171
13.	DETERMINATION OF TOTAL CARBON	185

✓ APPENDIX C - METHODS ADDED TO ANALYTICAL RADIOCHEMICAL MANUAL
IN 1965

1.	DETERMINATION OF AM-241 IN CPP FINAL PRODUCT	195
2.	DETERMINATION OF Ce-143 IN SAMPLES CONTAINING Np-239 .	199
3.	DETERMINATION OF Np-237 IN HIGH CONCENTRATION U-235 SAMPLES	205
4.	ABSOLUTE BETA COUNTING OF LOW-ACTIVITY LIQUID-WASTE SAMPLES	209
5.	DETERMINATION OF GROSS BETA ACTIVITY	215
6.	DISSOLUTION AND SEPARATION OF 10-DAY FISSION PRODUCTS IN CDE PLATEOUT AND OTHER SAMPLES	219

FIGURES

	<u>Page</u>
II-1. Organization of Atomic Energy Division Analytical Branch	3
III-1. Modified Zirconium Fuel Headend with Boric Acid Present	6
III-2. Apparatus for Dissolution and Extraction of Lanthanide from Irradiated Plutonium	26
VI-1. Chemist Training and Testing Program	68
B-2-1. Tolerance Levels of Diverse Ions in the Distillation-Colorimetric Measurement Procedure	92
B-2-2. Microdistillation Apparatus.	94
B-12-1. Tolerance of the Direct Procedure for Diverse Ions . .	172
B-13-1. Schematic of Carbon Apparatus	186
C-6-1. Outline of the Procedure for Dissolution and Separation	222
C-6-2. Special Digestion Apparatus.	223

TABLES

II-1. Distribution of Manpower in 1965	4
II-2. Determinations Made by the Analytical Branch in 1965 .	5
III-1. Effect of Individual Ions and Ion Combinations on the Direct Colorimetric Mercury Procedure	13
III-2. Recommended Visual EDTA Titration Methods	19
III-3. Summary of Separation Procedures	28
III-4. Thermal Stability of Particulate Filter Materials . .	35
III-5. Retention of Molecular Iodine on Filter Materials and Several Iodine-Species Adsorbers	36
III-6. Dissolution of Fused UO_2 - ZrO_2 -Zircaloy-4 Cermet . . .	41
V-1. 1965 Analytical Methods and Time Required for Analysis .	51
V-2. Iodine Loss in Polypropylene Dissolvers	57

VI-1.	Functions of AEC Laboratory Participants	62
VI-2.	Plans for the Immediate Future	63
VI-3.	Precision of Routine Analytical Methods	65
VI-4.	Variables Studied for Liquid Storage Stability	69
B-1-1.	Types of Samples Analyzable by Method	77
B-2-1.	The Effect of Diverse Ions on the Direct Lanthanum-Alizarin Complexone Colorimetric Procedure	93
B-3-1.	Scale Factors for ORNL Model Q-1165 Fluorophotometer	106
B-4-1.	Comparison of Procedures <u>D</u> and <u>E</u>	110
B-4-2.	Effects of Diverse Ions.	112
B-4-3.	Effect of Diverse Ions at Levels Above the Maximum Tolerance Level, Procedure E	114
B-4-4.	Enrichment Factors	122
B-6-1.	Probable Effects of Metal Ions on the Determination of Thorium	129
B-6-2.	Dissolution Techniques for Thorium Samples	131
B-9-1.	Effects of Diverse Metal Ions	152
B-9-2.	Effects of Diverse Anions	155
B-12-1.	Effect of Diverse Metal Ions at Ion to Iron Molar Ratios Above the Maximum Tolerance Ratio	173
C-2-1.	Factors for Calculating Radioactive Ce-143	203

ANNUAL REPORT OF DIVISION ANALYTICAL BRANCH FOR 1965

I. INTRODUCTION

This is the sixth^(1,2,3,4,5) annual report of the Analytical Branch. Until 1960, analytical progress was included in ICPP Operations weekly and monthly reports and also in the ICPP technical quarterly reports. For 1965, quarterly project reports were issued for the Burnup Determinations of Nuclear Fuel.

This annual report presents a complete years work on projects of interest to analytical chemists. Work that has been or will be published is only abstracted here allowing space for information, both positive and negative that will not be published elsewhere. New and improved methods are included in the appendixes.

It is hoped that this report will be of value to management, to those who submit samples, and to all analytical chemists. A summary of this annual report is provided for the benefit of the management.

This report has been organized according to analytical disciplines except for the Loss-of-Fluid Test (LOFT) project and the burnup determination of nuclear fuel project.

- (1) R. C. Shank et al, Annual Report of ICPP Analytical Section for 1960, IDO-14547 (April 14, 1961).
- (2) R. C. Shank et al, Annual Report of ICPP Analytical Section for 1961, IDO-14588 (May 31, 1962).
- (3) R. C. Shank et al, Annual Report of Division Analytical Branch for 1962, IDO-14605 (April 25, 1963).
- (4) R. C. Shank et al, Annual Report of Division Analytical Branch for 1963, IDO-14636 (June, 1964).
- (5) R. C. Shank et al, Annual Report of Division Analytical Branch for 1964, IDO-14655 (April, 1965).

II. GENERAL INFORMATION

The organization of the Analytical Branch is shown in Figure II-1 and 66 people were employed at the end of 1965. Table II-1 shows distribution of manpower in 1965, but the time of the branch manager, the two secretaries, and the three section chiefs are not included in the table.

The number of determinations made by the Analytical Branch, and the sources of samples are shown in Table II-2.

ANALYTICAL BRANCH

December 31, 1965

Figure II-1. ORGANIZATION OF ATOMIC ENERGY DIVISION ANALYTICAL BRANCH

TABLE II-1
DISTRIBUTION OF MANPOWER IN 1965

Section	ICPP Operations	ICPP Chem & Proc Dev	Plant Assistance	Analytical Development	Other FPCo	Outside PPCo ^(a)	Analytical ^(b)	TOTAL
Spectroscopy	3192.5	1430.0	2885.0	5962.5	5365.5	2843.0	8174.0	29852.5
Chemical Analysis								
Remote & Service Analysis	13212.0	3022.0	4898.5	234.5	5359.5	2323.0	12129.5	41179.0
Radio & Special Analysis	2472.5	1235.5	4343.5	226.0	8487.0	1422.0	6523.5	24710.0
Analytical Development	245.0	1896.0	533.5	13622.5	4910.5	116.0	8598.5	29922.0
Analytical Branch	19122.0	7583.5	12660.5	20045.5	24122.5	6704.0	35425.5	125663.5
Analytical %	15.2	6.0	10.1	16.0	19.2	5.3	28.2	100.0

(a) AEC Contractors other than Phillips Petroleum Company.

(b) Includes overhead items such as housekeeping, vacations, training, and other items not directly charges to analytical service or existing research projects.

TABLE II-2
DETERMINATIONS MADE BY THE ANALYTICAL BRANCH IN 1965

Section	ICPP Operations	ICPP Chem & Proc Dev	Plant Assistance	Analytical Development	Other PPCo	Outside PPCo ^(a)	Analytical	TOTAL
Spectroscopy	3807	685	931	299	3391	2719	663	12495
Chemical Analysis								
Remote & Service Analysis	20702	3676	6351	179	4730	1682	6345	43665
Radio & Special Analysis	1539	768	2950	33	5135	612	366	11403
Analytical Development	44	9	76	0	33	1	0	163
Quality Control ^(b)	0	0	0	0	47	0	8767	8814
Analytical Branch	26092	5138	10308	511	13289	5014	7374	67726
Analytical %	38.5	7.6	15.2	0.8	19.6	7.4	10.9	100.0

(a) AEC Contractors other than Phillips Petroleum Company.

(b) Reagents and controls prepared by this laboratory are not included in the total.

III. ANALYTICAL DEVELOPMENT

1. WET CHEMISTRY METHODS

1.1 Determination of Acidity in Zirconium Fuel Process Samples (S. S. Yamamura, M. A. Wade, W. A. Mickelson)

A portion of the modified plant zirconium fuel process headend is shown in Figure III-1. The new process requires the addition of boric acid to the dissolver solution for criticality control at increased capacity.

Figure III-1. MODIFIED ZIRCONIUM FUEL HEADEND WITH BORIC ACID PRESENT

The presence of boric acid requires accurate determination and control of process stream acidity to prevent precipitation. Acid analyses of streams 1, 2 and 3 by established procedures failed to provide an acid material balance. As a result, these methods were investigated to provide: (1) an accurate determination of the acidity of plant streams, especially the complexed dissolver product where precipitation stability is most sensitive to pH, and (2) total acidity method capable of giving an acid material balance for the headend process.

In the presence of boric acid, the acidity of the solutions depends on the relative concentrations of the fluoride, boric acid, and metal ions, as illustrated by the following equilibria:

Of special significance is the reaction of boric acid with fluoride ions according to reaction (1) to form a fluoborate complex and hydroxyl ions. High fluoride concentration favors the formation of the fluoborate complex with the accompanying release of hydroxyl acid-consuming ions. Low fluoride concentration and high hydroxyl ion concentration favor the reverse reaction. Fluoride-complexing metal ions also favor the reverse reaction by effectively reducing the fluoride concentration as shown by reaction (2).

In the routine acid method (Procedure B - See Appendix B, Method H⁺-Pot-4, Mod-6), the sample is pipetted into a solution of potassium oxalate preadjusted to pH 5.55, and the mixture is titrated back to pH 5.55 with standard sodium hydroxide. As noted above, the acid results obtained by this method for the three plant streams shown in Figure III-1 failed to provide a material balance. The reason for this is the different ratios of total (aluminum plus zirconium) metal to fluoride in the dissolver product and in the complexed dissolver product. These ratios affect the fluoride-boric acid reaction as well as the consumption of acid, as previously discussed, resulting in slightly higher acidity values for the dissolver product when determined by the routine method, than the "true" acidity of these solutions. However, the acidity values so obtained are considered to be satisfactory for the control of precipitation stability.

The fact that fluoride-complexing metal ions eliminate the complicating effect of boric acid by the reversal of reaction (1) suggested the addition of aluminum nitrate to the sample. This change led to a modified method which provides an acid material balance for the headend process. The principal changes are the addition of 1 mmole of aluminum nitrate to the sample and the use of a 1M potassium oxalate solution in place of the 0.4M solution prescribed for the routine procedure. Essentially this modified method determines the sum of nitric acid and hydrofluoric acid in the samples with no reaction between boric acid and fluoride.

Details of the new method (Procedure F) as well as Procedure B are described in Appendix B, Method H⁺-Pot-4, Mod-6.

1.2 Determination of Microgram Amounts of Boron (J. H. Sikes)

Currently, there are three spectrophotometric procedures for the determination of microgram levels of boron, each adapted to specific sample types. As a replacement for these methods, the reportedly versatile spectrophotometric curcumin procedure for boron^(6,7) was reinvestigated.

In the curcumin method, the boron-curcumin complex is formed in a nearly anhydrous sulfuric acid-acetic acid medium. The red complex is then measured spectrophotometrically by one of two ways. In one, the boron-curcumin complex is precipitated with water or dilute hydrochloric acid, separated from the uncomplexed curcumin by filtration, redissolved in a small volume of ethanol, and measured at 555 mμ. In the other, the sulfuric acid-acetic solution is diluted with a large volume of ethanol and the absorbance of the solution is measured at 555 mμ. The filtration technique was used in the present studies.

The effect of water on the color development was studied to establish the volume limits for aqueous samples. Up to ~250 μl of water had no effect, but 250 to 400 μl of water introduced a slight negative error. Above ~450 μl of water, the color development dropped off sharply with increasing amounts of water. Because of the desirability of maximum sensitivity and high versatility, a procedure based on the control of water at 400 μl was adopted.

The effects of aluminum, 347 stainless steel constituents, zirconium, and anions commonly found in solutions of these metals were studied by analyzing various synthetic samples containing known levels of boron and varying levels of the diverse ions. Significant amounts of stainless steel and zirconium did not interfere, but aluminum interfered slightly at all the concentration levels (2.75 to 11 mg) studied. Fluoride and nitrate, even in small amounts, interfered seriously.

The development of a satisfactory procedure is expected to require further extensive study. Because of other higher priority work, this investigation was suspended.

(6) M. R. Hayes, J. Metcalf, "The Boron-Curcumin Complex in the Determination of Trace Amounts of Boron", Analyst, 87, p 956 (1962).

(7) M. R. Hayes, J. Metcalf, AEA Report pG 391 (5) (1962).

1.3 Determination of Small Amounts of Carbon in Metals (J. H. Sikes)

The carbon content of metal is presently determined by burning the sample in a stream of oxygen in a Fisher induction carbon apparatus, absorbing the evolved carbon dioxide in a tared Ascarite tube, and weighing it. Because the Ascarite absorption tube weighs about 100 g, the results must be calculated from the difference between two large numbers and the precision is unsatisfactory for low-carbon samples that yield only a few milligrams of carbon dioxide.

To improve the reliability of the analysis for low-carbon samples, a titrimetric procedure⁽⁸⁾ is being investigated for the final measurement of the carbon dioxide. In this procedure, the evolved carbon dioxide is absorbed in an excess (10 ml) of 0.04M barium hydroxide - 1.0M barium chloride solution, and the excess barium hydroxide is titrated with standard 0.05N hydrochloric acid to a thymolphthalein end point. The difference between the titers for the blank and the sample is proportional to the amount of carbon dioxide absorbed. A difference of 1 ml of 0.05N hydrochloric acid is equivalent to 1.1 mg of carbon dioxide.

The titration procedure was evaluated by titrating aliquots of a standard sodium bicarbonate solution. Four aliquots of the bicarbonate solution equivalent to 0.9 to 3.6 mg of carbon dioxide were titrated. On the basis of the four results, the relative standard deviation was 0.5%.

The titrimetric procedure then was tested by analyzing an NBS stainless steel carbon standard. The effluent gas from the induction carbon apparatus was dispersed with a frit and the carbon dioxide was absorbed in 10 ml of the 0.04N barium hydroxide-1.0M barium chloride solution diluted to 120 ml with distilled water. The observed values were low by as much as 15%. Part of the cause for the low results has been traced to incomplete absorption of the carbon dioxide. Means of improving the method will be investigated.

1.4 Microdistillation-Colorimetric Fluoride Determination (M. A. Wade, S. S. Yamamura)

The colorimetric determination of micro quantities of fluoride has previously been described⁽⁹⁾. In subsequent studies the apparatus was modified to minimize the carry-over of perchloric acid, and an apparatus cleansing step was introduced to prevent cross contamination. Details of these changes are found in Appendix B, Method F-3, Mod-1.

(8) C. G. Golbeck, The Volumetric Determination of Carbon in Uranium Metal, USAEC Report TID-10160, p 164, 1951.

(9) R. C. Shank and Staff, Annual Report of Division Analytical Branch for 1964, IDO-14655, Section III-6, p 9, and Appendix B, p 161 (April 1965).

1.5 Separation of Lithium for Mass Isotopic Analysis (S. S. Yamamura, J. H. Sikes, D. M. Lund)

A preliminary separation of lithium as the hydroxide or fluoride salt was required for the mass isotopic analysis of lithium in lithium-aluminum alloy samples submitted by MTR Reactor Physics. Since these samples contained significant amounts of silicon they were dissolved with nitric and hydrofluoric acids. The procedure detailed below has been used satisfactorily for the isolation of 2- to 20- μ g amounts of lithium after the dissolution. The recovery of lithium is $> 90\%$.

PROCEDURE

1. Transfer an aliquot of the sample containing less than 3 mmoles of aluminum to a platinum dish.
2. Fume the sample over a hot plate three times with 3-ml portions of perchloric acid. On the first two evaporations, fume to near dryness without baking the sample. On the third evaporation, evaporate the sample to dryness.
3. Cool slightly, dissolve the salts with water, then transfer the solution with water rinses to a 50-ml centrifuge tube. Dilute to about 40 ml.
4. Add one drop of 0.2% methyl red indicator. Because sodium ions interfere in the mass isotopic analysis, an alcoholic solution of the acid form of the indicator should be used.
5. Using efficient magnetic stirring, add 1M ammonium hydroxide until the indicator just turns from red to yellow (pH 6).
6. Immerse the centrifuge tube in boiling water for 2 to 3 min.
7. Upon heating, the methyl red indicator reverts to the red acidic form. Add 1M ammonium hydroxide dropwise until the indicator again just turns to yellow.
8. Chill the sample to room temperature then settle the aluminum hydroxide precipitate by centrifugation.
9. Decant and filter the clear supernatant solution through a 0.45- μ membrane filter. Use a Fisher filtrator and filter directly into a clean 100-ml beaker. The precipitate need not be washed.
10. Pass the filtrate slowly through a 9-mm ID x 10-in. column of Dowex 1-X8, 50-100 mesh resin in the nitrate form.

11. Evaporate the column effluent to dryness in a platinum dish, then heat the dish to a dull red over a Meker burner to decompose the ammonium nitrate and to convert lithium nitrate to lithium oxide.
12. Cool the dish, then transfer the lithium to a small plastic container. If the lithium must be supplied as a solution of the fluoride salt, neutralize the lithium oxide with excess hydrofluoric acid, evaporate the solution to dryness, then transfer the residual lithium fluoride to a small plastic container.

1.6 Determination of Mercury

1.6.1 In Sagebrush (D. K. Oestreich, S. S. Yamamura)

To monitor the release of mercury from the Waste Calcination Facility, the Chemical and Process Development Branch submitted samples of sagebrush, from the vicinity of the calciner off-gas stack, for mercury analyses. Ten-gram samples were digested under reflux for 4 hr with a mixture of 5 ml of sulfuric acid and 35 ml of nitric acid. The digested samples were filtered through 0.45- μ Gelman Vinyl Metrical filters and diluted to volume with water. Aliquots of the solution then were analyzed for mercury by the routine colorimetric procedure, Method Hg-1, Mod-6⁽¹⁰⁾. The method was modified slightly to adapt it to the sagebrush samples with their very low levels of mercury. Five-centimeter cells were used for the absorbance measurements and 2- and 5- μ g mercury standards were used for the calibration.

1.6.2 By Spectrophotometric Dithizone Methods (J. H. Sikes, D. M. Lund, S. S. Yamamura)

The spectrophotometric method for the determination of mercury⁽¹¹⁾ was reinvestigated to establish and eliminate the cause of erratic results experienced during routine use. Simultaneously, a comprehensive study of the method was undertaken to establish its applicability and limitations and to adapt it to samples with very low concentrations of mercury. During the course of the investigation, no erratic results were observed, indicative that contamination or a similar phenomenon is the cause of faulty results in routine use.

The method consists of two procedures; a direct procedure involving one extraction and a longer but more selective procedure involving two extractions. In both procedures, the mercury is extracted as the dithizonate complex into carbon tetrachloride from an EDTA-citrate masking medium and the absorbance of the complex is measured spectrophotometrically at 510 m μ . In the double extraction

(10) This report, Appendix B.

(11) R. C. Shank et al, Annual Report of Analytical Chemistry Branch for 1963, IDO-14636, Appendix B, p 165 (June, 1964).

procedure, this is preceded by a preliminary extraction of the complex into xylene. The mercury is stripped from the xylene with hydrochloric acid, then reextracted into carbon tetrachloride as described above. The double extraction procedure is designed for those samples containing metal ions such as copper that partially coextract and interfere in the direct single extraction procedure.

To improve the versatility of the method, two major changes were made. The volume of the dithizone-carbon tetrachloride extractant was increased from 10 ml to 15 ml to increase the upper limit of the method and the complexing solutions previously specified were replaced by one modified complexing solution with greater masking capacity. These new conditions were used for most of the present study.

The effects of diverse ions and mixtures of ions on the direct single extraction procedure were studied by analyzing synthetic mixtures containing known levels of mercury and varying levels of the diverse ions. The results are summarized in Table III-1. Principal known interferences are copper(II) at greater than 25:1 copper to mercury molar ratios, silver(I) at greater than 0.1:1 ratios, and iodide. Iodide interferes in two ways. It inhibits the extraction of mercury and coextracts as free iodine. The tolerance of iodine was not established.

Because mercury must be in the (II) valence state, all samples currently are oxidized with nitric acid. The oxidized sample is diluted to 50 ml, then a maximum volume of 10 ml of the diluted sample is carried through the colorimetric procedure. The lower limit of the present colorimetric procedure is 5 μg of mercury, so the actual lower limit of the method is 25 μg in the original sample aliquot. Two different approaches were studied in an attempt to improve the sensitivity of the method and to adapt it to samples containing a total of less than 25 μg of mercury. In one, a potassium permanganate oxidation was substituted for the nitric acid oxidation. The excess permanganate was destroyed with hydroxylamine hydrochloride or with oxalic acid plus manganous sulfate. In the other approach, the mercury was separated on a cadmium sulfide disk, redissolved in a mixture of hydrochloric acid and potassium chlorate, then analyzed. In either case, the original sample was carried through in its entirety, so that the lower limit was potentially 5 μg of mercury. Neither approach proved satisfactory. The permanganate-oxidized samples invariably read 4 to 5% lower than those oxidized with nitric acid and the recovery of mercury through the sulfide disk separation step was only about 92%.

Table III-1

EFFECT OF INDIVIDUAL IONS AND ION COMBINATIONS
ON THE DIRECT COLORIMETRIC MERCURY PROCEDURE^a

<u>Ion or Mixture Investigated</u>	<u>Tolerance Level, Ion to Hg Molar Ratio^b</u>
Metal Ions	
Be(II), Bi(III), Ca(II), Cd(II), Ce(III), Co(II), Cr(III), Cs(I), Fe(III), Ge(IV), Ho(III), In(III), La(III), Mg(II), Mn(II), Mo(VI), Ni(II), Pb(II), Sn(II,IV), Sr(II), Th(IV), Tl(I), U(VI), V(V), Y(III), Zn(II), Zr(IV)	Each ion individually at 1000
Ag(I)	0.1 ^c
Au(III), Pd(II), Pt(IV)	Each ion alone at 50
Cu(II)	25 ^c
Common Anions	
Br ⁻¹	1000
Cl ⁻¹	7.5x10 ⁵
I ⁻¹	--- ^d
PO ₄ ⁻³	3.0x10 ⁴
SO ₄ ⁻²	1.3x10 ⁵
Synthetic Mixtures	
Simulated aluminum fuel dissolver product	
Al(III)	2x10 ⁴
Cr(VI), U(VI)	Each at 50
Cl ⁻¹ plus NO ₃ ⁻¹	6x10 ⁴

Table III-1 (Continued)

<u>Ion or Mixture Investigated</u>	<u>Tolerance Level, Ion to Hg Molar Ratio^b</u>
Simulated aluminum fuel dissolver product and calciner product	
Al(III), Zr(IV)	Each at 2000
Cr(VI), U(VI)	Each at 50
Cl ⁻¹ plus NO ₃ ⁻¹	~ 1x10 ⁴
Simulated calciner product fused with potassium pyrosulfate	
Al(III), Zr(IV)	Each at 2000
Cr(VI)	50
K(I)	2.4x10 ⁵
SO ₄ ⁻²	~ 1.3x10 ⁵

(a) Mercury level was maintained at 20 µg (1.0x10⁻⁴-mmole).

(b) Highest level studied.

(c) Maximum tolerance level.

(d) Iodide interferes at 1000:1. Its tolerance level was not established.

1.7 Separation of Plutonium for Mass Spectroscopic Analysis (S. F. Marsh)

Most plutonium-containing samples submitted for mass analysis contain fission products and actinide isobars from which the plutonium must first be separated. Even samples of originally pure plutonium may contain interfering levels of Am-241 grown in from the decay of 13-yr Pu-241.

The previously used separation procedures required several operations and were lengthy. Because glove box operations are required, a simple procedure was desired that would require neither elaborate nor expensive equipment. Such a procedure was developed which is based on the high selectivity of a strongly basic anion exchange resin for the nitrate complexes of the +4 metal ions in strong nitric acid.

The basis of the procedure is that plutonium is oxidized to +4 with sodium nitrite in 8M nitric acid before placement of the sample on the resin. The distribution coefficient for Pu(IV) is $\sim 10^4$ while the values for U(VI), Np(V), Am(III), and all aged fission products are low⁽¹²⁾.

A stepwise procedure, designed for isotope dilution mass analysis of samples containing uranium, americium, fission products, and fuel-cladding components is presented below.

PROCEDURE

1. To the sample containing about 0.1 to 1 μ g of plutonium in a small test tube, add an exact amount of a selected plutonium spike approximately equal to the amount of sample plutonium.
2. Mix thoroughly, then evaporate to near dryness under an infrared lamp. Heat gently to prevent spattering.
3. Let cool, add 1 ml of 8M nitric acid and 10 mg of sodium nitrite. (If the plutonium in the sample is in an oxidation state higher than +4, first add hydroxylamine hydrochloride.)
4. Mix until the sodium nitrite dissolves.
5. Transfer the sample to a small (eye dropper), 5- x 25-mm column of Dowex 1-X4; 200-400 mesh anion exchange resin that has been equilibrated with 8M nitric acid.

(12) J. P. Faris, R. F. Buehanan, "Anion Exchange Characteristics of Elements in Nitric Acid Medium". Anal. Chem. **36**, 1157 (1964).

6. Elute fuel cladding impurities, fission products, and americium with 8M nitric acid. Discard the effluent.
7. Elute uranium with 2 ml of 1M nitric acid and discard the effluent.
8. Elute plutonium with 2 ml of 0.2M nitric acid into a 5-ml conical centrifuge tube.
9. Evaporate to near dryness under an infrared lamp.
10. Insert a polyethylene stopper in the tube, seal the tube in a plastic bag and transfer to the mass laboratory.

1.8 Determination of Uranium

1.8.1 Pellet Fluorophotometric Method (D. M. Lund)

In the routine pellet fluorophotometric method for the determination of uranium, the uranium is separated from interfering ions prior to measurement. Two different extraction methods have been used for this separation. In one, the extractant is 1% tributylphosphate (TBP) in hexane and the salting solution is a mixture of aluminum nitrate and lithium nitrate. In the other, the extractant is 4-methyl-2-pentanone (hexone) and the salting solution is acid-deficient aluminum nitrate containing tetrapropylammonium nitrate (TPAN). The extraction of uranium is more nearly quantitative in the hexone procedure than in the TBP procedure; however, the coextraction of fission product Ru-106 is greater. Thus, when used for fission product samples, the Ru-106 alloys with the platinum dishes used to obtain the melt, resulting in a buildup of beta activity. Because many samples in this laboratory are fission product samples, the TBP extraction method has been adopted.

Subsequent analysis of a series of uranium samples by the TBP procedure in an interlaboratory testing program⁽¹³⁾ revealed that the extraction of the uranium was sufficiently low to be affected by the composition (salting strength) of the sample. A ten-fold increase in the concentration of the TBP extractant and a two-fold increase in the concentration of the aluminum nitrate in the salting solution increased the uranium extraction to ~ 95% to make the extraction less dependent on sample composition. However, these changes also substantially increased the coextraction of fission products, so that from an activity standpoint, the hexone procedure was now the more desirable of the two. Accordingly, the hexone extraction procedure has been adopted for the fluoro-

(13) Selected Measurement Methods Evaluation Program, administered by New Brunswick Laboratory, C. J. Rodden, Director. In this program, samples were distributed to various U. S. Laboratories to establish the reliability of the methods published in TID-7029, R. J. Jones, Editor, Selected Measurement Methods. USAEC, 1963.

photometric uranium method. With the hexone extraction procedure there will be a slow build-up of radioactivity, mainly 1-yr Ru-106, on the platinum dishes. A few dishes should therefore be used for the analysis of radioactive samples only, and set aside when the radiation level becomes excessive.

In a separate study the tolerance limit of the hexone procedure for sulfate was established to be 2.5 mmoles. Above this level, the aluminum sulfate precipitates and carries uranium. For sample containing greater than 2.5 mmoles of sulfate the excess sulfate must be removed by fuming.

Details of the revised fluorophotometric method for uranium are presented in Appendix B.

1.8.2 Total Uranium in an ETR Fuel Element (D. M. Lund, S. S. Yamamura)

To calibrate the fuel element gamma scanner, the Operations Analysis Group submitted 19 fuel plates from an ETR fuel element for total and isotopic uranium analysis. Each of the 37.25- x 2.78-in. plates were dissolved separately in aqua regia, then analyzed for uranium. The primary method of analysis was a well-established redox titrimetric procedure developed at the New Brunswick Laboratory⁽¹⁴⁾. National Bureau of Standards natural U_3O_8 (NBS Standard Sample 950a) was used for the standardization. Approximately one-third of the samples were also analyzed by isotope dilution mass spectrometry⁽¹⁵⁾ and by a rapid spectrophotometric method⁽¹⁶⁾.

The reliability of the titrimetric procedure was established by replicate analyses of two synthetic standards containing known amounts of natural uranium. On the basis of six results for one and five results for the other, the observed precision was 0.2% relative standard deviation. There was no bias. The agreement between the titrimetric results, the spectrophotometric and mass spectrometric results were generally within 1%.

(14) R. J. Jones, Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle, p 96, USAEC, TID-7029, 1963.

(15) Ibid, p 279.

(16) This report, Appendix B.

1.8.3 Extraction-Spectrophotometric Determination of Milligram Amounts of Uranium (S. S. Yamamura, D. M. Lund, D. K. Oestreich, F. A. Duce)

The extraction-spectrophotometric method for milligram levels of uranium was re-investigated to improve its versatility and further establish its applicability and limitations. The results of the studies are summarized in the revised method, U-Color-5, Mod-3 described in Appendix B. Included in the revision are expanded Discussion and Applicability sections wherein the factors affecting the extraction and absorptivity of the uranium complex and the effects of diverse ions are discussed. The range of the method has been expanded in both directions. This was accomplished by increasing the sample size, modifying the salting solution to accommodate higher levels of uranium, and using 5-cm absorption cells.

1.9 Evaluation of Titrimetric EDTA Methods of Analysis With Visual Indicator End Points (S. S. Yamamura)

In 1963, an experimental evaluation of visual titrimetric EDTA methods of analysis was begun⁽¹⁷⁾ to select, from the many methods published in the literature⁽¹⁸⁾, an abbreviated list of those found to be desirable. The criteria established for the selection of the methods were specificity, reliability; and the distinctness of the indicator color change at the end point. This study has been carried on intermittently over the past two years. As of this report, extensive data have been obtained for the elements magnesium, calcium, strontium, and barium of Group II-A; scandium, yttrium, and the lanthanides of Group III-A; and zinc of Group II-B. Recommended methods selected on the basis of these data are presented in Table III-2.

1.10 Use of Citrate-EDTA Masking for the Selective Determination of Iron With 1,10-Phenanthroline (S. S. Yamamura, J. H. Sikes)

The following is a summary of a paper which has been submitted for publication in Analytical Chemistry. Details of the method are presented in Appendix B, Method Fe-3, Mod-2.

Duo citrate-EDTA masking is recommended for high selectivity and versatility in the spectrophotometric determination of iron with 1,10-phenanthroline. Color development conditions and the results of comprehensive studies of diverse ion effects are presented.

(17) R. C. Shank et al, Annual Report of Division Analytical Branch for 1963, IDO-14636, Section III-12, p 28 (June, 1964).

(18) L. Meites, Handbook of Analytical Chemistry, Section 3, pp 166-200, 208-225, McGraw Hill, New York (1963).

Table III-2

RECOMMENDED VISUAL EDTA TITRATION METHODS

Metal Ion	Approximate No. of Methods Evaluated	Mode of Titration ^a	Recommended Procedure		Indicator Color Change and Remarks
			Indicator	Titration Conditions ^b	
<u>Group II-a</u>					
Mg ⁺²	20	D	Eriochrome Black T	NH ₃ buffer, pH 10-10.5	Distinct red-violet to blue
		D	Metalph-thalein	NH ₃ buffer, pH 10.5, 30-50% EtOH	Red-violet to colorless
		B(Ca ⁺²)	Metalph-thalein	NH ₃ buffer, pH 10.5	Distinct colorless to violet
		B(Mn ⁺²)	Eriochrome Black T	NH ₃ buffer + NH ₂ OH·HCl or ascorbic acid, pH 9.5-10.0	Blue to red-violet
		B(Zn ⁺²)	Eriochrome Black T	NH ₃ buffer, pH 9.5-10	Blue to red-violet
Ca ⁺²	25	D	Acid Alizarin Black SN	NH ₃ + NaOH, pH 11.3-12	Very distinct red to blue
		D	Eriochrome Black T + Mg-EDTA	NH ₃ buffer, pH 10.25 [±] 0.25	Red-violet to blue; fairly slow
		D	Metalph-thalein (Phthalein Complexone)	NH ₃ buffer, pH 10.5 [±] 0.25	Violet to colorless; best closest to pH 10.5

Table III-2 (Continued)

Metal Ion	Approximate No. of Methods Evaluated	Recommended Procedure			
		Mode of Titration ^a	Indicator	Titration Conditions ^b	Indicator Color Change and Remarks
Sr ⁺² , Ba ⁺²	20	B(Ca ⁺²)	Acid Alizarin Black SN	NaOH, pH 11.5-12	Distinct blue to red-violet
			Metalphthalein	NH ₃ buffer, pH 10.5	Distinct colorless to violet
		B(Mg ⁺²)	Eriochrome Black T	NH ₃ buffer, pH 10.25 [±] 0.25	Blue to red-violet
		D	Acid Alizarin Black SN	NaOH, pH 11.8-12	Red-violet to blue. Above ~ pH 12.2 purple hue of the indicator clouds the color change.
		D	Metalphthalein	NH ₃ buffer + NaCH ₃ , pH 10.5-11, 50% EtOH	Distinct purple to colorless
		R(Ca-EDTA)	Metalphthalein	NH ₃ buffer + NaCH ₃ , pH 10.5-11, 50% EtOH	Very distinct purple to colorless
		B(Ca ⁺²)	Acid Alizarin Black SN	NaOH, pH 11.5-12	Very distinct blue to red-violet
			Metalphthalein	NH ₃ buffer + NaCH ₃ , pH 10.5 [±] 0.25, 20-40% EtOH	Very distinct colorless to violet
<u>Group II-b</u>					
Zn ⁺²	25	D	Eriochrome Black T	NH ₃ buffer, pH 9-10.5	Very distinct violet to blue
		D	Eriochrome Red B	NH ₃ -NH ₄ Ac, pH 7-11.5 or NH ₃ buffer, pH 9-11	Very distinct red to yellow; wide applicable pH range

Table III-2 (Continued)

Metal Ion	Approximate No. of Methods Evaluated	Recommended Procedure			
		Mode of Titration ^a	Indicator	Titration Conditions ^b	Indicator Color Change and Remarks
Sc ⁺³	15	D	Xylenol Orange	Pyridine buffer, pH 5.5-6	Red-violet to yellow; good transition but slightly slow equilibrium.
		D	Zincon	Acetate buffer, pH 5.5-6	Distinct red-violet to yellow
				NH ₃ buffer, pH 9-10	Very distinct blue to yellow; sharpness of color change decreases with increasing salt concentration.
		R(Ce-EDTA)	Xylenol Orange	Pyridine buffer, pH 5.5-6.5	Red-violet to yellow
		B(Ce ⁺³)	Xylenol Orange	Pyridine buffer, pH 5.5-6.5	Yellow to red-violet
		B(Cu ⁺²)	SNAZOXS	Pyridine buffer, pH 5.5-6	Red to yellow or reddish-blue to green depending on the amount of Cu ⁺² introduced
		B(Zn ⁺²)	Eriochrome Black T	NH ₃ buffer, pH 9-10.5	Blue to violet
		D	Xylenol Orange	Acetate buffer, pH 2.2-4.5	Pink to yellow; best at pH 2.5-3

Table III-2 (Continued)

Metal Ion	Approximate No. of Methods Evaluated	Recommended Procedure			Indicator Color Change and Remarks
		Mode of Titration ^a	Indicator	Titration Conditions ^b	
Y ⁺³ Lanthanides	20	D	Arseneazo	Acetate or pyridine buffer, pH 5 [±] 0.25	Purple to orange-pink; color change is sudden but the color transition may be disagreeable to some individuals.
		R(Ce-EDTA)	Xylenol Orange	Pyridine buffer, pH 5.5-6	Distinct red-violet to yellow; easier pH adjustment than in the direct titration
		B(Ce ⁺³)	Xylenol Orange	Pyridine buffer, pH 5.5-6.5	Yellow to red-violet
		B(Cu ⁺²)	SNAXOXS	Pyridine buffer, pH 5.5-6	Red to yellow or reddish blue to green depending on the amount of Cu ⁺² introduced
		B(Zn ⁺²)	Xylenol Orange	Acetate buffer, pH 5.5-6	Yellow to red-violet
		D	Arseneazo	Pyridine buffer, pH 5.5-6.5	Purple to red-orange
		D	Arseneazo + Cresol Red	Pyridine buffer, pH 5.5-6.5	Purple to orange
		D	Xylenol Orange	Pyridine buffer, pH 5.5-6.5	Very distinct red-violet to yellow

Table III-2 (Continued)

Metal Ion	Approximate No. of Methods Evaluated	Recommended Procedure			
		Mode of Titration ^a	Indicator	Titration Conditions ^b	Indicator Color Change and Remarks
		B(Ce ⁺³)	Xylenol Orange	Pyridine buffer, pH 5.5-6.5	Very distinct yellow to red-violet
		B(Cu ⁺²)	SNAZOXS	Pyridine buffer, pH 5.5-6.5	Red to yellow or reddish-blue to green depending on the amount of Cu ⁺² introduced

^a D = direct titration with EDTA; R(M-EDTA) indicates replacement titrimetry. The compound enclosed in parenthesis is added to the sample and the metal, M, released is titrated with EDTA; B(M^{+Y}) indicates a back titration procedure. A known amount of EDTA is added to the sample and the excess EDTA is back titrated with the metal ion, M^{+Y}, enclosed in parenthesis.

^b All titrations are carried out in aqueous medium unless noted otherwise.

2. RADIOCHEMICAL METHODS

2.1 Determination of Am-241 in CPP Final Product (S. F. Marsh)

A two-step extraction procedure has been developed for the separation and radiometric determination of trace amounts of Am-241 in CPP Final Product samples which contain large amounts of enriched uranium and low amounts of thorium, neptunium, and plutonium.

In the first extraction, cations with valences of +4 and higher are extracted into 1.5M di-(2-ethylhexyl) phosphoric acid (D2EHP)-heptane from a 2M nitric acid - 0.2M sodium nitrite aqueous phase. The aqueous phase is separated and is diluted ten-fold with water, then the americium (as the stable +3 cation) is extracted into a fresh portion of the 1.5M D2EHP-heptane solvent. Mono- and divalent decay chain products remain in the aqueous phase. The organic phase is separated and americium is stripped into 2M nitric acid. An aliquot is mounted on a stainless steel planchet, evaporated to dryness, flamed, and the 5.476-Mev alpha disintegrations from Am-241 are measured with a silicon detector coupled to a pulse height analyzer.

Details of the procedure are given in Appendix C.

2.2 Determination of Ce-143 in the Presence of Large Amounts of Np-239 (S. F. Marsh)

In the routine method for radiocerium, based on the extraction of cerium as the tetrapropylammonium nitratocerate complex into nitroethane⁽¹⁹⁾, large amounts of Np-239 coextract and interfere with the determination of Ce-143 in young fission product samples.

An alternate procedure was developed based on the high distribution coefficient of Ce(IV) into di(2-ethylhexyl)phosphoric acid-heptane⁽²⁰⁾. After extraction, the organic phase is separated and contacted with hydrogen peroxide-hydrochloric acid. The Ce(IV) reduces to nonextractable Ce(III) which strips while the neptunium remains in the organic phase. The cerium is precipitated as cerous oxalate and counted.

Details of the procedure are given in Appendix C.

(19) S. F. Marsh, W. J. Maeck, G. L. Booman, and J. E. Rein, "Solvent Extraction Method for Radiocerium", Anal. Chem. 34, 1406 (1962).

(20) J. J. McCown, R. P. Larsen, "Radiochemical Determination of Cerium by Liquid-Liquid Extraction", Anal. Chem. 32, 597 (1960).

2.3 Separation of the Lanthanide Group from Irradiated Plutonium (S. F. Marsh)

The heavier members of the lanthanide fission product group were separated from an irradiated Pu-239 sample for decay scheme studies by the Physics Section. The heavier lanthanides are produced in appreciably higher yield in the fission of Pu-239 than in U-235. Because some of the nuclides of interest have half lives on the order of hours, the procedure had to be rapid. It also had to adapt to remote operation, apply to plutonium fuel, and give a product free of yttrium and cerium (which were of no interest, but contributed most of the activity).

