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MASTER

ANNUAL REPORT OF ICPP ANALYTICAL SECTION FOR 1961

Ralph C. Shank, et al.

PHILLIPS
PETROLEUM
COMPANY

ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION

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By

Ralph C. Shank and Staff

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ANNUAL REPORT OF ICPP ANALYTICAL SECTION OF 1961

By

Ralph C. Shank and Staff

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1. SUMMARY

ANALYTICAL SERVICE

A total of 58,467 determinations was made by the Analytical Section with an average force of 41. With the plant being down a large portion of the year, only 12% of Analytical's productive time was required to service it. Work from outside ICPP required almost 30% with the remaining time being spent on technical programs. Some new equipment was obtained and tested in preparation for servicing the Experimental Organic Cooled Reactor (EOCR).

2. INTRODUCTION

This is the second⁽¹⁾ Annual Report of the Analytical Section of the ICPP (Idaho Chemical Processing Plant). Until 1960, information concerning analytical progress was included in ICPP Operation's weekly and monthly reports and in ICPP Technical's quarterly reports. Limited reports of analytical work are still included in these monthly reports of Operations and Technical. However, the opportunity to present a complete year of work in an annual report seems worthwhile. Thus, things of interest to analytical chemists are collected into one volume where both negative and positive results can be presented in more detail. Work that has been or will be published is only abstracted, allowing space for information that will not be available elsewhere. Also opportunity is taken in the appendices to up to date routine method in use in this laboratory.

It is hoped that this report will be of value to management, to those who submit samples, and to analytical chemists from other installations.

⁽¹⁾ The first is Shank, R. C., et al., U. S. Atomic Energy Commission Report, IDO-14547, 1961.

3. GENERAL INFORMATION

3.1. Organization

At the start of 1961, 39 people were required to handle the Analytical load. Because of plant start up and other increases, the Section ended the year with 46 as shown in the organization chart (Figure 3.1.).

3.2. IBM Accounting System

The IBM accounting system as described last year was continued in 1961. A monthly manpower breakdown report is prepared from the IBM records. Table 3.1. Distribution of Manpower in 1961 and Table 3.2. Determinations Made by Analytical Section in 1961 were prepared by totaling these monthly reports. The accuracy of these reports is excellent because they are machine tabulations of daily reports by each individual. The IBM marksense cards are also used by the Accounting Branch to distribute Analytical costs and by supervision to determine source and kind of work load coming into the laboratory.

Fig. 3.1. Organization of ICFP Analytical Section.

Table 3.1. Distribution of Manpower^a in 1961

	<u>ICPP Operations</u>	<u>ICPP Technical</u>	<u>Outside ICPP</u>	<u>Analytical^b</u>	<u>Total Hours Worked</u>
Mass Analysis	4.8	13.9	32.9	48.4	6350
Special Analysis	5.1	11.8	48.8	34.3	14287.5
Analytical Development	0.4	58.5	12.3	28.8	24343.5
Shift Laboratory	18.5	41.9	8.4	31.2	28490.5
Spectrochem	1.3	43.1	21.2	34.4	11269
Section Total	7.9	39.5	19.8	32.8	84740.5

^a All figures expressed as per cent except last column.

^b Includes overhead items such as housekeeping, vacations, and other items not directly charged to analytical service or existing research projects.

Table 3.2. Determinations Made by Analytical Section in 1961

Source of Samples	Mass Lab	Special Analysis	Anal. Develop.	Quality Control*	Shift Control	Spectrochem	Total Number	Per Cent of Total Number
ICPP Operations	344	209		32	5177	144	5874	10.0
RaLa Process	6	33		14	167		1710	2.9
ICPP Technical	103	1639	132	72	26458	5854	34186	58.5
ICPP Miscellaneous		413		130	1153	17	1583	2.7
Inter Section	63	144		2764	1620	308	2135	3.6
Quality Control	444	54		1918	1518	15	2031	3.5
Other Phillips	1114	1988	92	34	1495	1082	5775	9.9
Outside Work**	1321	1827	25	25	296	1704	5173	8.9
GRAND TOTAL	3395	6307	249	4989	39392	9124	58467	100.0

*Reagents and controls prepared by this laboratory are not included in the total.

**AEC Contractors other than Phillips Petroleum Company.

4. SHIFT LABORATORY

George A. Huff, Group Leader; Ivan L. Doggett, Assistant;
Frank A. Duce, Benjamin R. Hunter, David M. Lund,
Howard A. Shogren, Shift Supervisors; Rodney J. Anderson,
Robert C. Girtton, Dale N. LeMaire, Chemists.

This laboratory analyzes unirradiated and irradiated materials. The Remote Analytical Facility is used to prepare and analyze irradiated samples. Operating procedures for remote equipment may be found in the "Analytical Control Laboratory Operating Manual," IDO-14396. As indicated in Table 3.2, 39,392 constituents were determined on samples from various sources. Samples analyzed generally conformed to the methods found in the "Manual of Analytical Methods Used by The Control Laboratory at The Chemical Processing Plant," IDO-14316. Non-routine samples were handled as time and manpower permitted.

Table 4.1 shows the various methods used in the laboratory and the average time required for analysis. This information was obtained from IBM records prepared daily by all laboratory personnel. It may be noted that some constituents require more or less time than reported last year. This variation in time is due to the number of samples being analyzed.

4.1. Routine Analyses

The majority of time utilized in this laboratory was devoted to routine analytical determinations. Samples requiring routine analyses were received from CPP Operations, CPP Technical and Phillips General Maintenance. Analytical data of this nature are required for operational, experimental, and accountability reasons.

Four chemists were trained to use the X-ray diffractometer. This was done in order to handle the sample load on a rotating shift basis.

Graphical representation showing standard deviation and bias over the range of the method have been developed for the methods listed below.

1. Acid, Oxalate, pH Titrimetric
2. Aluminum, Fluoride Complexing, Titrimetric
3. Boron, 1, 1' Dianthrimide, Colorimetric
4. Mercury, Thiocynate, Titrimetric
5. Specific Gravity, Westphal
6. Uranium, Extraction, Spectrophotometric

Data obtained using the above methods are now routinely corrected for bias and reported with precision.

Training for various personnel was completed on the methods listed below.

1. Boron, Mannitol Titrimetric
2. Density, Absolute
3. Density, Bulk
4. Density, Particle
5. Fluoride, Macro, Cerium Trifluoride, Titrimetric
6. Fluoride, Micro, Eriochrome Cyanide R, Colorimetric

4.2. Non Routine

4.2.1. Modifications of Methods

In order to analyze various samples received in the laboratory, slight modifications in methods were necessary. These changes were coordinated between personnel in this laboratory and the Analytical Development Group.

4.2.1.1. Aluminum, Fluoride Complexing, Titrimetric

The request from CPP Technical to determine aluminum on calciner product presented the problem of dissolving the sample and making it compatible with the existing method. These samples were partially dissolved by heating in 10 to 20% sodium hydroxide. The residue was dissolved with a few drops of 48% hydrofluoric acid. The solution was then analyzed for aluminum as outlined in the methods manual.

4.2.1.2. Boron, 1, 1' Dianthrimide, Colorimetric

During the color developing stage of this method, a brown interfering color was noticed. Pyrex glassware is used in this method. It is cleaned with nitric acid to eliminate boron contamination. It was determined that the nitric acid used to clean the glassware was decomposing the 1, 1' dianthrimide. By rinsing flasks thoroughly with sulfuric acid, after nitric acid cleaning, the interfering color was overcome.

4.2.1.3. Uranium, Lead Reduction, Titrimetric

Difficulty was encountered in using this method for samples containing tin. In order to overcome this problem, tin was volatilized from the sample prior to passing it through the lead reductor. This was accomplished by taking the sample to dryness over a low heat in the presence of concentrated hydrochloric acid and baking at a high heat for ten minutes. This step was repeated prior to passing the sample through the lead reductor.

4.2.1.4. Size Distribution, Screening

Size distribution on wet and dry samples has been accomplished by screening. The methods used are preliminary and are not found in the methods manual.

It is difficult to obtain a good sample aliquot on wet samples. This was overcome, in the laboratory, by using the entire sample.

Fine dry samples presented the problem of "balling up" and not passing through the screens upon shaking. This problem was overcome by alternately brushing with a fine brush and shaking the sample through each screen.

See section 7.2. for further information concerning size distribution of calciner solids.

4.2.2. Special Samples

Phillips Chemical Engineering Laboratory submitted sixteen uranium-zirconium alloy samples to be checked for uranium content and uranium isotope ratio. Three samples containing 98% uranium were dissolved in concentrated nitric acid. The remaining thirteen were 90%-99% zirconium. These samples were dissolved in 30 ml of 14M hydrofluoric acid added in 5 ml increments under reflux. Heat was provided by a boiling water bath. The reaction on acid addition is violent. After the reaction subsides, a solution containing 60 ml 14M hydrofluoric acid and 8 ml of 30% hydrogen peroxide was added through the condenser in 5 ml increments every 5 to 10 minutes.

Samples from the SL-1 incident were submitted by Idaho Operations Office, USAEC. They were analyzed for uranium content, and prepared for uranium isotope and radiochemical analyses.

Eight samples of uranium dioxide-beryllium oxide were received from Convair for uranium and radiochemical analyses. Two samples were unirradiated. One of these samples was heated in a tantalum crucible to 2500°C and melted. The other sample was not heated. Two samples had been irradiated and not exposed to heat. The other four samples were irradiated and melted in tantalum crucibles heated to 2500°C.

From previous experience on dissolving uranium dioxide-beryllium oxide, all samples were treated with boiling 10M sulfuric acid under reflux. The three premelt samples responded to this treatment and dissolved. The only postmelt sample that dissolved was not exposed to air on heating. It is believed that oxidizing conditions were not as severe as with the other four postmelt samples. The remaining four postmelt samples did not respond to this treatment. After prolonged refluxing (108 hours) only milligram quantities of uranium were dissolved. Many other combinations were tried such as sulfuric-nitric, sulfuric-phosphoric, nitric-hydrofluoric and potassium dichromate-hydrofluoric. None of the combinations were successful.

A portion of the unirradiated postmelt sample was fused with anhydrous potassium fluoride, dissolved in concentrated sulfuric acid and heated to fusion temperature again. This dissolved most of the sample leaving only a light gray residue. Although fusion was successful in dissolving the sample, this laboratory is not equipped to do this remotely. It was also concluded that a development program would be required to determine the accuracy of our methods due to the large amount of tantalum in the sample. Work on this project has been discontinued waiting for instruction from Convair.

Fifty-six unirradiated samples were dissolved and prepared for isotope ratio analysis. One hundred and eighty-six irradiated samples were dissolved and prepared for uranium isotope ratio, uranium content, and radiocesium analyses. These constituents were determined in order to obtain burnup on the samples. Sources for these samples are:

1. Phillips Reactor Engineering Development and Metallurgy Section
2. Battelle Memorial Institute
3. Westinghouse
4. Brookhaven National Laboratory through Phillips Project Engineering
5. GCRE through Phillips MTR Hot Cell
6. General Electric

Two unirradiated and fourteen irradiated fuel specimens from General Electric Aircraft Nuclear Propulsion Project were dissolved, diluted to volume and returned to General Electric for analysis. Five of these samples were analyzed for uranium isotope ratio and content before they were returned to General Electric.

Six irradiated thorium slugs from Phillips Reactor Physics Research Group were dissolved and analyzed for uranium content and isotope ratio, aluminum, thorium, cesium-137 and cerium-144. Through the cooperation of CPP Technical, this work was done in the multicurie cell. It was reported in IDO-14557.

Samples of coal and soil were submitted from Idaho Operations Office, USAEC through CPP Technical for carbonate analysis. The method suggested in the text, "Soil Chemical Analysis" by Jackson, was used for these samples. The method calls for the freeing of carbon dioxide in the sample by hydrochloric acid and heat. The carbon dioxide is trapped in excess standard sodium hydroxide. The excess sodium hydroxide is titrated with hydrochloric acid to determine the carbonate.