The aluminum-clad plutonium metal pellet was dissolved in a special extraction vessel (Figure III-2) with a calculated excess of aqua regia. Nitrite then was added to ensure complete oxidation of Pu(III) to Pu(IV) and the acid level was diluted to 1.5N for the initial extraction. Plutonium, zirconium, > 90% of the yttrium, and some iodine were separated from the lanthanides by an extraction into 1.5M di-(2-ethylhexyl)-phosphoric acid (D2EHP)-heptane. The organic phase was discarded and the aqueous phase was diluted five-fold with water to reduce the acidity to 0.3N. The lanthanides then were extracted into a fresh portion of 1.5M D2EHP-heptane, leaving behind the alkali metals, the alkaline earths, and most anionic species. The aqueous phase was discarded and, as the final step, the lanthanides were separated from cerium by a back extraction into 10N nitric acid-0.2M potassium bromate. Cerium, oxidized to the +4 oxidation state, remained in the organic phase as the strong D2EHP complex.

Manipulations were minimized by the use of a specially designed extraction system (Figure III-2). The extraction took place in the left tube. The application of reduced pressure to this tube regulated the rate of air bubbling through the solution, and therefore the degree of phase mixing. After the extraction, the unwanted phase was transferred to the right side tube by pressure from the syringe control. From this right tube, the unwanted phase was withdrawn and discarded. The capillary connection provided a precise separation of the two phases. After completion of the above separation procedure, the separated lanthanide fraction was transferred by vacuum to a clean sample bottle.

The individual lanthanides were chromatographically separated by Physics Section personnel by an α -hydroxyisobutyrate cation exchange procedure⁽²¹⁾. The decay scheme studies were reported to have been highly successful.

(21) L. Smith, D. C. Hoffman, J. Inorg. Nucl. Chem. 3, 243 (1956).

Figure III-2 Apparatus for Dissolution and Extraction of Lanthanide from Irradiated Plutonium

2.4 Separation of Lu-172 and Tm-172 from Adjacent Lanthanides (S. F. Marsh, B. A. Staples)

The two heavy lanthanide isotopes, 6.7-day Lu-172 and 64-hr Tm-172, were separated from target element and decay products for a study of their decay schemes by the Physics Section.

A cyclotron irradiation of enriched Yb-173 produced Lu-172 by: Yb-173 (p, 2n) Lu-172.

The Tm-172 was produced by double neutron capture on enriched Er-170 as follows:

The separations for both desired nuclides were by cation exchange chromatography with α -hydroxyisobutyric acid at controlled pH as the elutriant. The resin was Dowex 50 -X4, 325-400 mesh, in an 8-X 150-mm column. The Lu-172 was separated with pH 3.00 elutriant at a flow rate of 5 drops/min and the Tm-172 was separated with pH 3.10 elutriant at a flow rate of 6 drops/min. The separations required about 3 hr each. The separated activities were concentrated onto three to four cation exchange beads to serve as a point source for the decay scheme measurements.

A double separation procedure was required for the isolation of radiochemically pure Tm-172. After the irradiation, the sample was cooled for 50 hr during which time half of the Er-172 and 99% of the Er-171 decayed to their respective thulium daughters. The first separation then was performed and the unwanted Tm-171 fraction was discarded. After another 50 hr, a second separation yielded carrier-free Tm-172 essentially free of both Tm-171 and erbium nuclides.

2.5 Separations of Short-Lived Neutron-Deficient Isotopes (S. F. Marsh)

Assistance was given Physics Section personnel in the separation of short half-life, neutron-deficient isotopes formed by cyclotron irradiations at Boulder, Colorado. Various Calutron-enriched isotopes were bombarded with 12.5- to 28-Mev protons, and 40-Mev He^3 ions.

The experiments are summarized in the following table.

Table III-3

SUMMARY OF SEPARATION PROCEDURES

Target Material	Nuclear Reaction	Isotope Separated	Summary of Procedure
Sn-116	(p,n)	15-min Sb-116, 60-min Sb-116m	SnO ₂ target dissolved by Na ₂ O ₂ fusion. Take up melt in HCl. Selectively reduce Sb on surface of Fe metal.
Sn-117	(p,n)	2.8-hr Sb-117	
Sn-120	(p,2n)	38-hr Sb-119	
Sn-120	(p,3n)	5.1-hr Sb-118	
Sm-144	(p,n)	18-min Eu-144	Selective extraction of Eu into Li amalgam attempted (unsuccessful).
Er-166	(p,2n)	29-hr Tm-165	Separate by cation exchange, using ammonium α -hydroxyisobutyrate, pH 3.70.
Mo-97	(p,2n)	52-min Tc-96m	Dissolve MoO ₃ in NaOH. Scavenge with Fe(OH) ₃ . Ppt. tetraphenyl- arsonium pertechnetate, using perrhenate carrier.
Cu-63	(p,2n)	9.3-hr Zn-62	Adsorb Zn on anion exchange column from 1M HCl. Elute with 1M HNO ₃ .
Au-197	(p,3n)	9.5-hr Hg-195, 40-hr Hg-195m	Adsorb Au on anion column from 1M HCl. Hg is not adsorbed.
Cs-133	(He ³ ,n) (He ³ ,n)	20-hr La-135 4-hr La-133	Repeated La(OH) ₃ precipitations.
Zr-92	(He ³ ,n)	6.9-hr Mo-93m	Adsorb Mo on anion column from 4M HCl, Zr is not adsorbed. Elute Mo with 0.1M HCl.

2.6 Investigation of Yields of Some Radiochemical Methods (S. S. Yamamura, J. H. Sikes, G. J. Curtis)

Many radiochemical analytical methods rely on a gravimetric yield determination to translate the observed counting data into quantitative results. Because the reliability of the analytical results depend on the reliability of the observed yield, portions pertaining to the yield determination were investigated for a number of methods. Special attention was directed to the preparation and standardization of carrier solutions and the stoichiometry of the precipitate. The following are the most noteworthy observations and recommendations resulting from these studies:

1. For greatest reliability, the carrier spike should contain sufficient carrier to yield greater than 50 mg of precipitate. With 50 mg of precipitate, a weighing error of ± 0.5 mg causes only a 1% change in the calculated yield.
2. Cerous oxalate decahydrate loses weight continuously when stored in a vacuum desiccator containing Drierite (CaSO_4) desiccant. Recommended drying conditions are 5 to 10 min in a vacuum desiccator containing Drierite or 20 min in a vacuum desiccator without desiccant.
3. Cadmium is often standardized gravimetrically as $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ and strontium as $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The formulas of the precipitates are as shown, but the gravimetric standardization procedures are not always reliable.

The recommended standardization procedure for cadmium is direct EDTA replacement titrimetry per the following procedure: Add excess $\text{NaCeEDTA} \cdot 8\text{H}_2\text{O}$ and titrate with EDTA at pH 5.8-6.0 (pyridine buffer) to a xylenol orange end point⁽²²⁾.

Standard strontium carrier solution is best prepared by dissolving a weighed portion of anhydrous Reagent Grade strontium nitrate in water. The salt is converted to the anhydrous form at 110-200°C.

Apply the proper conversion factors to convert mg/ml cadmium to mg/ml $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ and mg/ml strontium to mg/ml $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

4. The formula $\text{K}_3\text{Co}(\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ is often assigned to potassium cobaltinitrite that has been dried at 110°C. The compound has been found to be the anhydrous salt, $\text{K}_3\text{Co}(\text{NO}_2)_6$.

(22) L. Meites, Handbook of Analytical Chemistry, McGraw-Hill, New York, 1963.

The use of an improper formula for potassium cobaltinitrite and the fact that two of four gravimetric standardization procedures were unsatisfactory suggest the need for re-emphasizing the importance of accurate standardization of carrier solutions and accurate yield determinations. The standardization procedure need not be the same procedure used for the analysis of samples, but it must accurately establish the actual concentration of the carrier solution. If the standardization procedure is a gravimetric one, the precipitation must be complete, and the stoichiometry of the precipitate must be well-defined to enable the use of a correct conversion factor. In the analysis itself, the precipitation need not be complete, but as in the standardization, the stoichiometry of the precipitate must be clearly defined and reproducible.

2.7 Revised Methods for the Determination of Beta Activity (D. M. Lund)

The two routine methods for the determination of gross beta activity of various CPP samples were revised to conform to latest laboratory practices. Method Act-1, Mod-2 is for low-level, waste samples. Method Act-2, Mod-1 is for high-level, process stream samples. Details of the two methods are presented in Appendix C.

3. ELECTROANALYTICAL STUDIES

3.1 Mathematical Analyses of Electrode Responses

The purposes of this project are to develop analysis methods based on electrochemical measurements and to develop a fundamental understanding of the electrochemistry of the species which are of direct concern to the atomic energy program. A detailed study of the electrochemistry of uranium is presently underway to obtain optimum measurement techniques, freedom from interferences, and the prediction of behavior in diverse chemical environments.

3.1.1 Second Order Reactions (D. T. Pence)

The following is an abstract of the paper published in Analytical Chemistry⁽²³⁾.

A generalized numerical method is presented for solving polarographic boundary value problems. Specific application is made to the interpretation of step-functional controlled-potential measurements of second-order homogeneous reactions following charge transfer. In this method the space and time co-ordinates are transformed into dimensionless parameters which automatically compensate for the time-dependent growth of the diffusion layer and permit the use of a logarithmic time scale. A numerical solution is obtained

(23) G. L. Booman, D. T. Pence, Anal. Chem. 37, 1366 (1965).

by solving simultaneously a series of finite-difference equations which describe the diffusion and kinetic processes for each normalized time increment. The method also is adaptable to first-order kinetic cases which have complex boundary value conditions and are difficult to solve analytically. An error analysis of the method is discussed.

3.1.2 Faradaic Current Considerations (G. L. Booman)

Mathematical relationships were derived to correct electrode response data for the changes caused by uncompensated cell resistance and finite double-layer capacity at the electrode surface. Expressions giving the potential-time function assuming immediate transition to the limiting current region and for the equivalent delay caused by the finite rise time of the potentiostat were presented in a published paper⁽²⁴⁾. This work also was extended to cases where both of these effects require simultaneous correction, and suitable equations were derived. Numerical evaluation will be required. The effects of a voltage dependent capacitance have not yet been included. Errors caused by the time constant of measurement circuits of the current follower type were evaluated both with and without zener diode limiting.

3.2 Uranium(V) Disproportionation Reaction in Perchloric Acid (D. T. Pence)

Work has continued on the investigation of the uranium(V) disproportionation reaction. To evaluate the effects of interfering anions in electroanalytical methods for uranium, the kinetics of the involved reactions must be understood. This requires studies of these reactions at short times. Because classical electrochemical methods are inadequate for a study of this nature, a controlled-potential electrochemical method using a step-potential pulse is being used. The electronic hardware necessary for this method is complete. A mathematical treatment was prepared and published⁽²⁵⁾ which is required for the interpretation of the experimental data. This treatment involves the numerical solution to the second-order differential equation describing the disproportionation of uranium(V).

During the past year, experimental data were collected concerning the uranium(V) disproportionation reaction in perchloric acid for various concentrations of uranium perchlorate. The calculated rate constants agree well with those obtained using slower methods. The experimental data are reliable to times as short as a few milliseconds without adjustment. However, the reliability of the data on the present instrument can be improved by a factor of 100 or more with respect to time by correcting for the following sources of error: the error in potential across the double-layer capacity because of the finite rise time of the potentiostat; the ohmic or IR losses because of the Faradaic and the

(24) G. L. Booman, W. B. Holbrook, Anal. Chem. 37, 795 (1965).

(25) G. L. Booman, D. T. Pence, Anal. Chem. 37, 1366 (1965).

double-layer charging currents; and, the error in current because of the current component necessary to charge the double-layer capacity. The theory has been developed to correct the error in potential across the double-layer capacity as a result of the finite rise time of the potentiostat and the ohmic losses because of Faradaic current. The theory for the error in the potential from the ohmic losses caused by the double-layer capacity charging current presently is being developed.

The precision of the experimental data using the controlled-potential apparatus with step-potential pulse and the data collection system is excellent---typically less than 1% relative standard deviation, and less than 0.2% under optimum conditions. The calculated rate constant for the disproportionation reaction of uranium(V) was 192 liter mole⁻²sec⁻¹ in 1M perchloric acid solutions and the diffusion coefficient was 7.1×10^{-6} cm²sec⁻¹ under the same conditions. These values have an estimated accuracy of $\pm 10\%$ and give a good fit to the model using second order kinetics in the rate determining step.

3.3 Controlled-Potential Coulometric Determination of Uranium (W. B. Holbrook, F. W. Dykes)

A new procedure reported last year⁽²⁶⁾ involved the reversed-phase chromatographic separation of uranium on a column of trioctylphosphine oxide (TOPO) coated on glass beads. Additional work was done to determine the effect of diverse ions. Matrices of type 304 stainless steel, and types 1100-S and 61-S aluminum alloys were without effect, as was concentrated nitric acid. The procedure requires about the same time as the method used previously⁽²⁷⁾, but may be advantageous in that a fusion step is eliminated and the number of volumetric transfer steps is reduced. This would be especially useful in automated procedures. Because of the urgency of other work, further development of this method has been postponed.

3.4 Instrument Design

3.4.1 Digital Timer and Waveform Generator (G. L. Booman)

A system of plug-in modules has been designed and constructed to give a flexible control of input signal waveforms and to generate crystal-controlled timing signals as required for the output data. Input functions such as pulse, square-wave, linear scan, linear scan and hold, stair-step, and bi-directional linear-scan waveforms can be scheduled by changing prewired plug-in boards. The basic waveform control element is a 0.01% precision, digital-to-analog converter module, with a rise time of less than 1 μ sec. Waveform generation is controlled by a buffer register, gating circuits,

(26) R. C. Shank and Staff, Annual Report of Division Analytical Branch for 1964, IDO-14655, Section IV (April 1965).

(27) G. L. Booman, W. B. Holbrook, Anal. Chem. **31**, 10 (1959).

and a two-decade reversible counter. The digital timing circuit can operate in exact logarithmic steps, with up to 25 points selectable for each time decade covered. With the high degree of flexibility given by the independent programming of input waveforms and output signal sampling schedules, electrochemical measurement techniques of a nearly unlimited spectrum can be quickly obtained. Use of this apparatus has not only overcome the need to photographically record the current-time electrode responses with the associated tedious reading, correcting for timing and amplitude nonlinearities; but has greatly improved the quality and precision of the data, through the ability to now collect data over four or more decades of time with a single transient experiment, thus ensuring data consistency without the uncertainties of varying electrode surface area or changes in surface conditions.

3.4.2 Transfer Function Analysis (G. L. Booman)

Simplified methods of circuit analysis were developed in cooperation with I. Shain (University of Wisconsin) and J. E. Harrar (Lawrence Radiation Laboratory). The following is an abstract of the paper published in *Analytical Chemistry*(28).

"The performance of operational amplifier instrumentation in controlled potential electrolysis experiments can be evaluated rapidly by a simplified transfer function analysis. The method provides explicit relations between the cell potential and the applied potential which clearly define the effectiveness of the compensation for IR drop in the cell and/or the current measuring device. The method is particularly useful in the evaluation of multi-amplifier circuits."

3.4.3 Electroanalytical Potentiostat Modification (J. P. Morgan)

The solid-state circuit described last year⁽²⁹⁾ was evaluated under experimental conditions with a passive electrical network used to represent the electrochemical cell impedance. By lowering the impedance level of the summing network, 90% rise times of 5 μ sec across the electrode double-layer capacitance could be obtained with passive elements representing a strongly acidic, aqueous electrolyte. The use of a recently available commercially current booster (Burr-Brown, Inc., Tucson, Model 1634-A) was found to give response times equivalent to the special circuit used earlier.

(28) I. Shain, J. E. Harrar, G. L. Booman, Anal. Chem. **37**, 1768 (1965).

(29) R. C. Shank and Staff, Annual Report of Division Analytical Branch for 1964, IDO-14655, Section IV (April 1965).

4. DEVELOPMENT IN SUPPORT OF LOFT PROGRAM

4.1 Gas-Particulate Sampler

The objective of this phase of the program is to test and, if necessary, to modify the LOFT gas-particulate sampler so that it performs its designated task. This task is to obtain representative fractions of the fission products in the containment shell atmosphere classified according to particulate matter, iodine activities differentiated by chemical species, and krypton-xenon. A total of 219 samplers are scheduled to be installed in the LOFT containment shell which will sample the atmosphere for up to 20-min periods on a preset time sequence, and then will be ejected and sent to the laboratory for fission product analysis.

The sampler basically consists of a hollow aluminum sphere which contains a cartridge filled with a series of filters and adsorbers. At a preset time, vacuum is applied to pull a sample of the containment atmosphere, sequentially, through the cartridge and hollow space. The proposed cartridge components are a filter for particulate matter and a series of selective adsorbers to discriminate between chemical species of iodine. These adsorbers are: silver-coated copper screens for readily adsorbed iodine species, charcoal paper for less readily adsorbed species, and granulated charcoal beds for such species as methyl iodide. The only fission products that should pass through the cartridge are krypton and xenon provided the sampling time is sufficient for these gases to attain sorption equilibrium on the cartridge components (mainly the charcoal beds).

Controlled experiments on a laboratory scale are underway to verify the predicted sorption properties of the various components of the cartridge for iodine species and for krypton-xenon under LOFT-simulated conditions. An overall performance test of the sampler is scheduled for next year in a fission product release facility, the Contamination Decontamination Experiment (CDE) to be operated under LOFT conditions.

4.1.1 Thermal Stability of Particulate Filter Materials (F. O. Cartan)

The last gas-particulate samplers will have remained in the containment shell for several days and may have been exposed to a peak temperature of $\sim 106^{\circ}\text{C}$. Hence, the cartridge components of the sampler must remain functional under these conditions.

Various particulate filter materials were tested for stability at temperatures of 105 and 145°C for 10-day periods. The results are summarized in Table III-4.

Table III-4

THERMAL STABILITY OF PARTICULATE FILTER MATERIALS

<u>Filter</u>	<u>10 days at 105°C</u>	<u>10 days at 145°C</u>
<u>Glass Fiber</u>		
Gelman A	no change	no change
Gelman E	no change	no change
<u>Fiber - Teflon</u>		
Fiberfilm	no change	no change
<u>Epoxy Membrane</u>		
Gelman Versapor	Discolored but functional	severely discolored but functional
<u>Asbestos-Cellulose</u>		
Hollingsworth-Vose HV-70	no change	discolored but functional
<u>Cellulose</u>		
Whatman 50	no change	discolored but functional
<u>Cellulose Membrane</u>		
Gelman α-6	no change	discolored but functional
<u>Cellulose triacetate Membrane</u>		
Gelman GA-6	no change	no change
<u>Vinyl Chloride Membrane</u>		
Gelman VM-6	discolored - melted at edge	
<u>Polystyrene Fiber</u>		
Microsorban	melted	

4.1.2 Iodine Retention of Particulate Filter Materials (F. O. Cartan)

In an ideal LOFT gas-particulate filter cartridge, the only iodine activity retained by the particulate filter should be that existing as or on particles. The retention of iodine in vapor form should be zero. Practically, however, all filter materials sorb some iodine vapor.

The retention of molecular iodine vapor at room temperature in a helium atmosphere and at 106°C in a steam-air atmosphere was measured for those particulate filter materials which were thermally stable (Section 4.1.1). Also tested in the steam-air atmosphere were charcoal-loaded filters and silver-plated copper screens. The results are summarized in Table III-5.

These studies will be continued with an evaluation of additional filter materials and sorbers and will be expanded to measure the sorption of other volatile iodine compounds such as hydriodic acid and methyl iodide.

Table III-5

RETENTION OF MOLECULAR IODINE ON FILTER MATERIALS AND SEVERAL IODINE-SPECIES ADSORBERS

Filter or Adsorber	Iodine Retention,	
	He at Room Temp	Steam-Air at 106°C
Fiberfilm (glass-Teflon)	Negligible	0.4
Gelman A (glass fiber)	1.0	0.7
Whatman 50 (cellulose paper)	1.0	---
HV-70 (asbestos-cellulose)	10	1.0, 1.2, 2.0 ^a
Gelman GA-6 (cellulose triacetate)	29	29
Gelman Versapor (epoxy)	91	99
Gelman AC-1 (charcoal-cellulose)	---	> 99
Whatman ACG/B (charcoal-glass fiber)	---	> 99
Silver-plated copper screens (four in series)	---	91

^a Three trials, each reported.

4.1.3 Sorption of Krypton, Xenon, and Iodine on Boron Nitride (F. O. Cartan, L. L. Dickerson)

Although activated charcoal is an effective sorber for iodine compounds, it also sorbs other vapor components expected in the LOFT atmosphere including water vapor, krypton, and xenon. A more specific sorber for iodine would simplify the analysis of the sampler components by gamma-ray spectrometry.

The structure of boron nitride is similar to that of graphite and its chemical and physical properties appear suitable for use as a sorbing medium. The sorption characteristics of krypton, xenon, and molecular iodine were measured for a batch of granular, -30+50 mesh, boron nitride which contained a small quantity of sodium silicate binder. The supplier of the boron nitride was Atlantic Equipment Engineers, Bergenfield, N.J.

For the measurement of krypton and xenon sorption, a gas chromatographic column of the material was prepared and gross retention times were measured. The column was 10 in. long, contained 1.1 g of the boron nitride, and was operated at room temperature. The retention times were 10.2 to 10.5 sec for krypton and 10.5 to 11.0 sec for xenon. The retention time for air was 10.2 to 10.5 sec; hence, neither krypton nor xenon were sorbed to any significant extent by boron nitride.

To measure the sorption of molecular iodine, 4 g of the boron nitride were loaded into 1-in. long cartridges, placed in a tube furnace, and streams of helium, air, and moist air, each containing tracers of I-131, were passed through. Downstream of the cartridges, activated charcoal cartridges were placed to trap the I-131 passing through the boron nitride. At room temperature, > 99% of the iodine was sorbed on the boron nitride both from dry air and helium. At 100°C, > 99% was sorbed both from helium and moist air. Unexpectedly, only 60 to 75% of the iodine was sorbed from dry air at 100°C. Purification of the air by passage through an activated charcoal trap before admission of the iodine increased the sorption to > 98%. A possible cause is an organic impurity in the air supply which reacted with the I-131 tracer to form a nonsorbing iodine compound. At higher temperatures, 220 to 240°C, the sorption of iodine was > 97% from all three atmospheres.

The strength of the sorption bonding was qualitatively measured by passing dry air and moist air at various temperatures through cartridges of boron nitride which previously had been loaded with small amounts of I-131 from helium flow-throughs. The flow rate of the two air streams was ~ 400-cc/min and the time of flow was 1 hr. Up to temperatures of 300°C, negligible amounts of iodine were desorbed. The sorbed iodine apparently is firmly bound to the boron nitride.

In one respect, boron nitride is superior to activated charcoal in that the sorptions of krypton and xenon are less. One disadvantage is the higher cost of the boron nitride, about \$0.50/g of powder compared to ~ \$0.001/g for activated charcoal.

A more thorough study of the sorptive properties of boron nitride for iodine species is planned.

4.2 Determination of Fission Products in LOFT Samples

Methods were developed for the separation of tellurium and iodine from other fission products applicable to young samples and for the determination of various fission products released during the meltdown of ~ 10-day cooled nuclear fuel. The latter method is applicable to various sample types including plateout coupons and reagents used for decontamination purposes.

4.2.1 Separation of Tellurium and Iodine from Other Fission Products (30) (Myra D. Anderson, T. R. Thomas)

To facilitate the measurement of biologically significant fission products in LOFT containment samples, a method was developed for the separation of tellurium and iodine from other fission products and from each other. After preliminary oxidation and reduction of iodine, tellurium is reduced to the metal and separated by filtration. Iodine is then absorbed as iodide by silver chloride. The tellurium metal and the silver iodide-silver chloride are dissolved separately, and the solutions are counted in a sodium iodide (thallium) well crystal. The procedure uses simple techniques and apparatus, and several samples can be processed concurrently. About 70 min are required to process one sample.

The determination of chemical yield is unnecessary, because quantitative separation and recovery of both tellurium and iodine are attained. Hydrazine hydrate completely reduces and precipitates tellurium, and digestion of the precipitate makes quantitative separation by filtration possible. Complete recovery of tellurium requires only the dissolution of the tellurium metal precipitate, and this is quickly accomplished by adding an acidified solution of hypochlorite. Preliminary oxidation and reduction assure complete exchange between radioactive and carrier iodine, and the difference in the solubilities of silver iodide and silver chloride assures complete absorption of the iodide. Quantitative recovery of the separated iodine is accomplished by dissolving all the silver chloride-silver iodide in a cyanide solution.

(30) Myra D. Anderson and T. R. Thomas, Separation of Tellurium and Iodine from Other Fission Products: Application to LOFT Samples, IDO-14664 (September, 1965).

The behavior of fission products other than tellurium and iodine was also studied. Other biologically significant fission products except ruthenium can be determined in the effluent solution from the tellurium and iodine separation, because they are not significantly retained by either the tellurium precipitate or the silver chloride. Ruthenium is significantly retained by the tellurium and variable amounts are lost, presumably by volatilization and plating out on apparatus; and therefore a separate aliquot of the initial sample will be used for the separation and determination of ruthenium. No isotopes which interfere in the determination of tellurium and iodine were observed to contaminate the tellurium and iodine fractions separated from a mixture of very young fission products.

Only one reagent, hydrofluoric acid, introduced in the tellurium and iodine separations seems likely to interfere in subsequent chemical separations of isotopes in the effluent solution. Masking the fluoride with aluminum may eliminate this interference. Conditions in the tellurium and iodine separation procedure were adjusted to avoid other interferences.

4.2.2 Determination of 10-Day Fission Products (S. F. Marsh, M. E. Kussy, W. J. Maeck)

A method was developed for the determination of various fission products released during the meltdown of ~ 10-day cooled nuclear fuel and collected on plateout coupons and other samples. In a series of sequential operations, separated fractions are produced that contain one or more fission products which are resolvable by simple gamma spectrum-stripping techniques.

The plateout coupons that can be handled are carbon steel and stainless steel; uncoated and coated with paint, plastic, and rubber materials. The method also is applicable to condensate solutions, acid mixtures and Turco solutions used for decontamination, and various filters used for the collection of particulate matter.

The major steps are: (1) digestion of samples in a specially designed all-glass reflux apparatus with a mixture of nitric, perchloric, and sulfuric acids, followed by hydrochloric acid; (2) distillation of iodine, ruthenium, and technetium into sodium hydroxide from which ruthenium is individually separated; and (3) treatment of the undistilled fraction with a series of sequential steps which gives separated fractions of barium, molybdenum, the lanthanides, and a final fraction of zirconium, niobium, and cesium. This procedure was not designed to produce highly pure fractions; rather it is a compromise between speed and purity. Therefore, gamma spectrometry is essential.

The method was successfully tested with gross fission products obtained by the dissolution of irradiated uranium samples. It also was used on plateout coupons and decontamination samples from the first melted fuel release test in the CDE Facility. Because only the more volatile fission products, mainly iodine with lesser amounts of tellurium, ruthenium, and technetium were released on this first test, the method was not used in its entirety. One unanswered question is whether refractory fission product oxides, especially the lanthanide oxides, will dissolve in the acid mixture used in the method.

Details of the method are given in Appendix C.

4.3 Dissolution of LOFT Fuel (M. A. Wade)

Methods are being investigated for the dissolution of melted LOFT fuel. In the LOFT test, the fuel is expected to melt and form a highly-refractory cermet of zircaloy-4, zirconia, and uranium. This melt will be very resistant to dissolution, much more so than unmelted fuel. The dissolution procedure adopted must satisfy the following requirements: (1) complete dissolution of the sample, (2) quantitative recovery of all fission products, including volatile iodine, ruthenium, krypton, and xenon, (3) use of techniques and equipment that are adaptable to remote operation, and (4) produce a final solution which is amenable to the desired radiochemical analyses.

A selected number of dissolutions, based on a literature survey, were experimentally evaluated on simulated LOFT melt-down fuel. The results of this study are summarized in Table III-6. Three methods appear promising: (1) dissolution with hydrofluoric acid with chromium(VI) added to solubilize uranium tetrafluoride, (2) fusion with potassium pyrosulfate, and (3) fusion with ammonium bifluoride, the latter two to be followed by dissolution of the melt in dilute hydrochloric acid. The hydrofluoric acid-chromium(VI) procedure is similar to a process developed by the Chemical and Process Development Branch for dissolution of PWR, UO_2 - ZrO_2 fuel (clad with zircaloy-4). These methods require the fabrication of special apparatus to withstand the highly corrosive nature of the reagents and to provide for the complete recovery of the fission products to be analyzed. Hydrofluoric acid dissolution requires either platinum, monel, or plastic equipment. Potassium pyrosulfate fusion can be done in quartz or platinum, and ammonium bifluoride fusion requires platinum.

A simulated LOFT fuel pin prepared by Battelle Northwest Laboratories was completely dissolved using the hydrofluoric-nitric-chromic acid system (Table III-6). This pin had been prepared by melting a zircaloy-2 clad, uranium dioxide pin supported on a uranium dioxide bed at 3000°C in an air atmosphere. The dissolution apparatus was a 250-ml Teflon FEP bottle attached to a water cooled polyethylene condenser.

Table III-6

DISSOLUTION OF FUSED UO_2 - ZrO_2 -ZIRCALOY-4 CERMET^a

Method of Dissolution	Comments
Liquid Systems	
2M HF-5M HNO_3	Zircaloy and UO_2 dissolved. A white residue of ZrO_2 remained.
22M HF-3M HNO_3 ^b followed by solid CrO_3	Complete dissolution of zircaloy and ZrO_2 . Green residue of UF_4 was dissolved by adding solid CrO_3 and heating.
Aqua Regia	UO_2 dissolves. No visible attack on zircaloy or ZrO_2 .
12M HCl	No visible effect.
HBr- CH_3OH	Rapid attack on zircaloy. No effect on ZrO_2 .
Fused Salt Systems	
$\text{K}_2\text{S}_2\text{O}_7$	Rapid and complete dissolution. Melt was dissolved in dilute HCl.
KF	Little effect, if any, on ZrO_2 .
KCl	No visible attack on zircaloy.
$\text{Na}_2\text{B}_4\text{O}_7$	Slow attack on zircaloy. Reaction eventually stops. Attacks quartz glass.
NH_4HF_2	Complete dissolution. The melt was dissolved in dilute HCl and the UF_4 was dissolved with Cr(VI).

^a Zircaloy-4 and UO_2 were fused in a carbon cup with a direct current arc which partially converted the Zr to ZrO_2 .

^b Nitric acid was added in the hope of dissolving the UF_4 .

5. REMOTELY OPERATED FACILITIES

5.1 Cell X Cave (F. W. Dykes)

The Model 7 manipulators used with the Cell X cave were equipped with pivot shield assemblies. These assemblies provide 4 in. of lead shielding for the manipulator openings on top of the cave. These openings previously were unshielded and created a high background in Cell X.

5.2 CPP Additional Alpha Handling Facility (F. W. Dykes)

This project, referred to in last year's report as the "Analytical Alpha Facility"⁽³¹⁾, was approved for construction by the AEC in March, 1965. The facility is similar to the Cell X installation in that it provides three glove boxes and a shielded cave connected as a single unit. In addition, a hood is connected to the last glove box. Thus, a facility is provided which is capable of efficiently handling samples of any activity level except high gamma activity. Completion of this project is being delayed by the long delivery time required for the shielded cave. Shipment of the cave is scheduled for March, 1966.

5.3 RAF Hot Cell (F. W. Dykes)

The Remote Analytical Facility (RAF) was designed to handle routine samples from the Idaho Chemical Processing Plant. The Analytical Chemistry Branch now receives many radioactive samples that are not of a routine nature. Most of these samples require special dissolution and processing steps that are difficult and sometimes hazardous to perform in the RAF. Inasmuch as the AEC has felt that there was not sufficient justification for a new facility for high level gamma activities, a proposal has been made to convert a portion of the RAF into a hot cell for nonroutine work.

The proposal provides a cell approximately 60-in. wide x 40-in. deep. An auxiliary area also is provided for unloading casks and handling transfers into and out of the cell. Two masterslave manipulators are provided for the cell and one for the auxiliary area. Shielding, equivalent to 8 in. of lead, is specified.

This proposal is awaiting action by the AEC.

(31) R. C. Shank and Staff, Annual Report of Division Analytical Branch for 1964, IDO-14655, Section V-1.1 (April, 1965).

6. BURNUP DETERMINATION OF NUCLEAR FUELS

The following are summaries published quarterly in Burnup Determination of Nuclear Fuels Project Report.

6.1 First Quarter

In this continuing program to develop methods for the accurate determination of the burnup of nuclear fuels, the main emphasis during January 1 to March 31⁽³²⁾ was the measurement of U-235 thermal fission yields for many stable and long-lived fission products. A capsule containing a weighed quantity of highly enriched U-235, irradiated to 11.5 atom percent fission, was dissolved and analyzed for the number of atoms of each uranium isotope and for the number of atoms of various stable and long-lived fission product nuclides. From these data, the capture-to-fission (α) and absolute fission yields were determined. The value for α_0 is 0.1716 ± 0.0019 . The fission yield values are:

<u>Mass</u> <u>Number</u>	<u>Element</u>	<u>Fission</u> <u>Yield</u>	<u>Mass</u> <u>Number</u>	<u>Element</u>	<u>Fission</u> <u>Yield</u>
83	Kr	0.496 ± 0.015	144	Ce	5.40 ± 0.07
84	Kr	0.453 ± 0.023	144	Nd+Ce	5.36 ± 0.06
85	Kr (10.8y)	0.270 ± 0.006	145	Nd	3.87 ± 0.06
86	Kr	1.84 ± 0.05	146	Nd	2.94 ± 0.03
131	Xe	2.90 ± 0.07	147	Sm	2.03 ± 0.05
132	Xe	4.22 ± 0.10	148	Nd	1.68 ± 0.02
134	Xe	7.74 ± 0.19	149	Sm	1.01 ± 0.01
137 (30.3y)	Cs	6.22 ± 0.14	150	Nd	0.63 ± 0.007
140	Ce	6.24 ± 0.07	151	Sm	0.398 ± 0.019
142	Ce	5.84 ± 0.07	152	Sm	0.236 ± 0.009
143	Nd	5.88 ± 0.07	154	Sm	0.050 ± 0.003
144	Nd	5.31 ± 0.06			

These values are tentative. Additional capsules will be similarly handled to produce refined data.

The conditions, established for the mass spectrometric analysis of krypton, xenon, and the lanthanides, to obtain the above fission yield data, are described. Also described is the preparation and standardization of the enriched isotope standard solutions that were used for the isotope dilution mass analysis of the lanthanides.

(32) W. J. Maeck, J. E. Rein, (eds.), "Burnup Determination of Nuclear Fuel", Project Report for the Quarter January 1 - March 31, 1965, IDO-14660 (June, 1965).

Separation methods were developed for the alkali metals, the alkaline earths, and ruthenium applicable to irradiated uranium and plutonium samples. These methods are designed for subsequent isotope dilution mass analysis to establish absolute fission yields. Also developed was a separation method for individual lanthanides, applicable to irradiated plutonium samples which will contain relatively high amounts of americium and curium.

6.2 Second Quarter

The main emphasis during April 1 to June 30⁽³³⁾ was the measurement of U-233 thermal fission yields for many stable and long-lived fission products. A capsule containing a weighed quantity of highly enriched U-233, irradiated to 11.4 atom percent fission, was dissolved and analyzed for the number of atoms of each uranium isotope and for the number of atoms of various stable and long-lived fission product nuclides. From these data the capture-to-fission ratio (α) and absolute fission yields were determined. The value for α_0 is 0.0986 ± 0.0015 . The fission yield values are:

<u>Mass Number</u>	<u>Element</u>	<u>Fission Yield</u>	<u>Mass Number</u>	<u>Element</u>	<u>Fission Yield</u>
83	Kr	1.02 ± 0.02	144	Ce	4.63 ± 0.08
84	Kr	1.68 ± 0.04	144	Nd+Ce	4.69 ± 0.08
85 (10.76y)	Kr	0.497 ± 0.011	145	Nd	3.40 ± 0.06
86	Kr	2.81 ± 0.06	146	Nd	2.54 ± 0.04
131	Xe	3.56 ± 0.07	147	Sm	1.82 ± 0.06
132	Xe	4.86 ± 0.10	148	Nd	1.31 ± 0.02
134	Xe	6.10 ± 0.13	149	Sm	0.751 ± 0.013
137 (30.3y)	Cs	6.69 ± 0.17	150	Nd	0.498 ± 0.008
140	Ce	6.54 ± 0.10	151	Sm	0.364 ± 0.012
142	Ce	6.66 ± 0.11	152	Sm	0.193 ± 0.007
143	Nd	5.87 ± 0.10	154	Sm	0.020 ± 0.006
144	Nd	4.74 ± 0.09			

These values are tentative. Additional capsules will be similarly handled to produce refined data.

6.3 Third Quarter

The main emphasis during July 1 to September 30⁽³⁴⁾ was additional measurements of U-235 and U-233 thermal fission yields from the second irradiated capsules of U-235 and U-233. Two capsules, one containing a weighed quantity of highly enriched U-233, and the

(33) W. J. Maeck, J. E. Rein, (eds.), "Burnup Determination of Nuclear Fuel", Project Report for the Quarter April 1 - June 30, 1965, IDO-14663 (September, 1965).

(34) W. J. Maeck, J. E. Rein, (eds.), "Burnup Determination of Nuclear Fuel", Project Report for the Quarter July 1 - September 30, 1965, IDO-14667 (December, 1965).

other highly enriched U-235, both irradiated to ~ 12 atom percent fission, were dissolved and analyzed for the number of atoms of each uranium isotope and for the number of atoms of the various stable and long-lived fission product nuclides. The absolute fission yield values determined on the second U-233 capsule are given below. Also reported is the weighted average of the absolute U-235 fission yields determined on the first and second U-235 capsules.

Mass Number	Element	Fission Yield %	
		U-233	U-235
83	Kr	0.985±0.024	0.497±0.009
84	Kr	1.63±0.04	0.920±0.016
85(10.76y)	Kr	0.484±0.012	0.265±0.004
86	Kr	2.74±0.07	1.81±0.03
131	Xe	3.44±0.09	2.84±0.05
132	Xe	4.71±0.12	4.24±0.08
134	Xe	5.93±0.15	7.62±0.15
137(30.3y)	Cs	6.60±0.17	6.21±0.10
140	Ce	6.30±0.13	6.30±0.06
142	Ce	6.35±0.14	5.87±0.05
143	Nd	5.57±0.12	5.89±0.06
144	Nd	4.48±0.09	5.36±0.05
144	Ce	4.46±0.13	5.40±0.05
144	Nd+Ce	4.48±0.09	5.40±0.05
145	Nd	3.22±0.06	3.88±0.04
146	Nd	2.41±0.04	2.95±0.02
147	Sm	1.78±0.07	2.13±0.05
148	Nd	1.25±0.02	1.68±0.02
149	Sm	0.710±0.013	1.00±0.01
150	Nd	0.471±0.009	0.630±0.006
151	Sm	0.363±0.019	0.431±0.016
152	Sm	0.166±0.006	0.226±0.005
154	Sm	0.024±0.005	0.056±0.001

In addition the values for the thermal capture-to-fission ratio (α) of U-233 and U-235 were determined. These values are:

U-233; 0.0942±0.0016
U-235; 0.1715±0.0024

All of the above values are tentative and as additional capsules are analyzed, refined data will be reported.

6.4 Fourth Quarter

The main emphasis during October 1 to December 31⁽³⁵⁾ was the development of an isotope dilution, mass spectrometric analysis method for ruthenium, and the determination of the absolute thermal fission yields of stable and long-lived isotopes of ruthenium for U-233 and U-235. The average values, determined on two each of dissolved, standard U-233 and U-235 burnup capsules, are:

<u>Isotope</u>	<u>Fission Yield, %</u>	
	<u>U-233</u>	<u>U-235</u>
Ru-101	3.19±0.06	5.03±0.06
Ru-102	2.40±0.04	4.18±0.05
Ru-104	0.998±0.019	1.81±0.02
Ru-106	0.255±0.006	0.385±0.007

These values are tentative. As additional capsules are analyzed, refined data will be reported.

(35) W. J. Maeck, R. M. Abernathey, J. E. Rein, (eds.), "Burnup Determination of Nuclear Fuel", Project Report for the Quarter October 1 - December 31, 1965, IDO-14676 (May, 1966).

IV. SPECTROSCOPY

1. SPECTROCHEMICAL ANALYSIS

1.1 Determination of Iridium in Aluminum (T. R. Lyon)

Three segments of aluminum wire were submitted for the determination of iridium. Preliminary studies showed that direct excitation of the samples was preferable over any involving dissolution of the sample. Synthetic standards were prepared by mixing aluminum and iridium powders. These standards and thin segments of the samples were both mixed with graphite and excited using D. C. arc. Replicate results of this method showed a coefficient of variation of 3.5%, but the results were higher than expected. In order to avoid any bias due to matrix effects, osmium was added as an internal standard, and both standards and samples were re-run after a potassium pyrosulfate-potassium chloride fusion. The fusion melt was ground to a fine powder and arced. This procedure confirmed the results of the direct method.

1.2 Determination of Boron in Thorium (T. R. Lyon)

Solutions of thorium alloyed with gold and boron were analyzed spectrochemically for boron using the rotating disk technique. Preliminary study showed that there was residual throrium interference even when second order dispersion was used. In order to avoid dilution of boron in the sample and to compensate for throrium interference, a separate working curve was established for three different concentrations of throrium. Standards for boron, over the range from 10- to 80- $\mu\text{g}/\text{ml}$ were prepared by adding boron to aliquots of solutions which contained only thorium and gold. The coefficients of variation for the five samples averaged 4.5%.

1.3 Separation and Determination of Sm-151 in CPP Feed Solutions (B. A. Staples, S. F. Marsh, G. D. Workman)

To evaluate the economics of a process for the separation of 90-yr Sm-151 from CPP waste tanks, an estimate of the amount present was needed. Because sampling of the waste tanks is difficult, the plant process streams which flow into the tanks were analyzed.

Samarium-151, with no high energy gamma or beta energies, is difficult to detect by counting techniques. The samarium concentration therefore was measured by isotope dilution mass spectrometry following chemical separation, based on a method previously developed in this laboratory^(36,37). The spike was Sm-144.

(36) W. J. Maeck and J. E. Rein, "Burnup Determination of Nuclear Fuels," Project Report for the Quarter January 1-March 31, 1965, IDO-14660 (June 1965).

(37) W. J. Maeck and J. E. Rein, "Burnup Determination of Nuclear Fuels," 1964 Annual Report, IDO-14656 (May 1965).

2. IMPROVED EQUIPMENT AND METHODS

2.1 Installation of Ion Pumps on MA 30 and MA 31 Mass Spectrometers (A. H. Toepfer, R. A. Nielsen, R. M. Abernathey)

The two single filament surface ionization mass spectrometers were altered to use high vacuum ion pumps to provide better vacuum conditions in the ion sources and analyzer tubes. Since these pumps do not require cold traps, the use liquid nitrogen was reduced. One high vacuum mercury diffusion pump and cold trap remains on the third stage of each vacuum lock.

One 100-liter/sec Ultek pump was installed on a short 30 degree bend adapter to the source block flange surface and one 50-liter/sec Ultak pump was installed on the analyzer pump lead.

For ion pump start-ups a high vacuum valve was welded to the original source pumping lead and connection made to a vacuum roughing pump. Similarly a connection was made through the analyzer pump flange, also equipped with a valve, to the same roughing pump. One common power supply for two ion pumps was installed in the control console of each instrument.

Prior to the installation, two mercury diffusion pumps with cold traps, two ion gauges and controls, and the Dewar flask elevator were removed from each mass spectrometer. Laboratory platform jacks were used to support the Dewar flasks used with each remaining cold trap. To prevent distortion and misalignment of the sources and analyzer tubes, mechanical support was provided for the ion pumps. Each source pump rests on a single ball bearing in the center of a steel base plate and the analyzer pumps hang from supports on the third stage manifolds.

The performance of the mass spectrometers has been improved. Because pressures in the 10^{-6} - and 10^{-7} -torr range are achieved, the peak shapes are better. Resolution is improved sufficiently to practically eliminate base line problems, resulting in better data. The better vacuum has reduced the occurrence of high voltage arcing and consequent damage to the power supplies. The operating cost has been reduced because the liquid nitrogen demand has been reduced to one-third of the former demand. The pump performance record is very satisfactory.

2.2 Installation of Microfocus X-ray Diffraction Unit (W. A. Ryder)

A Jarrell-Ash microfocus X-ray diffraction unit was received and installed. Slight modifications were made to the vacuum system to improve performance. This instrument can analyze areas down to 10 μ diameter. The determination of the lattice constants of irradiated beryllium and the identification of micro-sized areas on samples from the reactor fuel development program are the first studies to be undertaken with this unit.

2.3 Detection of Hydrocarbons in Reactor Containment Buildings (L. L. Dickerson)

As requested by LOFT administrators, a flame ionization instrument was purchased to measure the organic concentration in the EBR-II and LOFT containment building atmospheres. The instrument acquired was a Perkin-Elmer Model 213B Hydrocarbon Detector.

On April 6, 1965, the instrument was used to survey the atmosphere of the EBR-II reactor containment building for organic materials. Five sample points on the main floor of the containment shell were sampled. The locations were chosen as ones which might be expected to contain organic vapors. At all five locations there was less organic material detected by the instrument than from a Matheson standard gas certified as less than 2-ppm methane equivalents.

2.4 Conversion of CEC Vacuum System (L. L. Dickerson, R. M. Abernathey)

An all metal exhaust vacuum pump which uses polyphenyl ether as a pump fluid was installed on the CEC mass spectrometer. Installation of the pump required that the magnet poles be shifted 15 degrees clockwise to provide correct alignment with the exhaust port of the analyzer tube. The vapor pressure of polyphenyl ether is so low that a dry ice trap is no longer required in the exhaust system. Some advantages of the new pump are a higher and more uniform pumping speed and the elimination of a background problem with xenon.

2.5 Restoration of Spectrograph for SNAP Test (T. R. Lyon)

The Bausch and Lomb, dual-grating spectrograph located at Test Area North (TAN) was restored to operating condition for the SNAP Destruct Test. This spectrograph was part of the equipment in an unused laboratory in a building adjacent to the area used for that test. Nearness of the laboratory to the test site reduced transportation time considerably and speeded analysis of monitor samples.

The optical bench of the spectrograph was re-assembled and aligned, a faulty jog switch in the control panel was replaced, and the source unit was repaired and checked-out. The excitation cage was adapted for the rotating platform technique, and a calibration for routine analysis of beryllium filters and fall-out plates was completed. Photographic plate processing equipment was collected and installed in suitable darkroom facilities.

2.6 Analysis of Deliquescent and Pyrophoric Samples by X-ray Diffractometry (E. S. Bell, W. A. Ryder)

A modified sample holder and a new loading procedure were developed so that X-ray diffractometry could be used for analysis of deliquescent and pyrophoric samples. Previously, samples were loaded into thin walled capillary tubes in an inert atmosphere and the X-ray patterns obtained with Debye-Scherrer cameras.

A standard Norelco X-ray diffractometer sample holder was modified by covering the sample chamber with a rubber hydrochloride or "Surlyn" A ionomer resin window to prevent sample contact with the room atmosphere. Samples are ground, poured into the holder through a slot cut in the side of the holder, and sealed while in a dry argon atmosphere in an inflatable plastic glove box.

2.7 Silver Spark-Rotating Platform Technique for Spectrochemical Determination of Rare Earths (T. R. Lyon)

A silver-spark rotating-platform technique was adapted for the analysis of rare earth elements directly, either as a solution or as a solid after co-precipitation with a carrier. Platform electrodes were found to be more convenient and adaptable than conventional rods, and silver was shown to have some advantage over copper as an electrode material. Conditions pertaining to the preparation and excitation of samples were studied and reported at the Fourth National Meeting of the Society for Applied Spectroscopy. Interelemental effects were investigated, both for rare earths in a mixed rare earth matrix and for the effects of a "pure" rare earth matrix on rare earth impurities. The sensitivity of the method was shown to be comparable to the copper spark method for small samples, and while the sensitivity decreased with larger samples, good sensitivity was attained by proper selection of conditions and equipment.

2.8 Installation of Vacuum Lock on Tandem Mass Spectrometer (R. M. Abernathey, A. H. Toepfer, R. E. McAtee, G. D. Workman)

The bolted flange ion source on Mass Spectrometer TDD-1 was replaced with a Nuclide vacuum lock to reduce the time required to change samples. The result has about doubled output and improved operation. The lock requires about 5 min to change samples and produce operating vacuum in the range of 10^{-7} torr for a total of about 1 hr per sample. The original system required about 15 min to change samples and 1 hr to produce a marginal vacuum for a total of about two and one-quarter hours per sample. Ultimate vacuum is at least an order of magnitude better than before. The better vacuum improves resolution by reducing beam scattering and has reduced high-voltage arcing. Mechanical functioning has been very satisfactory.

V. CHEMICAL ANALYSIS

1. MANPOWER REQUIREMENTS FOR DIFFERENT ANALYSES

Table V-1 shows some of the general methods and average time required for analysis. These methods are used in the Chemical Analysis Section and time per analysis was obtained from total analysis and total hours accumulated from 1965 daily time records. The time per analysis applies only if three or more samples are analyzed for the same constituent at the same time. Time per single determination would be higher.

Table V-1

1965 ANALYTICAL METHODS AND TIME REQUIRED FOR ANALYSIS

<u>Method</u>	<u>Hours</u>
Acid, oxalate, pH titrimetric	0.30
Acid, oxalate, pH titrimetric (a)	0.33
Acid, simple volumetric	0.25
Aluminum, fluoride complexing, titrimetric	0.47
Biochemical oxygen demand	0.30
Boron, mannitol titrimetric	0.50
Boron, flame photometric	0.24
Carbonate, titrimetric	0.30
Cerium, radiochemical	2.00
Cesium, radiochemical	2.00
Chromium, diphenyl carbizide, colorimetric	0.50
Chromium, redox, titrimetric	0.58
Density, particle, mercury displacement	0.67
Density, absolute, helium displacement	0.33
Dibutylphosphate, colorimetric	0.83
Fluoride, macro, cerium trifluoride, titrimetric	1.00

Table V-1 Continued

Method	Hours
Fluoride, micro, distillation, colorimetric	0.83
Gamma, spectral	1.33
Gross activity	0.67
Iodine, radiochemical	0.67
Iron, column extraction, or the phenanthroline, colorimetric	0.33
Iron, column extraction, EDTA, complexometric	0.75
Mercury, dithizone, colorimetric	0.55
Mercury, Thiocyanate, titrimetric	0.25
Nickel, dimethylglyoxime, colorimetric	0.53
Nickel, dimethylglyoxime, precipitation, EDTA titration	0.75
Nitrate, Devarda alloy reduction, distillation, titrimetric	0.50
Nitrate, phenaldisulphonic acid, colorimetric	0.75
Ruthenium, radiochemical	2.33
Solids, undissolved, by filtration	0.83
Solids, total	0.42
Specific gravity, falling drop ^(a)	0.42
Specific gravity, Westphal balance	0.30
Strontium, radiochemical	2.00
Tributylphosphate, acid saturation, titrimetric	0.42
Uranium, extraction, spectrophotometric	0.47
Uranium, extraction, fluorophotometric	0.40
Uranium, extraction, fluorophotometric ^(a)	0.47
Uranium, mass isotopic distribution ^(b)	0.50
Uranium, mass isotopic distribution ^(a,b)	0.75

Table V-1 Continued

<u>Method</u>	<u>Hours</u>
Uranium, gravimetric	1.00
Zirconium, cupferron, amperometric	0.75

- (a) Method performed in Remote Analytical Facilities.
- (b) Separation of uranium by solvent extraction before mass assay.

2. ANALYTICAL SERVICES

2.1 Health and Safety Branch

2.1.1 Analysis of Polystyrene Filters for Selenium (I. L. Doggett)

Selenium on polystyrene filters, was determined colorimetrically by method Se-1, the Colorimetric Determination of Selenium. Details of this procedure are described in Appendix B.

2.2 Nuclear Safety Research Branch

2.2.2 Dissolution of Ternary Fuels (calcium, uranium, and zirconium oxides) (R. C. Girton, J. G. Scott)

Power Burst Fuel Engineering personnel requested dissolution of a sample containing oxides of calcium, uranium, and zirconium. Two 4 g pieces of unirradiated ternary fuel were used for the dissolution study. Usually this type of material is dissolved in various acid mixtures or in an acid solution using a sealed tube under pressure. An acid mixture dissolution was used.

One of the pieces was finely ground and added to 15 ml of a 6M nitric acid-0.005M mercuric nitrate solution. After the reaction subsided, 1 ml of concentrated hydrochloric acid and 5 ml of concentrated hydrofluoric acid were added. After this reaction stopped, the solution was decanted into a beaker and 10 ml of a 2:1 solution of sulfuric acid-hydrofluoric acid was added to the residue. The resulting solution was decanted and added to the first solution. Ten milliliters of a 2:1:1 sulfuric acid-hydrofluoric acid-aqua regia solution was added to the remaining residue, and complete dissolution was accomplished. The combined solutions were evaporated to sulfur trioxide fumes, and salts which precipitated during the evaporation process were dissolved by diluting the sample to 500 ml with water.

The dissolution time of the finely ground sample was 6-9 hr. The second sample was dissolved without grinding and dissolution time increased three-fold.

2.3 Nuclear Technology Branch

2.3.1 Analysis of Irradiated Thorium Samples (E. M. Fortsch, S. S. Yamamura, W. A. Mickelson, J. P. Clark)

During the past year several irradiated thorium and aluminum-clad thorium samples were dissolved and analyzed for aluminum, thorium, uranium, and Cs-137. Because of the large sample size and high radiation, several of the samples were dissolved in the Multicurie Cell. The remaining samples were dissolved in the Remote Analytical Facility. The methods used for dissolving the samples and determining the thorium and aluminum are described in Appendix B, Method Th-2, tentative. The uranium was determined by the isotopic dilution mass spectrometric procedure after ion-exchange separation as the chloride complex on Dowex 1-X8 and the Cs-137 was determined radiochemically.

2.4 Reactor Engineering Branch

2.4.1 Determination of Copper and Aluminum in Copper-Aluminum Alloys (E. M. Fortsch, S. S. Yamamura)

Copper and aluminum were determined in copper-aluminum alloy samples containing 6- to 40-% copper. The analyses were done chelometrically with EDTA after sample dissolution in a nitric-hydrochloric acid medium.

The sum of aluminum plus copper was determined by adding an excess of standard EDTA and back titrating with standard zinc. The copper was determined directly on a separate aliquot with EDTA after fluoride masking of the aluminum and the aluminum was calculated by difference. Both titrations were carried out at pH 5.5 using snazoxs indicator.

3. IMPROVEMENTS IN METHODS AND EQUIPMENT

3.1 Colorimetric Determination of Iodine (I. L. Doggett, J. G. Scott)

Iodide present in aqueous samples is oxidized to iodine with sodium nitrite in an acid medium. Sulfamic acid then is added to destroy any excess nitrite and the iodine is extracted into carbon tetrachloride. Potassium iodide and alcohol are added to the carbon tetrachloride to form the highly colored I_3^- species which is measured spectrophotometrically by comparison to standards. Details of this procedure are described in Appendix B, Method I-2.

3.2 Determination of Strontium in Stainless Steel (J. R. Fischer, J. G. Scott)

The large amount of precipitate formed from stainless steel components, when strontium is precipitated with sodium carbonate, interferes with strontium as the oxalate from a weak acid solution.

After addition of carrier to the sample, solid sodium acetate is added until the pH is approximately 4.5. An excess of saturated ammonium oxalate is added to the hot solution to precipitate strontium oxalate. After cooling, the sample is centrifuged, decanted and the precipitate dissolved with a minimum quantity of 6M nitric acid. The analysis can then proceed as described in Strontium Method, Sr-1(38) for radiochemical strontium separation.

3.3 Simultaneous Determination of Xe-133m and Xe-135 (A. C. Hill, J. G. Scott)

A method was developed for measuring the amount of 2.3-day Xe-133m and 9.2-hr Xe-135 without waiting for the decay of the Xe-135. Resolution is not good enough to separate the 0.23- and 0.25-Mev peaks of the two isotopes with a 3-x3-in. sodium iodide (thallium) crystal and a gain setting of 10-kev per channel, therefore, the area of the combined peaks is measured at two different times, 18 to 24 hr apart. By setting up decay equations for the two areas and solving these equations simultaneously, the concentrations of the two isotopes can be obtained.

Example:

Measurement of 2.3-day Xe-133m and 9.2-hr Xe-135 after 24 hr decay period, using simultaneous equations:

$$X = \text{Xe-133m}$$

$$Y = \text{Xe-135}$$

$$3031 = \text{number counts/min at time of first counting.}$$

$$929 = \text{number counts/min at time of second counting 24 hr later.}$$

$$\text{Decay of Xe-133} \quad \frac{1 \text{ day}}{2.3 \text{ day}} = 0.435 = 0.740 \text{ fraction remaining after } 24 \text{ hr.}$$

$$\text{Decay of Xe-135} \quad \frac{24 \text{ hr}}{9.2 \text{ hr}} = 2.61 = 0.165 \text{ fraction remaining after } 24 \text{ hr.}$$

(38) D. G. Olson, (ed.), Manual of Radiochemical Methods, IDO-14613, (January 1964).

$$X + Y = 3031$$

$$0.74 X + 0.165 Y = 929$$

$$0.575 Y = 1314$$

$Y = 2285$ = number of counts/min of Xe-135.

$X = 746$ = number of counts/min of Xe-133m in 0.23 and 0.25 energy peak at time of first counting.

This method can be applied to any combined peaks if the contributing isotopes are known. It is necessary, however, to have as many peak area measurements and decay equations as there are contributing isotopes.

3.4 Iodine Loss in Polypropylene Dissolvers (D. E. Filion, J. G. Scott)

Polypropylene dissolvers, used for dissolving irradiated fuel samples, were tested to determine the amount of iodine lost by plateout during dissolution. Six tests were made using I-131 tracer and less than one gram samples of cold zircaloy-uranium dioxide. Additional tracers of Cs-137, Ce-144, Ru-106 and Sr-90 were added to two of the tests. Carrier solutions were also added to the dissolver before dissolution. The polypropylene dissolver bottles were sealed by filling the sealing groove on the cap with silicone grease. A polypropylene reflux tube was connected to three wash solutions (water, 6M sodium hydroxide, and 0.1M sodium thiosulfate). No activity was found beyond the water wash.

A solution of concentrated nitric acid and concentrated hydrofluoric acid in a 1:2 ratio was used to dissolve the fuel. The dissolver was heated in a water bath to sustain the reaction and dissolution time was approximately 3.5 hr. The physical appearance of the dissolver was unchanged. Analysis of the dissolver solution, the three wash solutions, and sodium hydroxide and sodium thiosulfate rinses of the dissolver indicate a significant amount of radioactive iodine is retained by the dissolver unless a large carrier addition is made prior to dissolution. Gamma scans of the dissolvers also indicated high retention levels of iodine.

The mechanism of iodine retention on polypropylene has not been studied. Table V-2 summarizes the information obtained from this study.

Table V-2

IODINE LOSS IN POLYPROPYLENE DISSOLVERS

	Isotope Added	Amount of Cold Carrier Added, mg	Concentration of Added Isotope d/m	% Recovery
Test 1	I-131	40	2.00×10^6	91.1
Test 2	I-131	40	2.00×10^6	91.5
Test 3	I-131	4	2.00×10^6	66.5
Test 4	I-131	4	2.00×10^6	57.5
Test 5	I-131	4	1.00×10^6	75.5
	Cs-137	3.4	2.11×10^5	101
	Ce-144	5.2	3.20×10^6	102
	Ru-106	0.2	2.12×10^7	80
	Sr-90	4.4	1.50×10^4	98
Test 6	I-131	4	2.00×10^6	75.6
	Cs-137	3.4	2.11×10^5	88
	Ce-144	5.2	3.20×10^6	92
	Ru-106	0.4	2.12×10^7	84
	Sr-90	4.4	1.50×10^4	96

3.5 Determination of Inorganic Nitrate and Ammonia (H. A. Shogren)

The Kjeldahl procedure for nitrate and ammonia was modified to permit the direct titration of ammonia after its collection in boric acid. In the old procedure the ammonia was collected in an excess of standard acid and then back titrated with standard base. A mixed indicator of methyl red-bromocresol green is used which gives a sharper end point than the previously used methyl red indicator. This change has improved the accuracy of the method. Details of this procedure are described in Appendix B, Method NO₃-1, Mod-4.

3.6 High Activity Gamma Spectrometry (A. C. Hill, C. M. Wilcox, J. G. Scott)

A non-destructive gamma scan analysis of highly radioactive samples requires reducing the activity at the detector to reasonable levels for

measurement. This reduction can be accomplished by using an absorbing material or by increasing the distance between the source and the detector.

Approximately 38% of the original activity from a 0.662-Mev Cs-137 source containing 3.5×10^6 d/m (15 mr/hr) was detected using a 2-x3.25-x0.5-in. lead absorber with 1/4-in. hole drilled in the center. A lead absorber of the same dimensions, without the center hole, passed 23% of the original activity to the detector. These measurements were made at 10 cm with the source placed on top of the lead. The distortion of the spectrum with lead absorbers is prominent in the low energy range since the lead X-ray peak is present.

The effect of increased distance was measured by placing a Cs-137 source at 3 and 30.5 cm from the detector. At 30.5 cm, the counting rate was 2.8% of the rate at 3 cm. Unistrut channels with movable sample holders have been installed over the detector barricades, to permit raising the sample holders to a maximum distance of 9.5 ft above the detectors.

The study indicates the best spectrum is obtained by increasing the distance from the detector rather than using absorbers. If the activity of the sample must be shielded, a small unobstructed portion of the sample should be directed toward the detector.

3.7 Purification of Mercury (H. A. Shogren)

A simple procedure for purifying mercury developed by D. A. Cochran⁽³⁹⁾ was found to be satisfactory for general laboratory use.

The mercury is purified by counter-current washing with a dilute nitric acid-mercuric nitrate solution in a 3-ft column packed with Raschig rings. The Raschig rings break up the mercury into fine particles thus increasing the surface area exposed to the cleaning solution. Mercury purified by this procedure tested less than 1 ppm of impurities using an emulsification test described by O. H. Muller⁽⁴⁰⁾. Emission spectrographic analysis also showed the mercury to be equivalent to triple distilled mercury.

3.8 Improvements in the Waste Disposal System (Remote Analytical Facility) (G. A. Huff, F. W. Dykes, H. A. Shogren)

The procedure for packaging and removing radioactive solid waste from the Remote Analytical Facility has been improved. The material is sealed in metal cans and transported to the waste end where the cans are remotely handled and dropped through a chute in the shielding wall

(39) D. A. Cochran; General Electric Co., Richland, Document HW-84509 (1964).

(40) O. E. Muller, Chem. Eng. News, 20, 1528 (1942).

into a plastic bag. The bag is boxed and transferred to a dumpster for removal to the burial ground. As a result of this improvement personnel exposure to radiation and area contamination has been reduced.

3.9 New Design of Castle Manipulators Bellows (E. M. Fortsch)

The Remote Analytical Facility Castle Manipulator bellows were redesigned to obtain: (1) better movement of the manipulators, (2) better visibility and (3) longer wear. The new bellows are made from a neoprene impregnated nylon material instead of neoprene dipped canvas and are manufactured locally at a substantial reduction of cost. Assembly and details of the bellows are given in drawing number CPP-E-3957, "Castle Manipulator Bellows Seal Assembly and Details".

VI. STANDARDS AND QUALITY CONTROL

1. UMPIRE QUALIFICATION PROGRAM

(S. S. Yamamura, D. M. Lund, J. E. Rein)

Many private U. S. companies and foreign concerns are entering the atomic energy industry. As a result, the AEC will be transacting an increasing number of sales, leases, and purchases of fissionable material outside the AEC complex. The basis of the monetary payments or credits is the quantity and quality of the materials involved as established by analysis. Based on past experience, there will be inevitable differences and, hence, disputes between the AEC and other parties. Such disputes are best resolved by neutral umpire laboratories. To establish competent umpire laboratories, the Division of Nuclear Materials Management (DNMM) of the AEC in April, 1965, contracted the Atomic Energy Division of Phillips Petroleum Company to administer an Umpire Qualification Program⁽⁴¹⁾ in cooperation with the Oak Ridge Gaseous Diffusion Plant (K-25), the Paducah Gaseous Plant (PAD), New Brunswick Laboratory (NBL), Goodyear Atomic Corporation (GAT), Isochem, Rocky Flats (RF), and the Los Alamos Scientific Laboratory (LASL).

1.1 Umpire Service Needed

The types of materials which are currently being transferred within the AEC complex and which can be expected to be exchanged between the AEC and other parties include: uranium hexafluoride, uranyl nitrate (solution and crystal), uranium oxides (U_3O_8 , UO_2 , and UO_3), uranium metal, plutonium nitrate solution, plutonium dioxide, and plutonium metal. Of these, uranium hexafluoride, uranyl nitrate, and plutonium nitrate solution will be exchanged most frequently and highest priority has been assigned to them. The specifications of interest are various physical properties, impurities including nonradioactive metallic and nonmetallic elements, fission products, and certain actinide nuclides; and most important, concentration and isotopic assay of uranium and plutonium. Laboratories will be qualified on the basis of the results of actual analyses of specially prepared standards.

1.2 Implementation of Program

The program is being implemented as follows:

- Phase 1:
- a. Review the specifications for the various uranium and plutonium materials.
 - b. Establish the availability of adequate methods for the specification analyses.

(41) The program was originally identified as the Umpire Certification Program.

- c. Establish the basic requirements of a prospective umpire laboratory.
- d. Explain the objective of the Program to selected AEC laboratories and obtain their cooperation.

- Phase 2:
- a. On the basis of information obtained in Phase 1, inform laboratories seeking qualification what the Program entails, and to assess by means of a questionnaire, their interests, competences, and technical capabilities.
 - b. With the aid of the selected AEC laboratories, prepare standards of the various materials on the basis of information obtained in Phase 1:a and analyze each standard for the various specifications.

- Phase 3:
- a. Distribute the standards to those laboratories that qualify under Phase 2:a.
 - b. Qualify or reject the laboratories on the basis of a personal inspection of their laboratory facilities and statistical comparisons of their data with that obtained under Phase 2:b by the AEC laboratories.

1.3 Status of Program

With reference to the last section, Phase 1 has been completed for all uranium materials and Phase 1 has been started for plutonium materials. Phase 2 is underway for the uranium materials with the highest priority.

Technical personnel of Phillips visited five AEC laboratories to enlist their aid in the Program and to obtain information about the specifications of uranium materials and specification analysis methods for both uranium and plutonium materials. At K-25, the specifications for uranium materials were thoroughly reviewed with the aid of DNMM and Oak Ridge Operations personnel. Methods of analysis were reviewed at NBL, SRP, K-25, and GAT for uranium materials and at NBL, SRP, and RF for plutonium materials.

The AEC laboratories that are to prepare and analyze the various standards are summarized in Table VI-1. This distribution of work, except for three minor changes, is the same as agreed upon at the DNMM-sponsored meeting of June 18, 1965, attended by personnel from AEC Operations Offices and AEC-contractor laboratories. For the analysis of uranium hexafluoride, PAD has replaced Phillips Petroleum Company (PPCo) and for the analysis of the two uranyl nitrate solutions, GAT has replaced SRP. As shown in Table VI-1, one laboratory will prepare a given material which will be analyzed by that laboratory and three others.

An information-and-questionnaire letter was sent to the 31 commercial laboratories that had responded to the DNMM news release of the Program. Eight laboratories have requested qualification for various phases of the Program, eight have decided not to participate, and 15 have not yet replied.

1.4 Future Plans

Projected plans and completion dates for the various phases of the Umpire Qualification Program are summarized in Table VI-2. As indicated, the preparation and analysis of uranium standards with priority one (see Table VI-1) is expected to be completed in the fiscal year 1966. The distribution of standards to commercial laboratories will be started as soon as standards are obtained. A visit to Isochem is planned early in CY 1966 to discuss plutonium materials.

Table VI-1

FUNCTIONS OF AEC LABORATORY PARTICIPANTS

Materials	Priority	Standards	Function	
			Preparation	Standardization
1. UF_6	1	1	K-25	K-25, GAT, NBL, PAD
2. $\text{UO}_2(\text{NO}_3)_2$ Solution	1	2	PPCo	PPCo, K-25, GAT, NBL
3. U_3O_8	2	2	K-25	K-25, GAT, NBL, PPCo
4. $\text{UO}_2(\text{NO}_3)_2$ (U-233 enriched) Solution ^a	3	1	PPCo	PPCo, K-25, GAT, NBL
5. UO_2	3	^b	K-25	K-25, GAT, NBL, PPCo
6. UO_3	3	^b	K-25	K-25, GAT, NBL, PPCo
7. U-metal	3	^b	^c	^c , GAT, NBL, PPCo
8. $\text{Pu}(\text{NO}_3)_4$ Solution	1	2	Isochem	Isochem, NBL, RF, LASL
9. PuO_2	2	1	Isochem	Isochem, NBL, RF, LASL
10. Pu Metal	3	2	Isochem	Isochem, NBL, RF, LASL

^a Spectrographic standard only.

^b Not established.

^c Unassigned.

Table VI-2

PLANS FOR THE IMMEDIATE FUTURE

Materials	Work	Remarks
UO ₂ (NO ₃) ₂ Solution	Preparation and analysis	Will be started January, 1966. Estimated completion date is April, 1966.
UF ₆	Preparation and analysis	A work order for the preparation of the UF ₆ standard has been sent to K-25.
Pu(NO ₃) ₄ Solution PuO ₂ , and Pu Metal	Review of specifications and specification analysis methods; preparation of Pu(NO ₃) ₄ solution standard	A visit to Isochem is planned for early 1966. The prepara- tion of the standard Pu(NO ₃) ₄ solutions may be started before July 1966.
U ₃ O ₈ , UO ₂ , UO ₃ , and UO ₂ (NO ₃) ₂ Solution enriched in U-233.	Preparation and analysis	Planned for fiscal year 1967.
Pu standard materials	Preparation of PuO ₂ and Pu metal	Planned for fiscal year 1967.

2. QUALITY CONTROL

(J. E. Rein, G. J. Curtis)

The comprehensive quality control program on both routine and special methods was continued. The main features of this program are (1) the preparation and supplying of all reagents and standards for the methods, (2) the submission of unknown control samples and the record-keeping of results for transmittal to the statisticians, (3) the submission of controls and the record-keeping for the Training and Testing Program of the Chemical Analysis Section, (4) the maintenance of "bench" standards and control charts, and (5) the surveillance of the control data. "Bench" standards of known values are processed prior to samples to prevent the use of faulty apparatus or reagents.

2.1 Bias and Precision Data

Tables of current bias and of precision for routine methods, based on computer-calculated regression equations computed from control sample results, are now provided at 3-month intervals by Operations

Analysis. These tables provide a rapid means of correcting results for bias and of associating a precision uncertainty over the entire range of the methods and are used routinely by laboratory personnel. Table VI-3 is a summary of the precision data for routine methods for 1965. The handling and reporting of quality control data has been modified during the past year for greater efficiency. Previously, the control sample results were recorded on a raw data form which then had to be transferred to computer input sheets. The raw data form has been eliminated and the results are recorded directly onto the input sheets.

2.2 Training and Testing Program

The statistical test of pass-fail in connection with the Training and Testing Program of the Chemical Analysis Section has been transferred from the statisticians to this laboratory. A special test (see Figure VI-1) was devised by G. Booth which provides a rapid evaluation of the data.

2.3 Standards and Reagents

Routine

The numbers of standard solutions, reagents, and quality control samples prepared this year are summarized in Table II-2.

Storage of Uranium Standard Solutions

Standard uranium solutions stored in special dispensing bottles⁽⁴²⁾ remained stable throughout 1965. This was verified by periodic analyses of these solutions by the mass laboratory using the procedure previously described⁽⁴³⁾.

Storage Stability of Liquids

A major problem in analytical chemistry is the stability of standard solutions that are stored for extended time periods. Leakage through stoppers, reaction with the vessel surface, and transpiration are factors which cause changes in concentration. An experiment recently completed, investigated the effects of certain of these variables. The variables studied are summarized in Table VI-4. A total of 132 combinations of the above variables was evaluated. The containers were filled to several different levels with the various liquids, and weight changes were measured at intervals over a period of 1 yr. The results showed that the bottle type most often used for the storage of solutions in laboratories had the greatest weight losses for aqueous type media.

(42) R. C. Shank, and staff, Annual Report of Division Analytical Branch for 1962, IDO-14605, Section VII-2.2.1 (April 1963).

(43) R. C. Shank, and staff, Annual Report of Division Analytical Branch for 1964, IDO-14655, Section VII-2.2.2 (April 1965).

Table VI-3

PRECISION OF ROUTINE ANALYTICAL METHODS

Methods	Range and Units ^(a)	Precision ^(b)
Acid, visual indicator titrimetric	0.5 to 4.5 meq	0.01 to 0.04 meq
Acid, oxalate, pH titrimetric	0.5-meq base to 1.2-meq acid	0.01 meq, constant
Acid, oxalate, pH titrimetric, remote	0.5-meq base to 1.2-meq acid	0.01 to 0.06 meq
Aluminum, fluoride complexing, titrimetric	5 to 11 mg	0.15 to 0.21 mg
Beta activity, gross	45- to 355-d/m	8- to 48-d/m
Boron, mannitol complexing, titrimetric, high level	0.5 to 5.0 mg	0.02 to 0.28 mg
Boron, mannitol complexing, titrimetric, low level	0.1 to 1.5 mg	0.03 mg, constant
Ce-137	5×10^4 - to 9.9×10^5 d/m	1.2×10^4 - to 1.6×10^5 - d/m
Chromium, redox titrimetric	1.6 to 15.6 mg	0.12 to 0.5 mg
Chromium, diphenyl-carbazide colorimetric	0.005 to 0.05 mg	0.0005 to 0.0059 mg
Fluoride, pyrolysis, Ce(III) titrimetric	6 to 40 mg	1.0 to 2.9 mg
Iron, column extraction, EDTA titrimetric	2 to 25 mg	0.09 to 0.41 mg
Iron, orthophenanthroline colorimetric	2 to 98 μ g	1.1 to 4.8 μ g
Iron, column extraction, orthophenanthroline colorimetric	4 to 100 μ g	0.9 to 3.9 μ g

Table VI-3 Continued

Methods	Range and Units ^(a)	Precision ^(b)
Mercury, titrimetric, Hg(II) with KSCN	96 to 300 mg	1.2 to 1.9 mg
Mercury, dithizone colorimetric	50 to 300 µg	9.8 to 48.8 µg
Nickel, dimethylglyoxime colorimetric	0.01 to 0.1 mg	0.002 to 0.003 mg
Nickel, dimethylglyoxime precipitation, EDTA titrimetric	2 to 28 mg	0.1 to 1.5 mg
Nitrate, Devarda reduction, distillation, titrimetric	0.2 to 4.5 mmole	0.03 to 0.26 mmole
Phosphate, extraction, colorimetric	1 to 100 µg	1.1 to 4.4 µg
Reducing Normality, dichromate titrimetric	0.1- to 0.9-meq Fe(II)	0.01 meq, constant
Specific Gravity, Westphal	0.79 to 1.59 specific gravity units	0.001 to 0.003 specific gravity units
Specific Gravity, falling drop, remote	1.05 to 1.32 specific gravity units	0.001 to 0.005 specific gravity units
Tin, pyrocatechol violet colorimetric	15 to 150 µg	6.5 to 9.9 µg
Tributylphosphate, bromthymol blue titrimetric	1.5- to 12-% TBP	0.1% TBP, constant
Uranium, extraction tetrapropylammonium uranyl trinitrate spectrophotometric	3.5 to 20 mg	0.1 to 0.4 mg
Uranium, extraction, tetrapropylammonium uranyl trinitrate spectrophotometric	5 to 38 mg	0.10 to 0.63 mg
Uranium, mass isotopic distribution, hand pipetted	1.013% U-234 93.112% U-235 0.183% U-236 5.692% U-238	0.009% 0.076% 0.007% 0.060%

Table VI-3 Continued

Methods	Range and Units(a)	Precision(b)
Uranium, isotopic-dilution mass-spectrometric, hand pipetted	1.00 mg	0.008 mg
Uranium, mass isotopic distribution, remote pipetted	1.012% U-234 93.114% U-235 0.183% U-236 5.689% U-238	0.007% 0.053% 0.007% 0.037%
Uranium, isotopic-dilution mass-spectrometric, remote pipetted	1.00 mg	0.018 mg
Uranium, mass isotopic-distribution, high precision	1.0183% U-234 93.1389% U-235 0.1832% U-236 5.6611% U-238	0.0149% 0.0399% 0.0076% 0.0285%
Uranium, isotopic-dilution mass-spectrometric, high precision	1.00 mg	0.0039 mg
Uranium, extraction, dibenzoylmethane colorimetric	0.005 to 0.075 mg	0.002 to 0.009 mg
Uranium, ignition to U_3O_8 , spectrographic impurity correction	220.0 to 230.0 mg	0.12 mg
Uranium, extraction, pellet fluorophotometric	5×10^{-5} to 0.1-mg/ml	3.4×10^{-5} to 2.8×10^{-2} -mg/ml
Zirconium, cupferron amperometric	0.01 to 0.1 mmole	0.002 mmole, constant

(a) Amount in aliquot of control taken for analysis.

(b) In terms of standard deviation for a single determination over range of method.

NAME I. M. Wright

METHOD Cr-2, Mod-3

	<u>REPORTED</u>	<u>KNOWN</u>	<u>R-K</u>	<u>STD. DEV.</u>	<u>R-K/STD. DEV.</u>
1	<u>1.04</u>	<u>1.02</u>	<u>+0.02</u>	<u>0.04</u>	<u>+0.50</u>
2	<u>0.42</u>	<u>0.40</u>	<u>+0.02</u>	<u>0.03</u>	<u>+0.67</u>
3	<u>2.09</u>	<u>2.06</u>	<u>+0.03</u>	<u>0.06</u>	<u>+0.50</u>
4	<u>1.03</u>	<u>1.02</u>	<u>+0.01</u>	<u>0.04</u>	<u>+0.25</u>
5	<u>3.01</u>	<u>3.12</u>	<u>-0.11</u>	<u>0.10</u>	<u>-1.10</u>
6	<u>0.42</u>	<u>0.40</u>	<u>+0.02</u>	<u>0.03</u>	<u>+0.67</u>
7	<u>2.12</u>	<u>2.06</u>	<u>+0.06</u>	<u>0.06</u>	<u>+1.00</u>
8	<u>0.42</u>	<u>0.40</u>	<u>+0.02</u>	<u>0.03</u>	<u>+0.67</u>
9	<u>1.07</u>	<u>1.02</u>	<u>+0.05</u>	<u>0.04</u>	<u>+1.25</u>

$$\Sigma \left(\frac{R-K}{S.D.} \right) = \text{TOTAL} = \underline{+4.41}$$

$$\Sigma \left(\frac{R-K}{S.D.} \right)^2 = \text{SS} = \underline{5.68}$$

$$\text{SUM} = \text{ABSOLUTE VALUE OF TOTAL} \quad \text{FF} = \frac{\text{SS}}{9} = \underline{0.63 \text{ is } < 1.74[\text{F(N)}]}$$

$$\text{SUM} = \underline{4.41} \quad \text{TT} = \frac{\text{SUM}}{3} = \underline{1.47 \text{ is } < 1.67[\text{T(N)}]}$$

If TT is greater than T(N), then bias is significantly greater than zero.

If FF is greater than F(N), then STD. DEV. is significantly greater than one.

N is the number of analyses in the current quality control program.

BIAS IS: SIGNIFICANT _____ NOT SIGNIFICANT X

STD. DEV. IS: SIGNIFICANT _____ NOT SIGNIFICANT X

Figure VI-1 CHEMIST TRAINING AND TESTING FORM

Table VI-4

VARIABLES STUDIED FOR LIQUID STORAGE STABILITY

Containers	Stoppers	Aqueous Media	Organic Media
borosilicate glass	regular glass	water	ethanol
polyethylene	inverted glass	hydrochloric acid 1M and 12M	ethyl ether
polypropylene	plastic screw cap	hydrofluoric acid 1M and 12M	hexane
Teflon	plastic screw caps sealed with parawax	nitric acid sodium hydroxide 1M and 12M	hexone kerosene

This was the borosilicate glass bottle with a ground glass stopper. For water, the average weight loss for two bottles after 1 yr was 3.9%. In comparison, two bottles of the same type with stopcock grease applied to the stopper had an average weight loss of only 0.05%. Weight losses were observed for all of the liquids except the combination of 12M sodium hydroxide stored in the three types of plastic bottles. Of interest was that 12M nitric acid which gained ~ 0.1 wt % after 3 months of storage in polyethylene, then lost weight to give an overall loss of 0.02% at the end of the 1-yr period. A journal publication describing this work is planned.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

APPENDIX A
PUBLICATIONS AND OTHER ACTIVITIES

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

PUBLICATIONS AND PAPERS FOR 1965

1. U. S. ATOMIC ENERGY COMMISSION REPORTS

IDO-14642	W. J. Maeck	<u>Proposed Determination of Nuclear Fuel Burnup Based on the Ratio of Two Stable Fission Products of the Same Element</u>
IDO-14655	R. C. Shank and Staff	<u>Annual Report of Division Analytical Branch for 1964</u>
IDO-14656	W. J. Maeck J. E. Rein	<u>Burnup Determination of Nuclear Fuels: 1964 Annual Report</u>
IDO-14660	W. J. Maeck J. E. Rein	<u>Burnup Determination of Nuclear Fuels Project Report for the Quarter January 1 - March 31, 1965</u>
IDO-14663	W. J. Maeck J. E. Rein	<u>Burnup Determination of Nuclear Fuels Project Report for the Quarter April 1 - June 30, 1965</u>
IDO-14664	M. S. Anderson T. R. Thomas	<u>Separation of Tellurium and Iodine from Other Fission Products: Application to LOFT Samples</u>
IDO-14667	W. J. Maeck J. E. Rein	<u>Burnup Determination of Nuclear Fuels Project Report for the Quarter July 1 - September 30, 1965</u>
IDO-17128	B. R. Hunter G. B. Matheney E. L. Murri J. R. Palmer	<u>Sampling and Analysis of Fission Products During the Loss-of-Fluid Test (LOFT) an Interim Report</u>

2. JOURNAL ARTICLES

W. J. Maeck, M. E. Kussy, J. E. Rein, "Spectrophotometric Determination of the Lanthanides as Extracted Nitrate Complexes," Anal. Chem. 37, 103-106 (Jan 1965)

G. L. Booman, W. B. Holbrook, "Optimum Stabilization Networks for Potentiostats with Application to a Polarograph Using Transistor Operational Amplifiers," Anal. Chem. 37, 795-802 (June 1965).