A number of other organizations outside CPP have submitted samples to this laboratory which required special handling and preparation. The constituents determined on these samples were uranium, iron, copper, gold, hafnium, boron and aluminum.

Sources of these samples are:

1. Aerojet General through Idaho Operations Office, USAEC
2. Phillips Reactor Engineering Development and Metallurgy Section
3. Westinghouse
4. Phillips Engineering Test Reactor Health Physics
5. Phillips EOCR Group

The dissolution schemes used for various samples are shown in Table 4.2.

4.3. Remote Analytical Facility

Remote equipment was used throughout the year for samples from CPP Operations, CPP Technical and for special samples from sources outside CPP. Some operational problems were experienced, however these were few and not serious.

Maintenance was required on pneumatic cylinders for lift mechanisms, motors for stirring devices, solenoid valves, electronic circuits and leaking and plugged remote pipets.

The Model-B remote pipetter developed a leak in February. This unit functioned longer than any pipet used by the laboratory before maintenance was required. The unit was removed from the operation line, decontaminated and overhauled. Details on the problems encountered are discussed further in Section 7.25.1.

The Model-B specific gravity apparatus was moved into position 5-A in January of this year. This is an experimental model and it appears to be an improvement over the old units. Further information concerning this apparatus is given in Section 7.25.2.

Two simplified sample disposal units were installed in the A line. These units are located in the A line storage boxes. They are the same as the one installed in the B line last year. They consist of a water line and drain line. Bottles are rinsed and drained to the plant salvage tanks.

In June of this year, a new direct drive stirrer was installed in the water bath tank for the 8-A specific gravity apparatus. This replaced the defective magnetic stirrer.

During the month of June, a new Model-B titrator was installed in position 6-B in the Remote Analytical Facility. The unit has functioned properly since installation. It is a replacement for original obsolete equipment located in that position.

Table 4.1. Analytical Methods Used in The Shift Laboratory

<u>Method</u>	<u>Hours Per Analysis</u>
<u>Acid, Oxalate, pH Titrimetric</u>	0.27
<u>Acid, Oxalate, pH Titrimetric^a</u>	0.28
<u>Acid, Simple Volumetric</u>	0.33
<u>Aluminum, Aluminon Colorimetric</u>	0.82
<u>Aluminum, Fluoride Complexing-Titrimetric</u>	0.46
<u>Biochemical Oxygen Demand</u>	0.28
<u>Boron, 1, 1' Dianthrimide Colorimetric</u>	1.22
<u>Boron, Mannitol Titrimetric</u>	0.70
<u>Carbonate, Titrimetric</u>	0.32
<u>Chloride, Silver(I) Turbidimetric</u>	0.50
<u>Chloride, Silver(I) Titrimetric</u>	0.62
<u>Chromium, Diphenylcarbazide Colorimetric</u>	0.64
<u>Chromium, Redox Titrimetric</u>	0.81
<u>Density, Absolute</u>	0.86
<u>Density, Bulk</u>	0.33
<u>Density, Particle</u>	0.86
<u>Fluoride, Macro, Cerium Trifluoride, Titrimetric</u>	1.28
<u>Fluoride, Micro, Eriochrome Cyanine R, Colorimetric</u>	0.30
<u>Gross Activity</u>	0.41
<u>Hydrogen Peroxide, Potassium Permanganate, Titrimetric</u>	0.73
<u>Iodine, Radiochemical</u>	1.20
<u>Iron, Orthophenanthroline Colorimetric</u>	0.34
<u>Iron, Hydroxide Precipitation-Redox Titrimetric</u>	0.95
<u>Mercury, Dithizone Colorimetric</u>	0.42
<u>Mercury, Thiocyanate Titrimetric</u>	0.29
<u>Nickel, Dimethylglyoxime Colorimetric</u>	0.71
<u>Nickel, Dimethylglyoxime Precipitation EDTA Titration</u>	0.87
<u>Nitrate, Ferrous Nitrosyl Sulfate Colorimetric</u>	0.36
<u>Nitrate, Devarda Reduction Distillation-Titrimetric</u>	0.58
<u>Reducing Normality</u>	0.50
<u>Solids, Total at 400°C</u>	0.29
<u>Solids, Undissolved at 1000°C</u>	0.34
<u>Specific Gravity, Falling Drop^a</u>	0.48
<u>Specific Gravity, Westphal</u>	0.25
<u>Tributyl Phosphate, Acid Saturation</u>	0.36
<u>Uranium, Extraction-Spectrophotometric</u>	0.57
<u>Uranium, Fluorophotometric</u>	0.41
<u>Uranium, Fluorophotometric^a</u>	0.48
<u>Uranium, Direct Ignition to U₃O₈</u>	0.80
<u>Uranium, Mass Isotopic Distribution^b</u>	0.50
<u>Uranium, Mass Isotopic Distribution^{a,b}</u>	0.69
<u>Uranium, Pb Reduction, Titrimetric</u>	1.00
<u>Zirconium, Pyrocatechol Violet EDTA, Colorimetric</u>	1.39
<u>Zirconium, Cupferron Amperometric</u>	1.11

^aMethod performed in Remote Analytical Facility^bSeparation of uranium by solvent extraction before mass assay

Table 4.2. Dissolution Schemes for Various Samples

<u>Samples Submitted By</u>	<u>Sample</u>	<u>Method of Dissolution</u>
General Electric (ANP)	UO ₂ -BeO	10M sulfuric acid plus heat
Battelle Memorial Institute	UO ₂ -graphite	Equal volumes of concentrated nitric, sulfuric and perchloric acid plus heat
Battelle Memorial Institute	UO ₂ in stainless steel tube	6M sulfuric acid plus iron trigger plus heat UO ₂ in concentrated nitric acid plus heat
Battelle Memorial Institute	UO ₂ powder	Concentrated nitric acid plus heat
Battelle Memorial Institute	UO ₂ pellets	Concentrated nitric acid plus heat
Battelle Memorial Institute	UO ₂ -BeO	1M chromic acid, 14M hydrofluoric acid solution plus heat
Battelle Memorial Institute	UC pellets	Concentrated nitric acid plus heat
Battelle Memorial Institute	UO ₂ clad in zircaloy-2	UO ₂ dissolved out of cladding with 6M nitric acid plus heat
Battelle Memorial Institute	UO ₂ -ThO ₂	Aqua regia plus heat
Phillips Reactor Physics Research Group	Al clad thorium	Cladding dissolved in 6M nitric acid, 0.005M mercury solution plus heat. Thorium dissolved in 16M nitric acid, 0.05M hydrofluoric acid solution
Phillips Chemical Engineering Laboratory	98% U-2% Zr 90%-99% Zr-U	Concentrated nitric acid plus heat Hydrofluoric acid, hydrogen peroxide plus low heat

Samples Submitted By

Phillips Reactor Engineering
Development & Metallurgy Section

MTR Hot Cell (GCRE)

MTR Hot Cell (WCAP)

Convair

Sample

Al clad UO_2

UO_2 in stainless
steel tube

UO_2 in hastaloy

10% UO_2 -BeO

Method of Dissolution

6M nitric acid, 0.005M mercury solution plus
heat

UO_2 dissolved out with concentrated nitric
acid

UO_2 dissolved out with concentrated nitric
acid

10M sulfuric acid under reflux
Fusion also used - Fused with anhydrous
potassium fluoride, dissolved in concentrated
sulfuric acid and heated to fusion temperature
again

5. SPECIAL ANALYSIS LABORATORY

Dale G. Olson, Group Leader; Jack G. Scott, Assistant Group Leader
James E. Baker, Robert E. Foster, Ronald E. Ohlin, Jack L. Teague,
Chemists; Andrew C. Hill, Technician.

The major endeavor of this laboratory is radiochemical analysis. Non-routine analyses are also made on cold samples. Both types of analyses often require short development effort, usually consisting of adapting literature available methods.

5.1. Radiochemical Analyses

5.1.1. SL-1 Assistance

Many samples of various materials taken from the SL-1 reactor incident were analyzed. An effort was made to verify that a nuclear excursion had occurred and determine the flux at various locations. The specific activity of Cu^{64} in a brass buckle and screw was measured. Sodium²⁴ was sought in a blood sample. Metal particles and clothing fragments were dissolved and analyzed for Zr^{97} , Zr^{95} , Ce^{143} , Ce^{144} , Sr^{89} , Sr^{90} , Cs^{137} , $\text{Pu}^{238,239,240}$, Ru^{103} , Ru^{106} , I^{131} , Nb^{95} , Ba^{140} , Pa^{233} , Cr^{51} , Co^{60} , Fe^{59} , and Cd^{115} . Portions of stainless steel, not exposed to neutrons prior to the incident, were analyzed for Co^{60} . Particulate matter, vacuumed from the core, was photographed and then analyzed for radionuclides.

5.1.2. Burnup Measurement by Cs^{137} Determination

Cs^{137} measurements, to be used in determining burnup, were requested on samples of uranium-aluminum alloy from MTR, BMI, and BNL; stainless steel- UO_2 fuel pins from WCAP 2 and 4; and thorium slugs from MTR Reactor Engineering. The method used is that of the ASTM, E-10, Burnup Task Force. The burnup ranged from 1 to 60 per cent.

The laboratory participated in making a round-robin analysis of a mixed fission product sample provided by ORNL. Participation in this project was to assist the ASTM Task Force in evaluating their proposed method.

5.1.3. Analysis of Irradiated Stainless Steel

Activation products Cr^{51} , Fe^{59} , Co^{58} , and Co^{60} were used to calculate fast and slow neutron fluxes. Stainless steel samples were dissolved in aqua regia. Two radiocobalt methods (see Appendix III of IDO-14547 and Appendix III, this report) were used. Each method gave good separation from iron, however the latter method is shorter. Gamma analysis was used to separate Co^{58} and Co^{59} . Iron⁵⁹ was calculated from the difference between the integrated 1.33-mev photopeak area of the gross sample and the cobalt fraction. (For the Cr^{51} method, see IDO-14547, Appendix III).

5.1.4. Analytical Assistance in Detection and Evaluation of ICPP Criticality Incident

Radiochemical and gamma spectral analyses were used for the detection and evaluation of the CPP criticality incident of January. Detection of 30-minute Cs^{138} on the stack monitor filter gave evidence that criticality had occurred. Separations of Sr^{91} , Sr^{92} , Mo^{99} , Ba^{139} , Ba^{140} , and Ce^{143} were made and calculations completed to determine the total fissions occurring in the excursion (see Appendix III for details of the methods for Sr, Mo, and Ce).

Personnel neutron monitors stationed in the access corridor were counted to determine the neutron flux at various locations.

The exact location of the vessel in which criticality occurred was determined by analysis of stainless steel samples which were removed from the cell and analyzed for activation products Cr^{51} , Fe^{59} , Co^{60} , and Co^{60} .

A further discussion concerning the evaluation of critical incidents by radionuclide analysis is given in Section 7.5.

5.1.5. Analysis of Gold Wire Flux Monitor

A gamma spectral analysis for Au^{198} was made for GCRE (operated by Aerojet General). Because a resonance flux was present during irradiation, surface activation could have occurred. Therefore, there is some uncertainty in the amount of self absorption that must be applied as a correction factor when attempting to measure the absolute gamma emission. All assumed parameters used to make the calculation were reported to the requestor. The same wire was later analyzed by activating in a known flux and counting in the same configuration as the initial analysis. This comparison technique found the flux to be within 15% of the value determined by the original spectrometric analysis.

5.1.6. Analysis of Fission Gas Samples

Gaseous samples were analyzed to determine the migration of fission gases through a graphite vessel. Prompt and delayed gamma analyses were used to determine Kr^{85m} , Kr^{88} , Xe^{133} , and Xe^{135} .