M. A. Wade, S. S. Yamamura, "Microdetermination of Fluoride Using an Improved Distillation Procedure," Anal. Chem. 37, 1276-1278 (Sept 1965).

G. L. Booman, D. T. Pence, "Generalized Numerical Method for Stationary Electrode Polarography," Anal. Chem. 37, 1366 (October 1965).

G. L. Booman, J. E. Harrar, I. Shain, "Simplified Use of Transfer Functions in Analysis of Operational Amplifier Electroanalytical Instrumentation," Anal. Chem. 37, 1768 (December 1965).

3. PAPERS

M. A. Wade*, S. S. Yamamura, "Micro Determination of Fluoride Using an Improved Distillation Procedure", 20th Northwest Regional Meeting of the American Chemical Society, Corvallis, June 1965.

W. J. Maeck*, R. M. Abernathy, J. E. Rein, "Absolute U-235 Thermal Fission Yields of Cs-137 and Stable Kr, Xe, Nd, and Sm Isotopes," Burnup Symposium Co-sponsored by ANS and ASTM, Gatlinburg, June 1965.

S. F. Marsh*, R. E. Foster, "Chemical Separations in the Determination of Fission Yields," Burnup Symposium Co-sponsored by ANS and ASTM, Gatlinburg, June 1965.

T. R. Lyon, "Rare Earth Analysis by a Rotating Platform, Silver Spark Technique," National Meeting of Society for Applied Spectroscopy, Denver, August 1965.

J. E. Rein, "Separation of Inorganic Ions on Inorganic Compounds," 150th American Chemical Society National Meeting, Atlantic City, September 1965.

S. S. Yamamura, "The Use of Citrate-EDTA Masking for the Selective Determination of Iron with 1,10-Phenanthroline," 150th American Chemical Society Meeting, Atlantic City, September 1965.

* Presented paper.

APPENDIX B

METHODS ADDED TO ANALYTICAL MANUAL IN 1965

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

IDO-14316
H⁺-Pot-4:1
Mod-6

TITRIMETRIC DETERMINATION OF ACIDITY
OF HYDROLYZABLE ION SOLUTIONS

ABSTRACT

The basis of this method(1) is the addition of the sample to a potassium oxalate solution preadjusted to a known pH, then titration with standard sodium hydroxide to the same pH. Optimum conditions are described for various types of samples including acid-deficient samples.

APPLICABILITY

The various types of samples which can be analyzed by this method are summarized in Table I.

Table I. TYPES OF SAMPLES ANALYZABLE BY METHOD

Principal Elements in Sample	Procedure and Reference pH	Remarks
1. Al(III), U(VI), Zr(IV). (Zr in HF medium only)	B, 5.55	Any of the four ions can be together in mixtures. The polymerization of zirconium has been found to be negligible in samples containing hydrofluoric acid. Less than 0.01M concentrations of mercury do not interfere. If the mercury concentration in the sample is greater than 0.01M, use 20 ml of the 0.45M potassium oxalate reagent that is saturated with potassium chloride. These type of samples often contain small concentrations of chromium. The chromium can be neglected if its concentration is less than 5% of the major metal constituent(s).
2. $M(OH)^{+x}$ such as $Al(OH)_x^{+(3-x)}$	C, 5.55	The addition of an acid-deficient aluminum sample to the oxalate reagent usually results in the precipitation of aluminum hydroxide which can be solubilized only by the addition of excess acid. The excess acid then is back titrated with sodium hydroxide to the reference pH.

IDO-14316
H⁺-Pot-4:2
Mod-6

Table I. TYPES OF SAMPLES ANALYZABLE BY METHOD (Continued)

Principal Elements in Sample	Procedure and Reference pH	Remarks
3. Fe(III), Cr(III),	D, 5.80	Applicable only to acidic samples in which polymerization is negligible. Procedure C should be used to analyze acid-deficient samples. Stainless steel constituents, especially chromium, react very slowly with oxalate. For this reason, wait at least 2 hr after the addition of the sample to the oxalate before titrating.
4. Zr(IV) without HF present	E, 5.55	In the absence of complexing anions such as fluoride, zirconium forms polymeric species. These are usually very stable and are broken only by a preliminary digestion with sulfuric acid in a sealed container.
5. Metal ions, such as Al(III), U(VI), and Zr(IV), with both boron and fluoride present	F, 5.55	The acidity of these samples is dependent on the relative concentrations of the metal ions, boron (boric acid), and fluoride (See the <u>DISCUSSION</u> section). This procedure (2) provides the answer to the question, "What is the acidity of the sample if there were no reaction between the boric acid and fluoride?" Actually, there is some reaction between fluoride and boric acid and the question, "What is the free acidity of the sample?" might be raised. Procedure B provides the answer to this second question.

DISCUSSION

Free acid, N^a is defined as that amount of acid which would remain if the hydrolyzable metal ions were removed from the solution as neutral salts. Analogously, acid-deficiency, N^b , or "free-base" is defined as that amount of base which would remain if the hydrolyzable metal ions were removed from the solution as neutral salts.

In this method, hydrolyzable metal ions are removed by complexation with potassium oxalate. This is illustrated by equation 1 which describes the reaction of potassium oxalate with an acidic solution of aluminum

nitrate. In practice, the direct reaction of potassium oxalate (Diban), equation 2, is usually not practical, and the hydroxy complex must first be converted with excess standard acid to the neutral salt which then reacts with potassium oxalate according to equation 1.

Actually, the determination of acidity using oxalate complexation is quite complicated and requires a careful consideration of several equilibria. Oxalic acid is a dibasic acid which ionizes to give the

monovalent binoxalate and bivalent oxalate anions according to the reversible equations 3 and 4, respectively. Equation 5, similar to

IDO-14316
 H⁺-Pot-4:4
 Mod-6

equation 1, is the desired, predominant reaction, but it is accompanied by reactions 6, 7, and 8. Equation 6, together with the reverse of reaction 4, and reaction 7 show the consumption of hydrogen ions accompanying the formation of the metal binoxalate complex. These reactions causing a negative bias are observed especially at moderate acidities where monovalent binoxalate ions are stable and predominant. Equation 8, particularly troublesome at high pH, shows the hydrolysis of the metal ion and the release of acid.

In the recommended procedures, the pH of the oxalate complexing solution is controlled at a value where the release of acid via reaction 8 is offset by the consumption of acid via reactions 6 and 7. The optimum pH values are pH 5.80 for stainless steel samples and pH 5.55 for aluminum, uranium, and zirconium samples.

Besides pH, the sample to oxalate ratio must be controlled to guarantee reliable reproducible results (2). Significant differences have been noted with changes in the sample to oxalate ratio.

Dilution of the oxalate reagent with water also affects the results (2). This dilution effect is probably due to changes in the activity of the hydrogen ion resulting from changes in the salt concentration.

Mercury undergoes considerable hydrolysis even in the presence of oxalate. A special oxalate reagent saturated with potassium chloride is used to prevent this.

The determination of the acidity of STR (CPP-Process for Zircaloy-Clad fuel) solutions containing both boric acid and fluoride (Sample 4, Table I) presents a unique problem because the acidity is dependent on the relative concentrations of the fluoride, the boric acid, and the metal ions. This is illustrated by the following equilibria:

Of special significance is that boric acid reacts with fluoride ions according to reaction 1 to form a fluoborate complex and hydroxyl ions. Reaction 1 is reversible. High fluoride concentration favors the formation of the fluoborate complex with the accompanying release of hydroxyl ions which consumes acid. Low fluoride concentration and high hydroxyl ion concentration favor the reverse reaction. Fluoride-complexing metal ions also favor the reverse reaction by effectively reducing the fluoride concentration as shown in reaction 2.

The routine acid procedure, B, for zirconium samples containing HF provides acidity values which are probably close to, but slightly higher than, the free acidities of these solutions. However, these acidity values do not provide an acid material balance because of the usual variations in the compositions of the process solutions and the dependence of the acidity on the relative concentrations of fluoride, boric acid, and metal ions as noted above.

The fact that fluoride-complexing metal ions eliminate the complicating effect of boric acid by the reversal of reaction 1 has led to the development of a modified method, F, for the determination of acidity which provides an acid material balance. The principal modifications are the addition of 1 mmole of aluminum nitrate and the use of a 1M potassium oxalate solution in place of the 0.45M solution prescribed for Procedure B. Essentially Procedure F determines the sum of nitric acid and hydrofluoric acid in the sample with no reaction between boric acid and fluoride.

SPECIAL SAFETY PRECAUTIONS

1. Wear rubber gloves to avoid acid burns from concentrated sulfuric acid in Procedure E.
2. Heating the sealed tubes containing sulfuric acid in Procedure E, should only be done behind a safety glass shield.
3. Glass screw-cap test tubes have been known to break when strong pressure is applied. Wrap the test tubes in a cloth to avoid cuts (and sulfuric acid burns).

SPECIAL APPARATUS AND REAGENTS

The apparatus and reagents listed below include only those items which are essential for this method or which require special preparation. Apparatus and reagents normally available in the laboratory are not listed.

IDO-14316
H⁺-Pot-4:6
Mod-6

A. Apparatus

1. pH meter Beckman Model H-2 or Leeds and Northrup (L&N) Model 7664 with calomel (Beckman No. 4970 or L&N No. Std. 1199-30) and glass (Beckman No. 4990-80 or L&N No. Std. 1199-31) electrodes. The L&N electrodes specified above may be replaced with L&N miniature probe glass and calomel electrodes; however, these miniature electrodes are not recommended for the Remote Analytical Facilities where routine maintenance is not very practical.
2. Burets, micro, 10-ml, graduated in 0.02-ml increments.
3. Syringe Microburet, Model No. SB2, with assorted syringes, available from Micro-Metric Instrument Co., Cleveland, Ohio.
4. Test tubes, glass and plastic, with screw-caps. These test tubes should have a capacity of 15 to 25 ml.
5. Parafilm. This paraffin-coated film manufactured by Marathon Division of American Can Company is a stock item.

B. Reagents

1. Sodium hydroxide solutions, standards, $0.200 \pm 0.001N$ and $1.000 \pm 0.001N$.
2. Hydrochloric acid solution, standard, $0.200 \pm 0.001N$
3. Sulfuric acid solution, standard, $1.000 \pm 0.001N$.
4. Sulfuric acid, $26N$ ($13M$). Add cautiously, with cooling, 360 ml of concentrated sulfuric acid to 140 ml of water. Cool, dilute to 500 ml with water, and mix well. Transfer the sulfuric acid solution to 20-ml ampoules and seal the ampoules with a flame.
5. Potassium oxalate reagent I, $0.45M$, unadjusted. Prepare the $0.45M$ solution using 82.9 g of potassium oxalate monohydrate per liter of solution. Adjust portions of this solution as needed to pH 5.55 or 5.80 with $1M$ nitric acid. If subsequent readjustment to a higher pH is necessary, use $1M$ sodium hydroxide.
6. Potassium oxalate reagent II, $0.45M$, unadjusted, saturated with potassium chloride. Prepare the solution as directed above except dilute nearly to volume, saturate the oxalate solution with potassium chloride, then dilute it to volume. Crystals of potassium chloride should be visible at the bottom of the container. Adjust portions of this solution as needed to pH 5.55 or 5.80 with $1M$ nitric acid.

7. Potassium oxalate reagent III, 1.00M unadjusted. Prepare the 1.00M solution using 184.2 g of potassium oxalate monohydrate per liter of solution. Adjust portions of this solution as needed to pH 5.55 or 5.80 with 1M nitric acid.
8. pH 7.00 buffer solution.
9. Aluminum nitrate solution, 1M aqueous solution.

PROCEDURE

A. Bench Standard

Run a single determination on the bench standard prior to the analysis of samples. The composition of the bench standard should be similar to the samples. Limits will be specified by the Quality Control Laboratory.

B. Analysis of Samples Containing Major Amounts of Aluminum, Uranium, and Zirconium, and Small Amounts of Mercury.

NOTES: (a) This procedure is applicable to zirconium samples only if the samples contain hydrofluoric acid which prevents the polymerization of zirconium through complexation. In the absence of strong complexing agents such as fluoride, Procedure E must be used.

(b) Adjust a suitable portion of the 0.45M potassium oxalate reagent I or II to pH 5.55±0.05 with 1M nitric acid or 1M sodium hydroxide before analyzing the bench standard or the samples.

1. Wash the pH meter electrodes with distilled water and dry with an absorbent tissue.
2. Standardize the pH meter against a pH 7.00 buffer solution, then thoroughly wash the electrodes with water. Wipe the electrodes dry with tissue paper.
3. Pipet 20 ml of the 0.45M potassium oxalate reagent I, preadjusted to pH 5.55, into a 50-ml beaker. If the mercury concentration of the sample is greater than 0.01M, use instead 20 ml of the 0.45M potassium oxalate reagent II, preadjusted to pH 5.55.
4. Lower the pH electrodes into the solution and stir the solution for about 3 min with the aid of a magnetic stirrer and stirring bar.

IDO-14316
H⁺-Pot-4:8
Mod-6

5. Measure the pH of the solution. The pH must be in the range 5.50 to 5.60. If not, adjust the pH to within this range with either 0.200N sodium hydroxide or 0.200N hydrochloric acid. Carefully note the pH and record it for reference.
6. Pipet 200 μ of sample into the oxalate solution, stir, then observe the pH. If the pH is below 5.20, continue with step 7. If the pH is above 5.2, discard the solution and analyze the sample according to Procedure C which is specially designed for samples containing stable hydroxy-metal complexes.
7. Titrate with 0.200N sodium hydroxide to the exact pH recorded in Step 5.
8. Record the titer on the worksheet and calculate the acidity of the sample as described under CALCULATIONS, Section A.

C. Analysis of Low Acid or Acid-Deficient Samples Such as Diban.

1. Standardize the pH meter against pH 7.00 buffer solution, then adjust the 0.45M potassium oxalate reagent to pH 5.55 $\pm$ 0.05 (aluminum samples) or pH 5.80 $\pm$ 0.05 (samples containing iron, chromium, and nickel). Record the pH. Depending on the mercury content of the sample, use either reagent I or reagent II.
2. Standardize the 1.0-meq sulfuric acid spike as follows:
 - a. Pipet 1.00 ml of the 1.000 $\pm$ 0.001N sulfuric acid solution into a 50-ml beaker.
 - b. Pipet 20 ml of the 0.45M potassium oxalate reagent into the beaker.
 - c. Titrate with 0.200N sodium hydroxide to the exact pH recorded in step 1.
 - d. Record the titer on the worksheet and proceed with step 3.
3. Analyze the sample as follows:
 - a. Pipet 1.00 ml of the 1.000 $\pm$ 0.001N sulfuric acid solution into a 50-ml beaker.
 - b. Pipet 200 μ of the sample into the sulfuric acid. Cover the beaker with a watch glass and swirl the beaker intermittently over a period of 2 to 3 min.

- c. Pipet 20 ml of the 0.45M potassium oxalate reagent into the beaker. If the sample is of the stainless steel type that contains large amounts of chromium, cover the beaker with a 3- x 3-in. sheet of parafilm, swirl to mix, then let stand for 2 hr.
 - d. Immerse the pH electrodes into the solution and stir for 3 min.
 - e. Titrate with 0.200N sodium hydroxide to the exact pH recorded in step 1.
 - f. Record the titer on the worksheet and calculate the acidity, N^a or N^b , as described under CALCULATIONS, Section B.
- D. Analysis of Samples Such as Stainless Steels that Contain the Major Constituents Iron, Chromium, and Nickel.
- 1. Standardize the pH meter against a pH 7.00 buffer solution, then adjust the 0.45M potassium oxalate reagent I to pH 5.80±0.05 with 1M nitric acid or 1M sodium hydroxide. Record the exact pH.
 - 2. Analyze the sample as follows:
 - a. Pipet 20 ml of the potassium oxalate reagent I, preadjusted according to step 1, into a 50-ml beaker.
 - b. Pipet 200 λ of the sample into the oxalate reagent. Mix well by swirling or with magnetic stirring. Cover the beaker tightly with a 3- x 3-in. sheet of Parafilm and let stand for 2 hr to enable the chromium to react with the oxalate.
 - c. Remove the Parafilm covering, insert the pH electrodes, and observe the pH. If the pH is less than 5.4, continue with step d. If the pH is higher than 5.4, discard the solution and analyze the sample according to Procedure C which is specially designed for low acid or acid-deficient samples.
 - d. Titrate with 0.200N sodium hydroxide to the exact pH recorded in step 1.
 - e. Record the titer on the worksheet and calculate the acidity of the sample as described under CALCULATIONS, Section A.
- E. Analysis of Samples Containing Polymeric Species Such as Polymers of Zirconium.

- NOTE: (a) In this procedure, results are obtained from the difference of two large titers; therefore, standardize the sulfuric acid spike and analyze the sample in duplicate. Allowable limits for the difference between duplicates is 0.1N. If these limits are adhered to, results will be reliable to +0.1N standard deviation.
- (b) Strong sulfuric acid absorbs atmospheric moisture and loses strength. The 26N acid will be supplied in small sealed ampoules. Transfer the acid to a small screw-cap bottle and keep the bottle tightly capped when the acid is not being used. Request a new ampoule of sulfuric acid if the 26N sulfuric acid is left standing for over two weeks.
1. Standardize the pH meter against the pH 7.00 buffer solution, then adjust the 0.45M potassium oxalate reagent I to pH 5.55±0.05 with 1M nitric acid or 1M sodium hydroxide. Record the exact pH.
 2. Standardize the 5.2-meq sulfuric acid spike as follows:
 - a. Standardize the pH meter against the pH 7.00 buffer solution, then rinse the electrodes thoroughly with water and wipe dry with tissue paper.
 - b. Pipet 20 ml of the 0.45M potassium oxalate reagent from step 1 into a 50-ml beaker.
 - c. With the Syringe Microburet, pipet 200 λ of the 26N sulfuric acid solution into the oxalate reagent.
 - d. Immerse the pH electrodes into the solution and titrate with 1.000N sodium hydroxide to the exact pH recorded in step 1.
 - e. Record the titer on the worksheet and continue with the analysis of the sample, step 3.
 3. Analyze the sample as follows:
 - a. Pipet 200 λ of the 26N sulfuric acid solution into a glass (plastic, if the sample contains fluoride) screw-cap test tube. Use the Syringe Microburet to deliver the acid. Do not use the common hand micro pipet. The sulfuric acid does not drain completely and the use of water rinses is not allowed because complete depolymerization is obtained only with strong sulfuric acid.

- b. Pipet 200 λ of the sample, also delivered with the Syringe Microburet, cap tightly, then swirl the test tube to mix the acid and the sample.

Proceed with steps c, d, and e. Follow the directions specified to prevent the precipitation of insoluble sulfates and the loss of volatile acids.

- c. Heat the test tube in a beaker of boiling water FOR AT LEAST 1 HR BUT NOT MORE THAN 2 HR.
- d. Remove the test tube from the boiling water bath and quickly immerse it into an ice bath. Chill to room temperature.
- e. Open the test tube and rinse the sample into a 50-ml beaker. Use 20 ml of the potassium oxalate reagent from step 1 for the quantitative transfer.
- f. Immerse the pH electrodes into the solution and titrate with 1.000N sodium hydroxide to the exact pH recorded in step 1. The titration of these samples is characterized by a drifting pH because of slow equilibrium and the end point may be overshoot. If so, back titrate with 0.200N hydrochloric acid. Allow ample time for equilibrium. The titration may require as much as an hour for completion.
- g. Record the titer on the worksheet and calculate the acidity of the sample as described under CALCULATIONS, Section C.

F. Analysis of Metal Ion Solutions that Contain Both Fluoride and Boron.

1. Standardize the pH meter against the pH 7.00 buffer solution, then adjust the 1.00M potassium oxalate reagent III to pH 5.55 $\pm$ 0.05. Record the exact pH.
2. Determine the acid blank of the 1-mmole aluminum nitrate spike according to steps 3a, 3d, and 3e.
3. Analyze the sample as follows:
 - a. Pipet 1.00 ml of the 1M aluminum nitrate solution into a 50-ml beaker.
 - b. Pipet 200 λ of the sample into the beaker.

IDO-14316
H⁺-Pot-4:12
Mod-6

- c. Cover the beaker with a 3- x 3-in. sheet of Parafilm, then swirl the beaker to thoroughly mix the sample with the aluminum nitrate. Let stand 3 min.
- d. Remove the Parafilm and pipet 20 ml of the potassium oxalate reagent from step 1 into the beaker.
- e. Immerse the pH electrodes into the solution. Stir the solution for about 2 min then titrate with 0.200N sodium hydroxide to the exact pH recorded in step 1.
- f. Record the titer on the worksheet and calculate the acidity of the sample as described under CALCULATIONS, Section D.

CALCULATIONS

A. For Analyses According to Procedures B and D.

Record the data on the worksheet and calculate the results as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Sample volume, 0.200 ml
B	Volume 0.200N sodium hydroxide used, ml
C	Volume, 0.200N hydrochloric acid used, ml
D	Result, acid normality, <u>N^a</u> , of the sample
$D = \frac{0.200(B-C)}{0.200} = B-C$	

Report the results to the nearest hundredth as 1.00 N^a, 0.10N^a, 0.01N^a.

B. For Analyses According to Procedure C.

Record the data on the worksheet and calculate the results as follows:

IDO-14316
H⁺-Pot-4:13
Mod-6

<u>Column</u>	<u>Unit to Record</u>
A	Volume of 0.200N sodium hydroxide used to titrate the 1-meq sulfuric acid spike, ml
B	Sample volume, 0.200 ml
C	Volume of 0.200N sodium hydroxide used to titrate the sample, ml
D	Result, free base normality, $\underline{N}^b$, or free acid normality, $\underline{N}^a$.
	$D = \frac{0.200(C-A)}{0.200}$
	D = C-A
	If C-A is positive, D is the free acid normality, $\underline{N}^a$, of the sample.
	If C-A is negative, the absolute value of D is the free base normality or acid deficiency, $\underline{N}^b$, of the sample.
	Report the results to the nearest hundreth as 1.00 $\underline{N}^b$, 0.10 $\underline{N}^b$, and 0.01 $\underline{N}^b$.

C. For Analyses According to Procedure E.

Record the data on the worksheet and calculate the results as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Volume 1.000N sodium hydroxide used to titrate the 5.2-meq acid spike, ml
B	Sample volume, 0.200 ml
C	Volume of 1.000N sodium hydroxide used to titrate the sample, ml
D	Volume of 0.200N hydrochloric acid used to titrate the sample, ml
E	Result, normality of free acid, $\underline{N}^a$, or free base, $\underline{N}^b$, in the sample.

IDO-14316
H⁺-Pot-4:14
Mod-6

<u>Column</u>	<u>Unit to Record</u>
	$E = \frac{1.000C - 1.000A - 0.200D}{0.200}$
	$= 5(C-A) - D$

If E is positive, E is the free acid normality, N^a , of the sample.

If E is negative, the absolute value of E is the free base normality, N^h , of the sample.

Report the results to the nearest tenth as $2.1N^a$ and $0.2N^a$.

D. For Analyses According to Procedure F.

Record the data on the worksheet and calculate the results as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Sample volume, 0.200 ml
B	Volume 0.200N sodium hydroxide used to titrate the sample, ml
C	Volume 0.200N sodium hydroxide used to titrate the 1-mmole aluminum nitrate spike, ml
D	Volume 0.200N hydrochloric acid used, ml
E	Result, free acid normality, N^a , of the sample
	$E = \frac{0.200(B-C) - 0.200(D)}{0.200}$
	$= B - C - D$

Report results to the nearest hundreth as $1.00N^a$, $0.10N^a$, and $0.01N^a$.

REFERENCES

1. Booman, G. L., Elliott, Maxine C., Kimball, R. B., Cartan, F. O., Rein, J. E., ANAL. CHEM. 30, 284 (1958).
2. Wade, M. A., IDO Notebook U-1221, pp. 124-135, 1965.

April, 1965
S. S. Yamamura
J. E. Rein

IDO-14316

F-3:1

Mod-1

MICRODISTILLATION-COLORIMETRIC FLUORIDE DETERMINATION

ABSTRACT

A sensitive, highly specific procedure is described for the determination of 2.5 to 25 μ g of fluoride. Fluoride is separated from fluoride-complexing metal ions by steam distillation from a phosphoric acid medium. The fluoride then is determined in the distillate by a direct colorimetric procedure based on the reaction of the red lanthanum(III)-Alizarin Complexone (La-AC) chelate with fluoride to form a blue double-complex. A comprehensive discussion of the effects of diverse ions is presented under APPLICABILITY.

APPLICABILITY

This procedure is applicable to the determination of fluoride in aqueous samples containing high concentrations of diverse ions. A comprehensive study was made of the effects of various ions on the procedure. As shown by the data summarized in Figure 1, few ions interfere.

At a 500:1 diverse ion to fluoride molar ratio, Al(III), Cd(II), Ce(III), and Mn(II) cause a 5-to 10-% negative bias. However, these metals do not interfere at the 100:1 ratio.

Borate and silicate interfere seriously even at the 100:1 diverse ion to fluoride molar ratio by retarding the distillation of fluoride. This interference can be overcome if 60 ml of distillate are collected instead of 20 ml as described in the procedure. However, the distillate must be evaporated in a polyethylene beaker to less than 25 ml before the La-AC color reagent is added.

For samples that contain little or no metal ions or complexing anions, direct colorimetric measurement of the fluoride is possible with no distillation necessary. The effect of various diverse ions on the La-AC colorimetric fluoride procedure is summarized in Table I. In general, metal ions that complex fluoride interfere. Iron(III) in equimolar amounts is without effect but at this same level, aluminum(III) and zirconium(IV) interfere seriously. Sulfate and silicate interfere slightly at 77:1 molar ratio but phosphate at 2:1 and sulfite at 380:1 interfere seriously. The monovalent anions bromide, chloride, nitrate, and perchlorate at 3800:1 have no effect. Nitrite is reduced with hydroxylamine hydrochloride in the procedure and thus does not interfere at the 1500:1 molar ratio.

MEASUREMENT PROCEDURE

*NO INTERFERENCE EXPECTED

IDO-14316

F-3:3

Mod-1

Table I. THE EFFECT OF DIVERSE IONS ON THE
DIRECT LANTHANUM-ALIZARIN COMPLEXONE COLORIMETRIC PROCEDURE^a

<u>Ion Added</u>	<u>Diverse Ion to Fluoride Molar Ratio</u>	<u>Fluoride Found, %</u>
Bicarbonate	2310	100.0
Borate	500	100.3
Bromide	4600	98.3
Chloride	7700	98.6
Nitrate	3850	98.3
Nitrite	1540	99.7
Perchlorate	3850	100.0
Phosphate	2	87.5
Silicate	38	99.4
	77	94.9
Sulfate	77	95.4
	380	Interferes
Sulfite	380	Interferes
Aluminum(III)	1	Interferes
Barium(II)	770	99.7
Calcium(II)	770	100.8
Iron(III)	1	99.7
Magnesium(II)	190	100.6
Zirconium(IV)	1	Interferes

^a

All samples contained 25 µg of fluoride. Each value is the average of two or more determinations.

IDO-14316
F-3:4
Mod-1

CPP-S-3606

Fig. 2. MICRODISTILLATION APPARATUS

DISCUSSION

Phosphoric acid is used in the distillation because it forms strong complexes with such fluoride-complexing metal ions as aluminum(III), iron(III), zirconium(IV) and the rare earths, thus releasing fluoride for distillation as fluosilicic acid. As mentioned under APPLICABILITY, phosphate interferes seriously in the colorimetric procedure. The micro-distillation apparatus illustrated in Figure 2 contains a perchloric acid trap to minimize the carryover of phosphate. It is important that the rate of addition of water and the flow rate of the air be maintained at the levels specified in the procedure. Higher rates may cause such vigorous bumping that phosphate will be forced over.

Silicate causes a negative interference in the color procedure. Thus it is important that sodium hydroxide used in the procedure be stored in and dispensed with polyethylene ware.

Nitrate is reduced by cerium(III) or manganese(II) to nitrite during distillation from phosphoric acid. The nitrite, which interferes seriously in the color procedure, must be reduced with hydroxylamine hydrochloride prior to color development.

The absorbance of the blue, La-AC fluoride complex is proportional to the fluoride concentration over the range 2.5 to 25 μg . The colored complex is developed in a 20%(v/v) acetone-water or acetonitrile-water medium buffered with acetic acid and sodium acetate at pH 4.35 ± 0.05 . Under these conditions, full color development is obtained in 20 min and the colored complex is stable for 24 hr.

Although the calibration curve obtained by plotting absorbance vs fluoride concentration is linear as noted above, there is a small, constant negative intercept characteristic of the La-AC fluoride system. A small correction for this negative intercept is included in the calculations.

In routine analyses of samples of unknown fluoride concentrations, it is usual to distill samples of widely varying fluoride levels. To prevent cross contamination of low-fluoride samples with residual fluoride from a previous sample, clean out the distillation apparatus thoroughly after each distillation. The recommended cleansing procedure is described in Procedure E.

APPARATUS AND REAGENTS

A. Apparatus

1. Spectrophotometer, Beckman DU or DK or Cary Model 14.

IDO-14316
F-3:6
Mod-1

2. Absorption cells, Corex, 1-cm matched set.
3. Volumetric flask, 50-ml.
4. Pipets, volumetric, macro and micro, assorted sizes.
5. Distillation apparatus (see Figure 2).
6. Heating bath. The bath should be of a type that will maintain a temperature of $165 \pm 5^\circ\text{C}$ during the distillation. A glycerol bath (800-ml beaker of glycerol heated with a beaker-type heating mantle) has been found to be satisfactory. A fluidized-bed bath may be a more suitable substitute.
7. Lab Jacks.
8. Collection tubes. 50-ml polyethylene graduated cylinders.
9. Dropping bottles, polyethylene construction.
10. Pipets, volumetric, assorted sizes, polyethylene.

B. Reagents

NOTE: Use distilled water and C.P. or Analytical Reagent Grade chemicals throughout.

1. Fluoride stock solution, 1.00 mg/ml. Dissolve 1.1050 g of sodium fluoride in water and dilute to 500 ml with water.
2. Fluoride calibration standard I, 20.00 $\mu\text{g/ml}$. Dilute 10.00 ml of the fluoride stock solution to 500 ml with water. Store in a polyethylene bottle.
3. Fluoride calibration standard II, 10.00 $\mu\text{g/ml}$. Dilute 5.00 ml of the stock solution to 500 ml with water. Store in a polyethylene bottle.
4. Lanthanum nitrate stock solution, 0.0167M. Dissolve 3.616 g of lanthanum nitrate hexahydrate in water and dilute to 500 ml.
5. Alizarin Complexone stock solution, 0.0167M. Suspend 0.643 g of the reagent (obtainable from Burdick and Jackson Laboratories, Muskegon, Michigan) in 50 ml of water. Dissolve with 0.25 ml of concentrated ammonium hydroxide. Add 0.25 ml of glacial acetic acid and dilute to 100 ml. This solution is stable for two weeks.

IDO-14316

F-3:7

Mod-1

6. pH 4 buffer solution. Dissolve 60 g of sodium acetate trihydrate in 500 ml of water. Add 115 ml of glacial acetic acid and dilute to 1 liter with water.
7. Composite fluoride reagent. Mix in order and with swirling, 330 ml of acetone or acetonitrile, 68 ml of the buffer solution, 10.00 ml of the Alizarin Complexone stock solution, 10.00 ml of the cerium stock solution, and 75 ml of water. Warm to room temperature and dilute to 500 ml with water. This reagent, stored in a polyethylene bottle, is stable for five days. PREPARE A FRESH SOLUTION AFTER FIVE DAYS.
8. Hydrochloric acid, concentrated, and 1M.
9. Sodium hydroxide, carbonate-free, 1M and 0.5M.
10. Hydroxylamine hydrochloride solution, 2M. Dissolve 70 g of the salt in 500 ml of water.
11. Phosphoric acid. Heat 1 liter of phosphoric acid to 160°C in a 3-liter round bottom flask and bubble steam through the hot acid for 4 hr.
12. Perchloric acid. Purify the perchloric acid as described for the phosphoric acid. Dilute the purified perchloric acid with an equal volume of water.
13. Sodium hydroxide, 0.5M and 2M. Prepare aqueous solutions and store in polyethylene bottles.
14. Hydrochloric acid, 1M and 0.5M.

PROCEDURE

A. Blank

Process a blank with each series of samples. Substitute water for the sample aliquot and process according to the same procedure used for the sample.

- ##### B. Run a separate calibration with each series of samples. Use 1.00-ml of each of the two fluoride calibration standards, 10.00- and 20.00- μ g F/ml, respectively, and process these according to the procedure used for the analysis of the samples. Add 0.007 absorbance units to the absorbance of each of the standards. Divide the corrected

IDO-14316
F-3:8
Mod-1

absorbances by the micrograms of fluoride to obtain the calibration factor. The difference between the two factors should not exceed limits set by the Quality Control Laboratory. Also, the average of the two factors should agree with the established conversion factor within the specified limits. If either or both of the specifications are not met, reprocess the pair of calibration standards. Contact your supervisor if difficulties still are experienced.

C. Microdistillation of Fluoride

1. Clean the distillation apparatus as described in Procedure E.
2. Transfer 4 ml of 0.5M sodium hydroxide to the 50- μ l graduated cylinder collection tube with a polyethylene pipet.
3. Add 1 ml of 1:1 perchloric acid to the trap through the top of the distillation flask.
4. Assemble the apparatus with the condenser delivery tube extending below the surface of the sodium hydroxide in the collection tube.
5. Remove the bubbler tube and add an aliquot of the sample (5-ml or less) containing 2.5 to 25 μ g of fluoride and less than 1.75 mmoles of distillable anions to the distillation tube. The distillable inorganic anions include the halides, nitrate, and nitrite.
6. Replace the bubbler tube and add 3.0 ml of phosphoric acid.
7. Adjust the air flow rate so that 2 to 3 bubbles per sec emerge from the perchloric acid trap.
8. Raise the heating bath and adjust the temperature to $165 \pm 5^{\circ}\text{C}$.
9. Maintain the temperature at 165°C and admit water from the reservoir at a rate of 7 to 10 drops per min.
10. Collect 20 ml of distillate.
11. Remove the collection tube and wash down the condenser with 1 to 3 ml of water. Combine the washings with the distillate.
12. Continue according to D beginning at step 2.

IDO-14316
F-3:9
Mod-1

D. Colorimetric Fluoride Measurement

1. Pipet an aliquot of the sample (25 ml or less) containing between 2.5 and 25 μ g of fluoride to a 50-ml volumetric flask. The sample must be free of interfering ions and contain less than 3.0 mmoles of the ions chloride, nitrate, and perchlorate.
2. Add 1 drop of 0.2% phenolphthalein and 1 ml of 2M hydroxylamine hydrochloride.
3. Add 1M hydrochloric acid dropwise till colorless, then add one drop more. Let stand 3 to 5 min with occasional mixing.
4. Add 2M sodium hydroxide dropwise from a polyethylene pipet until basic, then add 0.5M hydrochloric acid until the solution just turns acidic.
5. Add 15 ml of the composite fluoride reagent and transfer the solution to a 50-ml volumetric flask.

NOTE: For samples analyzed directly (without distillation), the transfer is not necessary.

6. After 20 min, measure the absorbance against the reagent blank in a 1.0-cm cell at 617 m μ .
7. Calculate the concentration of fluoride as described on next page.

E. Distillation Apparatus Cleansing Procedure

Rinse the distillation apparatus thoroughly with water, and add 5 ml of concentrated perchloric acid to the distillation flask. Attach the condenser, stopper the flask (without inserting the bubbler tube) with a 14/35 g plug, then using a small flame, distill about 2 ml of perchloric acid. Finally, rinse the flask and condenser thoroughly with water. To clean the bubbler tube, immerse the tube in hot perchloric acid, then rinse thoroughly with water.

CALCULATIONS

Column

Unit to Record

A

Micrograms fluoride in the calibration standards.

IDO-14316
F-3:10
Mod-1

<u>Column</u>	<u>Unit to Record</u>
B	Absorbance of standards.
C	Corrected absorbances $C = B + 0.007$ $C' = B' + 0.007$
D	Calibration factor $D = C/A$ $D' = C'/A'$
E	Average calibration factor $E = 0.5 (D + D')$
F	Sample volume in ml.
G	Sample absorbance.
H	Result, $\mu\text{g F}^-/\text{ml}$. $H = \frac{G + 0.007}{EF}$

Report results to 3% relative significance.

REFERENCES

1. Wade, M. A., Yamamura, S. S., "Micro Determination of Fluoride Using An Improved Distillation Procedure", submitted for publication in Analytical Chemistry.
2. Yamamura, S. S., Wade, M. A., Sikes, J. H., Anal. Chem. 34, 1308 (1962).

December, 1965
S. S. Yamamura
M. A. Wade

IDO-14316
U-Fluor-1:1
Mod-6

EXTRACTION-FLUOROPHOTOMETRIC DETERMINATION OF URANIUM

ABSTRACT

A method is described for the determination of low level (< 0.1 mg/ml) uranium in aqueous and organic solutions. Uranium in aqueous samples is separated by extraction with hexone using an acid-deficient aluminum nitrate salting solution containing tetrapropylammonium nitrate (TPAN). Organic samples are analyzed directly.

The extracted uranium is fused with a sodium fluoride-lithium fluoride pellet and excited by ultraviolet light. The uranium fluorescence is read and converted to uranium concentration by comparison to a standard curve.

APPLICABILITY

The following procedures are applicable to aqueous samples containing from 5.0×10^{-5} -to 0.1 -mg/ml of uranium and to organic samples containing from 2.5×10^{-5} -to 5.0×10^{-2} -mg/ml of uranium. Aqueous samples that contain more uranium than 0.1 mg/ml may be diluted with dilute nitric acid; organic samples may be diluted with a pure solvent identical to the sample. Most cations and anions can be tolerated at high levels. See Procedure U-Color-4 as a guide for tolerance limits. Large amounts of sulfate precipitate aluminum in the salted aqueous phase and inhibit the extraction of uranium. The tolerance limit for sulfate is 2.5 mmoles in the sample aliquot. The tolerance limit for acid is 8 meq in the sample aliquot. Above this, the acid deficiency of the aluminum nitrate salting solution is exceeded and the decontamination factors for such fission products as zirconium are decreased. With a 0.5 -ml aqueous sample aliquot, as specified in the procedure, the tolerance limits are $5M$ for sulfate and $16N$ for acid. If either the levels of sulfate or acid exceeds these limits, the sample aliquot should be evaporated to near-dryness, then redissolved in $6M$ nitric acid. Water solutions and acid-deficient solutions should be acidified with concentrated nitric acid before proceeding with the analysis.

DISCUSSION

The conditions of the TPAN-hexone extraction were designed for the quantitative recovery of uranium, with high decontamination from fission products. The only fission product that measurably extracts is ruthenium. Upon fusion, the ruthenium alloys with the platinum dishes resulting in a buildup of beta activity, mainly from 1 -yr Ru-106. For this reason a separate set of platinum fusion dishes should be used for analysis of highly radioactive samples. These dishes should be checked periodically for radiation buildup and set aside if radiation levels become excessive.

Handle all platinum dishes with care because scratched or rough dishes adversely affect the fluorescence response.

IDO-14316
U-Fluor-1:2
Mod-6

APPARATUS AND REAGENTS

A. Apparatus

1. Rotating wheel stirrer.
2. Platinum fusion dishes.
3. Transite boards for carrying platinum dishes.
4. Pelletizer, syringe-type, to deliver ~ 216 mg of the sodium fluoride-lithium fluoride flux.
5. Ribbon burner with nichrome wire fusion rack.
6. Fluorophotometer, Oak Ridge Model Q-1165.

B. Reagents

1. TPAN Salting Solution. 2.8M Al, 2N^b, plus 0.1% TPAN. Prepare by dissolving 1050 g of aluminum nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, in a minimum amount of water (heat if necessary). Add 135 ml of concentrated ammonium hydroxide and 10 ml of a 10% solution of tetrapropylammonium hydroxide and dilute to about 950 ml with water. Stir until dissolved, then extract with 250 ml of hexone in a separatory funnel. Filter the aqueous phase through a large fine-porosity sintered-glass Buchner funnel, add 10 ml of 10% tetrapropylammonium hydroxide, and dilute to 1 liter with water.
2. Potassium permanganate, 0.2M. Dissolve 7.9 g of potassium permanganate, KMnO_4 , in distilled water and dilute to 250 ml.
3. Hydroxylamine hydrochloride, 2M. Dissolve 13.9 g of hydroxylamine hydrochloride, $\text{NH}_2\text{OH} \cdot \text{HCl}$, in distilled water and dilute to 100 ml.
4. Hexone.
5. Fusion flux. Homogeneously mix by weight 98% of sodium fluoride and 2% lithium fluoride.
6. Acetone.
7. Nitric acid, concentrated and 6M.

PROCEDURE

A. Calibration

1. Each of three shifts process a set of standards in the same manner as samples (Procedure D). Submit the resultant data to the Quality Control Laboratory for the preparation of a standard curve.

B. Bench Standard

Process a bench standard exactly as samples once each shift. Limits will be specified by the Quality Control Laboratory

C. Blank

Process a blank once each shift. Substitute 500 μ l of distilled water for aqueous samples (Procedure D), and 100 μ l of a suitable organic solvent for organic samples (Procedure E).

D. Aqueous Samples

1. Pipet 500 μ l of the sample into a 13-X 100-mm test tube. For neutral or acid deficient samples, add 100 μ l of concentrated nitric acid.

NOTE: As pointed out in the APPLICABILITY section, the tolerance limits for sulfate and acid are 2.5 mmoles and 8 meq, respectively. If either of these limits is exceeded, evaporate the sample to near-dryness without baking the sample. Redissolve the residue in 0.5 ml of 6M nitric acid (with heating if necessary), cool the test tube and contents to room temperature, then continue with step 2.

2. While swirling, add 0.2M potassium permanganate one drop at a time until the pink color just persists.
3. While swirling, add one drop of 2M hydroxylamine hydrochloride. If the pink color persists, add another drop. If the pink color still persists, too much potassium permanganate was added in step 2. Start again with a fresh aliquot.
4. Add 4 ml of the TPAN salting solution.
5. Pipet 2.00 ml of hexone into the test tube, stopper, mix on the rotating wheel for 3 min, then let stand until the phases separate. If complete separation does not occur, centrifuge for 2 min.

IDO-14316
U-Fluor-1:4
Mod-6

6. Place a pellet of the fusion flux into each of two platinum dishes with the pelletizer. The pellets should be of maximum size.
7. Pipet 200 μ l of the organic phase onto each of the two pellets. Each time rinse the pipet with acetone and add the rinsings to the pellet. If the pipet is Dri-filmed and drains thoroughly, the acetone rinse may be omitted. Hexone slowly dissolves Dri-film so that frequent treatment is necessary.
8. Place the pellets on a Transite board under an infrared lamp and evaporate to dryness.
9. Adjust the blue tip of the flame on the burner to midway between the top of the burner and the nichrome screen.
10. Fuse the pellets for 3 min. Do not let the dishes touch because they will fuse together.
11. Remove the pellets from the burner and place them on a Transite board. Let them cool for at least 1 min.
12. Measure the fluorescence according to Section F.

E. Organic Samples

1. Place a pellet of the fusion flux into each of two platinum dishes with the pelletizer. The pellets should be of maximum size.
2. Pipet 100 μ l of the sample onto each of the two pellets. Each time rinse the pipet with acetone and add the rinsings to the pellet. If the pipet is dri-filmed and drains thoroughly, the acetone rinse may be omitted.
3. Place the pellets on a Transite board under an infrared lamp and slowly evaporate to dryness.
4. Adjust the blue tip of the flame on the burner to midway between the top of the burner and the wire screen.
5. Fuse the pellets for 3 min. Do not let the dishes touch because they will fuse together.
6. Remove the pellets from the burner and place them on a Transite board. Let them cool for at least 1 min.
7. Measure the fluorescence according to Section F.

F. Operation of the ORNL Model Q-1165 Fluorophotometer

1. The fluorophotometer should be left on at all times. It is recommended that the instrument be left on with the coarse SENSITIVITY in position X1 when not in use.
2. Check the number 1 pellet slot to make sure that it is empty and clean and that the number 2 pellet slot contains the permanent fluorescence standard.
3. Rotate the carrier to place the number 1 slot in the measurement position. With COARSE SENSITIVITY at X1 and FINE SENSITIVITY at Zero Adj., zero the galvanometer needle with the ZERO SET knob.
4. Turn the FINE SENSITIVITY to 10 and zero the needle with the DARK CURRENT knob. Rotate the carrier to place the number 2 slot in the measurement position. Adjust the needle to read 5 on the upper galvanometer scale with the X1 control located at the top inside of the case. Alternately place slots 1 and 2 in the measurement position, adjusting the needle to 0 and 5 respectively until the readings stabilize.
5. Place the samples in positions 3 through 24. It is recommended that readings be taken in mid-scale; that is, from 3 to 7 (on the upper scale), by appropriate adjustment of the COARSE and FINE SENSITIVITIES.
6. Read FINE SENSITIVITY settings of 10, 100, and 1000 on the upper galvanometer scale; settings of 20 and 200 on the middle scale; settings of 40 and 400 on the lower scale.
7. Record the COARSE SENSITIVITY and FINE SENSITIVITY settings and the GALVANOMETER READING on the worksheet.

F. Removal of Flux from Dishes

Gentle tapping usually is sufficient. If not, dissolve the flux with warm water. Do not scrape because the dish is easily scratched (see DISCUSSION).

CALCULATIONS

Record the data on the worksheet as follows:

IDO-14316
U-Fluor-1:6
Mod-6

<u>Column</u>	<u>Unit to Record</u>
A	Sample dilution.
B	Galvanometer scale readings.
C	Coarse and fine sensitivity settings.
D	Scale factor (see Table I).
E	μ a of fluorescence (<u>B</u> times <u>D</u>) for sample.
F	Average μ a for sample.
G	Average μ a for blank.
H	Corrected μ a for sample (<u>F</u> - <u>G</u>).
I	Result; concentration of uranium, mg/ml (obtained from standard curve).

NOTE: For organic samples, divide I by 2.

Report results to two significant numbers, as 2.1×10^{-3} mg/ml.

Table I

SCALE FACTORS FOR ORNL MODEL Q-1165 FLUOROPHOTOMETER

<u>Sensitivity Settings</u>		<u>Scale Factor</u>
Coarse	Fine	
XI	10,20,40	1
XI	100,200,400	10
XI	1000	100
X5	10,20,40	5
X5	100,200,400	50
X5	1000	500
X25	10,20,40	25
X25	100,200,400	250
X25	1000	2500

IDO-14316
U-Fluor-1:7
Mod-6

REFERENCES

1. Centanni, F. A., Rose, A. M., DeSesa, M. A., Anal. Chem. 28, 1651 (1956).
2. ORNL Master Analytical Manual, Method Nos. 1 003080, 9 003080, 1960.
3. Hunter, B. R., Private Communication, February, 1960.
4. Lund, D. M., IDO Notebook No. 1327, pp. 1-4.

D. M. Lund
November, 1965

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

IDO-14316
U-Color-5:1
Mod-3

DETERMINATION OF MILLIGRAM AMOUNTS OF URANIUM
BY AN EXTRACTION-SPECTROPHOTOMETRIC MEASUREMENT
METHOD

ABSTRACT

A rapid, highly selective method is described for the determination of milligram amounts of uranium in a wide variety of samples. The uranium is extracted into hexone as the neutral tetrapropylammonium trinitratouranate ion pair from an acid-deficient aluminum nitrate salting medium, then measured at 452 mμ on a recording spectrophotometer. Known standards are processed simultaneously and the concentration of uranium in the sample is determined by comparison.

APPLICABILITY

This method is applicable to a wide variety of samples including those of the aluminum, stainless steel, and Zircaloy types. Two procedures, D and E are given. These are compared in Table I. Procedure D requires only a small volume of salting solution, is adaptable to remote use, and has adequate tolerance for diverse ions. It is therefore recommended for all samples except those with complex unknown compositions and those with less than 1 mg of U/ml. Procedure E is specially adapted to samples with complex unknown compositions and low levels of uranium. It has greater tolerance for diverse ions than does Procedure D and it is suitable for the analysis of samples with uranium concentrations down to 0.05 mg/ml. The ranges of Procedures D (1 to 30 mg U) and E (0.5 to 35 mg U) purposely overlap to minimize repeat determinations. When highest precision is desirable, Procedure E should be used for the analysis of samples that contain less than 5 mg of U/ml.

In Procedure E, 35 mg of uranium has been selected as the upper limit because the absorbance approaches 1.0 at this level. However, under the extraction conditions of E, the extraction is known to be quantitative up to at least 75 mg of uranium so that in emergencies, extracted samples with greater than 35 mg of uranium can be diluted with 1 or 2 parts of hexone for measurement. This approach will give results within about 3% of the true value....about 1.5% low when diluted two-fold and about 2-3% low when diluted three-fold. Possible reasons for the negative bias are given in the DISCUSSION section.

Table I. COMPARISON OF PROCEDURES D AND E

Item of Comparison	Procedure	
	D	E
Volume of salting solution used	6 ml	40 ml
Maximum sample size	1 ml ^a	10 ml
Water tolerance	1.75 ml	12 ml
Range of colorimetric procedure ^b	1-30 mg U for "cold" samples 5-30 mg U for samples that require remote handling	0.5-35 mg U
Lowest U concentration determinable ^b	1 mg/ml ("cold" samples) 5 mg/ml (samples that require remote handling)	0.05 mg/ml
Diverse ion tolerance	Excellent but generally less than Procedure <u>E</u> ; greater than moderate amounts of chloride interfere	Excellent; generally greater than Procedure <u>D</u> . High levels of chloride do not interfere
Principal advantages	Requires small volume of salting solution; Adaptable to remote use; Adequate tolerance for diverse ions	High tolerance for diverse ions including chloride, therefore more suitable than <u>D</u> for the analysis of samples with complex unknown compositions; Applicable to samples with very low U concentrations

^a Actually, the sample volume can exceed 1 ml if an evaporation step is used prior to extraction.

^b The range and applicability of both Procedure D and E have been broadened by the use of low-volume 5-cm absorption cells as recommended by Remote and Service Analysis personnel⁽¹⁾.

The effects of diverse ions have been studied extensively under the conditions of Procedure D(2,3) and Procedure E(5) and on the basis of these studies, the tolerance level of 43 metal ions and 18 anions have been established (Table II). Careful examination of Table II will show that most ions do not interfere even at high levels. Some of them (those in Table II identified by the letter b) do interfere under given conditions, and for these potential interferences, maximum tolerance levels are listed. The maximum tolerance level is defined as that level where the observed effect is 1%. The effects of a number of the interfering ions at levels above the maximum tolerance level have also been studied using Procedure E. These data are summarized in Table III. Noteworthy is the fact that sulfate does not interfere very seriously even at the 24 mmole (1.25 ml of the concentrated acid) level.

The diverse ions that do interfere affect the determination in different ways. Bismuth, perchlorate, tungstate, and vanadate precipitate under the conditions of the analysis and carry uranium. Cerium(IV), chloraurate (AuCl_4^-), perchlorate, vanadate, and Th(IV) form stable complexes with the tetrapropylammonium ion and prevent the complete extraction of uranium. Others such as Ho(III), Np(VI), and Pu (all valences) coextract with the uranium and absorb at 452-m μ , the working wavelength. Complexing anions such as citrate, phosphate, and sulfate above certain levels complex uranium to prevent quantitative extraction. Chloride alone does not interfere except at very high levels; however, when major amounts of iron(III) are also present, the chloride level must be less than 6 mmoles for Procedure E and less than 1 mmole for Procedure D. Above these limits, the iron(III)-chloride complex coextracts and interferes by altering the spectra of the uranium complex. The extraction of iron is strongly dependent on the chloride concentration as well as the total chloride level. In Procedure E, the addition of water effectively reduces the chloride concentration and the coextraction of iron.

The harmful effect of some of the interferences can be minimized or eliminated with simple manipulations. In the recommended procedures, a sequential potassium permanganate-hydroxylamine hydrochloride treatment is used routinely to guarantee that the uranium is in the extractable (VI) valence state. This treatment automatically reduces Ce(IV), Cr(VI), Mn(VII), and peroxide to eliminate their interferences. Volatile interferences such as perchloric acid can be removed by repeated evaporation of the sample with sulfuric acid. Sulfate, however, does tend to suppress the absorbance so that the final fuming should be to a small volume and standards should be processed with the samples through the same treatment. The tolerance for thorium can be increased by the use of a modified salting solution with a higher tetrapropylammonium nitrate concentration.

Table II EFFECTS OF DIVERSE IONS^a

Tolerance Level, mmole(s)			Tolerance Level, mmole(s)		
Ion	Procedure		Ion	Procedure	
	D	E		D	E
Metal Ions					
Al(III)	2.0 ^c	15.0	Mg(II)	0.75	5.0
Ag(I)	1.2	2.0 ^c	Mn(II)	0.50	5.0
Au(III)	Expected to Interfere		Mn(VII)	1.0 ^d	1.0 ^d
Ba(II)	0.025	1.0 ^c	Mo(VI)	0.10 ^b	0.35 ^b
Be(II)	1.0	2.0 ^c	Na(I)	1.2	5.0 ^c
Bi(III)	0.025	0.05 ^b	Nd(III)	0.10	0.55
Ca(II)	0.75	5.0 ^c	NH ₄ (I)	0.5 ^c	3.0
Cd(II)	0.50	5.0	Ni(II)	1.0	5.0
Ce(III)	0.50	5.0	Np(VI)	Expected to Interfere	
Ce(IV)	0.008 ^b	0.025 ^{b,d}	Pb(II)	0.25	5.0
Co(II)	1.2	5.0	Pt(IV)	0.0003 ^c	0.024
Cr(III)	1.5	5.0	Pu(IV, VI)	Expected to Interfere ^f	
Cr(VI)	0.1 ^{b,d}	0.5 ^{b,d}	Ru(III,IV)	0.01 ^c	0.13
Cu(II)	1.0	5.0	Sm(III)	0.10	0.52
Dy(III)	0.10 ^c	0.55	Sn(II,IV)	0.02 ^c	0.05 ^b
Er(III)	0.10 ^c	0.52	Sr(II)	0.50	5.0
Fe(III)	0.50	5.0	Th(IV)	0.008 ^b	0.025 ^b
H(I) as HNO ₃	10 ^b	50 ^b	V(V)	0.012 ^b	0.025 ^b
Hg(I,II)	0.50	2.5	W(VI)	0.01 ^c	0.06 ^b
Ho(III)	0.015 ^{b,c}	0.025 ^b	Y(III)	0.02 ^c	0.10
K(I)	0.50	8.0	Zn(II)	1.0	2.5
La(III)	0.50	5.0 ^c	Zr(IV)	0.25	2.5

Table II EFFECTS OF DIVERSE IONS^a (Continued)

Tolerance Level, mmole(s)			Tolerance Level, mmole(s)		
Ion	Procedure D	Procedure E	Ion	Procedure D	Procedure E
Anions					
Acetate	1.2	8.7 ^b	Iodide	0.05 ^{b,c,e}	0.10 ^{b,e}
Borate	0.025	3.0	Nitrate (as NH_3)	10	50
Bromate	0.50	1.0 ^c	Oxalate	0.050	4.0
Bromide	0.2 ^c	1.0	Perchlorate	0.10 ^b	0.50 ^b
Chloride (low Fe samples)	0.25	24.2 ^b	Peroxide (H_2O_2)	0.10 ^b	0.50 ^b
Chloride (high Fe samples)	Expected to Interfere	6.0 ^b	Persulfate	0.25	---
Citrate	0.25	2.5 ^b	Phosphate	0.25 ^b	1.0 ^b
Cyanide	0.25	0.25 ^c	Sulfate	0.25 ^b	12 ^b
Fluoride	0.25	20	Tartrate	0.05 ^c	2.5
Formate	1.2	5.0 ^c			

^a Unless noted otherwise, the tolerance level listed is the highest level studied and does not necessarily represent the maximum tolerance level.

^b Maximum tolerance level at or below which the error is 1% or less.

^c Conservative estimate based on the chemical properties of the elements and the observed effect of the ion in the other procedure.

^d Tolerance level with no hydroxylamine reduction. With reduction, tolerance is about same as lower valence ion listed.

^e After the extraction, wait 30 min before color measurement to allow the iodine to bleach out.

^f The interference of plutonium could possibly be eliminated or reduced by scrubbing the hexone phase with a salting solution containing organic complexing reagents⁽⁴⁾.

Table III. EFFECT OF DIVERSE IONS AT LEVELS ABOVE
THE MAXIMUM TOLERANCE LEVEL, PROCEDURE E^a

Metal Ion	Mmoles Present	Effect, %	Anion	Mmoles Present	Effect, %
Au(III)	0.04	-9	Acetate	17.4	-1.7
Bi(III)	0.50	-2.6	Chloride	36.3	-1.1
H(I) as HNO ₃	63 78	-1.1 -4.3	Citrate	5.0	-2.0
Hg(III)	0.10	-12.3	Iodide	0.5	Iodine Coextracts and Interferes
Mo(VI)	0.70	-2.0	Perchlorate	2.0	-2.7
Sn(II,IV)	0.25	-2.3	Peroxide (H ₂ O ₂)	1.0	-3.5
Th(IV)	0.05	-1.5	Phosphate	7.3	-1.5
V(V)	0.05	-1.5	Sulfate	18	-1.5
	0.10	-4.4		24	-2.1
W(VI)	0.10	-4.4			

^a The uranium level was maintained at 25 mg. Similar effects can be expected for Procedure D at diverse ion levels approximately 20% of the levels listed above.

DISCUSSION

The uranium must be in the (VI) oxidation state to be extractable, so in both Procedures D and E, a permanganate oxidation step is specified. If the uranium is DEFINITELY known to be in the (VI) state only, the addition of potassium permanganate is not necessary. The uranium can be assumed to be totally in the (VI) state when the sample contains strong oxidants such as chromium(VI) and when the prior history of the sample precludes the existence of uranium in oxidation states other than (VI).

The extraction of uranium(VI) and the absorbance of the extracted uranium complex are dependent on temperature, the TPAN concentration, the age and concentration of the salting solution, and the volume of hexone. Thus, standards must be processed each time a sample is run. Recent studies⁽⁵⁾ have shown that the calibration factors for D and E are significantly different so standards must be processed by the same procedure as that used for the analysis of the samples. The reasons for the observed difference between the factors for D and E are thought to be differences in the level and concentration of TPAN in the two extraction systems and differences in the distribution of hexone into the aqueous phase.

Two potentially serious sources of error are the improper measurement of the hexone and the loss of hexone in the extraction process before equilibration is attained. It should be kept in mind that a difference of one drop (~ 0.05 ml) of hexone will cause an error of 1%. Freshly-prepared salting solution contains a significant amount of suspended hexone which seriously effects the results. For this reason, requests for salting solution should be made well in advance so that properly aged salting solutions can be provided.

APPARATUS AND REAGENTS

A. Apparatus

1. Test tubes, glass, 15-x 125-mm.
2. Culture tubes, 25-ml, with polyethylene-lined screw caps.
3. Separatory funnels, 60-ml, Teflon stopcocks.
4. Polyethylene stoppers for above test tubes and separatory funnels.
5. Extraction apparatus for test tubes, pin wheel type⁽²⁾ is recommended.
6. Centrifuge, International Clinical, Model Cl.
7. Pipets, volumetric, assorted sizes.

U-Color-5:8, Mod-3

8. Pipets, micro, assorted size, with control syringe.
9. Pipets, Mohr, 5- and 10-ml sizes.
10. Cary Model 14 Recording Spectrophotometer, Beckman DK Recording Spectrophotometer, or equivalents.
11. Absorption cells, Corex, 1-cm. Teflon spacers should be placed in the bottom of the cell if scaled-down volumes are used in the method.
12. Absorption cells, Aminco, 5-cm, 13-mm O.D., 4.9-ml capacity. These cells should be fitted with Teflon sleeves with a diameter similar to that of standard 22-mm O.D. 5-cm cells.
13. Graduated cylinder, 50-ml.
14. Dropping bottles.

B. Reagents

NOTE: Prepare all reagents from C.P. or Analytical Reagent Grade stock and distilled water. Use distilled or treated water throughout the procedure.

1. Aluminum Nitrate Salting Solution, $2N^b$.

- a. 0.8%(0.04M) TPAN (tetrapropylammonium nitrate)

Dissolve 1050 g of aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$, in 75 ml of water and 135 ml of concentrated ammonium hydroxide with the aid of heating and stirring. Cool to room temperature, dilute to 900 ml with water, add 20 ml of 10% tetrapropylammonium hydroxide (Eastman Organic), and mix well. Extract the solution with 100 ml of hexone for 3 min. Let stand for about 1 hr to allow the phases to separate then drain off the lower phase into a 1-liter bottle. Finally, add 80 ml of 10% tetrapropylammonium hydroxide and mix well. THE SOLUTION IS SUITABLE FOR USE AFTER 3 DAYS (See the DISCUSSION Section). The preparation of a 4-liter batch is recommended. To prepare a 4-liter batch, multiply all additions by four and extract the solution one-half at a time with 200-ml portions of hexone.

- b. 5.0% in TPAN

Neutralize 100 ml of 10% tetrapropylammonium hydroxide solution to pH 7 with 5M nitric acid. Transfer to a large evaporating dish and allow the TPAN solution to stand until a

U-Color-5:9, Mod-3

thick slurry of crystals forms. This may take as long as 4 days. Transfer the crystals to a 400-ml beaker with 20 ml of water. Add 210 g of aluminum nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Stir and add water until a volume of approximately 165 ml is reached. Add 27 ml of concentrated ammonium hydroxide and stir without heating until solution is complete. Filter and dilute to 200 ml with water.

2. Hexone - Shell Oil Company methyl isobutyl ketone or Eastman white label 4-methyl-2-pentanone.
3. Potassium permanganate solution, 0.2M. Dissolve 31.6 g of potassium permanganate, KMnO_4 , in 100 ml of water. Store in a dark bottle.
4. Hydroxylamine hydrochloride, 2M. Dissolve 27.8 g of hydroxylamine hydrochloride, $\text{NH}_2\text{OH} \cdot \text{HCl}$, in water and dilute to 200 ml.
5. Nitric acid, concentrated.
6. Uranium stock solution, 250 mg U/ml. Ignite approximately 300 g of NBS U_3O_8 at 900°C for 1 hr. Let cool, then weigh to the nearest 0.001 g, 295 ± 1 g of the oxide into a 500-ml Erlenmeyer flask. Cover the flask with a reflux head and dissolve the U_3O_8 in nitric acid with the aid of heat. Lengthy digestion with nitric acid may be necessary to completely dissolve the oxide. When the dissolution is complete, evaporate the solution to the appearance of uranyl nitrate crystals. Cool slightly, then quantitatively transfer the contents of the Erlenmeyer flask with water rinses to a tared (to ± 0.001 g) 1-liter volumetric flask. Cool the flask and contents to room temperature, dilute to volume with water, mix thoroughly, and weigh. Store the solution in sealed ampoules in 50-ml units. From the weight of the U_3O_8 , its purity, and the weight of the solution, calculate the uranium concentration in mg/g. Label the ampoules accordingly.
7. Calibration and Bench Standards. Four standards are necessary for this method. The approximate concentration of each and the recommended dilutions are:
 - a. Standard I, 25 mg U/ml. Dilute a weighed (to ± 0.0001 g) 25-ml aliquot of the stock solution to 250.0 ml with 0.1M nitric acid.
 - b. Standard II, 10 mg U/ml. Dilute a weighed 10-ml aliquot of the stock solution to 250.0 ml with 0.1M nitric acid.
 - c. Standard III, 5 mg U/ml. Dilute a weighed 5-ml aliquot of the stock solution to 250.0 ml with 0.1M nitric acid.

U-Color-5:10, Mod-3

- d. Standard IV, 2 mg U /ml. Dilute a weighed 2-ml aliquot of the stock solution to 250.0 ml with 0.1M nitric acid.

From the weight of the aliquot and the concentration of the stock solution, calculate the concentration of uranium in the standards in mg/ml and label the standards accordingly. One 50-ml ampoule of the stock solution will provide sufficient stock solution to prepare the entire series of four standards. Supply four fresh standards at least every 3 months.

PROCEDURE

A. Use and Care of Cells

One cell is recommended for a series of measurements of standards and samples. Clean cells between measurements by rinsing at least three times with acetone. Dry with clean air.

After the final measurement, rinse the cell thoroughly in order with water and acetone, then air dry.

B. Blank

A blank is not necessary in this method. All measurements are made against air.

C. Calibration and Bench Standard

The use of four calibration standards is intended to promote efficiency by reducing repeat analyses. If only samples with similar concentrations are being analyzed, the use of two appropriate standards will suffice.

PROCESS CALIBRATION STANDARDS WITH EACH RUN by the same procedure as that used for the analysis of samples. Use 1.00-ml aliquots of the standards for both Procedure D and Procedure E. Divide the observed absorbances by the milligrams of uranium in each standard to obtain the conversion factor. For each of the two groups of standards, the difference between the two factors should not exceed limits set by the Quality Control Laboratory and the average of the two factors should agree with the established conversion factor within the specified limits. If either or both of the specifications are not met, reprocess the pair or pairs of calibration standards immediately. Contact your supervisor if difficulties still are experienced.

D. Analysis of Samples (Procedure D)

Procedure D is recommended for all samples including highly radioactive samples that require remote handling. It is not recommended for samples with complex unknown compositions and

samples that contain appreciable amounts of chloride. If remote analysis is not required, the uranium concentration must be at least 1 mg/ml; however, if the extraction must be performed remotely, only 1-cm cells can be used for the final measurement so the uranium concentration should be greater than 5 mg/ml. The tolerance of Procedure D for diverse ions and the recommended pretreatment for volatile interferences are discussed under APPLICABILITY.

1. To a 15- x 125-mm test tube or a 25-ml screw-cap culture tube, pipet 1 ml or less of sample containing 1 to 30 mg of uranium and less than 10 meq of acid.

NOTES: 1. If the extraction of uranium, steps 1 through 8, is to be done remotely, the sample aliquot must contain at least 5 mg of uranium.

2. If the evaporation step is used in step 4, the sample can be larger than 1 ml.

2. Add one drop of concentrated nitric acid, then with continuous swirling, add 0.2M potassium permanganate one drop at a time until the pink color remains for 30 sec. Continue with step 3a. If the uranium is definitely known to be only in the (VI) valence state, omit this step and proceed with step 3b.
3. a. While swirling continuously, add one drop of 2M hydroxylamine hydrochloride. If the pink color still persists, add another drop. If the pink color still remains, too much excess permanganate was added in step 2. Start again with a fresh aliquot.
 b. Hydroxylamine hydrochloride will also reduce chromium(VI), cerium(IV), and peroxide, which are potential interferences. Add one drop of concentrated nitric acid, then with continuous swirling, add 2M hydroxylamine hydrochloride dropwise until the yellow-orange color of the chromium(VI) and cerium(IV) is "bleached" and the evolution of nitrogen ceases. Cerium(III) is colorless and chromium(III) is bluish-violet or green. Do not add more than five drops of 2M hydroxylamine hydrochloride.
4. Using the approximation one drop $\approx$ 0.05 ml to determine the volumes of reagents added in steps 2 and 3, estimate the total volume of the treated sample. If the total volume exceeds 1.5 ml, evaporate the sample to less than 1.5 ml, then let it cool to room temperature.
5. With a Mohr pipet, add 6 ml of salting solution. Use the 0.8% TPAN salting solution except for samples that contain interfering levels of thorium in which cases the 5% TPAN salting solution should be used.

U-Color-5:12, Mod-3

6. Pipet EXACTLY 5.00 ml of hexone, stopper, and extract for 3 min with the extraction wheel.
7. Centrifuge for 1 min to separate the two phases.
8. With a transfer micropipet, transfer the organic phase to a 1-cm (5-to 35-mg of uranium) or a 5-cm (1-to 7-mg of uranium) optical cell. Select the cell on the basis of the yellow color of the hexone phase. In doubtful cases, use the 5-cm cell first. This will permit subsequent measurement in a 1-cm cell.
9. Scan the sample with the recording spectrophotometer from 480 m μ to 440 m μ . Use air as the reference and a scan speed of 5A/sec.
10. Determine the uranium concentration of the sample as described under CALCULATIONS.

E. Analysis of Sample (Procedure E)

This procedure is primarily intended for samples that contain between 0.05 and 2-mg of U/ml; however, it is also applicable to samples with higher uranium concentrations. Procedure E is recommended for samples with unknown compositions and samples that contain large amounts of chloride. The effects of diverse ions and the recommended pretreatment for volatile interferences are discussed under APPLICABILITY.

1. To a 60-ml separatory funnel, pipet a sample (10 ml or less) that contains between 0.5 and 35 mg of uranium and less than 50 meq of acid. Dilute to 5 ml with water. If the sample aliquot is larger than 5 ml, omit the water and proceed with step 2.
2. Add five drops of concentrated nitric acid, then with continuous swirling, add 0.2M potassium permanganate one drop at a time until the permanganate color lingers for at least 30 sec. Continue with step 3a. If the uranium is definitely known to be in the (VI) valence state only, omit this step and proceed with step 3b. Refer to the DISCUSSION Section.
3. a. While swirling continuously, add 2M hydroxylamine hydrochloride one drop at a time until the permanganate is decolorized, then add five drops more.
b. Hydroxylamine hydrochloride will also reduce chromium(VI), cerium(IV), and peroxide which are potential interferences. Add five drops of concentrated nitric acid, then with continuous swirling, add 2M hydroxylamine hydrochloride dropwise until the yellow-orange color of the chromium(VI)

or cerium(IV) is "bleached" and the evolution of nitrogen ceases. Cerium(III) is colorless and chromium(III) is bluish-violet or green. When large amounts of oxidant are present, immerse the separatory funnel in a beaker of boiling water to promote complete reduction. Cool to room temperature and continue with step 4.

4. Using the approximation one drop $\approx$ 0.05 ml to determine the volumes of reagents added in steps 2 and 3, estimate the total volume of the treated sample. If the total volume is less than 12 ml, proceed to step 5. If the volume exceeds 12 ml, start again with a slightly smaller aliquot. In some cases, additional sample is not available. If so, evaporate the sample under a heat lamp to less than 12 ml, cool to room temperature, then continue with step 5.
5. With a graduated cylinder, add 40 ml of the 0.8% TPAN salting solution.
6. Pipet EXACTLY 5.00 ml of hexone, stopper and extract for 1 min.
7. Wait several minutes for the phases to separate, then drain off the lower aqueous phase.
8. With a transfer micropipet, transfer the organic phase to a 1-cm Corex (for 5 to 35 mg of U) or a 5-cm cylindrical (for 0.5- to 7 mg of U) optical cell. Select the cell on the basis of the yellow color of the hexone phase. In doubtful cases, use the 5-cm cell first. This will permit subsequent measurements in a 1-cm cell. Occasionally, a precipitate is present or an emulsion will persist such that a sufficient volume of the hexone phase cannot be removed for spectrophotometric measurement. Drain the organic phase completely into a clean 15- x 125-mm test tube and centrifuge it for 1 min.
9. Scan the sample with the recording spectrophotometer from 480 to 440 m μ . Use air as the reference and a scan speed of 5A/sec.
10. Determine the uranium concentration as described under CALCULATIONS.

CALCULATIONS

- A. Determine the absorbance by drawing a line tangent to and connecting the absorbance minimums on each side of the 452-m μ peak as shown below.

U-Color-5:14, Mod-3

The absorbance is the height of the peak in absorbance units as shown in the above drawing. It is equal to the difference between the absorbance reading at the 452-m μ peak and the absorbance reading on the tangent line at 452 m μ .

B. Record the data on the worksheet as follows:

Column	Unit to Record
A	Mg of uranium in each of the standard aliquots.
B	Absorbance of each of the calibration standards.
C	Conversion factor obtained by dividing the absorbance by the mg of uranium in the standard aliquot. $C = B/A, C' = B'/A'$
D	Average conversion factor. $D = 0.5 (C + C')$
E	Sample size in ml.
F	Absorbance of sample.
G	Enrichment factor (see Table I). This factor is based on the use of normal uranium for the calibration.
H	Results, mg U/ml. $H = \frac{F G}{D E}$

Report results to three significant numbers as 0.124, 1.24, and 12.4.

Table IV. ENRICHMENT FACTORS

% Enrichment	Factor	% Enrichment	Factor
0.7 (normal)	1.000	88.1 - 90.0	0.9889
80.0 - 82.0	0.9899	90.1 - 92.0	0.9887
82.1 - 84.0	0.9897	92.1 - 94.0	0.9884
84.1 - 86.0	0.9894	94.1 - 96.0	0.9882
86.1 - 88.0	0.9892	96.1 - 98.0	0.9879
		98.1 - 100.0	0.9877

REFERENCES

1. Duce, F. A., Oestreich, D. K., Personal Communication, October, 1965.
2. Maeck, W. J., Booman, G. L., Elliott, M. C., Rein, J. E., Anal Chem 31, 1130 (1959).
3. Ibid, 30, 1902 (1958).
4. Shank, R. C., et al , Annual Report of Division Analytical Branch for 1964, IDO-14655, Appendix B, pp 73-79 (April, 1965) and Rein, J. E., This Manual, Method U Color-4, Mod-3, December, 1964.
5. Yamamura, S. S., Lund, D. M., IDO Notebook U-1151, pp 5-40, 1965.

U-Color-5:16, Mod-3

SAMPLE CODE _____

LOG NO. _____

CHARGE NO. _____

ACTIVITY _____ mr/hr

CHEMICAL ANALYSIS

DETERMINATION Uranium

A	B	C	D	E	F	G	H
Mg U in Standards	Absorbance of Standards	Conversion Factor	Average Conv. Factor	Sample Size, ml	Sample Absorbance	Enrichment Factor	Result U/ml
25.00	0.600	0.024					
			0.024	10.00	0.480	1.000	2.00
10.00	0.240	0.024					

Calculations:

ANALYZED BY _____ RESULTS 2.00 mg/ml

$$C = \frac{B}{A} = \frac{0.600}{25.00} = 0.024 ; \quad C' = \frac{0.240}{10.00} = 0.024$$

$$D = 0.5 (C+C') = 0.5 (0.024+0.024) = 0.024$$

$$H = \frac{F G}{D E} = \frac{(0.480)(1.000)}{(0.024)(10.00)} = 2.00 \text{ mg U/ml}$$

COLORIMETRIC DETERMINATION OF SELENIUM⁽¹⁾ABSTRACT

The sample is acidified with formic acid and 3,3'-diaminobenzidine is added. The diphenylpiaszelenol thus formed is extracted into toluene at pH 6 to 7 and the absorbance is measured at 420 mμ.

APPLICABILITY

The method, as written, is applicable to fairly pure selenium solutions. The linear range of the method is 2.5 to 50 μg of selenium. Strong oxidizing agents, which oxidize the 3,3'-diaminobenzidine, must be absent. The major diverse ion interferences are Cu(II), Fe(III), and V(V)⁽²⁾.

DISCUSSION

Selenium reacts with 3,3'-diaminobenzidine to form an intense yellow compound, piaszelenol, with maximum absorbance at 420 mμ.

Aqueous solutions of 3,3'-diaminobenzidine are unstable at room temperature, but are stable for several days if kept refrigerated.

The formation of piaszelenol is sensitive to acid concentration, temperature, and time. The conditions cited in the procedure must be followed carefully to obtain reliable results.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, Griffin, 100-ml.
2. pH meter.
3. Centrifuge.
4. Centrifuge tubes, 15-ml.
5. Separatory funnels, 125-ml.
6. Micropipets, various sizes.
7. Macropipets, various sizes.

IDO-14316
Se-1:2

8. Beckman Model DU spectrophotometer, or equivalent.
9. Absorption cells, 1-cm Corex, calibrated to ± 0.002 absorbance units with a processed standard in the cells at 420 m μ .

B. Reagents

Distilled water and C.P. or Reagent Grade chemicals are used.

1. Formic acid, 2.5M. Dilute 34 ml of 88% formic acid to 100 ml with water.
2. 3,3'-diaminobenzidine, 0.5%, prepared from Aldrich Chemical Co. reagent. Dissolve 0.5 g of the reagent in water and dilute to 100 ml. Keep refrigerated. Prepare fresh at least once per week.
3. Ammonium hydroxide, 6M. Mix 1 volume of concentrated ammonium hydroxide with 1 volume of water.
4. Toluene.
5. Standard selenium solution, 100 $\mu\text{g}/\text{ml}$. Dissolve 14 mg of selenium dioxide in water and dilute to 100 ml.

PROCEDURE

A. Calibration and Bench Standard

A separate calibration is required for each series of samples. Use 0.100-ml and 0.200-ml aliquots of the 100 $\mu\text{g}/\text{ml}$ standard selenium solution. Process these according to C. Divide the absorbances by the respective micrograms of selenium in each aliquot to determine the conversion factor. If the difference between the two conversion factors does not agree within limits set by the Quality Control Laboratory, process another pair of standards. Contact your supervisor if agreement still is not obtained.

D. Blank

Process a reagent blank according to C substituting water for the sample.

C. Samples

1. Pipet a sample aliquot containing from 2.5 to 50 μg of selenium, in a maximum volume of 40 ml, into a 100-ml beaker. Dilute high concentration samples with water to meet the required concentrations.

2. Add 2 ml of 2.5M formic acid.
3. Dilute to approximately 50 ml with water.
4. Add 2 ml of 0.5% diaminobenzidine solution.

Keep this reagent refrigerated when not in use. The reagent decomposes at room temperature to cause low results.
5. Adjust the pH to 2 to 3 with 6M hydrochloric acid or 6M ammonium hydroxide and let stand at room temperature for at least 30 min.

The minimum period for full color development is 30 min. Once developed, the color is stable indefinitely.
6. Adjust the pH to 6 to 7 with 6M ammonium hydroxide and quantitatively transfer the solution to a 125-ml separatory funnel with the aid of water rinses.

Erratic results will be obtained if the pH exceeds 10.
7. Add exactly 10 ml of toluene and extract for 30 sec with vigorous shaking.
8. Transfer the toluene phase to a 15-ml centrifuge tube and centrifuge for 5 min.
9. Place the reagent blank in the cell and adjust the controls of the spectrophotometer so that the net absorbance is zero at 420 mμ.
10. Fill a matched cell with the sample and measure the absorbance at 420 mμ.

CALCULATIONS

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms of selenium in the calibration standards.
B	Absorbance of standards.
C	Calibration factor
	$C = \frac{B}{A}$
	$C' = \frac{B'}{A'}$

/IDO-14316
Se-1:4

<u>Column</u>	<u>Unit to Record</u>
D	Average calibration factor. $D = \frac{C+C'}{2}$
E	Sample volume, in ml.
F	Sample absorbance.
G	Results, $\mu\text{g/ml}$ of selenium in sample. $G = \frac{F}{DE}$

REFERENCES

1. Cheng, K. L., Anal. Chem. 28, 1738 (1956).
2. Hoste, J., Anal. Chim. Acta 2, 402-8 (1948).

I. L. Doggett
October, 1965

TITRIMETRIC DETERMINATION OF THORIUM (AND ALUMINUM) IN THORIUM
METAL AND THORIUM METAL SLUGS CLAD WITH ALUMINUM

ABSTRACT

Thorium is determined by reverse ethylenediaminetetraacetic acid (EDTA) titrimetry after it is selectively extracted into hexone from high lithium nitrate salting medium and stripped into water. The sum of thorium plus aluminum is likewise determined by reverse EDTA titrimetry without prior separation of the thorium. Aluminum is obtained by difference (8).

APPLICABILITY

This method, a modification of two existing methods (1,4) for the determination of macro amounts of thorium and aluminum, was developed specifically for the analysis of relatively pure thorium metal and thorium metal slugs clad with pure aluminum.