5.1.7. Phosphate Distribution in Liquid-Liquid Extraction Systems Using P^{32} Tracer

Liquid beta counting was used to determine the efficiency of a mixer-settler scrubber unit. Empirical calibrations were made by pipetting 4 ml of solution into a 7/8 inch diameter plastic cup and counting with the liquid surface about 1 cm from the detector face. Aqueous samples were counted with 2.6% and the organic samples with 2.9% geometry. Reproducible counting configuration thus permitted a direct measurement of phosphate concentration.

5.1.8. Radiochemical Analysis for General Dynamics (Fort Worth) Field Release Test III

Melt down tests of high temperature fuel required fission product analyses of irradiated pre-melt, post-melt residue, total effluent, and off-gas collector samples. Conventional separations followed by gamma analysis and nuclide nullification were used to determine Zr^{95} , Nb^{95} , Ba^{140} , La^{140} , and Ce^{144} .

5.1.9. Uranium Distribution in DBP and TBP Systems.

Radiometric analysis gave measurements of uranium distribution in dibutylphosphate and tributylphosphate. Uranium-233 was spiked in normal uranium and counted.

5.1.10. Neutron Activation Analysis

5.1.10.1 Aluminum Alloys

Aluminum alloys of cobalt, gold, indium, lutetium, and tungsten were checked for composition by comparison to known standards.

5.1.10.2 Hydrazine

The chloride impurity was measured on liquid samples of hydrazine by comparison with standard solutions.

5.1.11. Decontamination of Stainless Steel

Samples of stainless steel, typical of reactor vessel material, were gamma analyzed for Ag^{110} during a series of decontamination experiments. Proposed methods were tried on small samples, and the effectiveness evaluated by comparing pre- and post-treatment gamma scans. Quantitative decontamination data thus were made available within minutes.

5.1.12. Plutonium Defect Test

Radiochemical support was given G. E. Hanford in analysis of a planned plutonium fission break in an ETR loop. One pre-rupture and 7 post-rupture coolant samples were analyzed for $Sr^{89,90,91,92}$, Zr^{95} , Nb^{95} , Mo^{99} , Ru^{103} , Ru^{106} , I^{131} , Te^{131} , Cs^{137} , Ba^{139} , Ba^{140} , rare earth fraction, and gross alpha. The overall activity increase was much less than had been anticipated.

5.2. Special Analysis

5.2.1. Uranium in Fuel Pieces

Reliable uranium analyses are essential for reactor measurement and accountability purposes. During the year three uranium methods were used, each giving better data than the previous one. The first method involved nitrate removal, lead reduction, ceric redox titration, and an impurity iron determination. The second method required an impurity removal by mercury cathode electrolysis, zinc reduction to U(III), air oxidation

to U(IV), and a ceric redox titration (Section 7.23). This method was limited to a dilute sulfuric acid medium. The final method requires an impurity removal by extraction and fusion, followed by a coulometric measurement of the U(VI) to U(IV) reduction at a controlled potential (Section 7.1.1.4.).

Aluminum clad fuel plates, batch melt pieces, and fabrication heat samples used in reactivity measurements were analyzed during the year.

5.2.2. Physical Properties

5.2.2.1. Flash Point

The inadvertent addition of gasoline to a fuel oil tank was verified for GCRC by flash point measurement.

5.2.2.2. Viscosity and Specific Gravity

The viscosity and specific gravity were determined on organic coolant for the Naval Reactor Facility to follow the effect of radiation damage.

5.2.3. Water Analysis

Reactor water samples from the SPERT reactors, loop samples from MTR and ETR, and leaching pond samples from the MTR area were analyzed.

5.2.3.1. Chloride

An adapted method (2), based on the bleaching of the mercury(II)-diphenylcarbazone complex by chloride, gave desirable results. The detection range is 10 to 240 μg of chloride in 100 ml of sample. A Mohr titrimetric method was used on high range samples.

5.2.3.2. Ammonia

A Nessler colorimetric method (3) was used on samples for the range of 0.25 to 2.5 ppm ammonia.

5.2.3.3. Phosphate

Microgram quantities of phosphate were determined by an extraction-spectrophotometric method based on the molybdophosphoric acid complex.

5.2.3.4. Nitrate

Small amounts (30 to 120 μg) of nitrate were determined by a phenol-disulfonic acid colorimetric method.

(2) Gerlach, J. L., Frazier, R. G., Anal. Chem, 30 1142 (1958).

(3) Snell, F. D., Snell, C. T., "Colorimetric Methods of Analysis," p.814
Van Nostrand, New York, 1949.

5.2.3.5. Sulfate

The direct titration of sulfate with barium perchlorate in an 80% alcohol medium was used to determine as little as 0.5 ppm of sulfate (4).

5.2.4. Total Phosphate in Aqueous and Organic Samples

Samples pretreated with fuming perchloric acid were analyzed by the colored molybdophosphoric acid complex method.

5.2.5. Steel Specification Confirmation

Chromium and silicon were analyzed volumetrically and gravimetrically to type a steel sample submitted by ANL, Idaho Division.

5.2.6. Iron Oxide

Samples of high fired iron oxide were analyzed for the ratio for Fe_2O_3 and Fe_3O_4 by a volumetric iron analysis.

5.2.7. OMRE Fuel Plate Film

The fouling film removed from a fuel plate from the OMRE was analyzed for radioactive nuclides and for manganese concentration. The manganese concentration varied from 5 to 25%. Activities detected were Mn^{56} , Co^{56} , Co^{60} , and/or Fe^{59} , and long lived fission products.

5.2.8. Tin in Zircaloy Dissolutions

Samples of Zircaloy dissolved in a mixture of nitric-hydrofluoric acid were analyzed for tin by the pyrocatechol violet spectrophotometric method. The range of the method is 15 to 100 μg of tin. See Appendix II, Method Sn-1.

(4) Fritz, J. S., Yamamura, S. S., Richard, M., Anal. Chem. 29, 158 (1957).

6. SPECTRAL ANALYSIS

Thomas D. Morgan, Group Leader

6.1. Mass Analysis Laboratory, P. Goris

6.1.1. Surface Ionization Mass Spectrometry

6.1.1.1. Analyses, R. A. Nielsen

The isotopic analysis of uranium for determination of burn-up was requested on an expanded scale by BMI, GCRE, and WCAP. Outside contractors such as AGN, General Dynamics, BNL, GE, and Westinghouse were also provided uranium analytical service for purposes such as fuel assay. This was in addition to the CPP plant feed and product analyses which were required whenever there was production.

The SL-1 incident resulted in a few uranium identifications and boron isotopic determinations.

Services within the Company, other than for CPP Operations, were provided for MTR and CPP Technical Groups, and the Operations Analysis Branch.

6.1.1.2. Development

6.1.1.2.1. Uranium Determination

Uranium-233 of about 99.9% purity was obtained for use as a spike for uranium isotope dilution analysis to replace the 98% purity used previously. Improvement in analysis of samples containing low uranium concentration was such that this is now the most reliable method for low levels of uranium in use here.

A special program was arranged with the Analytical Development Group to determine if a new system of storing U-233 standard solution resulted in uranium concentration changes with time. Initially, aliquots of a standard U-235 solution were accurately pipetted for later analysis with the U-233 standard. The same pipet used for the U-235 solution is used to pipet U-233 from the storage vessel at intervals of two weeks. The total amount of U-235 remains constant so that concentration changes in the U-233 solution would be indicated. During the first six weeks of this test, no significant change was observed.

6.1.1.2.2. Boron

The following is the abstract of the paper published as IDO-14549.

"Surface ionization results for natural boron isotopic analysis are in agreement with other recent investigations indicating a B^{11}/B^{10} atom ratio nearer to 4.00 than the more commonly accepted value of 4.31 based on BF_3 analysis."

6.1.1.2.3. Porous Filament

Porous filaments give improved sample bonding and emission and are used for micro uranium determinations and for precise isotopic analysis. The porous filament also was used for obtaining the Sr^+ spectrum from $\text{Sr}(\text{NO}_3)_2$. Results show that fractionation effects observed with a single filament source can be eliminated for strontium.

6.1.1.2.4. Two-Stage Mass Spectrometer

Design specifications were prepared for a two-stage surface ionization mass spectrometer which is required for completion of atomic fuel burn-up studies in which it is necessary to make measurements such as the slight increase in U-236 from neutron capture of U-235 during fission. Included in the design are:

- a. Triple filament surface ionization source
- b. Two-stage magnetic analyzer
- c. Electron multiplier collection and pulse counting equipment
- d. Ionic vacuum pumps

AEC approval was obtained for purchase of this instrument and preparations were completed for issuing invitations for construction bids. Three manufacturers expressed interest in competing for the contract.

6.1.1.2.5. Plutonium-Uranium Determination

The simultaneous mass spectrometric determination of plutonium and uranium by the isotope dilution technique was performed as a cooperative project with Matthew T. Laug of the Idaho Division of Argonne National Laboratory because the mass spectrometer at EBR II is more sensitive than the machines at CPP. The following is a summary of the paper accepted for publication in Nucleonics.

This method, specifically developed for power reactor fuel dissolver samples, provides both the determination of the concentration and of the isotopic distribution of plutonium and uranium with a single separation. The separation procedure involves oxidation of plutonium to the ~~4~~6 valence state with potassium permanganate (which also provides chemical exchange of spike and sample plutonium), extraction of the plutonium and the uranium as tetrapropylammonium nitrate complexes into hexone from an acid deficient aluminum nitrate salting solution, addition of iodide (as a solution of tetrahexylammonium iodide in hexone) to the separated organic phase, and stripping of the plutonium and the uranium into hydrochloric acid. The concentrated level of the hydrochloric acid controls the ratio of uranium to plutonium stripped. The strip phase is fumed with nitric acid before mass analysis.

For mass analysis, an instrument with a triple filament surface ionization source and an electron multiplier is used. The ions collected and measured are singly charged metal ions. Stable scans are obtained with 1×10^{-9} gram of plutonium; for practical analytical work, an amount 100-fold greater is used. Uranium, vaporized at a lower

temperature than plutonium, is scanned. Then the side filament temperature is increased for plutonium scanning. A ratio of uranium:plutonium of 10-25:1 gives excellent scans for both elements. With expended power reactor fuels with a ratio of uranium:plutonium of 250:1, a concentration level of 4M for the hydrochloric acid strippant gives a product with a ratio of 12.5:1.

With uranium-233 and plutonium-242 as the added isotopes, a series of simulated zirconium-containing and stainless steel-containing power fuel dissolver samples were analyzed. Concentration results and isotopic distribution results both for plutonium and uranium were on the order of 1% standard deviation.

6.1.2. Consolidated Mass Spectrometer, Robert M. Abernathey

6.1.2.1. Analysis

Analysis of gases from loop water of experiments at MTR-ETR continued throughout the year on a reduced scale. Fission gases from WCAP-2 and AGN fuel pins, which were punctured in the MTR-ETR and the AREA hot cells, constituted an appreciable load.

Many special analyses were made such as gases from irradiated boric acid capsules, polyethylene pyrolysis, and butyl bromide experiments.

Boron isotopic analyses were completed on samples from the SL-1 incident and other sources.

6.1.2.2. Development

Fission gas collection apparatus was designed and constructed for use at the AREA hot cell. Improvements in design were based on experience with the apparatus installed in the MTR-ETR hot cell last year. The out-of-cell parts, including manifold, gauges, and pumps, are mounted on a 2 ft. X 3 ft. tool stand. It is compact, easy to operate, and readily portable. The fuel puncturing device, designed by Hot Cell Personnel, is a hydraulic punch similar in operation to a madden valve. Two hydraulic pumps outside the cell are the only controls. Samples can be changed in less than two minutes and pumpdown is very rapid because of the quick change and small volume.

6.2. Spectrochemical, G. V. Wheeler

6.2.1. Emission Spectrography, Kenneth R. Arnold, George W. Dickinson, Burton E. Ginther

6.2.1.1. Analyses

Qualitative and quantitative analyses were made for nearly every organization at NRTS. A one month delay for this service was frequently experienced because of manpower shortage. Addition of one man to the staff in the latter half of the year partially relieved this situation. More manpower is required to provide all of the requested service and to carry out development projects. The calciners provided the source of the largest sample loads. The direct reader has been very useful in making rapid, accurate analyses for Al, B, Li and Na on calciner product and scrubs.