An independent study of the effects of diverse ions on the determination of thorium has not been made, but on the basis of the two reports cited above (1,4) the discussions of the nitrate extraction system by Grimaldi (3) and by Morrison and Freiser (5) the selectivity of the EDTA titration (6), and the chemical properties of thorium, the effect of diverse ions can be predicted (Table I).

Table I. PROBABLE EFFECTS OF METAL IONS ON THE
DETERMINATION OF THORIUM

Metal Ions	Effect
Bi(III), Ce(IV), Cr(VI), Hg(II), Pa(V), Pu(V), Sc(III), Tl(III), V(V), Zr(IV)	Serious positive interference
Ce(III), Fe(III), Gd(III), In(III), Sn(IV), Y(III), Yb(III)	Slight positive interference ^a
Ba(II), Be(II), Ca(II), Co(II), Cr(III), Cu(II), La(III), Mg(II), Mn(II), Mo(VI), Nd(III), Ni(II), Pb(II) ^b , Th(IV), U(VI), Zn(II)	No interference ^a

^a The interference of metal ions that are partially extracted (see references 1 and 3) will increase as the diverse metal ion to thorium ratio is increased.

^b Some metal ions such as Pb(II) precipitate as nitrate salts in the high nitrate salting medium, and therefore, may interfere.

IDO-14316
Th-2:2
Tentative

Metallic interferences are those metal ions that both coextract with thorium under the recommended extraction conditions and form a stable complex with EDTA at pH 2.5 to 3.0 (6), the pH maintained during the final EDTA titration.

Complexing anions such as citrate, fluoride, and phosphate which complex thorium even at low pH cause low results. Sulfate which forms a moderately stable complex with thorium will probably interfere if present in large amounts. Except for sulfate and phosphate which are not volatilized readily, the interference of complexing anions can be prevented by fuming the sample initially with perchloric acid. Of course, nitric acid should be admitted with the perchloric acid if the sample contains organic reagents.

DISCUSSION

This section is devoted to two areas which are likely to cause the most difficulty - the extraction of the thorium and the dissolution of the thorium samples.

The thorium is pre-separated from aluminum and other diverse ions by extraction into hexone from 1M nitric acid saturated with lithium nitrate. The hexone phase containing the thorium is scrubbed with fresh nitric acid-lithium nitrate salting solution to remove entrained diverse ions, then the thorium is stripped with water. For quantitative extraction and recovery of the thorium, the 1M nitric acid salting solution must be saturated with lithium nitrate. The solubility of lithium nitrate is very dependent on the temperature of the solution, and upon cooling, copious amounts of the salt will crystallize out. Warm the reagent in a bucket of hot water and dissolve the salts completely before use.

The dissolution characteristics of thorium metal and thorium slugs clad with aluminum varies widely from sample to sample. Such variation creates many unexpected, difficult problems especially when the samples are highly radioactive and are not amenable to bench-type maneuvers or close visual examination. The following information (Table II), drawn from reference books and our own experiences (2,8) is intended as a guide for the dissolution of thorium samples.

IDO-14316

Th-2:3

Tentative

Table II. DISSOLUTION TECHNIQUES FOR THORIUM SAMPLES^a

Type of Sample	Dissolution Procedure and Remarks
ThO ₂	Heat the sample plus HClO ₄ to fumes of HClO ₄ . Cool slightly, add 2 to 3 drops of 2 to 3M HF, then again heat to HClO ₄ fumes. Repeat the HF addition and fuming until dissolution is complete.
Th Metal	<ol style="list-style-type: none"> 1. Decompose the sample first with conc HCl (2.5 ml/g). Usually, a black "sandy" residue remains undissolved. Decompose the black residue with a minimum of conc HNO₃ after which a white or dirty white residue may remain. Heat the solution, then add 3M HF dropwise to dissolve the residue. This procedure has been found to be reliable when other elements, such as Al, that complex fluoride are absent or present only in small amounts. 2. An alternate procedure which has been used successfully to dissolve unirradiated samples is the following: <ol style="list-style-type: none"> a. Decompose the sample with HCl and HNO₃ as described above. b. Add HClO₄ and evaporate to HClO₄ fumes. c. Add 2 to 3M HF dropwise to dissolve the residue. 3. Large solid thorium samples are best dissolved with a conc HNO₃-0.04M HF mixture. This procedure is not recommended for finely-divided samples which tend to be pyrophoric. Finely-divided samples such as filings and turnings are best dissolved by procedure 1 described above.
Th metal clad with Al	<ol style="list-style-type: none"> 1. According to our past experience, this type of sample is best dissolved by chemically or mechanically removing the aluminum first, then dissolving the thorium separately with HNO₃ plus HF (2). The following procedure has been used: <ol style="list-style-type: none"> a. Dissolve the aluminum cladding with 6M HNO₃-0.005M Hg(NO₃)₂.

IDO-14316
Th-2:4
Tentative

Table II. DISSOLUTION TECHNIQUES FOR THORIUM SAMPLES^a (Continued)

Type of Sample	Dissolution Procedure and Remarks
	<ul style="list-style-type: none"> b. Using vacuum, transfer the solution to a polyethylene beaker or bottle. Rinse the dissolution container and the thorium slug with water and transfer the solution to the same beaker or bottle. c. If the aluminum solution contains a solid residue, filter the residue and dissolve it with 1:1 HNO₃-HF. Combine the dissolved residue with the filtrate. d. Dissolve the thorium slug from a and b with conc HNO₃-0.04M HF. Usually, a clear solution is obtained. If a residue remains, filter the residue, and dissolve it with fuming perchloric acid and 1:1 HNO₃-HF. Combine the dissolved residue with the filtrate. e. Dilute each of the two solutions from c and d to a suitable volume. Store each separately in polyethylene containers.
	<p>2. Milner (4) recommends the following procedure for the dissolution of Th-Al binary alloys:</p> <ul style="list-style-type: none"> a. Dissolve a 1-g sample with 10 ml of conc HCl plus 5 mg of sodium silicofluoride (Na₂SiF₆). b. Add 5 ml of HClO₄ and evaporate to strong fumes to volatilize fluoride. c. Dilute to a suitable volume with dilute nitric acid.
ThO ₂ in the presence of Al	<p>The HClO₄-HF procedure described above for the dissolution of ThO₂ is ineffective when the ThO₂ is accompanied by Al. The reason for this is thought to be the "removal" of fluoride through complexation by Al(III). The use of fluosilicic acid is said to overcome this.</p>

Table II. DISSOLUTION TECHNIQUES FOR THORIUM SAMPLES^a (Continued)

Type of Sample	Dissolution Procedure and Remarks
Thorium Ores	See references 3 and 7.

^a Hydrofluoric acid is used in many cases. Fluoride-resistant ware made with materials such as Teflon or Teflon-FEP should be used whenever HF is used in high concentrations. If the use of glassware is necessary, the contact time of the HF on the glass should be kept to a minimum.

In general, it is best to avoid the use of sulfate reagents which often lead to the precipitation of insoluble thorium sulfates. If sulfate reagents (sulfuric acid, potassium pyrosulfate, potassium bisulfate) are necessary and insoluble thorium sulfates are formed, they might be dissolved by metathesizing the insoluble sulfate to thorium hydroxide with sodium hydroxide, then dissolving the thorium hydroxide with cold nitric acid. An important point to remember is that the thorium sulfate salts are less soluble at high temperatures and usually form when the samples are heated.

APPARATUS AND REAGENTS

The apparatus and reagents listed below include only those items which are essential for this method or which require special preparation. Apparatus and reagents normally available in the laboratory are not listed. Refer to the procedure for specific requirements. Use distilled or deionized water throughout the procedure.

A. Apparatus

1. Separatory funnels, 125-ml capacity, equipped with Teflon stop-cock plugs and polyethylene stoppers.
2. Buret, 10-ml, with 0.02- or 0.05-ml graduations.
3. Millipore filter holders for 1-in. and 47-mm dia filters, available from Millipore Filter Corporation, Bedford, Massachusetts.

4. Membrane filters, 1-in. and 47-mm dia, of two types, Alpha-6 (for routine filtrations) and VM-6 (for filtration of highly acidic solutions), available from Gelman Instrument Co., Ann Arbor, Michigan. The two types of filters have been found to be satisfactory for the many different types of filtration problems normally encountered in the laboratory including filtrations of highly acidic or basic solutions and filtrations or organic solvents. In certain cases, Millipore membrane filters type HA, a stock item, can be used.

B. Reagents

1. Thorium solution, standard, 0.05M. Prepare a 0.05M solution using 27.61 g of thorium nitrate tetrahydrate per liter of solution (prepared with water). Standardize the thorium solution against standard EDTA according to Procedure C beginning at step 12.
2. EDTA, 0.05M. A standardized solution will be provided by the Quality Control Laboratory.
3. Salting solution, 1M HNO₃-saturated LiNO₃. Add 575 g of LiNO₃ to 64 ml of conc HNO₃ plus 600 ml of water. Warm the solution and stir until dissolution is complete, then dilute to 1 liter with water. Mix well, then transfer the solution WITHOUT WATER RINSES to a 1-liter screw-cap bottle. Upon standing at 23°C, LiNO₃ salt will settle out to a depth of about 1.5 in.
4. Xylenol orange, 0.2% aqueous solution.
5. Chloroacetic acid, 2M aqueous solution. Use 94.5 g of the acid per 500 ml of solution. Chloroacetic acid "works slowly" but can cause severe burns. Use rubber gloves to avoid contact with the chemical.

PROCEDURE

A. Bench Standard

Run a single determination on the bench standard before analyzing samples. Use Procedure C if only thorium is being determined and both Procedures C and D if both thorium and aluminum are being determined. Limits will be specified by the Quality Control Laboratory.

B. Sample Dissolution

Dissolve a weighed portion of the sample and dilute to a convenient volume. Suggested methods for the dissolution of samples were described in the DISCUSSION section.

C. Determination of Thorium

1. The salting reagent used in the extraction process will contain a layer of lithium nitrate salt. Warm the solution and shake thoroughly to dissolve the salt.
2. Pipet an aliquot of the sample containing between 0.1 and 0.45 mmole of thorium into a 50- or 100-ml beaker. For best results, select a sample containing between 0.25 and 0.45 mmole of thorium. If the HF concentration of the sample exceeds about 1 to 2M, use a quartz or Vitreosil beaker to minimize the introduction of metal ions from the glassware.
3. Add 2 ml of conc HClO_4 and evaporate the sample to near dryness. Use a transite board on the hot plate to avoid baking the sample and cover the beaker with a Speedivap cover glass to avoid loss of sample.
4. Add 5 ml of the salting solution to the beaker and heat gently to dissolve the salts.
5. Transfer the sample quantitatively to a 125-ml separatory funnel. Use an additional 20 ml of the salting solution to rinse the sample into the funnel.
6. Pipet 25 ml of hexone and extract for 30 sec.
7. Let the two phases separate, then drain and discard the lower aqueous layer.
8. Scrub the residual hexone phase with 15 ml of the salting solution. Let the two phases separate, then drain the lower aqueous layer.
9. Repeat step 8.
10. Strip the thorium with two 15-ml portions of water. Each time, shake for about 15 sec. On the second contact with water, use only gentle mixing to avoid the formation of an emulsion.
11. Drain the lower aqueous phase from each of the two contacts with water into a 150-ml beaker. Rinse the sides of the separatory funnel with a stream of water and drain the wash into the beaker.
12. Add 10.00 ml of standard 0.05M EDTA and 2 ml of 2M chloroacetic acid and dilute to about 100 ml.

IDO-14316
Th-2:8
Tentative

13. Adjust the pH (with the aid of a pH meter) to 3.0 ± 0.1 with 4 to 6M NH_4OH .
14. Add 4 drops of 0.2% xylenol orange indicator.
15. Titrate the excess EDTA with 0.05M thorium solution to a color change from yellow to red or reddish-orange.
16. Record the titer on the worksheet and calculate the results as described under CALCULATIONS.

D. Determination of the Sum of Thorium Plus Aluminum

This procedure can also be used for the direct determination of thorium in the absence of interfering metal ions.

1. Pipet an aliquot containing between 0.25- and 0.45-mmole of thorium plus aluminum into a 150-ml beaker. If the dissolution requires much HF, use a quartz or Vitreosil beaker to minimize the introduction of metal ions from the glassware.
2. Add 2 ml of perchloric acid, cover the beaker with a Speedivap cover glass, and evaporate to near dryness. Use a transite board on the hot plate to avoid baking the sample.
3. Cool slightly and rinse down the cover glass and the beaker walls with water. Swirl the contents of the beaker to dissolve the solids. If necessary, heat gently.
4. Pipet 10.00 ml of 0.05M EDTA and 2 ml of 2M chloroacetic acid and dilute to about 100 ml with water.
5. Adjust the pH (with a pH meter) to 3.0 ± 0.1 with 4 to 6M NH_4OH .
6. Heat to near boiling, then chill to room temperature.
7. Add 4 drops of 0.2% xylenol orange indicator and titrate the excess EDTA with 0.05M thorium to a color change from yellow to red or reddish orange.
8. Record the titer on the worksheet and calculate the results as described under CALCULATIONS.

E. Determination of Aluminum

1. Determine the sum of aluminum plus thorium according to Procedure D.
2. Determine thorium alone according to Procedure C.

3. Obtain aluminum by difference (See CALCULATIONS).

CALCULATIONS

Record the data on the worksheet and calculate the results as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Molarity of EDTA solution.
B	Molarity of thorium solution.
C	Sample weight, grams.
D	Sample dilution, ml.
E	Sample aliquot analyzed, ml.
F	Volume of thorium solution used, ml.
G	Result, mmole(s) thorium (or the sum of aluminum plus thorium) per gram or per ml of sample thorium. $G = \frac{D[10.00(A) - BF]}{CE}$
H	Result, mmole(s) aluminum per gram or per ml of sample $H = \text{mmole(s) Al} = \text{mmole(s) Th} + \text{Al minus mmole(s) Th}$

Report the results to four significant figures as 3.017 mmoles Th/g and 0.3017 mmole Th/ml.

REFERENCES

1. Banks, C. V., Edwards, R. E., Anal. Chem. 27, 947 (1955).
2. Fortsch, E. M., Private Communication, 1965.
3. Kolthoff, I. M., Elving, P. J., Treatise on Analytical Chemistry, pp. 176-179, Interscience, New York, 1961.
4. Milner, G. W. C., Woodhead, J. L., A. E. R. E. Rept. C/R 1400, 1954.

IDO-14316
Th-2:10
Tentative

5. Morrison, G. H., Freiser, H., Solvent Extraction in Analytical Chemistry, pp. 137-142, Wiley, New York, 1957.
6. Welcher, F. J., The Analytical Uses of Ethylenediamine Tetraacetic Acid, Van Nostrand, New York, 1958.
7. Wilson, C. L., Wilson, D. W., Comprehensive Analytical Chemistry, pp. 528-531, 1962.
8. Yamamura, S. S., IDO Notebook U-455, pp. 25-40, 1961.

S. S. Yamamura
May, 1965

COLORIMETRIC DETERMINATION OF IODINE

ABSTRACT

A method is described for the determination of microgram quantities of iodine in aqueous and in carbon tetrachloride samples. Iodide in aqueous samples is oxidized to iodine which then is extracted into carbon tetrachloride as the I_3^- species. For carbon tetrachloride samples, potassium iodide and alcohol are added to form the I_3^- species. The absorbance of this species is measured at 360 m μ .

APPLICABILITY

This method is designed for the determination of iodine that is scrubbed from gas streams into sodium hydroxide or into carbon tetrachloride solutions. The lower limit of detection is 2.5 μ g of iodine and the linear range is 5 to 80 μ g for aqueous samples and 2.5 to 40 μ g for carbon tetrachloride samples.

DISCUSSION

The method is based on the absorbance measurement of the triiodide species (I_3^-), formed by reaction of I_2 with I^- , that has an intense color in a carbon tetrachloride-ethanol medium. For aqueous samples, the acidic form of this species is extracted into carbon tetrachloride-ethanol. For carbon tetrachloride samples, potassium iodide and ethanol are added to form the species insitu. The wavelengths of maximum absorbance are 292 and 360 m μ . The latter is used because it is more intense. Once formed, the color is stable for at least 24 hr.

APPARATUS AND REAGENTS

A. Apparatus

1. Separatory funnels, 60-ml.
2. Assorted pipets.
3. Volumetric flasks, 10-ml.
4. Beckman Model DU spectrophotometer, or equivalent.
5. Absorption cells, Corex, 1-cm, calibrated to ± 0.0002 absorbance units with a processed standard in the cells at 360 m μ .

IDO-14316

I-2:2

B. Reagents

Distilled water and C.P. or reagent grade chemicals are used throughout the procedure.

1. Carbon tetrachloride.
2. Nitric acid, 6M.
3. Sodium nitrite, 1M. Dissolve 6.9 g of sodium nitrite in water and dilute to 100 ml.
4. Sulfamic acid, solid.
5. Potassium iodide, 2% in 95% ethyl alcohol. Dissolve 2 g of potassium iodide in ethanol and dilute to 100 ml with ethanol.
6. Standard iodine solution in carbon tetrachloride, 100 µg/ml. Dissolve 0.1000 g of iodine in carbon tetrachloride and dilute to 1 liter.
7. Aqueous standard iodine solution, 100 µg /ml. Dissolve 0.1308 g of potassium iodide in water and dilute to 1 liter.

PROCEDURE

A. Calibration and Bench Standard

A separate calibration is required for each series of samples.

1. Process 100- and 200-µl aliquots of the aqueous standard beginning with step C-1.
2. Process 100- and 200-µl aliquots of the carbon tetrachloride standard beginning with step D-1.

Divide the absorbance by the respective micrograms of iodine in each aliquot to determine the conversion factor. If the difference between the two conversion factors does not agree within limits set by the Quality Control Laboratory, process another pair of standards. Contact your supervisor if agreement still is not obtained.

B. Blank

Process the appropriate reagent blank with each series of samples. Begin with step C-1 substituting water for the sample or at step D-1 substituting carbon tetrachloride for the sample.

C. Aqueous Samples

1. Pipet up to 10 ml of the sample, containing 5 to 80 μg of iodine, into a 60-ml separatory funnel.
2. Add distilled water to a total volume of approximately 10 ml.
3. Acidify with 6M nitric acid using pH paper. Final solution must be acidic as the extracted complex is HI_3 .
4. Accurately pipet 10 ml of carbon tetrachloride into the separatory funnel.
5. Add approximately 0.5 ml of 1M sodium nitrite. Iodide oxidizes to iodine.
6. Stopper the funnel and extract for 1 min. Invert the funnel and vent it several times during the extraction.
7. After the phases separate, cautiously add solid sulfamic acid until the reaction ceases, then add the same amount again. Because this reaction foams vigorously, add the sulfamic acid slowly.
8. Extract for approximately 15 sec.
9. Drain the carbon tetrachloride phase into a container. A 15-ml sample bottle may be used as the container.
10. Continue the analysis with a 5-ml or less aliquot, starting at step 1, Section D. Iodide precipitates if more than 5 ml of the carbon tetrachloride is used in Section D.

D. Carbon Tetrachloride Samples

1. Pipet up to 5 ml of the sample, containing 2.5 to 40 μg of iodine, into a 10-ml volumetric flask. Iodide precipitates if more than 5 ml is used.

IDO-14316
I-2:4

2. Add 1 ml of 2% potassium iodide in 95% ethanol. The I_3^- species forms in situ.
3. Dilute to 10 ml with 95% ethanol.
4. Place the reagent blank in the cell and adjust the controls of the spectrophotometer so that the net absorbance is zero at 360 mμ.
5. Fill a matched cell with the sample, and measure the absorbance at 360 mμ.

CALCULATIONS

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms iodine in the calibration standards.
B	Absorbance of standards.
C	Calibration factor. $C = \frac{B}{A}$ $C' = \frac{B'}{A'}$
D	Average calibration factor. $D = \frac{C + C'}{2}$
E	Sample volume, in ml.
F	Sample absorbance.
G	Result, μg/ml of iodine in sample. $G = \frac{F}{D E}$

IDO-14316
I-2:5

REFERENCE

1. Ovenston, T. C. J., Reese, W. T., Anal. Chim. Acta 5, 123 (1961).

I. L. Doggett
August, 1965

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

IDO-14316
NO₃-1:1
Mod-4

DETERMINATION OF INORGANIC NITRATE AND AMMONIA

ABSTRACT

Inorganic nitrate is reduced to ammonia with Devarda alloy in a sodium hydroxide medium, the ammonia is steam distilled, collected in boric acid, and titrated with standard acid. Ammonia is separately determined by omitting the Devarda alloy.

APPLICABILITY

This method is applicable to the determination of nitrate in aqueous solutions and to solids that are either soluble in sodium hydroxide or from which the nitrate is leachable by sodium hydroxide. Nitrite also is reduced to ammonia and therefore is an interference. However, for most samples which contain nitrate and nitrite, the procedure is used and the results are reported as total nitrate. Interferences are ammonia and compounds which release alkaline vapor during the distillation. By omitting the Devarda alloy, ammonia can be determined in the presence of nitrate. Any compounds that release alkaline vapors will be determined as ammonia.

Both nitrate and ammonia can be determined. The result with Devarda alloy present is the sum of the two. The result for ammonia (with no Devarda alloy) is subtracted to give nitrate.

The sample aliquot should contain the equivalent of 0.24 to 4.5 mmoles of distillable ammonia.

DISCUSSION

The results will be low if all connections on the Kjeldahl distillation apparatus are not tight. High results can be obtained if ammonia fumes are present in the laboratory. For this reason, open bottles of ammonia should not be near the working area.

The boric acid in which the distilled ammonia is collected is not appreciably ionized at the pH level of the titration and thus does not affect the titration.

SAFETY PRECAUTIONS

Concentrated sodium hydroxide is very dangerous. Contact with the skin and eyes must be avoided. Wear rubber gloves when handling this reagent and when washing the Kjeldahl flasks after the analyses are complete. If the reagent comes in contact with the skin or eyes, wash immediately with copious quantities of water followed by a boric acid rinse.

IDO-14316
NO₃-1:2
Mod-4

APPARATUS AND REAGENTS

A. Apparatus

1. Kjeldahl distillation apparatus.
2. Kjeldahl flasks, 800-ml.
3. Erlenmeyer flasks, 500-ml.
4. Buret, 50-ml, graduated in 0.1-ml divisions.

B. Reagents

NOTE: All reagents should be C.P. or Analytical Reagent Grade. Use distilled water for the preparation of all reagents and throughout the procedure.

1. Sulfuric acid, standard, 0.1000N.
2. Sodium hydroxide, 15M.
3. Bromcresol green - methyl red mixed indicator. Dissolve 1 g of bromcresol green and 0.5 g methyl red in ethyl alcohol and dilute to 500 ml with ethanol.
4. Devarda alloy.
5. Boric acid solution, 40 g/liter.

PROCEDURE

A. Blank

Process a blank once each shift according to C omitting step 5.

B. Bench Standard

Analyze the bench standard according to C. Limits will be specified by the Quality Control Laboratory.

C. Samples

NOTE: For the determination of alkaline volatile matter (such as ammonia), omit the Devarda alloy in step 8.

1. Add 50 ml of the boric acid solution to a 500-ml Erlenmeyer flask.

2. Add 3 drops of the indicator solution.
3. Immerse the delivery tube of the Kjeldahl apparatus well below the surface of the boric acid.
4. Start the flow of cooling water through the condenser.
5. Pipet an aliquot of the sample containing from 0.25 to 4.5 mmoles of distillable ammonia (sum of nitrate plus volatile alkaline matter) into an 800-ml Kjeldahl flask.
6. Dilute to about 450 ml with distilled water.
7. Add 50 ml of 15M sodium hydroxide.
8. Add 5 g of Devarda alloy and immediately attach the flask to the connecting trap of the Kjeldahl apparatus.
9. Heat the flask moderately until the foaming stops.
10. Apply high heat and distill over 350 ± 10 ml of distillate.

If any solution threatens to foam over, cool the flask before continuing the distillation. If any solution carries over into the Erlenmeyer flask, discard the sample, and distill about 250 ml of water to clean the system.

If any Devarda alloy carries into the trap or condenser, the system may plug causing sodium hydroxide to be expelled. This is a safety hazard. Also if this occurs, discard the sample, and clean the apparatus.
11. Lower the Erlenmeyer flask until the delivery tube is above the solution.
12. Turn off the heater and allow the distillate to drip into the flask as the system cools.
13. Rinse the condenser tip with distilled water and remove the Erlenmeyer flask.
14. Add 3 to 5 drops of indicator solution and titrate with the standard acid to an endpoint of blue to pink.

The color is blue on the basic side and goes through a gray or colorless transition near the endpoint to a pink color on the acid side. Titrate to the appearance of

IDO-14316
NO₃-1:4
Mod-4

the pink color. Titrate the bench standard and blank first and set them aside as a visual reference. Titrate all samples to the same endpoint.

15. Dispose the waste Devarda alloy by transferring it to a beaker, rinsing out as much sodium hydroxide as possible, and then redissolving the Devarda alloy with nitric acid in a hood.

CALCULATIONS

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Volume of sample, ml.
B	Normality of acid.
C	Volume of acid used for sample, ml.
D	Volume of acid used for blank, ml.

Results:

- (a) Nitrate in samples free of ammonia

$$\text{molarity} = \frac{B(C-D)}{A}$$

- (b) Ammonia

$$\text{molarity} = \frac{B(C-D)}{A}$$

- (c) Nitrate in samples that contain ammonia

$$\text{molarity} = (\text{molarity result with Devarda alloy}) - (\text{molarity result without Devarda alloy})$$

Report results to 3 significant figures as 4.28M, 0.428M, 0.0428M.

IDO-14316

NO₃-1:5

Mod-4

REFERENCES

1. Hillebrand, W. F., Lundell, G. E. F., Applied Inorganic Analysis, p. 629, Wiley, New York, 1950.
2. Snell, F. D., Biffen, F. M., Commercial Methods of Analysis, p. 150, McGraw-Hill, New York, 1944.
3. Lyper, H. A., et al, Methods of Analysis, A.O.A.C., 7th ed., p. 14, Association of Official Agricultural Chemists, Washington, D. C., 1950.
4. Wade, M. A., IDO Notebook U-666, p. 50, 1964.
5. Oestreich, D. K., Private Communication, June, 1965.

H. A. Shogren
July, 1965

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

SPECTROPHOTOMETRIC DETERMINATION OF MILLIGRAM LEVELS
OF PHOSPHOROUS AS MOLYBDIVANADOPHOSPHORIC ACID

ABSTRACT

An intense yellow coloration forms upon the addition of an excess of molybdate to an acidified solution mixture of vanadate and phosphorous as orthophosphate. This is the basis of a simple colorimetric procedure described herein for the determination of milligram amounts of phosphate. An extensive discussion of the effects of diverse ions and of color development conditions are included in the APPLICABILITY and DISCUSSION sections, respectively.

APPLICABILITY

This procedure for milligram amounts of phosphate, based on a method by Kitson and Mellon(1) is especially suited for aluminum-based samples such as the calcine glass samples for which it was originally tested. However, because only a few ions interfere seriously, this method is applicable also to a wide variety of samples. The effects of diverse metal ions and anions are shown in Tables I and II, respectively. Included in Tables I and II is a column of remarks to guide the analyst in the analysis of samples with interfering or potentially interfering substances.

The linear range of the method is 1 to 40 ppm of phosphorous. With the prescribed dilution to 100 ml, this corresponds to a range of 0.1 to 4 mg of phosphorous or 0.3 to 12 mg of phosphate.

DISCUSSION

According to Kitson and Mellon(1) the following conditions must be controlled for complete, reproducible color development:

Acidity. The optimum acidity of the reaction medium is about 0.5N. The permissible variation from this acidity depends on the acid used. With nitric acid, the acid recommended for this procedure and most generally used, full color development is obtained in the range of 0.2- to 1.6N^A. With hydrochloric acid, perchloric acid, and sulfuric acid, the minimum acidity is 0.2N also, but for these acids, the maximum permissible acidity is 1.0%, 0.7, and 0.9N respectively.

* Although the maximum permissible acidity is stated to be 1N, Kitson and Mellon(1) contradict themselves by listing chloride as a serious interference. In independent studies(2), chloride did not interfere as shown in Table II.

IDO-14316
P-Color-2:2

Table I. EFFECTS OF DIVERSE METAL IONS

Phosphate Added, Mg	Ion Added	Ion to Phosphate Molar Ratio ^a	Absorbance ^b	Remarks
10.00	None	-	0.586	Based on 10 detns., the std dev is 0.0031 absorbance unit and the 95% confidence limits are 0.586±0.007 absorbance unit for a single detn. and 0.586±0.005 for the average of 2 detns.
8.00	None	-	0.475	Based on 35 detns., the std dev is 0.0015 absorbance unit and the 95% C.L. are 0.475±0.003 absorbance unit for a single detn. and 0.475±0.002 absorbance unit for the average of 2 detns.
10.00	Al(III)	80	0.587	Bi(III) interferes seriously at Bi(III) to phosphate molar ratios exceeding 2:1.
8.00	Bi(III)	2.0	0.472(2)	
		5.0	Precipitates	
10.00	Ca(II)	80	0.587	
10.00	Cd(II)	80	0.589	
10.00	Ce(III)	80	0.590	
8.00	Co(II)	20	0.476(2)	Co(II) absorbs at the working wavelength. Run reagent blank, sample blank (sample without vanadate and molybdate color reagents), and sample and measure the absorbance of each vs water. Apply reagent and sample blank corrections to the sample.
		100	0.480	
8.00	Cr(III)	5	0.460(2)	Cr(III) absorbs at the working wavelength. Apply sample blank correction, as per Co(II). The reason for the interference decrease with increasing Cr(III) to phosphate ratio is not known.
		10	0.456(2)	
		60	0.465	
		100	0.475(2)	

IDO-14316
P-Color-2:3

Table I. EFFECTS OF DIVERSE METAL IONS
(Continued)

Phosphate Added, Mg	Ion Added	Ion to Phosphate Molar Ratio ^a	Absorbance ^b	Remarks
10.00	Cu(II)	80	0.589	Cu(II) does not absorb at the working wavelength.
10.00	Fe(III)	40	0.588	Fe(III) absorbs slightly at the working wavelength.
		80	0.568	For example, at the 80:1 ratio [8.4 mmole Fe(III)], the sample blank absorbance vs water is 0.003.
10.00	Hg(II)	40	0.589	Measure within 10 min after color development to avoid the formation of a precipitate.
		80	0.587	
10.00	K(I)	80	0.583	
10.00	Mg(II)	80	0.589	
10.00	Mn(II)	80	0.589	Mn(II) absorbs slightly at the working wavelength. Apply sample blank correction as per Co(II).
	Mn(VII)	12	0.587	Reduce Mn(VII) to Mn(II) with NaNO ₂ .
10.00	Ni(II)	80	0.591	Ni(II) absorbs at the working wavelength. Apply sample blank correction as per Co(II).
10.00	Pb(II)	10	0.593	Measure within 5 min after color development to avoid the formation of lead molybdate precipitate.
		20	0.600(3)	
10.00	Sr(II)	80	0.590	
8.00	Th(IV)	0.1	0.468(2)	Serious interference.
10.00	U(VI)	80	0.584	U(VI) absorbs at the working wavelength. Apply sample blank correction as per Co(II).
8.00	W(VI)	0.5	0.458(2)	Serious interference.

IDO-14316
P-Color-2:4

Table I. EFFECTS OF DIVERSE METAL IONS
(Continued)

Phosphate Added, Mg	Ion Added	Ion to Phosphate Molar Ratio ^a	Absorbance ^b	Remarks
8.00	Zr(IV)	0.05	0.451(2)	Serious interference. Interference can be minimized by the addition of a 2.5:1 NaF-Al(NO ₃) ₃ masking mixture.

^a
10.00 mg PO₄⁻³ = 0.1053 mmole; 8.00 mg PO₄⁻³ = 0.0842 mmole.

^b
Single detn except where noted otherwise by the numbers in parenthesis.

IDO-14316
P-Color-2:5

Table II. EFFECTS OF DIVERSE ANIONS

Ion Added	Ion to Phosphate Molar Ratio ^a	Absorbance ^a	Remarks ^b
Chloride (as NaCl)	50	0.585(2)	Though stated by Kitson and Mellon(1) to be a serious interference at greater than a 2.5:1 Cl ⁻ /PO ₄ ⁻³ weight ratio, independent studies(2) show that chloride does not interfere at the 100:1 molar ratio. In fact, color development is rapid and complete in 0.5M HCl.
Chloride (as HCl)	100	0.584(2)	
Citrate	7	0.581	At high levels, citrate bleaches the color.
	12	0.538	Moderate amounts of citrate can be destroyed by digesting with nitric acid (5 ml) and perchloric acid (1 ml).
Fluoride (as HF)	5	0.583	Fluoride interferes at greater than 25:1 mole ratios; however, the fluoride can be masked effectively* with 5 mmoles of Al(NO ₃) ₃ .
	25	0.579	
	60	Interferes	
	60*	0.588(2)	
Nitrate (as NaNO ₃)	100	0.586(2)	
Nitrate (as HNO ₃)	93	0.584	
	186	0.576	
Nitrite (as NaNO ₂)	60	0.584	
	120	0.570(2)	
Oxalate	5	0.583	Moderate amounts of oxalate can be destroyed by
	7	0.581	digesting with nitric
	12	0.528	acid (5 ml) and perchloric acid (1 ml).

IDO-14316
P-Color-2:6

Table II (Continued)

Ion Added	Ion to Phosphate ^a Molar Ratio	Absorbance ^a	Remarks ^b
Perchlorate (as HClO_4)	138	0.582	
	276	0.578	
Silicate	20	0.591	At greater than 20:1 silicate, introduces a positive bias.
	40	0.601	
	80	0.633	
Sulfate (as H_2SO_4)	120	0.578(2)	
	240	0.535(2)	
Tartrate	24	0.581	Moderate amounts of tar- trate can be destroyed by digestion with nitric acid (5 ml) and perchloric acid (1 ml).
	48	0.554	

^a

Phosphate maintained at 10.00 mg (0.1053 mmole). Single determination except when noted otherwise by the numbers in parenthesis.

^b

Based on 10 detns at the 10.00 mg level, the std dev is 0.0031 absorbance unit and the 95% confidence limits are 0.586 ± 0.007 absorbance unit for a single detn and 0.586 ± 0.005 absorbance unit for the average of 2 detns.

Vanadate and molybdate level. An excess of vanadate and molybdate is necessary.

Order of reagent addition. The order of reagent addition is: acid, vanadate, then molybdate. This order should be maintained to avoid complications(1).

Phosphate concentration. The linear range of the method is 1 to 40 ppm of phosphorous corresponding to 0.3 to 12 mg of phosphate per 100 ml of solution.

Color development time. Generally, the color development is complete in 3 to 10 min. The resulting color is stable for at least 1 week.

APPARATUS AND REAGENTS

A. Apparatus

1. Spectrophotometer, Beckman, Model B or Model DU, or Cary, Model 14 with 1-cm Corex cells.
2. Volumetric flasks, 100-ml.
3. Pipets, volumetric, assorted sizes.
4. Pipets, micro, assorted sizes with syringe.

B. Reagents

1. Phosphate calibration and bench standard I, 2.00 mg PO_4^{-3} /ml. Dissolve 1.3906 g of diammonium hydrogen phosphate in water and dilute to 500 ml.
2. Phosphate calibration and bench standard II, 1.50 mg PO_4^{-3} /ml. Dissolve 1.0430 g of diammonium hydrogen phosphate in water and dilute to 500 ml.
3. Ammonium molybdate reagent, 5% (w/v). Dissolve 25 g of ammonium molybdate, $(\text{NH}_4)_7\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, in warm water and dilute to 500 ml with water.
4. Ammonium vanadate, 0.25% (w/v). Dissolve 2.50 g of ammonium vanadate, NH_4VO_3 , in 500 ml of boiling water. Cool slightly, add 20 ml of concentrated nitric acid, cool to room temperature then dilute to 1 liter with water.
5. Nitric acid, 5M. Dilute 160 ml of concentrated nitric acid to 500 ml with water.

PROCEDURE

A. Blank

Run a reagent blank with each set of standards and samples.

B. Sample Blank

When samples contain metal ions that absorb at the working wavelength of 270 m μ , process a sample blank with the samples. The sample blank contains the sample aliquot identical to that used for the analysis, and all the reagents except the ammonium molybdate and the ammonium vanadate.

C. Calibration and Bench Standard

Process a pair of calibration standards with each series of samples. Use 4.00-ml portions of the two calibration standards and process these according to D. Divide the absorbance by the milligrams of phosphate in the standards to obtain the conversion factor. The difference between the two factors should not exceed limits set by the Quality Control Laboratory. Also, the average of the two factors should agree with the established conversion factor within the specified limits. If either or both of the specifications are not met, reprocess the pair of calibration standards. Consult your supervisor if difficulties still are experienced.

D. Recommended Procedure

1. Pipet a sample containing 1 to 10 mg of phosphate into a 100-ml volumetric flask.
2. Add 10 ml of 5M nitric acid. Swirl to mix.
3. Add 10 ml of 0.25% (w/v) ammonium vanadate. Swirl to mix.
4. Add 10 ml of 5% (w/v) ammonium molybdate, dilute to volume with water, and mix well.
5. Let stand 5 min, then measure the absorbance of the sample against the reagent blank at 470 m μ in 1-cm cells.

NOTES: (a) With samples containing metal ions that absorb at 470 m μ , measure the absorbances of the sample, the sample blank, and the reagent blank against water. Then, subtract the total absorbance of the reagent blank plus the sample blank from the sample absorbance to obtain the net absorbance of the sample.

(b) When samples contain lead(II) or mercury(II), develop the color only a few samples at a time and measure the sample absorbance immediately after 3 min to avoid the interference due to the formation of a precipitate.

6. Record the data on the worksheet and compute the results as described under CALCULATIONS.

CALCULATIONS

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit of Record</u>
A	Mg phosphate in calibration standards.
B	Absorbance of standards.
C	Conversion factor. $C' = \frac{B'}{A'}$ $C'' = \frac{B''}{A''}$
D	Average conversion factor. $D = 0.5(C' + C'')$
E	Sample volume in ml.
F	Sample absorbance.
G	Results, mg PO_4^{-3} /ml. $G = \frac{F}{DE}$

Report results to three significant figures as 111, 11.1, and 1.11 mg PO_4^{-3} /ml.

REFERENCES

1. Kitson, R. E., Mellon, R. G., Ind. Eng. Chem., Anal. Ed. 16, 379 (1944).
2. Yamamura, S. S., IDO Notebook U-850, pp 111-150.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

VOLUMETRIC DETERMINATION OF CHROMIUM(VI)

ABSTRACT

In this method, chromium(VI) is titrated directly with iron(II) in a sulfuric acid-phosphoric acid medium to a visual ferroin indicator endpoint.

APPLICABILITY

This method is limited to samples in which chromium(VI) is the only strong oxidant. By strong oxidant is meant the capability of oxidizing iron(II) to iron(III) in acid medium. Nitrate, either as nitric acid or as the neutral salt, has been tested as an interference. A volume of 5 ml of concentrated acid, 78.5 mmole, did not interfere. This method will not determine total chromium if some is present in the +3 valence state. For such determinations, methods Cr-3 for milligram levels and Cr-4 for microgram levels are recommended. The range of the method, as written, is 0.03- to 0.3 mmole (1.6 to 16 mg) of chromium(VI) in the sample aliquot.

DISCUSSION

The indicator for this method is ferroin (iron(II)-1,10-orthophenanthroline). Because it consumes chromium(VI), the blank for the method is negative and is determined by a titration with standard potassium dichromate solution. The indicator solution is stable for long periods of time, up to one year. The indicator solution should be changed if more than 50 μ l is required to obtain a sharp endpoint.

SAFETY PRECAUTIONS

Rubber gloves are recommended for handling the strong acids used in this method.

APPARATUS AND REAGENTS

A. Apparatus

1. Buret, 10-ml graduated in 0.05-ml divisions.
2. Beakers, 250-ml.
3. Graduated cylinder, 25-ml.

IDO-14316
Cr-2:2
Mod-1

4. Magnetic stirrer and Teflon-coated stirring bars.

B. Reagents

NOTE: Use distilled water and C.P. or Analytical Reagent Grade chemicals throughout.

1. Potassium dichromate solution, 0.1000N. Dissolve 4.9035 g of dried (at least 1 hr at 110°C) National Bureau of Standards potassium dichromate in distilled water and dilute to 1 liter in a volumetric flask.
2. Ferrous ammonium sulfate solution, 0.1M. Dissolve 39.2 g of ferrous ammonium sulfate hexahydrate in 500 ml of cold 0.5M sulfuric acid and dilute to 1 liter with 0.5M sulfuric acid.
3. Ferroin indicator solution, 0.025M. G. F. Smith Chemical Company, Reagent No. 165, Columbus, Ohio.
4. Sulfuric acid, 9M.
5. Phosphoric acid, 7M.