6.2.1.2. Development

6.2.1.2.1. Radioactive Spectrographic Facility

Approval was obtained to construct the facility which was designed last year for handling radioactive samples. Negotiations for the construction contract were completed and installation is expected early next year. This facility will permit general spectrographic analysis of "hot" samples which can be adequately shielded by two inches of lead.

6.2.1.2.2. Hollow Cathode Studies

Because of high priority work in the laboratory, only minor progress in design improvements was made on the development of the hollow cathode technique for isotopic analysis.

6.2.1.2.3. Pellet Method for Boron and Sodium in Alumina

A method using pelleted samples and a rotating platform, spark technique was developed for analyzing alumina for boron in the range of 0.03 to 4% and for sodium in the range of 0.1 to 8% with an estimated precision of $\pm 5\%$ relative in the higher ranges to $\pm 20\%$ relative at the detection limit.

6.2.1.2.4. Turbine Oil Wear Products

A preliminary study and calibration was made for analysis of wear products in turbine oil for AGN.

6.2.1.2.5. Impurities in Hafnium

The following is an abstract of IDO-14558 entitled "Spectrographic Determination of Impurities in Hafnium" by B. E. Ginther and G. V. Wheeler:

"A spectrographic method using d-c arc excitation in a controlled atmosphere was developed to analyze for seven impurity elements in radioactive hafnium samples. Analysis requires as little as 35 mg. of hafnium oxide."

6.2.2. Flame Photometry, Kenneth R. Arnold, George W. Dickinson, Burton E. Ginther

6.2.2.1. Analyses

The analytical load for flame photometry has been large and steady throughout the year. Included in the samples were calciner feed, mix, and scrub solutions, Westinghouse reactor waters, loop water from MIR-ETR, and lithium aluminate from Analytical Development.

6.2.2.2. Development

A method for analyzing boron is under development in cooperation with the Analytical Development Group. The method will include flame photometer determination of boron in an organic phase. (Section 7.10)

Flame burner variations including oxygen sheaths were studied and complete spectra were recorded photographically to determine background effects and optimum boron emission wavelengths. Effects of various cations and anions are being determined.

6.2.3. X-Ray, Walter A. Ryder

6.2.3.1. Analyses, Gerald L. Sanford

The major x-ray diffraction sample load was calciner products which were analyzed for alpha-alumina. To have enough instrument time for these analyses, chemists from the **Shift Laboratory** operated the equipment on extra shifts. A summer employee also assisted with this load. A variety of other analyses were made including barium fluozirconate, ammonium phosphomolybdate, Nb-PbCl₂, and Zr-DBP studies of CPP Technical. Samples such as corrosion products and stainless steels were submitted from many NRTS sites.

6.2.3.2. Development

6.2.3.2.1. Shielded Diffractometer

A shielded x-ray diffractometer for analysis of radioactive product from the Demonstrational Waste Calciner Facility has been delivered and installation was completed. Preliminary tests indicated that samples equivalent to 10 mg of radium can be handled easily. Samples at the 100 mg radium level are shielded sufficiently for personnel protection but the background interferes with quantitative analysis of alpha alumina at low level. Slight modifications in the shielding, use of electronic discrimination, and use of high intensity x-ray tubes are being considered to solve this problem.

6.2.3.2.2. High Temperature Diffractometer

A high temperature diffractometer was installed. Preliminary tests indicated that it performs satisfactorily. This equipment was obtained for use in connection with the ARCO process.

6.2.3.2.3. Iron in EOCR Coolant

The measurement of iron content of terphenyls was investigated by x-ray fluorescence. See Section 9.2. for details.

6.2.4. Infrared Spectrophotometry Laboratory, Robert M. Abernathy

6.2.4.1. Analyses

All of the high percentage D₂O samples from SPERT II were analyzed for purity by infrared absorption. The accountability for heavy water at this station is based on these measurements. Infrared techniques also were used for identification of many samples such as cellulube for ETR Operations, TBP and Amsco for CPP Technical, and plastic from the ETR reactor tank.

6.2.4.2. Development

6.2.4.2.1. Determination of D₂O

Sample handling procedures, purity range, precision and accuracy for the infrared absorption method of heavy water purity analysis was studied. The following is an abstract of a paper presented at the Gatlinburg Conference on Analytical Chemistry.

"The practical application of heavy water purity determination by infrared absorption spectroscopy using standard laboratory equipment has been demonstrated in connection with the operation of heavy water moderated Special Power Excursion Reactor Test (SPERT II) Facility at the NRTS."

6.2.4.2.2. Micro Techniques

A procedure was developed for small amounts of Amsco in uranium-nitric acid solution. The Amsco is extracted with carbon tetrachloride and measured in a sealed sodium chloride cell at 3.42 and 3.51 microns. The go - no go level of 100 ppm is measured in a 1 mm. path length cell. A 1 cm pathlength cell permits detection of 1 ppm.

7. ANALYTICAL DEVELOPMENT GROUP

James E. Rein, Group Leader; Glenn L. Booman, Assistant Group Leader.

7.1 Electroanalytical Development, Glenn L. Booman

7.1.1. Coulometry, Wayne B. Holbrook

7.1.1.1. Multipurpose Coulometer

Construction and preliminary checkout of this instrument was completed in April, and it was transferred to the Special Analysis Group for routine use in April. The precision of coulometric uranium analysis based on randomly submitted controls, is 0.22% relative standard deviation for samples without any preliminary treatment, and 0.45% relative standard deviation for samples undergoing a uranium separation by extraction followed by a bisulfate fusion (5). (Also see Section 7.1.1.4.).

7.1.1.2. Circuitry Design

Further study of possible circuit configurations and detailed circuit analysis of promising approaches has resulted in the selection of a potentiostat-integrator system with single feedback loops and power supplies for the potentiostat, separate and floating from those for the integrator. A circuit of this type is being built for high precision uranium analysis. Electrical tests of integrator performance showed that a coefficient of variation of less than 0.01% is obtainable with an exponential input signal, similar to that obtained during a controlled-potential titration. A commercial d.c. to 1-megacycle, 10-watt power amplifier (Krohn-Hite Co. Model DCA-10) is being evaluated for use with a fast response, high current potentiostat system. Stabilizing circuits for potentiostats were successfully tested using cell analogs.

7.1.1.3. Cell Design

Satisfactory controlled-potential coulometry is very dependent on adequate cell design. Specifications for the electronic control circuits cannot be written without knowledge of the range of cell impedances and the rate of change of these impedances. Reasonably short analysis time requires sufficient stirring in a limited volume of solution to effect the necessary mass transfer to the electrode-solution interface. The stirring rate necessary to obtain effectively complete sample reaction in less than 1 hour could not be obtained in a precision rotating cell design because at the greater than 1000 rpm speeds required, a smooth mercury-solution layer could not be obtained.

Preliminary results on shaft-driven disc stirrers are encouraging. Stirrers in the form of circular discs tapered from the top outside edge toward the bottom inside edge gave superior performance. Radius, angle of taper, and single and double taper designs are parameters now being studied. A coulometer cell apparatus is being fabricated having a short

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

sturdy stirrer shaft and using a 1.5-inch precision inside-diameter tube 4 inches long to contain the solution and mercury.

7.1.1.4. Chemical Studies

A program to develop a method to determine directly the uranium concentration in unirradiated uranium-aluminum alloy fuel plates was investigated. The cell, stirrer, and multipurpose coulometer now used for routine samples were used in this program. It was found that the aluminum 61S constituents in the fuel plates gave a high bias of about 0.2%. It was necessary to go to an extraction, fusion procedure (5). This extraction is not directly compatible to high sulfate containing samples. It was therefore preferable to dissolve the fuel plates in nitric acid with mercury (II) as catalyst. The large amounts of mercury used resulted in partial extraction and positively biased results. This problem was remedied by the addition of ammonium chloride to the sodium bisulfate flux used for the fusion. This flux caused partial reduction of the uranium, necessitating addition of a nitric acid fuming to the procedure. See Appendix II, Method U-Coul-1 for details. It was noted that direct analysis of an ORNL uranium metal sample dissolved in nitric acid gave a high bias of 2%. A bisulfate fusion completely corrected the bias. A possible cause was the presence of a carbon impurity (700 ppm carbon content) which gave rise to a reducible species.

7.1.2. High Resolution Polarography, Fred O. Cartan

The IBM-650 circuit analysis procedure was refined and several circuit variations were analyzed. A 2-feedback loop circuit was selected for construction. This will consist of a resistance compensator section and a grounded 3-terminal high-gain amplifier section, both having bandwidths of about 30 megacycles. Construction has been started on the resistance compensator section. Designing on the basis of cell-current measurement with a current transformer has resulted in simpler apparatus, requiring only one low-power amplifier to operate floating from ground.

7.2. Demonstrational Calciner Program, Fred O. Cartan

The objective of the ICPP Demonstrational Waste Calciner project is to evaluate fluidized bed calcination for the disposal of radioactive waste. The feed will be first cycle raffinate from aluminum-uranium fuel reprocessing. The product is a porous solid, principally low fired alumina, with roughly spherical, white particles. Product sizes range from 100 to 3000 μ diameter. The maximum activity level is roughly 0.2 curie per gram.

The method for particle density, reported last year (6), was lengthy and has been modified. Methods have been developed for measuring incipient fluidization velocity and particle size distribution of fines in the calciner off-gas scrubber liquor. The problem of disposing of active analytical sample wastes is under consideration.

(6) Shank, R. C., U. S. Atomic Energy Commission Report, IDO-14547, pp.75-82 1961.

The status of methods is discussed for the measurement of bulk density, particle size distribution, and nitrate content in plant (high activity) samples.

7.2.1. Methods for Nonradioactive Samples

7.2.1.1. Absolute Density, Fred O. Cartan

The present method is based on displacement with carbon tetrachloride. Though precise, it is tedious. A Beckman air pycnometer, Model 930 has been evaluated as a possible replacement. The results have been erroneous, apparently due to the sorption of air (or certain components of air) on the calciner product. Water vapor and carbon tetrachloride vapor were not successful as surface poisons to prevent the sorption. Parts have been ordered for the conversion of this instrument to a gas purgeable model.

7.2.1.2. Particle Density, George J. Curtis

Considerable difficulty has been experienced with the mercury displacement method for particle density. The fault was traced to the presence of appreciable amounts of fines in the samples.

An improved apparatus has been developed consisting of a simple pycnometer, a filling apparatus, and a pressure chamber. The pycnometer is a modified Aminco penetrometer cell. The filling apparatus speeds the filling operations and pressurization permits the use of samples as small as 100 mesh. A precision of 0.005 density unit standard deviation was obtained for replicate measurements on a calciner product sample.

A description of the apparatus will be prepared for publication in Analytical Chemistry. Details of the procedure are given in Appendix II, Method Density-Solid-3, Mod-1.

7.2.1.3. Incipient Fluidization Velocity, Fred W. Dykes

Incipient fluidization velocity is the minimum fluid velocity in a vertical direction, calculated on the basis of an empty bed, at which fluidization starts in a bed of solids.

The apparatus that was assembled for this measurement is shown in Figure 7.1. The calciner product sample is poured into the fluidization tube to a fixed height of 4 inches. The height is not critical; this value was a compromise between oscillation of the water manometer and a satisfactory pressure reading. As the air flow velocity is slowly increased, the pressure drop across the bed increases until the fluidization point is reached, then it levels off. The data plotted are pressure drop vs. air velocity. The intercept of the initial and final slopes is taken as the point of incipient fluidization velocity. The repeatability of measurement was 5%.

With various pilot plant samples, this variable was found to be a function of particle size and shape. Samples of mixed sizes were characterized by indistinct incipient fluidization velocity points.

7.2.1.4. Particle Size Distribution of Fines in Scrubber Liquors, Rodney J. Anderson

Of two methods tried, wet screening and a sedimentation method, the former proved convenient.

In the wet screen procedure, a single 325 mesh screen is used. The sample is briskly shaken and an aliquot is poured onto the screen. After thorough water rinsing accompanied by constant rotation of the screen, the screen and solids are placed in a 110° C. oven for 4 hours. A separate aliquot is analyzed for total solids with the same drying conditions.

For the sedimentation method, an Andreason Sedimentation pipet was tried. Settling times were impractically long due to the small particle size of the majority of the fines.

7.2.1.5. Measurement of Particle Growth by Neutron Activation Analysis, William J. Maeck, S. Fredric Marsh

At the request of CPP Technical, an evaluation was made of a spike technique for evaluating the growth phenomena of alumina particles in the calciner operation. Natural indium was selected as the spike with the subsequent determination of its build up in the particles by neutron activation and counting.

Three 100-mg samples of 400-micron diameter product were spiked with 0.12 µg of indium (equivalent to 6 mug of indium per particle). The samples were irradiated in the MTR and analyzed by gamma ray spectrometry. The precision of the lower indium level was better than 10% and at the higher level a standard deviation of 5% was obtained. There were no experimental difficulties and it seems likely that this technique would give useful ratios of indium to alumina, as well as providing a means for individual particle analysis.

7.2.2. Methods for Radioactive Samples

7.2.2.1. Bulk Density, Fred W. Dykes

A direct reading (Mettler) balance with an extended length balance pan has been ordered for installation in the Remote Analytical Facility. The balance proper will be located above the shielding, minimizing remote operation, maintenance costs, and avoiding air current problems.

The correlation of bulk density and bulk dielectric constant was evaluated. An apparent linear relationship was obtained; however, there was considerable scatter. Differences were observed within screened fractions of the same sample. Part of the variation is attributed to differences in moisture content.

The measurements were made at 4 to 5 megacycles using a coaxial capacitor and a Sargent oscillometer. No corrections were made for sample conductivity.

FIGURE 7.1
APPARATUS FOR MEASUREMENT OF INCIPIENT FLUIDIZATION VELOCITY

1. AIR METERING VALVE
2. FLOWMETER
3. FLUIDIZATION TUBE WITH FRITTED GLASS PLATE
4. SCREW CLAMP (RESTRICTOR)
5. H₂O MANOMETER
6. DAMPING BULB
7. DUST FILTER

CPP-S-2187

7.2.2.2. Particle Size Distribution, Fred O. Cartan

7.2.2.2.1. Air Classifier

This technique is well suited to remote operation because of the small sample requirement.

A prototype apparatus (Figure 7.2) has been tested. The indentations in the elutriation tube reduce slugging. Also the resulting turbulence aids in the scattering of solids into the air stream. Helical disengaging grooves in the cyclone-type separator provide for the separation of solids over a wide range of air flows.

7.2.2.2.2. Particle Size Transducers

Various transducers have been investigated for remote analysis applicability.

7.2.2.2.2.1. Reflectance Transducer (Figure 7.2.)

Calcliner product particles were blown through an intense light beam. The reflected light was measured with either a photomultiplier or a lead sulfide photoconductor, both without optics. Larger pulses were available from the photomultiplier; however, in either case the noise level was equivalent to a 10- μ particle. The pulse widths were sufficiently narrow so that an acceptable counting rate was obtained. The photomultiplier pulse width was on the order of 300 μ sec. The slow decay of the response of the lead sulfide cell stretched the output pulse to the range of 1 to 1.5 msec.

7.2.2.2.2.2. Impact Transducer (Figure 7.4.)

Calcliner particles were blown through a tube onto the diaphragm of a capacitor-type microphone. The transducer output was found to change with particle size, velocity of the transport air stream, position of the tip of the tube, and "loading" of the microphone diaphragm caused by the air stream. Noise was related to the velocity of the transport air stream with a sharp increase being observed at the onset of turbulent flow. With a rubber-damped microphone diaphragm, pulse widths of approximately 200 μ sec were obtained. The observed noise corresponded to a 90- μ particle.

7.2.2.2.2.3. Capacitance Transducer

Calcliner product particles were blown through an air capacitor which was part of a balanced a.c. bridge. The transducer was insensitive; only the largest particles (1 to 1.5 mm) produced an output above that of the noise level (primarily due to static charge of the particles).

7.2.2.2.2.4. Charge Transducer

Calcliner particles were blown through a polyethylene tube located between the plates of a shielded air capacitor. The capacitor output was amplified and recorded on an oscilloscope. Pulses were observed due to particles charged by friction, but they did not have reproducible heights.

FIGURE 7.2

PROTOTYPE AIR CLASSIFIER FOR REMOTE MEASUREMENT
OF PARTICLE SIZE DISTRIBUTION

- 1 NEEDLE VALVE
- 2 FLOWMETER
- 3 ELUTRIATION TUBE
- 4 COARSE GLASS FRIT
- 5 ANTI SLUG INDENTATION
- 6 CYCLONE SEPARATOR
- 7 GRADUATED TUBE
- 8 DUST FILTER

CPP-S-2188

FIGURE 7.3
REFLECTANCE TRANSDUCER

FIGURE 7.4
IMPACT TRANSDUCER

CPP-S-2189

Varying radiation levels of the sample may make application of either charge or capacitance transducers difficult.

7.2.2.3. Analytical Waste Disposal, Fred W. Dykes

The disposal of analytical wastes from calciner product analyses is a severe problem. Wastes will be: (1) a caustic slurry (nitrate determination), (2) an organic slurry or powder (alpha Al_2O_3 content) and (3) dusty solids (bulk density and particle size distribution). At the maximum activity levels anticipated, the shielding capacity of the remote storage and analytical areas will not permit the accumulation of samples.

Analytical wastes will be canned in the Remote Analytical Facility. Commercial cans and a modified canning apparatus will be used. Low level wastes will be disposed directly to ground burial. High level wastes will be dropped through a lock into the calciner product storage tanks.

7.2.2.4. Determination of Nitrate, Marvin A. Wade

The Devarda alloy reduction, caustic slurry distillation of ammonia was satisfactorily adapted on a semimicro scale. The ammonia distillate is collected in boric acid and titrated with a standard acid rather than being collected in excess standard acid followed by standard base back titration. This simplifies the remote operation.

7.3. Radiochemical Methods, William J. Maeck

7.3.1. Solvent Extraction Method for Radiocerium, S. Fredric Marsh

The following is the abstract of the paper submitted for publication in Analytical Chemistry. Details of the method are reported in Appendix III.

"In this method, radiochemical cerium, in fission-product mixtures, is oxidized to the quadrivalent state with divalent silver and extracted as the tetra-n-propylammonium nitratocerate ion association complex into nitroethane. Cerium is then stripped from the organic phase with hydrogen peroxide-hydrochloric acid and precipitated as cerous oxlate. This method is rapid, safe, and requires a minimum of laboratory technique. It is applicable to aluminum, thorium, zirconium, and stainless steel nuclear-fuel matrices, and tolerates up to 1 ml of concentrated nitric, sulfuric, perchloric, hydrochloric, and hydrofluoric acids, and 0.25 ml of concentrated phosphoric acid. The relative standard deviation is 1%.

7.3. 2. Ion Exchange Method for Radiosodium, S. Fredric Marsh

The ion exchange method of Wish (7) has been modified for the determination of radiosodium in less than 1-week cooled fission product samples. The sample is made 0.1M in hydrochloric acid, adsorbed on a Dowex 50 X 8 cation exchange column (100-200 mesh resin), and eluted with 0.125M sodium dichromate. Incomplete separation of sodium and tellurium resulted from the use of 0.25M sodium chloride eluant as

(7)Wish, L; U. S. Naval Radiological Defense Laboratory Report,
USNRDL-TR-484 (1960).

recommended in the original work. Eluting with sodium dichromate gives complete separation by oxidizing tellurium to the anionic form, which washes through prior to the sodium fraction. Volume collections of effluent have been established to give 100% recovery of sodium activity with insignificant foreign activity.

Details of the method are presented in Appendix III.

7.3.3. Determination of Radiocobalt, S. Fredric Marsh

A modified procedure for the determination of radiocobalt was developed and submitted for publication as a "Short Communication" in Talanta. Details of the procedure are reported in Appendix III.

In this procedure, cobalt is first precipitated as the hydroxide, then converted to the ammine complex with ammonia. After a ferric hydroxide scavenging, the solution is buffered with acetic acid, **thiocyanate is added**, and the cobalt thiocyanate complex is extracted into hexone. Following an ammonium thiocyanate scrub, the cobalt complex is stripped with water and made slightly acid with hydrochloric acid. Mercuric thiocyanate is added to precipitate cobalt mercuric tetra-thiocyanate, which is filtered, dried, and weighed for the yield determination.

7.3.4. Solvent Extraction Method for Radiochromium, Maxine E. Kussy

This study was undertaken to develop a solvent extraction procedure for radiochromium that does not require close control of pH nor a gravimetric yield determination, and also is applicable to either reactor cooling water samples or to high-level fission product samples.

The method is based on a preliminary hydrolytic separation of chromium (III), oxidation to chromium (VI), and extraction from hydrochloric acid as an ion association complex with the tetrabutylammonium ion into hexone. Chromate is stripped from the organic phase with caustic and the yield is determined spectrophotometrically.

Decontamination of both fission products and stainless steel activation products is excellent.

Details of the procedure are presented in Appendix III.

7.3.5. Determination of Radiosilver, Maxine E. Kussy

A program was undertaken to develop a solvent extraction procedure for the determination of fission product silver as well as neutron induced silver activity in high-level activity samples. Because of the increased specificity generally obtained in basic medium extraction systems, extraction of the silver diethyldithiocarbamate complex from an ammoniacal system was investigated. A procedure was developed involving an initial precipitation of silver chloride, an ammonia dissolution, an iron scavenging, extraction of the silver diethyldithiocarbamate complex into benzene, stripping with 6M HNO₃, and reprecipitation of silver chloride for a yield determination. Decontamination from 1-day old fission products was excellent. Gamma ray photopeaks attributable to 7.5-day

silver-111 and 3.1-hour silver-112 were observed in the separated silver fraction.

Although the decontamination associated with the above method is excellent, development work is continuing. A procedure based upon the extraction of the silver tetrahexylammonium iodide ion association complex into hexone from a strongly basic medium is being investigated. Satisfactory extraction and decontamination have been obtained; however, difficulty in stripping the silver from the organic phase is being encountered. It is presumed that a procedure based on this approach will be shorter than that described above.

7.3.6. Determination of Radiomanganese, S. Fredric Marsh

The increasing use of stainless steel clad power reactor fuels has prompted the development of a method for the determination of radio-manganese in the presence of fission and stainless steel activation products.

The extraction of manganese as the tetra-n-propylammonium permanganate complex was studied. The ion association complex, only slightly soluble in non-polar solvents such as chloroform and benzene, was rapidly reduced by more polar solvents. Because of this instability, a spectrophotometric yield determination of the extracted complex was not feasible. In addition, technetium and chromium coextracted from sulfuric and nitric acid, the medium studied.

Manganese is separated from technetium and chromium by precipitation of manganese dioxide from a hydrogen peroxide-sodium hydroxide solution (8). However, iron, which is a major constituent of most samples containing manganese, coprecipitates as the hydroxide, carrying technetium activity with it. Iron, aluminum, and other elements which hydrolyze readily, are homogeneously precipitated by raising the pH of a boiling ammonium chloride solution to 6.5 to 7.5 (9). Silver permanganate, which forms as a crystalline precipitate in nitric acid, was studied as a possible gravimetric form for manganese; however, the high solubility of the compound prevented its use.

Ion exchange techniques have been applied for the separation of high purity manganese-54 (see Section 7.4.3.). This procedure could be combined with a gravimetric yield determination, but would be quite time consuming.