PROCEDURE

A. Blank

NOTE: Do in duplicate at least once per week.

1. Place 50 ml of water in a 250-ml beaker.
2. Add 25 ml of 9M sulfuric acid.
3. Add 10 ml of 7M phosphoric acid.
4. Add 50 μ l of 0.025M ferroin indicator solution.
5. Titrate with the 0.1000N potassium dichromate solution to a color change from orange to colorless. The titer will be small, on the order of 0.05 ml.

B. Bench Standard

Rather than a separate bench standard, control is maintained in Procedure C for the standardization of the ferrous ammonium sulfate solution.

C. Standardization of Ferrous Ammonium Sulfate Solution

NOTE: Process duplicates once each shift. Correct each titer for the blank. The allowable difference between duplicates is 0.03 ml. If this difference is exceeded, process another pair. If agreement is still not obtained, clean the glassware and repeat. Plot the difference between duplicates and the average titer corrected for the blank on the provided quality control chart. Proceed with samples if the average titer agrees within 2% of the titer obtained on the preceeding standardization. If it does not, obtain new potassium dichromate and ferrous ammonium sulfate solutions from the Quality Control Laboratory. Also return the quality control chart to the Quality Control Laboratory and obtain a new one.

1. Pipet 5.00 ml of the 0.1000N potassium dichromate solution into a 250-ml beaker.
2. Add a stirring bar and start the stirring.
3. Add 50 ml of water.
4. Add 25 ml of 9M sulfuric acid.
5. Add 10 ml of 7M phosphoric acid.
6. Add 50 μ l of 0.025M ferroin indicator solution.
7. Titrate with the ferrous ammonium sulfate solution to a color change from blue-green to orange.

D. Samples

1. Pipet a sample aliquot containing from 0.03 to 0.3 mmole of chromium(VI) into a 250-ml beaker. For highest reliability, select the aliquot to contain an amount of chromium(VI) toward the upper limit.
2. Continue with steps 2 through 7 of Procedure C.

IDO-14316
Cr-2:4
Mod-1

CALCULATIONS

1. Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Titer of blank, ml.
B	Titer of two standardizations, ml.
C	Titer of two standardizations corrected for blank, ml, and calculated difference between the duplicates.
D	Average titer of two standardizations corrected for blank.
E	Normality of ferrous sulfate solution $E = \frac{0.50}{D}$
F	Volume of sample, ml.
G	Titer of ferrous sulfate for sample, ml.
H	Titer of ferrous sulfate for sample corrected for blank, ml.

2. Calculate the chromium(VI) content of the sample in whatever units the customer desires, as follows:

(a) Normality of chromium(VI)

$$= \frac{EH}{F}$$

(b) Molarity of chromium(VI)

$$= \frac{EH}{3F}$$

(c) mg/ml of chromium(VI)

$$= \frac{52.00 EH}{3F} = \frac{17.33 EH}{F}$$

Report results to 0.1% significance.

IDO-14316
Cr-2:5
Mod-1

REFERENCES

1. Kolthoff, I. M., Belcher, R., Volumetric Analysis, Volume III, Interscience, New York, 1957.

R. E. Foster, Jr.
J. E. Rein

July, 1965

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TITRIMETRIC DETERMINATION OF PEROXIDE

ABSTRACT

A rapid titrimetric method is described for the determination of micro amounts of peroxide. This method is especially applicable to reactor loop water samples. Hydrogen peroxide is reacted with iodide in acid medium to liberate free iodine which is then titrated with thiosulfate to a visual starch endpoint.

APPLICABILITY

This procedure is especially applicable to reactor loop-water samples. The procedure is not specific and any constituents which oxidize iodide will interfere. Nitrite is present in some loop-water samples but usually at insignificantly small levels compared to peroxide.

DISCUSSION

The basis of the method is the oxidation of iodide to iodine in an acid medium by the peroxide followed by back titration of the iodine to iodide with standard thiosulfate to a visual, starch indicator endpoint. Because the reaction rate between peroxide and iodide is slow, molybdenum(VI) is added as a catalyst.

As shown by the above equations, one mole of peroxide is equivalent to two moles of thiosulfate.

APPARATUS AND REAGENTS

A. Apparatus

1. Flasks, Erlenmeyer, 250-ml.
2. Buret, 10-ml with 0.05-ml graduations.
3. Magnetic stirrer and Teflon-coated stirring bars.

B. Reagents

All reagents used should be of Analytical Reagent Grade or equivalent. Use distilled water for the preparation of all reagents and throughout the procedure.

1. Sulfuric acid, 2M.
2. Potassium iodide.
3. Ammonium molybdate, neutral 3% solution. Dissolve 3 g of ammonium molybdate in 100 ml of water and adjust to pH 7 with 0.5M sulfuric acid or 1M ammonium hydroxide.
4. Sodium thiosulfate solution, 0.01N, standardized daily.
5. Potassium bromate solution, 0.0600N. Dissolve 1.6718 g of potassium bromate (99.9% pure) in distilled water and dilute to 1 liter.
6. Bench Standard, potassium bromate solution, 0.00075N. Dilute 25 ml of the 0.0600N potassium bromate solution to 2000 ml with distilled water.
7. Starch solution, 1%. Add a water slurry of 5 g of starch to 1 liter of boiling water and allow to boil for 5 min. When cool, transfer to a glass-stoppered bottle, add two drops of toluene as a preservative, and store in a refrigerator.

PROCEDURE

A. Standardization of Thiosulfate Solution.

Process a 1-ml aliquot of the standard 0.0600N potassium bromate solution according to C below.

$$\text{Normality of thiosulfate} = \frac{0.0600}{\text{ml thiosulfate}}$$

B. Bench Standard.

Process 50 ml of the 0.00075N potassium bromate standard according to C below. Limits will be specified by the Quality Control Laboratory.

C. Analysis of Samples

1. Pipet an aliquot of the sample containing from 170 to 1700 μg of peroxide into a 250-ml Erlenmeyer flask. The recommended aliquot for reactor loop water is 50.0 ml.

2. Add 10.0 ml of 2M sulfuric acid.
3. Add 1 ± 0.1 g of potassium iodide and three drops of the ammonium molybdate solution.
4. Titrate with the standardized thiosulfate solution to a pale yellow straw color. Add 1 ml of the starch indicator solution and titrate from a dark blue to colorless endpoint.

CALCULATIONS

A. Record data on worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Volume of sample, in ml.
B	Normality of thiosulfate solution.
C	Volume of thiosulfate solution, in ml.
D	Result, ppm of peroxide.

B. Calculate as follows:

$$D = 1.7 \times 10^4 \frac{BC}{A}$$

REFERENCE

1. Kolthoff, I. M., Sandell, E. B., Textbook of Quantitative Inorganic Analysis, p 600, Macmillan Company, New York 1949.

D. K. Oestreich
March, 1965

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

COLORIMETRIC DETERMINATION OF IRON WITH 1,10-PHENANTHROLINE

ABSTRACT

Two procedures are described for the determination of iron with 1,10-phenanthroline. In one, the direct procedure, the color is developed directly in an aqueous EDTA-citrate medium using hydroxylamine hydrochloride for the reduction of iron(III) to iron(II). In the second, a column extraction-colorimetric measurement procedure, the iron is separated initially by selective extraction from 7M hydrochloric acid into 2-octanone sorbed on a column of Fluoropak. The iron(III)-2-octanone solution is stripped from the column with 2-propanol, and the iron is determined in situ in the effluent with 1,10-phenanthroline using hydroquinone for the reduction of iron(III) to iron(II). In both procedures, the absorbance of the red iron(II)-1,10-phenanthroline complex is measured spectrophotometrically at 507 mμ.

In general, both procedures are highly selective. The column extraction procedure tolerates higher ratios of diverse ions. Each method tolerates a few ions that interfere in the other one.

APPLICABILITY

Each of the two procedures for the colorimetric determination of iron is highly selective and applicable to a wide variety of samples. The effects of diverse ions on each of the two procedures and the iron concentration limits for the two procedures are described below.

DIRECT PROCEDURE (A) USING EDTA-CITRATE MASKING^(3,4)

This procedure is recommended for all samples except those containing Co(II) and Ru(III,IV) and those containing diverse ions at ion to iron molar ratios exceeding the tolerance ratio.

Figure 1 gives the tolerance ratios of 54 elements. These ratios were established by analyzing synthetic samples containing 54.6 μg of iron and varying concentrations of the diverse ions. A "t" test at the 95% confidence level was used to establish interference. For a single determination at the 54.6-μg iron level, the allowable limits were ± 0.60 μg of iron.

As can be seen from a study of Figure 1, most cations and anions do not interfere at diverse ion to iron molar ratios greater than 100:1. In most cases, the tolerance ratio given is the highest ratio that was studied and does not necessarily represent the maximum tolerance ratio. Maximum tolerance ratios are given for the metal ions Ag(I), Co(II), Cr(III,VI), and Ni(II). The effects of these ions at higher ratios are shown in Table I. The ions As(III), Ga(III), Ge(IV), Ir(IV), Sb(III,V),

Li		Be		ELEMENT VALENCE		TOLERANCE OF METHOD FOR DIVERSE IONS										B		C		N		O		F									
				TOLERANCE:		a. HIGHEST RATIO STUDIED. IRON LEVEL MAINTAINED AT 0.001 MMOLE.										200				3000(a) -3(NH ₄ ⁺) 12000(a)		500C		1000									
Na		Mg		ION TO IRON MOLAR RATIO		b. MAXIMUM PERMISSIBLE RATIO AT OR BELOW WHICH THERE IS NO INTERFERENCE.										1000		500		1000		6000		18000									
(a)		(a)		(CODE)		c. SEE TEXT FOR ADDITIONAL INFORMATION.										(a)		(a,c)		(a)		(a)		(a)									
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br	
+1		+2		+3		+4		+4		+3		+2				+2		+2		+2		+2		+3		+4		+3					
3000		200		250		250		400		100(b) +6		1000(a,c) +7				INTERFERES		12.5		25		1000		200		1000		1000					
(a)		(a)		(a)		(a)		(c,f)		100(b,c)		100(a,c)				(c)		(b,c)		(b,c)		(a)		(a)		(a)		(a)					
Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I	
				+3		+4		+5		+6				+3,+4		+3		+2		+1		+2		+3		+2,+4		+3				-1	
				80		1000		200		250				INTERFERES		30		37.5		50		1000		200		200		80				3000	
				(a)		(a)		(c)		(a)				(c)		(a,c)		(a,c)		(b,c)		(a)		(a)		(a)		(a)				(a)	
Cs		Ba		La		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At	
		+2		+3		+4				+6				+4		+4		+4				+2		+3		+2		+3					
		400		200		100				500				30		30		30				200		100		1000		1000					
		(a)		(a)		(a)				(a,c)				(a,c)		(a,c)		(a,c)				(a,c)		(a)		(a)		(a)					
Fr		Ra		Ac		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu	
						+3																		+3									
						1000																		1000									
						(a)																		(a)									
H						Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf											
+1 (H ⁺)						+4				+6																							
18000						1000				1000																							
(b,c)						(a)				(a)																							

CPP-S-3397

Figure 1. Tolerance of the Direct Procedure for Diverse Ions

IDO-14316
Fe-3:3
Mod-2

Sn(II,IV), and Tl(III), which are potential interferences in the column extraction-colorimetric measurement procedure, do not interfere.

Table I. EFFECT OF DIVERSE METAL IONS AT ION TO IRON MOLAR RATIOS ABOVE THE MAXIMUM TOLERANCE RATIO

<u>Diverse Ion</u>	<u>Diverse Ion to Iron Molar Ratio^a</u>	<u>Interference, %</u>
Ag(I)	200	- 5.2
Co(II)	12.5	- 1.6
	25	- 1.8
	50	- 4.1
	100	- 6.1
Cr(III,VI)	200	+ 2.7
Ni(II)	25	- 2.0
	50	-12.5

^a These data were obtained using 54.6 µg (~0.001 mmole) iron.

The effects of the noble metals, iridium, osmium, rhodium, ruthenium, palladium, and platinum were studied at approximately 30:1 molar ratios. Ruthenium interfered at this ratio. However, at tracer levels, ruthenium is not expected to interfere.

In the procedure, 1.25 mmoles of EDTA and 2.50 mmoles of citrate are used for masking. As much as 2.50 mmoles of citrate or EDTA or 1.0 mmole of oxalate or tartrate can be present in addition without any adverse effect.

A precipitate is formed under the recommended analysis conditions in the presence of the ions Ag(I), Hg(II), and silicate. The precipitate must be removed by centrifugation or filtration prior to measurement of the absorbance of the iron complex.

Tungsten(VI) precipitates as tungstic acid in acid medium and coprecipitates iron. The precipitation is avoided by adding the EDTA-citrate reagent to the sample first, then adding the pyridine before the addition of the hydrochloric acid.

Many metal ions are colored or form colored complexes with EDTA under the analysis conditions. These include Co(II), Cr(III), Cu(II), Dy(III), Ho(III), Ir(IV), Mn(II), Mo(V,VI), Nd(III), Ni(II), Os(IV), Pd(II), Pt(II,IV), Rh(III), Ru(III,IV), Ti(IV), U(IV,VI), and V(IV,V). The preparation of a sample blank is included in the recommended procedure

IDO-14316

Fe-3:4

Mod-2

to correct for the absorbance of these ions at the 507-m μ wavelength. The sample blank is similar to the sample and contains all the reagents except the 1,10-phenanthroline chromogen. The net absorbance of the sample is then the gross absorbance of the sample vs water less the total absorbance of the reagent blank plus the sample blank, each measured vs water.

Cobalt(II) and ruthenium(III,IV) are the only known interferences. The interference of cobalt is somewhat unusual. The pink cobalt(II)-EDTA complex absorbs at the 507-m μ wavelength. The yellowish-orange cobalt(II)-1,10-phenanthroline complex, apparently more stable than the cobalt(II)-EDTA complex, also absorbs at 507 m μ but not as much as the cobalt(II)-EDTA complex. The net effect is that the subtraction of the sample blank results in an over correction, and hence, a negative bias. Samples that contain cobalt should be analyzed according to the column extraction-spectrophotometric measurement Procedure, B. As an alternative, simulated standards containing cobalt can be processed to obtain correction factors for cobalt.

The absorbance of the red iron(II)-1,10-phenanthroline complex is linear with iron concentrations up to at least 200 μ g per 25 ml of final solution (8 ppm); however, the range specified for this procedure is 1 to 100 μ g of iron. For samples that contain less than 10 μ g of iron, 5.00-cm cells are recommended.

COLUMN EXTRACTION-COLORIMETRIC MEASUREMENT PROCEDURE (B)

This procedure, somewhat longer than the direct procedure, is recommended for samples containing diverse ions at ion to iron molar ratios exceeding the tolerance ratios given in Figure 1 for the direct procedure. It is also recommended for samples containing Co(II) and Ru(III,IV) which interfere in the direct procedure even at low concentrations.

As in the macro procedure for iron, Method Fe-4, selectivity is obtained through a preliminary extraction of the iron into 2-octanone (1,2). The sample is adjusted to 7 ± 1 M in hydrochloric acid and passed through a column of Fluoropak saturated with 2-octanone. Iron(III) is extracted quantitatively and diverse cations and anions are washed from the column with additional 7 M hydrochloric acid.

A study of the effects of diverse ions has shown that the metal ions: Bi(III), Cd(II), Ce(III), Cr(III), Cu(II), Co(II), Hg(II), Ni(II), Th(IV), U(VI), and Zn(II) at a 5000:1 diverse ion to iron molar ratio, V(IV), at a 2500:1 ratio and Mo(VI), Ti(IV), and Zr(IV) at a 1000:1 ratio do not interfere. Mo(VI), which partially coextracts with iron is complexed with hydrogen peroxide. V(IV), which partially coextracts even in the presence of hydrogen peroxide, is eluted during the 7 M hydroxhloric acid wash with additional hydrogen peroxide.

The complexing anions citrate, oxalate, and tartrate at 2500:1 anion to iron molar ratio and phosphate at a 5000:1 ratio do not interfere. Fluoride at a 5000:1 ratio gave high erratic results because iron was introduced from the Pyrex column through etching. No fluoride interference is expected if columns of polyethylene or Teflon are used.

Potentially interfering elements are gallium, gold, and thallium which coextract quantitatively and antimony, arsenic, germanium, iridium, and tellurium which partially coextract. A special study was made of the effects of gallium, gold, tellurium, and thallium on the determination of iron with 1,10-phenanthroline. This study showed that gallium did not interfere at a 100:1 molar ratio, but did interfere at 200:1. Gold at 50:1 does not interfere; however, because gold solutions absorb at the working wavelength of 507 mμ, a comparison against a sample blank without chromogen is necessary. Tellurium interferes even at a 10:1 ratio. With chloride masking, thallium at 500:1 does not interfere.

The sample taken for analysis should contain between 5 and 100 μg of iron. For samples that contain less than 100 μg of iron, 5.00-cm cells are recommended.

DISCUSSION

Direct Procedure

The development of the iron(II)-1,10-phenanthroline complex is dependent on the concentrations of the 1,10-phenanthroline chromogen, the hydroxylamine reductant, and the EDTA and citrate masking agents. Because changes in pH alter the "effective" concentrations of hydroxylamine and 1,10-phenanthroline, the color development is also dependent on pH.

In the procedure, the pH is controlled at 5.0 to 6.5 by a mixture of pyridine and concentrated hydrochloric acid. The capacity of this buffer is large enough to maintain the pH at 5.0 to 6.5 even upon the addition of samples with up to 18 meq of acid or 5 meq of base.

The hydroxylamine and 1,10-phenanthroline levels are maintained at 2 mmoles and 0.10 mmole, respectively, and the EDTA and citrate levels are maintained at 1.25 mmoles and 2.50 mmoles, respectively. Under these conditions, complete color development is obtained in 25 min at room temperature. At much higher EDTA-citrate levels, complete color development is obtained only with heating. Heating at 60°C for 15 min, cooling, then allowing to stand for 25 min has been found to be satisfactory. The 25-min standing period is necessary because the iron(II)-1,10-phenanthroline complex dissociates at elevated temperatures. Once formed, the iron(II)-1,10-phenanthroline complex is stable for very long periods.

IDO-14316
Fe-3:6
Mod-2

Column Extraction-Colorimetric Measurement Procedure

In the column separation procedure, the iron is extracted from a 7M hydrochloric acid medium into 2-octanone sorbed on Fluoropak. The extracted iron and the 2-octanone solvent are then eluted with 2-propanol and the iron is determined colorimetrically with 1,10-phenanthroline in the 2-propanol-2-octanone medium.

For quantitative extraction, the iron must be in the +3, ferric, state. Proper preparation of the column also is essential. The column packing should not contain excessive amounts of free unabsorbed 2-octanone, and in packing the column, excessive pressure which tends to "squeeze out" sorbed 2-octanone should be avoided.

Hydroquinone rather than hydroxylamine hydrochloride is used for the reduction of iron(III) to iron(II) because the latter reacts with 2-octanone to form the oxime. This side reaction results in insufficient reductant and incomplete color development.

The rate of color development of the iron complex is fairly slow so that a 15-min waiting period is used. Once formed, the color is stable for long periods of time.

APPARATUS AND REAGENTS

A. Apparatus

1. Spectrophotometer, Beckman Model B, DU, or DK, or Cary Model 14 recording spectrophotometer.
2. Absorption cells, 1.00-cm and 5.00-cm.
3. Flasks, volumetric, 25-ml and other sizes.
4. Pipets, volumetric, 25-ml and other sizes
5. Pipets, Mohr, 5- and 10-ml sizes.
6. Water bath, at 60°C.
7. Ion exchange columns, 7.2-mm i.d. x 15-cm with a 25-ml reservoir, a Teflon-plugged stopcock, and a glass wool plug to support the column packing.
8. Beakers, assorted sizes.
9. Polyethylene wash bottles.
10. Glass stirring rods.

IDO-14316

Fe-3:7

Mod-2

B. Reagents

All reagents used should be C.P. or Analytical Reagent Grade stock. Use distilled water for the preparation of all reagents and throughout the procedure.

1. Reagents for both procedures

- a. Standard iron stock solution, 1.0000 mg Fe per ml. Dissolve 7.0250 g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 100 ml of 0.05M hydrochloric acid and dilute to 1 liter with water.
- b. Iron calibration standard I, 40.0 μg Fe/ml. Dilute 10.00 ml of the iron stock solution to 250 ml with 0.005M hydrochloric acid.
- c. Iron calibration standard II, 60.0 μg Fe/ml. Dilute 15.00 ml of the iron stock solution to 250 ml with 0.005M hydrochloric acid.
- d. Iron calibration standard III, 6.00 μg Fe/ml. Dilute 3.00 ml of the iron stock solution to 500 ml with 0.005M hydrochloric acid.
- e. Iron calibration standard IV, 12.0 μg Fe/ml. Dilute 3.00 ml of the iron stock solution to 250 ml with 0.005M hydrochloric acid.
- f. 1,10-phenanthroline reagent, 0.05M. Dissolve 4.96 g of 1,10-phenanthroline monohydrate in 500 ml of 95% ethanol.
- g. Pyridine.
- h. Hydrochloric acid, concentrated.

2. Reagents used in the direct procedure only.

- a. Hydroxylamine hydrochloride solution, 2M. Dissolve 70 g of hydroxylamine hydrochloride in 500 ml of water.
- b. EDTA-Citrate reagent. Dissolve 93 g of disodium EDTA dihydrate and 113 g of diammonium citrate in water and dilute to 1 liter.

3. Reagents used in the column extraction-colorimetric measurement procedure only.

IDO-14316
Fe-3:8
Mod-2

- a. Iron bench standard, 50 μg Fe/ml. Prepare a matrix solution containing 0.10 mole of each of the metals: cadmium, chromium, copper, mercury, nickel, uranium, and zinc. Introduce all the metals except uranium as nitric acid solutions of the spectrographic grade metals. Admit the uranium as the nitrate salt. Pipet 50.00 ml of the 1.00-mg Fe/ml stock solution to the matrix solution and dilute to 1 liter with water. Store in a Pyrex bottle.
- b. Fluoropak, 20 to 70 mesh, available from Wilkens Instrument & Research, Inc., Box 313, Walnut Creek, California.
- c. Hydroquinone, 0.1M aqueous solution. Prepare a new solution when significant discoloration occurs.
- d. Hydrochloric acid, 7M.
- e. 2-Octanone.
- f. 2-Propanol.
- g. Hydrogen peroxide, 30%.

PROCEDURE

A. Direct Procedure

1. Blank

Process a reagent blank with each series of standards and samples. In addition, process a sample blank if the sample contains colored ions other than iron. The reagent blank contains all the reagents used in the procedure except the sample aliquot. The sample blank contains the sample aliquot and all the reagents except the 1,10-phenanthroline chromogen.

Most reagent grade acids and salts contain traces of iron. Therefore, when large amounts of reagents are used to dissolve or prepare the sample, prepare a solution of the reagents, and process an aliquot of the solution as a sample to enable appropriate correction.

2. Calibration and Bench Standard

The use of four calibration standards is intended to promote efficiency by eliminating many repeat analyses. If only samples with similar concentrations are being run, the use of two appropriate standards will suffice.

IDO-14316

Fe-3:9

Mod-2

A separate calibration is required for each series of samples. Use 1.00-ml portions of each of the four calibration standards and process these according to 3 beginning at step c. Use 1.00-cm cells for standards I and II (40- and 60- μ g Fe/ml, respectively) and 5.00-cm cells for standards III and IV (6- and 12- μ g Fe/ml, respectively). Divide the absorbances by the micrograms of iron to obtain the conversion factors. The difference between the two conversion factors for each of the two groups should not exceed limits set by the Quality Control Laboratory. Also, the average of the two conversion factors should agree with the established conversion factor for each group within the specified limits. If either or both of the specifications are not met, reprocess the pair or pairs of calibration standards. Contact your supervisor if difficulties still are experienced.

3. Analysis of Samples

- a. If the sample is a solid, dissolve a weighed portion of the solid with a minimum of reagents (fusion fluxes, acids, etc.) and dilute with water to a convenient volume.

NOTE: If large amounts of reagents are used to dissolve the sample, it will be necessary to determine the amount of iron introduced through the reagents.

- b. Pipet an aliquot of the sample (15 ml or less) containing 2 to 100 μ g of iron into a 25-ml volumetric flask.

NOTE: If the sample solution contains colored ions other than iron(II,III), a sample blank must be run. The sample blank is processed as is the sample except that the 1,10-phenanthroline reagent is deleted.

- c. With a Mohr pipet, add 0.5 ml of concentrated hydrochloric acid.

NOTE: If a cloudy precipitate forms at this point the sample could contain tungsten. Discard the sample and pipet a new one. Omit the acid and continue with step 4.

- d. With a Mohr pipet, add 1 ml of 2M hydroxylamine hydrochloride and swirl to mix.
- e. Add 5 ml of the EDTA-citrate reagent and swirl.
- f. With a Mohr pipet, add 2 ml of the 0.05M 1,10-phenanthroline reagent.
- g. Swirl to mix, then add 3 ml of pyridine.

IDO-14316
Fe-3:10
Mod-2

- h. If the hydrochloric acid was omitted at step c, add 0.5 ml of concentrated hydrochloric acid.
- i. Dilute to volume with water, stopper, and mix well. Let stand for at least 25 min. Samples containing large amounts of organic complexing agents such as citrate, EDTA, and tartrate must be heated for 15 min at 60°C, cooled to room temperature, then allowed to stand for at least 25 min.
- j. If the sample contains a precipitate, settle the precipitate by centrifugation, then transfer the clear solution to the cell with a pipet.
- k. Measure the absorbances of the blank solutions and the sample against water at 507 mμ in 1.0- or 5.0-cm cells. When measuring the absorbances of a series of samples with absorbances that vary widely, measure the lighter samples first in 5.0-cm cells. This will permit subsequent measurements in 1.0-cm cells if the absorbance is too high.
- l. Record the data on the worksheet and determine the iron concentration as described under CALCULATIONS.

B. Column Extraction-Colorimetric Measurement Procedure

1. Blank

Run a blank with each series of samples substituting distilled water for the sample aliquot.

2. Bench Standard

Run a single determination on the bench standard provided. Proceed with a 1.00-ml sample according to 4 and 5. Limits will be specified by the Quality Control Laboratory. This standard is to be processed in addition to the calibration standards below to ensure that the column separation of iron is proceeding correctly.

3. Calibration

The use of four calibration standards is intended to promote efficiency by eliminating many repeat analyses. If only samples with similar concentrations are being run, the use of two appropriate standards will suffice.

A separate calibration is required for each series of samples. Use 1.00-ml portions of each of the four calibration standards and process these according to 4 and 5. Use 1.00-cm cells for standards I and II (40- and 60- μ g Fe/ml respectively) and 5.00-cm cells for standards III and IV (6- and 12- μ g Fe/ml, respectively). Divide the absorbances by the micrograms of iron to obtain the conversion factors. The difference between the two conversion factors for each of the two groups should not exceed limits set by the Quality Control Laboratory. Also, the average of the two conversion factors should agree with the established conversion factor for each group within the specified limits. If either or both of the specifications are not met, reprocess the pair or pairs of calibration standards. Contact your supervisor if difficulties still are experienced.

4. Column Preparation

- a. Half fill a 600-ml beaker with 20- to 70-mesh Fluoropak.
- b. Drench with 2-octanone.
- c. Filter on a large Buchner funnel and suck air through the 2-octanone-saturated Fluoropak for 10 to 15 min.
- d. Store in a screw-capped wide mouth jar.
- e. Transfer about 15 ml of the 7M hydrochloric acid to the empty column.
- f. Transfer the treated Fluoropak to the column reservoir and with the aid of a glass stirring rod, slurry the Fluoropak with the 7M hydrochloric acid. Open the stopcock and as the Fluoropak settles, tamp gently. Avoid excessive pressure. Prepare a bed 5 in. (12.5 cm) high. Do not allow the column to run dry.

5. Column Extraction-Spectrophotometric Measurement Procedure

- a. Prepare the column as described in B-4.
- b. Pipet a sample containing from 5- to 100- μ g of iron into the column reservoir.
- c. Add an equal volume of concentrated hydrochloric acid and 5 drops of 30% hydrogen peroxide. Use a stream of 7M hydrochloric acid delivered from a squeeze bottle to mix the contents of the reservoir.

IDO-14316
Fe-3:12
Mod-2

NOTE: When sample volumes greater than 10 ml must be taken, pipet the sample into a beaker, adjust the acidity then transfer quantitatively in small portions to the column reservoir.

- d. Pass the sample through the column at the rate of 3- to 5-ml/min. Collect the column effluent in a 250-ml beaker or Erlenmeyer flask.
- e. Wash the column well using 25 ml of 7M hydrochloric acid added in 5-ml increments. Drain the wash solution until the acid level is at the top of the Fluoropak bed.
- f. Strip the iron and 2-octanone with 15 to 18 ml of 2-propanol added in small portions. Collect the column effluent in a 25-ml volumetric flask containing 0.5 ml of 0.1M hydroquinone.
- g. Add 2 ml of the 0.05M 1,10-phenanthroline in ethanol reagent, mix, then add 3 ml of pyridine.
- h. Cool to room temperature and dilute to volume with 2-propanol. Mix well.
- i. After 15 min, read the absorbance at 507 mμ against the blank. The color is stable for several hours.

CALCULATIONS

A. Direct Procedure

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms iron in the calibration standards.
B	Absorbance of the reagent blank.
C	Absorbance of the calibration standards.
D	Conversion Factor

$$D = \frac{C-B}{A}, \quad D' = \frac{C'-B}{A'}$$

$$\bar{D} = 0.5 (D+D')$$

IDO-14316
Fe-3:13
Mod-2

<u>Column</u>	<u>Unit to Record</u>
E	Sample size, in g or in ml.
F	Dilution factor.
G	Absorbance of the sample.
H	Absorbance of the sample blank.
Results, $\mu\text{g Fe/ml}$ or per g	$= \frac{F(G-H-B)}{D E}$
Report the results to 3 significant figures as 606, 60.6, 0.606 $\mu\text{g Fe/ml}$ or g.	

B. Column Extraction-Colorimetric Measurement Procedure

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms iron in the calibration standard.
B	Absorbance of the calibration standard.
C	Conversion factor: $C = \frac{B}{A}, C' = \frac{B'}{A'}$
D	Average conversion factor: $D = 0.5 (C+C')$
E	Sample size, in ml.
F	Dilution factor, if used.
G	Absorbance reading of samples.
H	Result, $\mu\text{g Fe/ml}$ of sample: $H = \frac{FG}{CE}$

Report the results to 3 significant figures as 606, 60.6, 6.06, and 0.606 $\mu\text{g Fe/ml}$.

IDO-14316
Fe-3:14
Mod-2

REFERENCES

1. Fritz, J. S., Hedrick, C. E., Anal. Chem. 34, 1411 (1962).
2. Wade, M. A., Yamamura, S. S., Anal. Chem. 36, 1861 (1964).
3. Yamamura, S. S., IDO Notebook U-850, pp. 39-51, 67-79, 1964.
4. Yamamura, S. S., Sikes, J. H., Paper has been submitted for publication in Analytical Chemistry.

S. S. Yamamura
March, 1965

DETERMINATION OF TOTAL CARBON

ABSTRACT

A method is described for the determination of total carbon in various alloys. Carbon is converted to carbon dioxide in a Fisher Induction Carbon Apparatus and then determined gravimetrically after absorption on Caroxite.

APPLICABILITY

This procedure is applicable to the determination of carbon in various alloys of iron, such as cast iron, ferro-chrome alloys, ferro-vanadium alloys, and ferro-chrome silica alloys. It is also applicable to the analysis of tungsten carbides and uranium-aluminum alloys. The lower limit is 0.05% carbon.

DISCUSSION

The Fisher Induction Carbon Apparatus is schematically illustrated in Figure 1. Oxygen is purified by passing it through magnesium perchlorate (tube A) to remove water vapor, then through Indicarb (tube B) to remove carbon dioxide. The purified oxygen then flows over the heated sample in the induction chamber D where combustion takes place. The gaseous products of combustion are usually carbon dioxide, carbon monoxide, sulfur dioxide, and water. The gas then flows through manganese dioxide (tube E) where the sulfur dioxide is removed and through magnesium perchlorate (tube F) where the water is removed. Carbon monoxide is catalytically oxidized to carbon dioxide in the catalytic chamber G and the carbon dioxide then is absorbed on Caroxite in the tared absorption bulb H.

The sample must fuse completely during the heating cycle to obtain quantitative oxidation of the carbon. Care must be exercised in both the sample preparation and in the packing of the sample in the boat to obtain proper fusion. The ideal particle size of samples is 150 to 840 μ . However, the size may vary considerably outside these limits by exercising caution in packing the boat. Large chunks or turnings are inefficiently heated and should be avoided. Large particles in the presence of extremely small particles may cause erroneous results due to isolation of the small particles. At the conclusion of an analysis, examine the sample to ensure that proper fusion has taken place. If it has not, disregard the results and repeat the analysis with another sample.

SCHEMATIC OF CARBON APPARATUS

- A - WATER ABSORBER - MAGNESIUM PERCHLORATE
- B - CARBON DIOXIDE ABSORBER - INDICARB
- C - FLOW METER
- D - COMBUSTION TUBE
- E - SULFUR DIOXIDE ABSORBER - MANGANESE DIOXIDE
- F - WATER ABSORBER - MAGNESIUM PERCHLORATE
- G - CATALYST - CONVERT CARBON MONOXIDE TO CARBON DIOXIDE
- H - CARBON DIOXIDE ABSORPTION BULB - CAROXITE

Figure 1. Schematic of Carbon Apparatus

SPECIAL PRECAUTIONS

A. Safety

1. Never open the breech to insert or remove a sample while the instrument is in operation.
2. Do not use more than 2 g of uranium-aluminum alloy samples as the material reacts violently when fused.

B. Procedure

1. When transferring the sample to the boat, exercise care to avoid isolated particles.
2. Evenly distribute the sample in the boat.

APPARATUS AND REAGENTS

A. Apparatus

1. Fisher Induction Carbon Apparatus (Figure 1).
2. Ceramic boats.
3. Ceramic shields.
4. Oxygen supply with pressure regulator.
5. Positive manometer.
6. Absorption bulb.
7. Alignment tool (to position boat).
8. Spanner wrench.

B. Reagents

1. Magnesium perchlorate.
2. Caroxite or Indicarb.
3. Manganese dioxide.
4. Ascarite.
5. Combax accelerator.

6. Alundum.
7. Magnesium ribbon.
8. Bench standards, NBS standards of various carbon content.

PROCEDURE

A. Filling the Absorption Tubes

These tubes need be refilled only when the Indicarb is exhausted or when the magnesium perchlorate starts to cake.

1. Using the special spanner wrench, unscrew the knurled retaining collars that hold the absorption tubes.
2. Push the rubber gaskets and washers mounted under the retaining collars toward the center, then remove the tubes without removing the sealing gasket.
3. Empty the tubes and refill with fresh absorbers. Pack the absorbers loosely in the tubes using glass wool plugs at each end of the tubes. Fill the tubes to within 0.5 in. of the top. DO NOT PACK TIGHTLY. Fill one tube with manganese dioxide and place it in the position labeled "SO₂". Fill two tubes with magnesium perchlorate and place them in the two positions labeled "H₂O". Fill the fourth tube with Caroxite and place it in the position labeled "CO₂".
4. Tighten the knurled collars to seal the system.
5. Change the glass wool plug in the end of the combustion tube. Lightly tamp this new plug into the rear of the combustion tube.

B. Filling the Sample Absorption Bulb

This bulb needs to be refilled when the Caroxite shows by a color change from brown to white that it is two-thirds exhausted. (Indicarb will change from purple to gray.)

1. Remove the exhausted Caroxite or Indicarb.
2. Place a glass wool plug in the bottom of the bulb, fill the bulb one-half full with Caroxite or Indicarb, and cover with a plug of glass wool.
3. Add a 0.5-in. layer of magnesium perchlorate and cover with a plug of glass wool.

C. Leak Checking

1. With the breech secured, turn the circuit breaker to the "ON" position and allow the instrument to warm up.
2. Adjust the oxygen pressure to 3 to 5 in. of mercury.
3. Turn on the Flush switch and close the exit needle valve (while the oxygen is flowing).
4. Pinch the rubber tubing leading from the oxygen cylinder to the mercury pressure gauge. A drop in pressure indicates a leak. Leaks most frequently occur at either end of the combustion tube or in the purification-absorption train. Always check for leaks after a combustion tube has been replaced or the purification-absorption train has been refilled.

D. Special Instructions for the Use of the Fisher Induction Carbon Apparatus.

1. Turn the circuit breaker to the "ON" position. Allow the instrument to warm up for 30 sec before pressing the start button. Allow the instrument to warm up for 10 min the first time after a new rectifier tube has been installed.
2. Turn on the oxygen cylinder and adjust the pressure to 0.5 lb/in.².
3. Turn on the oxygen wall valve.
4. Rotate the needle valve on the exit train clockwise until closed, then counter-clockwise about a half turn.
5. Turn the Flush switch to the "ON" position.
6. Adjust the needle valve on the oxygen line until the pressure is between 3 and 4 in. of mercury and the float in the flowmeter is in the "Operating Range."

E. Bench Standard

Run a single determination on the bench standard according to Procedure G. Select a bench standard with the same approximate concentration as the samples.

IDO-14316
C-1:6

F. Sampling

1. Select the sample size as follows:

<u>Estimated % C</u>	<u>Sample Size</u>
< 0.2	2.5 g
0.20 - 1.0	1.5 g
> 1.0	1.0 g

Caution: Do not use more than 2.0 g of uranium-aluminum alloy as the material reacts violently when fused.

G. Burning the Sample

1. Check to ensure that the boat fits inside the ceramic shield.
2. Fill the boat to one-fourth of its depth with alundum.
3. Add a very thin layer of Combax accelerator.
4. Weigh the sample and transfer it to the boat distributing it evenly along the length of the boat.
5. Add a very thin layer of Combax accelerator and a thin layer of alundum over the sample.
6. Place a ceramic shield inside the breech of the instrument leaving about one-fourth of the shield sticking out.
7. Place the boat inside the shield and align the boat inside the shield using the special alignment tool.
8. Using the alignment tool, position the shield and boat inside the combustion tube.
9. Secure the breech.
10. Tare an absorption bulb and attach it at the exit.
11. Push the "Start" button and hold it in the "In" position for 2 to 3 sec until the sample heat indicator glows. The combustion will be completed automatically and the instrument will be returned to standby condition.

12. After the automatic timer turns off and the instrument is on standby, wait 5 min, detach the absorption bulb, and weigh it. The gain in weight is carbon dioxide.

CALCULATIONS

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Weight of sample, g.
B	Tare weight of absorption bulb, g.
C	Gross weight of absorption bulb, g.
D	Weight of CO ₂ , g.

$$D = C - B$$

Result: Carbon,

$$\% = \frac{27.27D}{A}$$

Report results to three significant figures.

REFERENCE

1. Fisher Modern Laboratory Appliances, "Fisher Induction Carbon Apparatus Catalog No. 10-465."

D. N. LeMaire
December, 1965

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

APPENDIX C

METHODS ADDED TO ANALYTICAL
RADIOCHEMICAL MANUAL IN 1965

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

DETERMINATION OF AM-241 IN CPP FINAL PRODUCT

ABSTRACT

A procedure is described for the separation and radiometric determination of americium from thorium, uranium, neptunium, and plutonium. Cations whose valences are +4 and higher are extracted from 2M sodium nitrite into 1.5M di(2-ethylhexyl) phosphoric acid (D2EHP)-heptane. The aqueous phase, which contains the unextracted Am(III), is diluted tenfold with water, and americium is extracted into a fresh portion of the D2EHP-heptane extractant. The organic phase is separated, and americium is back extracted into 2M nitric acid.

APPLICABILITY

This procedure is designed for CPP Final Product Samples which contain high levels of uranium, low levels of thorium, neptunium, and plutonium, and trace levels of americium. The separation is based on the difference in the distribution coefficients into D2EHP-heptane of +3 cations and those of higher valence cations. Actinium and transamericium actinide cations, in the +3 oxidation state, will accompany the americium.

DISCUSSION

This separation procedure is based on the high selectivity of D2EHP for multivalent cations as a function of acid concentration. From 2M acid, trivalent and lower valent cations are not extracted; from 0.2M acid, trivalent cations are extracted away from divalent and monovalent cations. In this way, all cations having higher valence are first extracted and separated from americium. Then americium is extracted and separated from all cations of lower valence. Finally the americium is back extracted into 2M acid and an alpha counting plate is prepared for the radiometric measurement.

SAFETY PRECAUTIONS

Because of the high levels of radionuclides anticipated in these samples, Health Physics procedures will be followed with the necessary precautions. Particular emphasis should be given to the requirement necessary for the handling of alpha emitting nuclides including the use of a glove box.