The method of Kolthoff and Sandell (10) for the homogeneous precipitation of manganese dioxide from sulfuric acid with bromate oxidation is being investigated. The manganese dioxide precipitate is dissolved in hydrochloric-sulfuric acid, niobium holdback is added, and the sample is fumed, cooled, and carefully diluted. Niobium is hydrolyzed by

(8) Matuszck, J. M., Sugihara, T. T., Anal. Chem. 33, 35 (1961).

(9) Lundell, G. E. F., Knowles, H. B., J. Am. Chem. Soc. 45, 676 (1923).

(10) Kolthoff, I. M., Sandell, E. B., Anal. Chem. 1, 181 (1929).

digestion in a boiling water bath which scavenges the acid-insoluble elements present. Addition of potassium bromate to the filtrate reprecipitates manganese dioxide which is dissolved in sulfuric acid and diluted with dibasic sodium phosphate solution. After adjusting the pH to 4.5, urea is added and the solution heated in a boiling water bath. The homogeneous release of ammonia produces a dense, crystalline precipitate of manganese ammonium phosphate monohydrate, which is oven dried at 105°C for a yield determination.

This procedure will be evaluated on samples containing various aged fission products, as well as stainless steel activation products.

7.3.7. Determination of Radioniobium, William J. Maeck

The conventional niobium procedure based on the hydrolytic precipitation of Nb_2O_5 occasionally gives very low yields as well as being time consuming. The latter is due to two lengthy heating steps.

A modified procedure, based on the following steps, is being evaluated: isotopic exchange with inactive added carrier through fluoride complexing, hydrolytic precipitation from a basic medium, dissolution with an acid-peroxide mixture, and precipitation of the oxide from acid solution upon destruction of the peroxide complex.

Reducing agents such as sodium formate and ascorbic acid have been studied as reagents for destruction of the peroxide complex. The precipitation was not reproducible and the precipitates were of questionable composition. The use of strong oxidants also will be investigated.

7.3.8. Determination of Zirconium-97, William J. Maeck

Zirconium-97 is a useful nuclide for evaluating a nuclear reaction, such as a criticality incident. (see Section 7.5.) Generally zirconium-97 is beta counted after equilibrium of 74-minute niobium-97 is attained. In the presence of significant amounts of 65-day zirconium-95, half life data and beta absorption curves are required to resolve the various isotopes.

A suggested faster and more convenient procedure is: quantitative separation of the zirconium isotopes followed by selective milking and counting of the 74-minute Nb-97 activity. A solvent extraction procedure based on a recently improved TTA-extraction procedure for zirconium (11) is amenable to this type of approach and is being evaluated. After extraction of the zirconium-TTA complex, the organic phase is scrubbed with 3M HClO_4 containing a few drops of hydrogen peroxide. This removes any coextracted niobium activity. The scrub is taken as time zero. Following a suitable grow-in time, the Nb-97 is stripped with the scrub solution, counted, and the time is noted. The Zr-97 content can then be calculated. The decontamination associated with this procedure is shown in Figure 7.5.

(11) Marsh, S. F., Maeck, W. J., Booman, G. L., Rein, J. E., Anal. Chem. 33, 870 (1961).

To evaluate the procedure, six 1-mg pieces of enriched uranium were irradiated in a thermal neutron region of the MTR at a flux of 3×10^{12} n/cm.²/sec. for 20 minutes. After cooling for 1 day, the samples were dissolved and analyzed for zirconium-97 by counting the 660-keV photopeak of the separated niobium-97. The standard deviation of the method, based on the six individual samples, was 2.8% for a single determination. The half life of the separated niobium-97 fractions was 74.0 ± 1.2 min. compared to a literature value of 74 minutes (12). Evaluation of the procedure is continuing.

7.3.9. Determination of the Branching Ratio of the 740-760-keV Level of Molybdenum-99, S. Fredric Marsh

This isotope has very desirable characteristics for use as a fission monitor for short cooled samples. Because the principal gamma ray of molybdenum-99 at 180-keV is coincident with the 140-keV gamma ray of the 6-hour technetium-99 m daughter, the 740-760 keV photopeaks are superior for measurement. There is discrepancy in the literature for the branching ratio through this level. A coordinated effort with MTR Physics (Edward C. Yates) was made to determine this value.

A high specific activity sample of molybdenum-99 was prepared by irradiating an enriched molybdenum-98 sample, as molybdenum oxide, in the MTR at a flux of 3×10^{14} n/cm.²/sec. for 48 hours. The molybdenum was separated from its technetium-99 daughter-activity by anion exchange chloride complexing. The sample was dissolved in ammonium hydroxide, made acidic with hydrochloric acid, placed on a column, and the molybdenum was eluted with 1M HCl (13). An essentially weightless source was prepared and counted by ~~4πB-δ~~ coincidence counting. The branching ratio, through this 740-760-keV level, was determined to be $16.25 \pm 0.45\%$, compared to a recent literature value of 14.0% (13).

(12) Sullivan, W. H., Trilinear Chart of Nuclides, U. S. Atomic Energy Commission, TIS, Oak Ridge.

(13) Miller, C. F., U. S. Naval Radiological Defense Laboratory Report, USNRDL-TR-160 (1957).

FIGURE 7.5 DECONTAMINATION IN ZIRCONIUM-97 METHOD

7.4. Radionuclide Separation and Purifications, William J. Maeck

7.4.1. Separation of Zirconium-97, Niobium-97 for Gamma Spectrometry, S. Fredric Marsh

At the request of R. L. Heath, MTR Physics Section, the separation procedure for Nb-97, described in Section 7.3.8, was applied to an irradiated sample of zirconium-96. Gamma spectra of 17-hour zirconium-97, 60-second niobium-97m, 74-minute niobium-97, and the equilibrium mixture were obtained. These will be added to Mr. Heath's "Scintillation Spectrometry Gamma-Ray Spectrum Catalog" (IDO-16408). It is believed that this will be the first presentation of the gamma spectra of the individual components of this equilibrium mixture.

7.4.2. Separation of Niobium-92 from Molybdenum-92, William J. Maeck

At the request of MTR Physics, niobium-92 was separated from a fast-neutron irradiated sample of molybdenum-92 for nuclear decay scheme studies. The procedure involved the addition of niobium carrier and hydrofluoric acid to insure exchange, precipitation of niobium hydroxide, dissolution in a nitric acid-hydrogen peroxide mixture, and heating to expel the peroxide and simultaneously precipitate niobium pentoxide. The cycle was repeated twice. The resulting niobium-92 fraction was reported to be exceedingly pure.

7.4.3. Purification of Mn-54, S. Fredric Marsh

The MTR Physics Section is evaluating various materials for use as fast neutron flux monitors. Iron, which produces 291-day manganese-54 by an (n,p) reaction, appeared promising. The use of iron required an accurately known value for the pile neutron cross section of manganese-54 in order to correct for any parasitic capture.

A high-purity manganese-54 source was requested for a 20-day irradiation in the MTR core. The cross section determination, based on pre- and postirradiation activity measurements, required a source free of any impurities that would activate.

In the separation procedure, high-purity carriers and quartz-distilled reagents were used where applicable. The source of the manganese-54 was an ash residue from an OMRE coolant sample. The sample, dissolved in 10M HCl, was passed through an anion resin (Dowex 1, X 8) column in the chloride form. The chloride effluent, containing the manganese, was repeatedly fumed with nitric acid to remove the chloride, then was diluted to 1M in nitric acid. An oxidation to permanganate was made with potassium periodate and the solution was passed through an anion (Dowex 1, X 8) column in the nitrate form. The adsorbed permanganate, after washing the column with large amounts of 1M HNO₃, was eluted with a 1M HCl-3% H₂O₂ mixture. High purity aluminum nitrate was added and a scavenging precipitation was made at pH 6.0. The manganese was precipitated as the hydroxide, was ignited to the oxide, and was sealed in quartz for irradiation.

This product was highly pure. No activity was noted at the end of the 20-day irradiation other than that contributed by impurities in the quartz capsule.

7.4.4. Purification of Uranium-239, Maxine E. Kussy

At the request of MTR Physics, a rapid method was developed for the separation of 23-minute uranium-239 in high purity from fission products and 23-day neptunium-239 for nuclear data measurements. The starting sample was U_3O_8 , almost 100% enriched in the 238 isotope, irradiated in the MTR.

After dissolution in nitric acid, the uranium was extracted into hexone under acid-deficient aluminum nitrate salting conditions. The separated organic phase was scrubbed once with a solution of acid-deficient aluminum nitrate containing EDTA and hydroxylamine to remove the trace of extracted neptunium.

The gamma ray spectrum of the separated uranium fraction was free both of neptunium-239 and of fission product activity. The MTR Physics Group observed several gamma rays of uranium-239, previously unreported.

7.4.5. Purification of Uranium-233 and Uranium-236, Maxine E. Kussy

Two samples, one enriched in the 233 isotope and the other in the 236 isotope, were received from MTR Physics for decontamination of foreign activity for nuclear data measurements.

The samples of U_3O_8 were dissolved in nitric acid and extracted into hexone from an acid-deficient aluminum nitrate salting medium for fission product and daughter product decontamination. A solution of tetrahexylammonium iodide in hexone was added to the organic phase and the coextracted plutonium was stripped into 5M HCl. The uranium then was stripped into water and was converted to U_3O_8 by ignition at 850°C for 20 hours. Excellent purity of both samples was reported.

7.4.6. Purification of Plutonium-240, Maxine E. Kussy

A sample of plutonium-240 was decontaminated of uranium and decay chain activities for MTR Physics. Uranium was extracted into hexone from an acid-deficient aluminum nitrate medium containing hydrazine and EDTA. The plutonium was then oxidized to +6 by the addition of potassium permanganate and was extracted into hexone. Freedom from all foreign activity was reported.

7.4.7. Separation of Uranium from Sulfuric Acid Media, Maxine E. Kussy

The extraction of uranium was studied from 50% solution of sulfuric acid (which may result from the dissolution of uranium-aluminum alloys in sulfuric acid) with the acid-deficient aluminum nitrate-tetrapropylammonium nitrate-hexone system. This system is normally used to separate uranium prior to coulometric analysis (see Section 7.1.1.4.).

Aluminum sulfate precipitates in the salting solution under the conditions of the routine method, carrying the uranium and causing low results. By increasing the volume ratio of the aqueous phase to that of the organic phase from 2:1 to 7:1, the extraction of uranium was increased to a satisfactory level of 99.7%.

7.5. Evaluation of Critical Incidents, William J. Maeck, S. Fredric Marsh, Maxine E. Kussy

7.5.1. SL-1 Incident

Assistance was provided to evaluate the magnitude of the nuclear reaction of the SL-1 incident. A brass screw from the cigarette lighter of one of the victims was analyzed for neutron-induced copper-64 activity. While some copper-64 activity was indicated, the amount was not sufficient to accurately determine the magnitude of the neutron flux to which the individual had been exposed.

A piece of clothing from one of the victims was analyzed for short-lived fission product activity. The hot sample (approximately 50R/hr) was digested in fuming nitric acid, filtered, and aliquots were analyzed for cerium-143 and zirconium-97. Unfortunately, the time delay between the incident and the sampling, along with a high concentration of long-lived fission products in the sample (the reactor had been down only about 10 days before the incident) again resulted in not being able to positively identify the sought for nuclides nor in being able to accurately calculate the fissions that occurred in the incident.

7.5.2. CPP Incident

Samples from the vessel that went critical in January were analyzed for selected nuclides to determine the magnitude of the incident. Molybdenum-99 was separated by a solvent extraction procedure (14) and was determined by gamma spectrometry. Based on this, the computed magnitude was 6×10^{17} fissions. Zirconium-97 was separated by a TTA extraction, and the short-lived 74-minute niobium-97 daughter was allowed to grow in. The niobium activity was used as the basis to compute the level of zirconium-97. This separation was necessary because of the large amount of zirconium-95 originally present in the sample. A value of 4×10^{17} fission was obtained. Cerium-143 was separated by a carrier-free solvent extraction procedure and analyzed by gamma spectrometry. After corrections for cerium-144 and some extraneous zirconium-niobium-95 activity, the computed value was 6×10^{17} fissions.