APPARATUS AND REAGENTS

A. Apparatus

Am-1:2

1. Separatory funnels, 50- and 125-ml.
2. Counting planchets, stainless steel.

B. Reagents

1. Nitric acid, 2M and 2.5M.
2. Sodium nitrite solution, 1M.
3. Organic extractant, 5 volumes of di-(2-ethylhexyl)phosphoric acid: 1 volume of triethylhexylphosphate: 5 volumes of n-heptane.

PROCEDURE

1. Pipet 1 ml of the sample into a 60-ml separatory funnel which contains 5 ml of 2.5M nitric acid and 1 ml of 1M sodium nitrite. The nitrite ensures the oxidation of all plutonium to at least the tetravalent state.
2. Add 5 ml of the organic extractant. Thorium, uranium, neptunium, and plutonium extract.
3. Extract for 2 min.
4. After the phases separate, drain the aqueous phase into a 125-ml separatory funnel. The americium remains in the aqueous phase as it does not extract from 2M acid.
5. Discard the organic phase.
6. To the aqueous phase in the 125-ml separatory funnel, add 45 ml of water and 10 ml of the organic extractant.
7. Extract for 2 min. Americium extracts from the diluted acid; divalent and monovalent contaminants do not extract.
8. Discard the aqueous phase.
9. Back extract the americium into 5 ml of 2.5M nitric acid. Evaporate a known portion of the strip solution on a stainless

steel planchet and measure the 5.476-Mev peak of Am-241 by alpha spectrometry.

CALCULATIONS

<u>Symbol</u>	<u>Unit Represented</u>
A	Sample volume, mL.
B	Aliquot pipetted for counting.
C	Volume factor. $C = \frac{5}{AB}$
D	Gross alpha activity of sample, counts.
E	Counting time, minutes.
F	Alpha activity of sample, count/min. $F = \frac{D}{E}$
G	Background, counts/min.
H	Counts corrected for background. $H = F - G$
I	Gross activity of standard alpha source, counts/min.
J	Known value of standard alpha source, disintegrations/min.
K	Calibration factor, disintegrations/count. $K = \frac{J}{I}$
L	Alpha activity of sample, disintegrations/min/mL. $L = CHK$.
M	% Am-241 in sample. Determined from alpha pulse height analysis.
N	Am-241 in sample, disintegrations/min/mL. $N = \frac{LM}{100}$

Am-1:4

REFERENCES

1. Healy, T. V., "Rapid Solvent Extraction Methods for Fission Product Separation and Analysis", Radiochim. Acta 2, 52 (1963).

S. F. Marsh
February 1965

DETERMINATION OF Ce-143 IN SAMPLES CONTAINING Np-239

ABSTRACT

A procedure is described for the separation and radiometric determination of Ce-143 in samples containing high levels of Np-239. The separation is based on the high distribution coefficient of tetravalent cerium into di-(2-ethylhexyl) phosphoric acid-heptane. After the extraction, the organic phase is separated and contacted with hydrogen peroxide-hydrochloric acid which reduces cerium to the nonextractable trivalent state. The small amount of neptunium which distributes into the aqueous phase is reextracted with a fresh portion of the organic extractant. Cerium is then precipitated from the aqueous strip solution as cerous oxalate for radiometric assay.

APPLICABILITY

This procedure is specifically designed for young fission product samples, in which 56-hr Np-239 may interfere with the gamma counting of 33-hr Ce-143. Resolution of these two nuclides by gamma scintillation spectrometry is very difficult because of the similarity of their gamma spectra and half lives. For fission product samples aged greater than three weeks, the routine tetrapropylammonium nitratocerate extraction procedure (3) is recommended.

DISCUSSION

The separation of neptunium and cerium can be difficult because hexavalent neptunium is formed in the presence of any oxidant sufficient to form tetravalent cerium (the extractable form), and neptunium(VI) is extracted into most systems used to extract cerium(IV). In this procedure, most of the neptunium is coextracted with cerium. However, the hydrogen peroxide-hydrochloric acid strip solution which reduces cerium to the nonextracted +3 valence state, reduces neptunium to a more highly extracted form. It is at this point in the procedure that the main separation is accomplished. The small amount of neptunium that distributes into the strip solution is reextracted by contact with fresh organic extractant. Precipitation of cerium, as the oxalate, provides a solid, stoichiometric form for the yield measurement.

SAFETY PRECAUTIONS

Because the samples will contain varying levels of radionuclides, Health Physics procedures are to be followed. The fuming with perchloric acid must be restricted to hoods which are designated for use with this acid.

APPARATUS AND REAGENTS

A. Apparatus

1. Bunsen Burner.
2. Centrifuge and 50-ml centrifuge tubes.
3. Separatory funnel, 125-ml.
4. Glass fiber filters, H. Reeve Angel 934AH, 2.4-cm diameter.
5. Filtering assembly.
6. Ultrasonic vibrator.

B. Reagents

1. Concentrated acids; nitric, perchloric.
2. Freshly-prepared 8M nitric acid-1M potassium bromate.
3. Hydrochloric acid, 3M.
4. Hydrogen peroxide, 30%.
5. Oxalic acid, saturated solution in water.
6. Organic extractant; 5 volumes of di-(2-ethylhexyl) phosphoric acid: 1 volume triethylhexylphosphate: 14 volumes of n-heptane.
7. Cerium carrier, 27.5 mg/ml as $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$. Dissolve 33 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 1 liter of 0.01M HNO_3 .

PROCEDURE

1. Pipet the sample into a 50-ml test tube, add 1 ml of cerium carrier, and 1 ml of concentrated perchloric acid.
2. Heat to fumes of perchloric acid.

The cerium carrier is made to a concentration of 27.5 mg/ml $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ standardized by an EDTA titration, as described in method Ce-1, IDO-14613.

Use a hood designed for perchloric acid fuming. Fuming with perchloric acid volatilizes hydrochloric and nitric acids, oxidizes contaminants present in a reduced form, and distills any ruthenium which may be present.

Ce-2:3

It may be desirable to vent the fumes through some type of trapping system to avoid the possible plating of radio-ruthenium on the hood and duct work surfaces.

3. Cool and transfer the contents of the test tube to a 125-ml separatory funnel with 10 ml of freshly prepared 8M nitric acid-1M potassium bromate.

The nitric acid-bromate mixture oxidizes cerium(III) to (IV). Neptunium oxidizes to (VI).
4. Add 10 ml of the organic extractant mixture.
5. Extract for 2 min.

Ce(IV), Np(VI), and Zr(IV) extract.
6. Discard the aqueous phase.
7. Scrub the organic phase with 10 ml of 8M nitric acid-1M potassium bromate for 1 min.
8. Discard the aqueous phase.
9. Strip the cerium into 5 ml of 3M hydrochloric acid containing four drops of 30% hydrogen peroxide for 2 min. Discard the organic phase.

Cerium is reduced to (III); neptunium is reduced to (V), then to (IV). The (V) to (IV) reduction is slow and some of the neptunium strips as (V). Zirconium remains in the organic phase.
10. Scrub the aqueous strip solution with a fresh 5-ml portion of the organic extractant mixture for 1 min.

Any stripped neptunium (V) will by this time have been reduced to (IV), which will reextract into the organic phase.
11. Drain the aqueous strip solution into a 50-ml test tube, add 20 ml of water, and heat to near boiling. Add 20 ml of saturated oxalic acid solution and allow at least 5 min for cerous oxalate crystals to form.

Precipitation from a hot solution results in a denser, cleaner precipitate. (It is sometimes desirable to initiate crystallization by holding the tube in an ultrasonic mixer.)

Ce-2:4

12. Centrifuge the precipitate and decant the solution.
13. Wash the precipitate with water in the ultrasonic mixer. The ultrasonic mixing improves the washing of the precipitate.
14. Filter the cerous oxalate on a glass fiber filter.
15. Wash with water, ethanol, and ether.
16. Dry for 5 min in a vacuum desiccator. Weigh the precipitate as $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$.

CALCULATIONS

A. Calculation of concentration of cerium carrier.

<u>Symbol</u>	<u>Unit Represented</u>
A	Volume of cerium carrier titrated, ml.
B	Molarity of EDTA solution.
C	Volume of EDTA used in titration, ml.
D	Concentration of cerium carrier, in mg of $\text{Ce}_2(\text{C}_2\text{O}_4)_3$.
	$10\text{H}_2\text{O}/\text{ml. } D = \frac{BC584}{A}$

B. Calculation Chemical Yield

<u>Symbol</u>	<u>Unit Represented</u>
D	Concentration of Cerium carrier, in mg of $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}/\text{ml}$.
E	Volume of cerium carrier used, in ml.
F	Tare weight of filter, in mg.
G	Weight of filter and precipitate, in mg.

<u>Symbol</u>	<u>Unit Represented</u>
H	Weight of cerium precipitate, in mg. H = G-F.
I	Chemical yield. $I = \frac{H}{DE}$

C. Calculation of radioactive cerium-143.

<u>Symbol</u>	<u>Unit Represented</u>
I	Chemical yield.
J	Sample aliquot volume, in ml.
K	Counting time, in min.
L	Branching ratio. See Table I.
M	1/TPA. Factor for the reciprocal of the combined detection efficiency, peak to total ratio, and absorbance. See Table I.
N	Counts in the integrated peak at 0.294 Mev. See Table I.
O	Ce-143, disintegrations/min/ml. $O = \frac{NM}{LJKL}$

Table I

FACTORS FOR CALCULATING RADIOACTIVE Ce-143

<u>Isotope</u>	<u>Half-Life</u>	<u>Index γ-Ray (Mev)</u>	<u>Branching Ratio</u>	<u>1/TPA at 3 cm</u>	<u>1/TPA at 10 cm</u>
Ce-143	33.4 hr	0.294	0.426	9.74	50.8

REFERENCES

1. Healy, T. V., "Rapid Solvent Extraction Methods for Fission Product Separation and Analysis", Radiochim. Acta 2, 52 (1963).

Ce-2:6

2. McCown, J. J., Larsen, R. P., "Radiochemical Determination of Cerium by Liquid Liquid Extraction", Anal. Chem. 32, 597 (1960).
3. Marsh, S. F., Maeck, W. J., Booman, G. L., Rein, J. E., "Solvent Extraction Method for Radiocerium", Anal. Chem. 34, 1406 (1962).

S. F. Marsh
B. A. Staples
October 1965

DETERMINATION OF NEPTUNIUM-237 IN HIGH CONCENTRATION URANIUM-235 SAMPLES

ABSTRACT

A double extraction method is described for the determination of Np-237 in samples containing 100-350 mg/ml of enriched uranium. The neptunium is reduced to Np(IV) with ferrous sulfamate, extracted from 1M nitric acid into 0.5M thenoyltrifluoroacetone(TTA)-xylene and stripped into 8M nitric acid. The strip solution is diluted to 1M in nitric acid and the neptunium is again extracted into 0.5M TTA-xylene. An aliquot of the TTA-xylene phase is alpha counted for Np-237.

APPLICABILITY

This method is especially suited for the determination of neptunium in CPP final product samples which contain about 300 mg/ml of highly enriched uranium. Samples containing up to 1 mg/ml of plutonium also can be analyzed.

DISCUSSION

If the neptunium product from this method is not sufficiently pure, additional extraction steps can be added. The recovery of neptunium is about 95 $\pm$ 5% with two extractions. A Np-239 internal standard should be used to correct for losses if additional extractions are made or if better accuracy is desired for the two-step method.

Process each sample in duplicate. The gross alpha counts of the duplicates should agree within 10%. Analyze the duplicate, with the highest count rate, for any impurities by α -pulse height spectrometry.

SAFETY PRECAUTIONS

Samples that contain neptunium and plutonium should be handled in a glove box. After the analysis is completed, the area should be surveyed by Health Physics.

APPARATUS AND REAGENTS

A. Apparatus

1. Separatory funnel, 60-ml.
2. Electric stirrer with glass paddles to fit separatory funnels.
3. Volumetric pipets, assorted sizes.

Np-2:2

4. Micropipets, assorted sizes.
5. Infrared lamp.
6. Counting planchets, stainless steel, 2.5-cm dia.
7. Standard Pu-239 alpha counting source.
8. Zinc sulfide alpha detector and proportional counter.

B. Reagents

1. Ferrous sulfamate, saturated. To a saturated solution of sulfamic acid, add an excess of ferrous sulfate. Prepare fresh daily.
2. Nitric acid, 8.0M, 3.3M, and 1.0M.
3. TTA, 0.5M, in xylene. Dissolve 111 g of TTA in xylene and dilute to 1 liter.
4. Ethylenediamine.

PROCEDURE

NOTE: Analyze duplicate samples.

1. Add 3 ml of 3.3M nitric acid, 6 ml of saturated ferrous sulfamate, and up to 1 ml of sample to a 60-ml separatory funnel. Mix well.
2. Let the solution stand for 5 min.
3. Add 10 ml of 0.5M TTA-xylene and extract for 10 min. Discard the aqueous phase.
4. Scrub the TTA-xylene phase with 10 ml of 1M nitric acid. Discard the aqueous phase.
5. Strip the neptunium into 2 ml of 8M nitric acid for 15 min. Discard the organic phase.

This gives a final nitric acid concentration of ~1M. The ferrous sulfamate solution should be prepared daily.

Neptunium reduces to Np(IV).

Vigorous mixing is essential because the neptunium is being stripped from a volume of 10 ml into a volume of 2 ml. It is easier to siphon away the organic phase with a transfer pipet than to decant it from the separatory funnel.

Np-237

6. Add 10 ml of water and 4 ml of saturated ferrous sulfamate to the 8M nitric acid phase.
This dilutes the acidity from 8M to 1M which is necessary for the second extraction of the neptunium into TTA-xylene.
7. Extract the neptunium into 4 ml of 0.5M TTA-xylene for 10 min. Discard the aqueous phase.
Vigorous mixing is essential because of the TTA-aqueous volume differences.
8. Scrub the TTA-xylene phase with 4 ml of 1M nitric acid. Discard the aqueous phase.
9. Pipet up to a 1-ml aliquot of the TTA onto a stainless steel planchet and evaporate to dryness under a heat lamp. Cover the residue with 2 or 3 drops of ethylenediamine and again evaporate to dryness. Flame the planchet.
Pipet the sample, one drop at a time, onto the center of the planchet, allowing each drop to dry before adding another. By keeping the alpha activity confined to the center of the planchet, the counting efficiency is increased.
10. Count for gross alphas.
The alpha count rate should not exceed 2×10^5 cpm. Duplicates should agree within 10%.
11. Alpha pulse height the duplicate with the highest count rate.
This establishes the degree of purity of the Np-237 on the planchet. If the alphas from isotopes other than Np-237 exceed 20% of the total, discard the two plates, and repeat the analysis.
12. Calculate the Np-237 content of the samples according to the next section.

CALCULATIONS

<u>Symbol</u>	<u>Unit Represented</u>
A	Sample volume, ml.
B	Volume of final TTA phase pipetted for counting.
C	Volume factor, $C = \frac{4}{A B}$

Np-2:4

<u>Symbol</u>	<u>Unit Represented</u>
D	Gross alpha activity of sample, counts.
E	Counting time, min.
F	Alpha activity of sample, cpm. $F = \frac{D}{E}$
G	Background, cpm.
H	Counts corrected for background, cpm $H = F G$
I	Gross activity of standard alpha source, cpm.
J	Known value of standard alpha source, dpm.
K	Calibration factor, disintegration/count. $K = \frac{J}{I}$
L	Alpha activity of sample, d/min/ml $L = CHK$
M	Percent Np in sample. Determined from alpha pulse height analysis.
N	Np in sample, d/min/ml. $N = \frac{L M}{100}$

REFERENCE

1. Murray, B. B., Analysis for Neptunium-237 in Nitric Acid Solutions, DP-316, 1958.

R. C. Girton
January, 1965

ABSOLUTE BETA COUNTING OF LOW-ACTIVITY LIQUID-WASTE SAMPLES

ABSTRACT

A method is described for the determination of the disintegration rate of liquid-waste samples that normally contain low levels of activity. The sample is evaporated to dryness on a 1-in. microscope coverglass, the activity is measured on a beta proportional counter, the counting rate is converted to a disintegration rate from geometry factors obtained with Tl-204.

APPLICABILITY

This method is directly applicable to all Chemical Processing Plant liquid waste samples discharged to ground. These include Waste Monitoring Station, SFW, SF-WG, WG-100, WH-101, WL-106, and WL-107 samples.

APPARATUS AND REAGENTS

A. Apparatus

1. Microscope coverglasses, 1-in. diameter.
2. Mounting plates, aluminum, 2.50- x 3.25-in.
3. Template, aluminum mounting plate with 1-in. diameter hole in center.
4. Saran Wrap or equivalent plastic material.
5. Masking tape, double coated, 2-in. wide.
6. Nuts, 0.375-in. stainless steel.
7. Evaporating dish, glass, 600-ml.

DISCUSSION

As in any counting method, extreme care must be exercised to avoid contamination. Cross contamination of samples could result if the equipment and preparation area are not kept free of activity.

All glassware and equipment as well as the sample preparation area should be routinely checked by Health Physics personnel for contamination. A blank determination should be made routinely to insure against contamination of reagents.

IDO-14316
Act-1:2
Mod-2

B. Reagents

Nitric acid, concentrated, C.P. reagent grade.

PROCEDURE

NOTE: Special precautions should be taken to avoid contamination during the preparation of low activity samples. Glassware used for this method should be kept separate. If there is any doubt about the cleanliness of the equipment, do not use it, but replace it with new.

A. Background

Determine the background for the beta proportional counters once each shift. Mount a microscope coverglass as described in step g of Procedure D-1 and place it on the first shelf of the counting chamber.

Activate the counter and allow it to operate for 1,000 sec. Calculate the background as counts per second.

B. Instrument Performance

Place the gross beta calibration standard on the fifth shelf of the counting chamber and activate the counter. Allow the counter to accumulate 10,000 counts. Divide the known value by the determined value of the standard to obtain the performance factor.

C. Blank

Pipet 1 ml of distilled water onto a microscope coverglass and process according to Procedure D-2. If the counting rate of the distilled water exceeds the background by 10%, repeat the blank analysis using a new pipet and fresh distilled water. To determine the blank for Waste Monitoring samples add 10 ml of concentrated nitric acid to 500 ml of distilled water in a 600-ml evaporating dish and process according to Procedure D-1. If the counting rate exceeds the background by 10%, repeat using freshly distilled water, new concentrated nitric acid, a new evaporating dish, and a new pipet.

D. Samples

1. Waste Monitoring Station Samples.

- a. Transfer 500 ml of the sample to an evaporating dish and add 10 ml of concentrated nitric acid.

- b. Evaporate the solution to a volume less than 10 ml. (Do not allow the sample to go to dryness.)
- c. Transfer the sample to a 10-ml volumetric flask with the aid of distilled water rinses, and make up to volume with distilled water. Mix the sample thoroughly.
- d. Pipet duplicate 1-ml aliquots of the concentrated sample onto separate tared microscope coverglasses which are supported by 0.375-in. stainless steel nuts on a piece of transite.
- e. Evaporate the aliquot to dryness under the infrared lamps. To avoid spattering, the samples should be evaporated almost to dryness with the heat lamps set at low. After the sample is almost dry, turn the lamps to high for about 2 min to insure thorough drying.
- f. Reweigh the coverglasses to determine the net weight of solids. (The geometry of counting is dependent upon this weight.)
- g. Mount the microscope coverglasses on the aluminum plates as follows:
 1. Attach a strip of the double-coated masking tape to one of the aluminum mounting plates.
 2. Using the template, inscribe a 1-in. diameter circle on the masking tape.
 3. Place the microscope coverglass, containing the evaporated sample, on the inscribed circle.
 4. Cover the microscope coverglass with a strip of the Saran Wrap and press down firmly to the masking tape.
- h. Count each of the two samples on the first shelf of the beta proportional counter to an integrated count of 10,000 counts or for a minimum of 10 min.

If the count rate exceeds 10,000 cpm, the linearity limit of the counters, start over at step 1-a with appropriately smaller aliquots.

- i. The allowable range of the two samples is 10%. If this is exceeded the entire analysis should be repeated. The range is calculated as follows:

$$200 \frac{X_1 - X_2}{X_1 + X_2}$$

IDO-14316
Act-1:4
Mod-2

where X_1 refers to the highest sample count and X_2 is the lowest sample count.

2. Liquid Waste Samples Other Than Waste Monitoring Station

NOTES: (a) In most cases these samples may be pipetted directly. If the total beta-gamma activity is greater than 1 mr/hr at contact the samples should be analyzed by Act-2, Mod-1 of this manual.

(b) These samples do not contain added solids and it is unnecessary to determine the weight of the small amount of dissolved solids present.

- a. To WG-100 and WH-101 samples add 3 drops of concentrated nitric acid and shake. Let stand 10 min before pipetting aliquots. (The dilution error is negligible for a 5-ml sample.)
- b. Pipet duplicate 1-ml aliquots onto 1-in. microscope cover-glasses supported by 0.375-in. stainless steel nuts on a piece of transite.
- c. Evaporate slowly under infrared lamps as per step 1-e.
- d. Mount the microscope coverglasses on the aluminum mounting plates per step 1-g.
- e. Count each of the two samples on the first shelf of the beta proportional counter to an integrated count of 10,000 counts or for a minimum of 10 min.

If the count rate exceeds 10,000 cpm, the linearity limit of the counters, start over at step 2-a with appropriately smaller aliquots.

- f. The allowable range of the two samples is 10%. If this is exceeded the entire analysis should be repeated. The range is calculated as follows:

$$200 \frac{X_1 - X_2}{X_1 + X_2}$$

where X_1 refers to the highest sample count and X_2 is the lowest sample count.

E. Calculations

The following information should be recorded on the Chemical Analysis Work Sheet. (a) circuit (counter used), (b) sample volume, (c) dilution or concentration volumes, (d) gross wt, (e) tare wt, (f) net wt, (g) counts, (h) time in seconds, (i) counts per second, (j) background, (k) counts corrected for background, (l) performance factor, (m) counts corrected for performance, (n) counts per minute, (o) volume factor, (p) counts corrected for volume, (q) geometry factor, and (r) the time and date of counting. Compute the results in units of beta disintegrations per minute per milliliter as follows:

$$\text{dpm/ml} = \frac{(\text{c/m})(\text{vol factor})}{0.37 - (0.0025 \text{ net wt})}$$

where:

dpm/ml = disintegrations per minute per milliliter

c/m = counts per minute

vol factor = sample volume corrected for concentration

net wt = wt of solids on coverglass in mg.

This expression is approximately valid up to a net wt of 75 mg of solids. In cases where a negligible amount of solids is present the relationship simplifies to the following.

$$\text{dpm/ml} = \frac{(\text{c/m})(\text{vol factor})}{0.37}$$

Report results to two significant figures as 0.25, 2.5 or 25 dpm/ml.

REFERENCES

1. Reynolds, S. A., Brooksbank, W. A., Jr., Nucleonics, 11, No. 11, 46, (November, 1953).

D. M. Lund
May, 1965

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

IDO-14316

Act-2:1

Mod-1

DETERMINATION OF GROSS BETA ACTIVITY

ABSTRACT

A method is described for the determination of gross beta activity in samples that normally contain high levels of activity. Following dilution of the sample to an appropriate activity range, an aliquot is evaporated to dryness on a 1-in. microscope cover-glass and counted on a beta proportional counter at about 10% geometry.

APPLICABILITY

This method is applicable to all Chemical Processing Plant samples except those which are normally low in activity. Low activity samples include Waste Monitoring Station, SFW, SF-WG, WG-100, WH-101, WL-106 and WL-107 and are to be analyzed by method Act-1, Mod-2 of this manual.

DISCUSSION

As in any counting method, extreme care must be exercised to avoid contamination. Cross contamination of samples could result if the equipment and preparation area are not kept free of activity.

All glassware and equipment as well as the sample preparation area should be routinely checked by Health Physics personnel for contamination. A blank determination should be made routinely to insure against contamination of reagents.

APPARATUS AND REAGENTS

A. Apparatus

1. Microscope cover glasses, 1-in. diameter.
2. Mounting plates, aluminum 2.50-x 3.25-in.
3. Template, aluminum mounting plate with 1-in. diameter hole in center.
4. Saran Wrap or equivalent plastic material.
5. Masking tape, double-coated, 2-in. wide.
6. Nuts, 0.375-in. stainless steel.

IDO-14316
Act-2:2
Mod-1

B. Reagents

1. Nitric acid, 0.1M.

NOTE: Special care should be used to insure contamination-free acid. Discard this reagent if 1 ml, carried through the procedure, gives a counting rate more than 10% that of the background.

PROCEDURE

NOTE: Use only new or decontaminated glassware. If decontaminated glassware is used, a blank should first be processed to insure that the equipment does not contain residual activity. This is especially important when analyzing samples with levels toward the lower range.

A. Background

Determine the background for the beta proportional counters once each shift. Mount a microscope cover glass as described in step 4 of PROCEDURE D and place it on the fifth shelf of the counting chamber.

Activate the counter and allow it to operate for 1,000 sec. Calculate the background as counts per second.

B. Instrument Performance

Place the gross beta calibration standard on the fifth shelf of the sample pig and activate the counter. Allow the counter to accumulate 10,000 counts. Divide the known value by the determined value of the standard to obtain the performance factor.

C. Blank

Pipet 1 ml of the 0.1M nitric acid reagent onto a microscope coverglass and process according to PROCEDURE D. If the counting rate of the nitric acid exceeds the background by 10%, repeat the blank analysis using a new pipet. If the counting rate remains high, obtain new reagent and a new pipet.

D. Samples

1. In most cases, samples must be diluted. Measure the total beta-gamma radiation level of the sample, at contact, with a portable Health Physics survey instrument. Dilute 1000 fold

IDO-14316

Act-2:3

Mod-1

for each R of activity by pipetting an aliquot of the sample into a volumetric flask and diluting to volume with the 0.1M nitric acid reagent. To insure proper mixing of diluted samples, use the procedure described on page 121 of the "REMOTE AND SERVICE ANALYSIS GROUP OPERATING MANUAL."

2. Pipet duplicate 1-ml aliquots of the diluted sample onto separate microscope coverglasses which are supported by 0.375-in. stainless steel nuts on a piece of transite.
3. Evaporate slowly, without spattering, to dryness under the infrared lamps. In order to avoid spattering, the sample should be evaporated almost to dryness with the heat lamps set at low. After the sample is almost dry, turn the lamps to high for about 2 min to insure thorough drying.
4. Mount the microscope coverglasses on the aluminum plates as follows:
 - a. Attach a strip of the double-coated masking tape to one of the aluminum mounting plates.
 - b. Using the template, inscribe a 1-in. diameter circle on the masking tape.
 - c. Place the microscope coverglass, containing the evaporated sample, on the inscribed circle.
 - d. Cover the microscope coverglass with a strip of the Saran Wrap and press down firmly to the masking tape.
5. Count each of the two samples on the fifth shelf of the beta proportional counter to an integrated count of 10,000 counts or for a minimum of 10 min.

If the count rate exceeds 10,000 cpm, the linearity limit of the counters, start over at step 1 with appropriately smaller aliquots.
6. The allowable range of the two samples is 10%. If this is exceeded the entire analysis should be repeated. The range is calculated as follows:

$$200 \frac{X_1 - X_2}{X_1 + X_2}$$

where X_1 refers to the highest sample count and X_2 is the lowest sample count.

IDO-14316
Act-2:4
Mod-1

E. Calculations

The following information should be recorded on the Chemical Analysis Section Worksheet: (a) circuit (counter used), (b) sample volume, (c) dilution volumes, (d) counts, (e) time in seconds, (f) counts per second, (g) background, (h) counts corrected for background, (i) performance factor, (j) counts corrected for performance factor, (k) volume factor, (l) counts corrected for volume factor, (m) geometry factor, and (n) the time and date of counting. Compute the results in units of beta disintegrations per minute per milliliter, corrected for background and scaler performance.

$$\text{dpm/ml} = (60) (\text{CC performance})(\text{vol factor})(\text{geometry}).$$

60 = conversion factor from seconds to minutes.

CC performance = computed counts per second corrected for background and performance factor of the counter.

vol factor = volume factors computed from sample dilution volumes and aliquot pipettings.

geometry = geometry factor of the fifth shelf of the counter. This factor is 10 for the beta proportional counters in the Remote and Service Analysis Laboratory, and 16.5 for the counters in the Radio and Special Analysis Laboratory.

Report results to two significant figures such as 25, 2.5×10^3 or, 2.5×10^9 dpm/ml.

D. M. Lund
March 1965

DISSOLUTION AND SEPARATION OF 10-DAY FISSION
PRODUCTS IN CDE PLATEOUT AND OTHER SAMPLES

ABSTRACT

A procedure is described for the determination of various fission products that are released and collected on plateout coupons and other samples during the meltdown of ~ 10-day cooled nuclear fuel. It is designed to produce separated fractions that contain one or more fission products which are resolvable by simple gamma spectrum stripping techniques. Samples are digested with a mixture of acids and the fission products are sequentially separated into fractions by distillation, precipitation, and solvent extraction steps.

APPLICABILITY

The procedure is designed for carbon steel and stainless steel coupons; uncoated, and coated with paint, plastic, and rubber materials. The procedure also is applicable to condensate samples, acid mixtures and Turco solutions used for decontamination, and various filters used for the collection of particulate matter. As stated above, the procedure was designed to produce fractions of fission products resolvable by simple gamma spectrum stripping techniques. Some degree of cross contamination between fractions can be expected. If more precise results are desired, the use of radiochemical procedures for the individual nuclides is recommended.

DISCUSSION

The major steps in the procedure are (1) addition of carriers; (2) digestion of sample and carriers in a specifically designed all-glass reflux apparatus with a mixture of nitric, perchloric and sulfuric acids, followed by hydrochloric acid; (3) distillation of iodine, technetium, and ruthenium into sodium hydroxide while the digestion is in progress; (4) separation of the ruthenium from the sodium hydroxide fraction by reduction to the hydrous oxide; and (5) sequential separations on the undistilled fraction; for tellurium by reduction to the metal with iron powder, for barium by precipitation as the sulfate, for molybdenum by extraction as the α -benzoinoxime complex, and for the lanthanides by precipitation as the oxalate. The gamma spectrum of the remaining solution is analyzed for zirconium-niobium and for cesium activities. The procedure is outlined in Figure 1.

Further discussion of the chemistry involved in the procedure is presented at each individual step in the PROCEDURE section. During the course of the procedure, many aliquots are removed. The analyst must record all such information.

Fiss Prod-1:2

Because the fission products are released from the melted fuel as a function of their boiling points, many samples will contain only the more volatile ones. For this reason, after each sequential operation in the procedure, the remaining fraction should be analyzed by gamma spectrum. Once the spectrum is resolvable, further chemical separations are unnecessary.

SAFETY PRECAUTIONS

Follow Health Physics procedures consistent with the activity levels of the samples. Specific hazards are mentioned at appropriate places in the PROCEDURE.

APPARATUS AND REAGENTS

A. Apparatus

1. Special digestion apparatus (Fig. 2).
2. Bunsen burner.
3. Glass rod (hooked end) for coupon removal.
4. Small plastic bags.
5. Millipore filter assembly.
6. Millipore filters, 1.2- μ ; glass fiber filters, H. Reeve Angel 934AH, (all filters 2.4-cm dia).
7. Beakers, 600-ml, 500-ml, 250-ml (graduations marked).
8. Centrifuge and 50-ml centrifuge tubes.
9. Ice bath (large Petri dish).
10. Magnet stirrer-hot plate.
11. Separatory funnels, 500-ml.

B. Reagents

1. Concentrated acids; nitric, perchloric, sulfuric, hydrochloric.
2. Hydrochloric acid, 4M.
3. Sodium hydroxide, 10M.
4. Concentrated ammonium hydroxide.
5. Cresol red indicator, 0.5% in ethanol.
6. Sodium iodide solution, 0.1 mg/ml.
7. Iron metal powder.
8. α -Benzoinoxime in ethyl acetate, 1% solution.
9. Methanol.
10. Ethanol.

Fiss Prod -1:4

Figure 1. OUTLINE OF THE PROCEDURE
FOR DISSOLUTION AND SEPARATION

Figure 2. Special Digestion Apparatus

Fiss Prod-1:6

11. Saturated bromine water.
12. Saturated oxalic acid.
13. Carriers; 20 mg/ml each of iodine (as iodate), lanthanum, ruthenium, tellurium, and zirconium; 10 mg/ml of molybdenum; and 3 mg/ml of barium.

PROCEDURE

1. Place the sample in the dissolver section of the digestion apparatus.
2. Add 20 mg each of the I, La, Ru, Tc, and Zr carrier solutions, and 10 mg of the Mo carrier solution.

The iodine carrier is added as HIO_3 to delay its distillation until exchange with the fission product iodine takes place.
3. Add 25 ml of sulfuric acid, 15 ml of nitric acid, and 10 ml of perchloric acid.

Mark the height of the sulfuric acid on the digestion apparatus with a marking pen (See Step 13 for reason).
4. Add 120 ml of 10M sodium hydroxide to the trap and connect the trap section to the dissolver section.
5. Seal all joints of the apparatus with concentrated sulfuric acid.
6. Pack the trap in ice.
7. Start the flow of cooling water through the condenser.
8. Adjust the air flow to 5 to 10 bubbles per second.

The flow is maintained from this point through step 24.
9. Heat the dissolver section with a Bunsen burner. Adjust the flame to maintain the frothing within the cooling water condenser section.

Whenever the heating of the dissolver section is stopped, the sodium hydroxide may be sucked into the dissolver section. Be certain to maintain sufficient air flow to prevent this.

Fiss Prod-1:7

10. Heat for at least 15 min or until the frothing noticeably subsides.

The frothing is the reaction of the coating material of the plateout coupons with the hot acids.
11. Remove the burner.
12. Stop the flow of cooling water, disconnect the cooling water lines, and drain the condenser.

The removal of water from the condenser allows the digestion to continue at a higher temperature. Also, the perchloric acid becomes concentrated to distill ruthenium as RuO_4 .
13. Replace the burner and heat for 45 min or until sulfuric acid starts fuming.

This step is attained when the 25-ml mark on the dissolver section step 3) is reached.
14. Remove the burner and let the dissolver section contents cool to the finger touch point.

After 10 min of cooling, the dissolver section may be immersed in warm water to hasten in cooling.
15. For samples of plateout coupons, open the joint above the condenser and lift the coupon with the glass rod hook above the sulfuric acid level.
16. Rinse the coupon with ~ 10 ml of water.

Caution. Water is dropping into concentrated sulfuric acid and will spatter.
17. Remove the coupon and place it in a plastic bag for a gamma scan.
18. Close the apparatus.
19. Slowly add 5 ml of concentrated hydrochloric acid through the reagent funnel.

The addition of hydrochloric acid to concentrated sulfuric acid causes a vigorous reaction.
20. Replace the burner and heat to dense fumes of sulfuric acid. Continue for ~ 5 min.

The remainder of the iodine distills, presumably as iodine monochloride, and is absorbed in the sodium hydroxide.

Fiss Prod-1:8

21. Remove the burner and let the dissolver section contents cool to the finger touch point.
22. Add 50 ml of 4M hydrochloric acid through the reagent funnel.
23. Replace the burner and boil the solution for 5 min.

The hot hydrochloric acid leaches most of the adsorbed activity from the dissolver section surfaces and from the undissolved residue.
24. Remove the burner and set aside the dissolver section and contents to cool.

Treatment of the contents starts with step 31.
25. Stop the air flow.

The air flow has been maintained without interruption from the time it was started (step 8) until now.
26. Disconnect the trap section and quantitatively transfer the sodium hydroxide to a 600-ml beaker with the aid of water rinsings.
27. Dilute to a final volume of 400 ml with water.
28. Heat to near boiling.
29. Add 5 ml of ethanol while stirring vigorously. Continue to stir until precipitation of the hydrous ruthenium oxide appears to be complete.

The ethanol reduces the ruthenium to the (IV) valence state which precipitates as $\text{RuO}(\text{OH})_2$.
30. Heat again to near boiling, then set the solution aside to cool. (The next operation on this solution is step 38).

The $\text{RuO}(\text{OH})_2$ precipitate will coagulate on standing. In the meantime, continue with the next step on the solution from the dissolver section.
31. Transfer the dissolver section contents (step 24) equally to two 50-ml centrifuge tubes.

32. Centrifuge, then decant the supernatant solutions through a glass filter in a Millipore filter assembly. Leave the assembly set up for step 34.

Centrifugation of the undissolved residue speeds the filtration time.
33. Add 3 ml of 4M hydrochloric acid to each centrifuge tube and heat over a burner with agitation.
34. Transfer the solids to the glass fiber filter (step 32) and thoroughly wash them with hot 4M hydrochloric acid. Mount the solids for a gamma scan. Label it Residue.

The filtered and washed solids usually retain low levels of fission product activity and must be counted to obtain a total fission product balance. Gamma scan the filtrate to establish whether further steps are necessary.
35. Transfer the filtrate from the Millipore filter assembly to a 250-ml beaker with the aid of water rinses.
36. Add 30 mg of iron metal powder and 1 ml of the sodium iodide solution.

Iron metal reduces tellurium to the metal. Iodide catalyzes the reaction.
37. Heat with stirring for 30 min. (The next operation on this solution is step 41).

If a magnet stirrer-hot plate is used, the iron metal serves as the stirring bar.
38. Filter the coagulated ruthenium oxide precipitate (from step 30) through a glass fiber filter in a Millipore filter assembly.
39. Wash the precipitate with ethanol. Mount the precipitate for a gamma scan. Label it Ru.

The major activity should be Ru-103.
40. Measure the volume of the filtrate and prepare an aliquot for a gamma scan. Label it I-Tc.

The major activities should be I-131 and Tc-99m.
41. Filter the tellurium precipitate (from step 37) through a glass fiber filter in a Millipore filter assembly. Mount the precipitate for a gamma scan. Label it Te.

The major activity should be Te-132. Do not wash the precipitate with alcohol or ether unless the vacuum flask is changed. These solvents would interfere in the subsequent separations.

42. Transfer the filtrate from the Millipore filter assembly to a 250-ml beaker with the aid of water rinses.
43. Heat the solution nearly to boiling and dropwise add 5 ml of the barium carrier solution while vigorously stirring.
44. Boil the solution for 2 min.
45. Cool and after the precipitate of barium sulfate settles, filter it through a 1.2- μ Millipore filter in a Millipore filter assembly.
46. Wash the precipitate with water. Mount the precipitate for a gamma scan. Label it Ba.

The major activity should be Ba-140. Gamma scan the filtrate to establish whether further steps are necessary.
47. Transfer the filtrate from the Millipore filter assembly to a 500-ml separatory funnel.
48. Slowly and with constant swirling, add 50 ml of concentrated ammonium hydroxide, then 5 ml of concentrated nitric acid, and finally 5 ml of saturated bromine water.

The molybdenum oxidizes to the (VI) valence state and the solution is at the proper acidity for the extraction of the α -benzioxime complex.
49. Cool the mixture.
50. Contact the mixture with two separate 25-ml volumes of 1% α -benzioxime-ethyl acetate, for 1 min each time.
51. Combine the two organic phases and add 10 ml of methanol with swirling.

The complex precipitates upon the addition of the methanol.
52. When precipitation of molybdenum- α -benzioximate is complete, filter the precipitate through a glass fiber filter in a Millipore filter assembly.

53. Wash the precipitate with ethanol. Mount the precipitate for a gamma scan. Label it Mo.
The major activity should be Mo-99. Gamma scan the filtrate to establish whether further steps are necessary.
54. Transfer the filtrate from the Millipore filter assembly to a 400-ml beaker with the aid of water rinses.
55. Place the beaker in an ice bath.
56. Add 50 ml of saturated oxalic acid solution and 0.5 ml of 0.5% cresol red indicator solution.
57. With vigorous stirring, add concentrated ammonium hydroxide (~ 20 ml) until the indicator color just changes from red to yellow.
At the indicator color change, the pH is 2 at which value the lanthanide oxalate precipitates almost completely.
58. Continue to stir while the solution cools.
59. After precipitation of the lanthanide oxalate is complete, filter the precipitate through a glass fiber filter in a Millipore filter assembly.
60. Wash the precipitate with ethanol. Mount the precipitate for a gamma scan. Label it La.
The major activities should be La-140, Nd-147, and Ce-141, -144.
61. Measure the volume of the filtrate and prepare an aliquot for a gamma scan. Label it Zr-Nb-Cs.
The major activities should be Zr-Nb-95 and Cs-137. For low enrichment uranium fuel, Np-239 may be present.

CALCULATIONS

No formal information is presented because it mainly is based on gamma spectrometry and due to the large variations between samples.

M. E. Kussy
S. F. Marsh
W. J. Maeck
November, 1965

**PHILLIPS
PETROLEUM
COMPANY**

ATOMIC ENERGY DIVISION