7.5.3. Development of Methods

Based on the experience gained in evaluating the critical incidents in Sections 7.5.1. and 7.5.2., this study was undertaken.

One primary purpose of radiochemical analysis of fissioned material is to establish the number of fission events. A study of the correlation of the fission yields of selected nuclides was made.

(14) Maeck, W. J., Rein, J. E., Anal. Chem. 33, 237 (1961).

Six 1-mg. pieces of enriched uranium metal were individually put into crimped aluminum metal envelopes, placed in a polyethylene bag, and inserted in standard Marlex rabbits. These were irradiated for 20 minutes in a 3×10^{12} n/cm.²/sec. flux in the MTR VG-33 graphite facility. The flux level was assumed to be constant over the irradiation period and the neutrons to be fully thermalized. The aluminum envelopes and the uranium were dissolved in a nitric acid-hydrofluoric acid mixture. Analyses were made for strontium-91, strontium-92, zirconium-95, zirconium-97, molybdenum-99, barium-140, and cerium-143 (Table 7.1.). The methods and nuclear data (gamma branching ratios and half lives) are described briefly at the end of this section. The sources of error for the data in Table 7.1. include the radiochemical separation, the uranium analysis, counting, irradiation time, and flux.

TABLE 7.1. ANALYTICAL RESULTS FOR SELECTED NUCLIDES

<u>Nuclide</u>	<u>Atoms per Mg. U</u>	<u>Standard Deviation</u>
Sr-91	1.46×10^{11}	14.0%
Sr-92	1.28×10^{11}	13.0%
Zr-95	1.82×10^{11}	4.0%
Zr-97	1.55×10^{11}	2.6%
Mo-99	1.69×10^{11}	4.8%
Ba-140	1.46×10^{11}	4.2%
Ce-143	1.50×10^{11}	3.7%

A compilation of the averaged atom ratio of each nuclide to molybdenum-99 is presented in Table 7.2. The error of the uranium analysis, the irradiation time, and flux variations are cancelled.

TABLE 7.2. FISSION YIELD RATIOS TO Mo-99

<u>Nuclide Ratio</u>	<u>Atom Ratio</u>	<u>Standard Deviation</u>
Sr-91/Mo-99	0.86	8.5%
Sr-92/Mo-99	0.76	11.4%
Zr-95/Mo-99	1.07	3.2%
Zr-97/Mo-99	0.92	4.5%
Ba-140/Mo-99	0.86	4.2%
Ce-143/Mo-99	0.89	3.7%

The experimentally determined fission yields, compared to literature values, are presented in Table 7.3. The experimental fission yields were computed by multiplying the "atom ratios" in Table 7.2. by 6.06 (the fission yield of molybdenum-99).

TABLE 7.3. COMPARISON OF EXPERIMENTAL AND LITERATURE FISSION YIELD VALUES OF URANIUM-235

Nuclide	Experimental (a)	Literature		
		Katcoff (b)	Blomeke and Todd (c)	Steinberg and Glendenin (d)
Sr-91	5.22 ± 0.45	5.81	5.9	5.0, 5.1, 5.9
Sr-92	4.61 ± 0.53	5.30	6.1	5.0
Zr-95	6.49 ± 0.21	6.2	6.4	6.0
Zr-97	5.58 ± 0.26	5.9	6.2	6.1, 5.5
Ba-140	5.22 ± 0.24	6.35	6.3	6.1, 6.3, 6.3
Ce-143	5.39 ± 0.20	6.0	6.2	5.4

(a) Error in units of absolute standard deviation.

(b) Katcoff, S., Nucleonics 18, No. 11 (1960).

(c) Blomeke, J. O., Todd, M. F., U. S. Atomic Energy Commission Report-ORNL-2127, Part 1, Vol. 1 (1957).

(d) Steinberg, E. P., Glendenin, L. E., Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 7, p. 3, Geneva (1956).

The lack of agreement in the literature values of the fission yields is noteworthy. This is most apparent for strontium-91 and strontium-92 which have gaseous precursors of 10-second krypton-91 and 3-second krypton-92. The relatively large imprecision in the experimental values for these two nuclides is attributed to this same cause, as well as to the escape of fission fragments from the targets. The targets had large ratios of surface area to volume. Based on this, neither strontium-91 nor strontium-92 are recommended for use as fission monitors.

The nuclide barium-140 also has a gaseous precursor, 16-second xenon-140, and it is noted that the fission yield is again low. Its use as a fission monitor is also questionable.

The nuclides zirconium-97, molybdenum-99, and cerium-143 have high yields, little or no gaseous precursors, and improved radiochemical procedures are available for their separation and determination. The fission yield for zirconium-97 and cerium-143 are not in disagreement with the literature values (Table 7.3). The use of these three nuclides is recommended for fission monitoring critical incidents.

BRIEF DESCRIPTION OF METHODS AND NUCLEAR DATA

Unless stated otherwise, nuclear data constants are those of Katcoff, S., Nucleonics 18, No. 11 (1960). Fission yield values are underlined.

Sr-91

Separated by chromate-oxalate precipitation method 4 hours after irradiation. Counted 20 hours after separation. Measured the 1.02-mev Sr^{91} peak with a branching ratio of 0.33.

Sr-92

Separated by chromate-oxalate precipitation method 4 hours after irradiation. Counted immediately. Measured the 1.37-mev Sr^{92} peak with a branching ratio of 0.92.

Zr-95

Separated by a TTA extraction [Marsh, S. F., et al., Anal. Chem. 33, 870 (1961)] 15 days after irradiation to allow for decay of 17-hour Zr^{97} . Measured the 740-keV peak with a branching ratio of 1.00.

Zr-97

Zirconium was extracted by the same TTA method as for Zr^{95} . Organic phase contacted with $\text{HClO}_4\text{-H}_2\text{O}_2$ to strip coextracted niobium. After 1-hour, the Nb^{97} daughter was stripped with $\text{HCl-H}_2\text{O}_2$ and counted in a well crystal. Measured the 660-keV peak with a branching ratio of 0.99. Confirmed results by a second milking 2 hours afterwards.

Mo-99

Analyzed by solvent extraction of the -benzoinoxime complex [Maeck, W. J., Rein, J. E., Anal. Chem. 33, 237 (1961)]. Measured the

740-760 kev peak with a branching ratio of 0.1625 (see Section 7.3.9.).

Ba-140

Separated by BaCl_2 precipitation method. Allowed La^{140} to grow into equilibrium and measured 1.6-mev peak with a branching ratio of 0.98.

Ce-143

Separated 1 day after irradiation by the method described in Section 7.3.1. Measured the 295-300 kev peak with a combined branching ratio of 0.48.

7.6. Determination of Fissionable Materials by Neutron Bombardment and Fission Fragment Counting, Fred O. Cartan and William J. Maeck

Present methods for the determination of uranium-235 include mass spectrometry, gamma ray pulse height analysis, alpha pulse analysis, in-pile fission counting, and delayed neutron counting. These require elaborate and expensive equipment as well as careful sample preparation. Calculations indicate that considerably less than 1 mg of uranium-235 can be determined by slow neutron activation analysis. Generally, in this technique a specific nuclide is chemically isolated and the 235 content is calculated based on a fission yield value for this nuclide and by comparison to known standards. Direct counting of the total induced fission product activity also has been employed but is limited to low beta-gamma activity in the original sample.

Because each fission event is accompanied by the release of two fission fragments, each carrying from 80 to 100 mev of energy, it seemed feasible to measure this large energy release as the basis for a specific method for the determination of fissionable isotopes.

Scintillation counting was investigated. Irradiation, with a laboratory 5-curie plutonium-beryllium source, of uranium-235 dissolved in a liquid phosphor, was investigated; however, light pulses were not observed greater than those produced by the normal beta, gamma, or alpha rays. This was attributed to the low efficiency of the liquid phosphor for heavy ionizing particles.

The use of solid $\text{ZnS}(\text{Ag})$, which scintillates with alpha particles and is insensitive to beta and gamma rays as well as neutrons, was investigated. Uranium-235 was added to an aqueous suspension of ZnS and was precipitated as the phosphate. The mixture was filtered onto a flat 1-inch filter disc,

placed on a photomultiplier tube, exposed to the 5-curie neutron source (moderated by paraffin) and the output was observed on an oscilloscope. In addition to the normal alpha pulses, some extremely large light pulses were observed. These were not noted in either the absence of uranium or the neutron flux and were concluded to be scintillations caused by fission fragments in the ZnS. A scaler and discriminator were incorporated into the design so that alpha pulses were rejected and only the large fission pulses were counted.

Because the mean free path of the fission fragments is very small, homogeneity of uranium and phosphor is important. Preliminary studies have been made with six samples containing 0.3 to 2.4 mg. of fully enriched uranium. The total uranium content was held constant at 3.0 mg., by adding normal uranium, to eliminate the bias caused by variations in the uranium to zinc sulfide phosphor ratio. The counting plates were prepared by precipitating the uranium as the phosphate, slurring with 10 mg. of zinc sulfide, filtering on a 1-inch disc of filter paper, and covering the precipitate with transparent tape. A coefficient of variation of 4% was obtained. Using a 2-curie source, 2.4 mg. of enriched uranium gave approximately 950 counts per minute. With the high discriminator setting, background is essentially nil (< 0.2 count per minute). Counting plates made with 3 mg. of normal uranium gave a counting rate equivalent to 0.7 - 0.8% enrichment. Arsenate, peroxide, and other uranium precipitants, as well as precipitation and filtration parameters, are being investigated. Improvements in the counting apparatus and chamber also are being studied for increased reliability.

7.7. Extraction of the Elements as Quaternary (Propyl, Butyl, and Hexyl) Amine Complexes, William J. Maeck, Maxine E. Kussy

The following is the abstract of the paper published in Analytical Chemistry 33, 1775 (1961).

The distribution of 57 metallic ions have been measured for three quaternary amines, tetrapropyl, tetrabutyl, and tetrahexyl, into methyl isobutyl ketone from five media, HNO_3 , H_2SO_4 , HF , HCl , and NaOH , over the concentration range of 0.2 to 5N. Distribution data are presented as plots of percent extraction vs. normality in a series of 5 periodic charts. Many separations for radiochemical and general analytical applications are proposed.

7.8. Adsorption of the Elements on Inorganic Exchangers, William J. Maeck, Maxine E. Kussy

The use of inorganic adsorbents, such as hydrous zirconium oxide, zirconium molybdate, zirconium phosphate, and zirconium tungstate, for the separation of the alkali and alkaline earth metals has become popular in recent literature. It seems likely that other metal ions, also of importance to the nuclear energy field, would be uniquely separable. A study has been initiated to determine the distribution coefficients of selected metal ions over the pH range of 1 to 5 in nitric acid.

7.9. Determination of Total Cobalt, S. Fredric Marsh

A method was needed for the determination of total cobalt, as an impurity in various ferrous and nonferrous alloys. The method of Dean (14) was selected for evaluation.

The basic features of this method are formation of the cobalt complex with 1-nitroso-2-naphthol-3, 6-disulfonate, selective adsorption on an alumina column in the perchlorate form, elution of this red complex with 1M sulfuric acid, and spectrophotometric measurement.

The method was verified and added to the Analytical Manual without modification. (see Method Co-1 in Appendix II for details).

7.10. Extraction, Flame Photometric Determination of Boron, William J. Macck, Burt E. Cinther, Maxine E. Kussy

A reliable method for the determination of boron, applicable to a variety of samples, long has been needed. The method selected for evaluation is based on the extraction of the complex of BF_4^- with quaternary ammonium ions from a hydrofluoric acid medium into hexone, followed by a direct flame photometric determination of the boron in the separated organic phase.

Boron extracts quantitatively from an aqueous phase 3M in H_2SO_4 , 3M in HF, and 0.3M in the tetrabutylammonium ion. Extraction is complete in 1 minute and pretreatment (to form the extractable complex is not necessary. Flame response is linear with boron concentration for the range 0 to 100 ppm of boron.

In an anion interference study, 25mmoles of sulfate and chloride did not affect the extraction of boron nor the flame response. Nitrate at this level depressed the flame response causing low bias. No interference was noted at the 10-mmole level. Phosphate distributes into the organic phase and enhances the emission causing high bias. Studies to extend the tolerable range of nitrate and phosphate are underway.

Of 22 metal ions studied, the only interferences were Cr(VI), Cu(II), Fe(III), Nb(V), Ti(IV), V(V) and W(VI). Tolerance to the first three is greatly increased by reduction to non-extractable valence states. Additional interference studies as well as means of eliminating interferences are in progress. See Section 6.2.2.2. for a discussion of flame excitation studies.

7.11. Separation of Cadmium in Copper-Cadmium Alloys, William J. Macck, Maxine E. Kussy, Stanley S. Yamamura

At the request of Aerojet General (GCRE), cadmium was separated from a neutron-irradiated copper alloy clad with nickel for the purpose of nuclear data measurements. The main steps in the procedure were (1) hydrochloric acid-hydrogen peroxide dissolution, (2) adsorption of

(14) Dean, J. A., Anal. Chem. 23, 1096 (1951).

cadmium as a chloride complex on an anion exchange resin, (3) removal of silver activity by repeated silver chloride scavengings and by passage through a lead column reductor, (4) precipitation of the cadmium with benzotriazole (to separate it from lead introduced from the reductor), and (5) final precipitation as cadmium sulfide. Because of the high Ag-110 activity, the separation was more difficult than anticipated.

7.12. Direct Spectrophotometric Fluoride Determination, Stanley S. Yamamura, Marven A. Wade, John H. Sikes

The following is an abstract of a paper that will be submitted for publication in Analytical Chemistry.

"The formation of a lilac-blue color by the unique reaction of fluoride with the cerium(III) chelate of alizarin complexone (3-amino-methylalizarin-N,N-diacetic acid) has been made the basis of a simple, direct colorimetric method for microgram levels of fluoride. The color is developed in a 20% (v/v) acetonitrile:water or acetone:water medium to enhance the sensitivity for fluoride and to improve reagent stability. For example, in 20% (v/v) acetonitrile:water, the sensitivity is nearly twice as great as in water alone. The cerium(III)-alizarin complexone and cerium(III)-alizarin complexone-fluoride chelates are not stable in water, but in an acetonitrile medium, these complexes are stable for several days enabling the use of a pre-mixed composite reagent. The effect of common ions depend on the cerium(III) to alizarin complexone molar ratio. At a 1 to 1 ratio, high levels of common anions such as bromide, chloride, nitrate, nitrite, and perchlorate and small amounts of borate, silicate, sulfate, and sulfite are without effects. Phosphate interferes seriously. Greater tolerance to sulfate and phosphate is obtained at a cerium(III) to alizarin complexone ratio of 1 to 2.5, but at this ratio, a small positive salt effect is observed. The reason for the greater sulfate and phosphate tolerance based on a critical analysis of various equilibria is presented. Data are also presented to show the applicability of the method for the direct determination of fluoride in natural waters."

7.13. Extraction - Spectrophotometric Determination of Zirconium, Marven A. Wade, Stanley S. Yamamura

The following is the abstract of a paper that will be submitted for publication in Analytical Chemistry. Details of the method are reported in Appendix II, Method Zr-3.

"The blue complex formed between zirconium and pyrocatechol violet at pH 5.2 is the basis of a sensitive method for the determination of zirconium. The molar absorptivity is 44,000 at the 650-mu peak for the linear range of 10 to 100 µg. of zirconium in a final volume of 50 ml. Prior to color development, zirconium is separated from interfering metal ions by a thenoyltrifluoroacetone extraction. Consequently, most cations do not interfere even at 100 to 1 mole ratio to zirconium. Of those that interfere at lesser ratios, niobium(V), titanium(IV), and tungsten(VI) are tolerated at 10 to 1 and scandium at a 1 to 1 mole ratio. The relative standard deviation of the overall method, including extraction, is less than 1% at the 50-µg. zirconium level."

7.14. Colorimetric Boron Determination, Stanley S. Yamamura, John H. Sikes

Additional studies have been made to develop a suitable method for the determination of low levels of boron in nuclear fuels. Methods based on boric acid catalysis of the conversion of yellow curcumin to red-brown rosocyanin were found to be unsuitable because of the need for rather precise control of color development conditions. In addition, common anions and various sugars, used to prevent volatilization of boric acid, interfered. Separation studies with Dowex 50-W resin show that columns must be washed thoroughly with water immediately before use. Otherwise, greater than 100% of the added boron is recovered.

7.15. Separation and Isotopic Analysis of Boron, Marven A. Wade, Stanley S. Yamamura, Paul Goris

The introduction of enriched boron ($B^{10}:B^{11}$ ratio $>1:4$) as a burnable poison in various reactor materials has increased the demand for isotopic boron analysis. The surface ionization mass spectrometer and the Consolidated gas mass spectrometer are employed for isotopic boron analyses. With the Consolidated instrument, absolute sample purity is not required. Consequently, ion exchange separation methods are being investigated to supplement the methyl borate distillation technique widely used. Studies have shown that aluminum matrix alloy samples dissolve in hydrochloric acid. Stainless steel samples are dissolved electrolytically in nitric acid. Hydrochloric acid cannot be used because of the possibility of forming negative chloro-complexes which pass through the cation resin. After dissolution, a suitable aliquot is passed through a Dowex 50-W-X8 column in the hydrogen form and is evaporated nearly to dryness in a quartz round-bottom flask. A small aliquot is then vacuum dried in a conical quartz tube, methyl alcohol is added to the solid boric acid, and the mixture is moderately heated to bleed methyl borate into the inlet system of the gas mass spectrometer (15). Experiments with known samples indicate that boron loss is negligible and that accurate measurements of the isotope ratios are obtained.

7.16. Analysis of Copper-Lead and Niobium-Lead Mixtures, Marven A. Wade, Stanley S. Yamamura

The ARCO process studies were continued by CPP Technical during the first half of the year. In one study, copper was introduced into the lead chloride process to catalyze the dissolution of UO_2 -type fuels. In another study, the behavior of niobium was investigated. Niobium is one of the major fission products and has been considered as a cladding material. Methods for the analysis of copper-lead and niobium-lead samples from these studies are described below.

(15)Abernathey, R. M., U. S. Atomic Energy Commission Report IDO-14503 (1960).

7.16.1. Determination of Copper(II) and Lead(II)

The sum of copper plus lead was determined by direct titration with EDTA at pH 5 to 6 to a naphthylazoxine end point (16). A pyridine buffer was employed. Copper was then determined on a separate aliquot by measuring the blue Cu-EDTA complex at 735 mμ. Lead was obtained by difference.

In the spectrophotometric copper procedure, the Cu-EDTA complex is developed in a 0.5M EDTA-0.5M citrate medium adjusted to pH 5.0 ± 0.6 . Under these conditions, Co(II), Cr(III), Fe(II), and Ni(II) are the only common metal ions which form colored EDTA complexes absorbing at 735 mμ. Because of the significant differences between the reduction potential of copper ($E^\circ\text{Cu(II)}-\text{Cu(0)} = 0.34$ volt) and the other metals (for example, $E^\circ\text{Ni(II)}-\text{Ni(0)} = -0.25$ volt) the selective reduction of copper onto metallic tin ($E^\circ\text{Sn(II)}-\text{Sn(0)} = -0.14$ volt) followed by redissolution and measurement of the blue Cu-EDTA complex was investigated briefly. At equimolar ratios, none of the metals, cobalt, chromium, iron, and nickel, interfered, but at 20 to 1, nickel interfered seriously.

7.16.2. Determination of Niobium and Lead

The composition of the various types of niobium samples from the ARCO studies pertaining to niobium are shown in Table 7.4.

TABLE 7.4. COMPOSITION OF ARCO-TYPE NIOBIUM SAMPLES

<u>Type of Dissolution</u>	<u>Vapor Phase (Sublimate)</u>	<u>Melt Phase</u>
1. Molten PbCl_2	NbCl_x (high)	PbCl_2 (high)
	PbCl_2 (low)	Pb (high)
		Nb (unreacted coupon)
		Nb (black sandy material)
		NbCl_x (low)
2. Molten PbCl_2 with Cl_2 purge	NbCl_x (high)	PbCl_2 (high)
	PbCl_2 (low)	NbCl_x (low)
		Nb (unreacted coupon)

The vapor phases from both dissolution schemes were dissolved in dilute hydrofluoric acid and treated with hydrogen sulfide to precipitate the lead. The lead sulfide precipitate was boiled with hydrochloric

(16) Fritz, J. S., Lane, W. J., Bystroff, A. S., Anal. Chem. 29, 821 (1957).

acid to remove sulfide, then digested with nitric acid. A measured excess of EDTA was added and the excess was back titrated with manganese(II) at pH 9 to 10 to an eriochrome black T end point. Niobium was determined by evaporating an aliquot of the filtrate to fumes of sulfuric acid and measuring the absorbance of the blue peroxy complex at 360 mμ.

The melt phase from dissolution type (1) contained an unreacted niobium coupon which was removed manually, cleaned, and weighed. The lead chloride, lead metal, and niobium sand were dissolved successively with 0.01M nitric acid, concentrated nitric acid, and nitric-sulfuric acid mixture, respectively. The various fractions were separated by filtrations. Lead was determined complexometrically and niobium was determined colorimetrically. The NbCl_x compound is converted to insoluble niobic acid during the dilute nitric acid treatment and accompanies the niobium sand fraction.

The melt phase from dissolution type (2) also contained an unreacted niobium coupon which was separated and weighed. The lead chloride was dissolved in dilute nitric acid and filtered to isolate the niobium residue. Each fraction was determined as described above.

Details of the colorimetric niobium procedure are described in Appendix II, Method Nb-1, tentative.

7.17. Recovery of Tungsten from Tungsten-Aluminum Alloy, Stanley S. Yamamura

MTR Reactor Physics is measuring the resonance integral of tungsten-184 and -186. Because of the high cost of producing these pure isotopes, a method, suitable for the quantitative recovery of the enriched tungsten from the tungsten-aluminum powder alloy samples, has been developed.

The tungsten-aluminum alloy is dissolved with 9M hydrochloric acid in a 2-liter beaker placed in a 4-liter beaker to guard against loss. The black insoluble residue, containing approximately equal amounts of aluminum and tungsten, is separated by filtration and "dissolved" in aqua regia. Most of the tungsten is precipitated as tungstic acid during the aqua regia treatment. The remainder is precipitated by acidifying with hydrochloric acid and digesting with cinchonine. The soluble tungsten in the original filtrate is also precipitated with cinchonine. The tungstic acid is then separated by filtration, dissolved in sodium hydroxide, and reprecipitated. Finally the tungstic acid is ignited to the oxide at 800°C.

Recovery studies with various alloys prepared with pure aluminum and normal tungsten metal by MTR Metallurgy indicate that more than 94% of the tungsten, added initially, is recovered.

7.18. Determination of Thorium and Aluminum in Irradiated Thorium Slugs, Stanley S. Yamamura

Samples of irradiated thorium slugs clad in aluminum were dissolved in nitric-hydrofluoric acid mixtures and were analyzed for thorium and aluminum. After fuming with perchloric acid to volatilize the fluoride thorium was separated from aluminum by extraction into hexone from 1M nitric acid saturated with lithium nitrate. The thorium was stripped with water and determined complexometrically. A measured excess of EDTA was added and the excess was back titrated with thorium at pH 3 to an alizarine red S end point. The sum of thorium plus aluminum was determined on a separate sample aliquot by a similar procedure. Aluminum was obtained by difference.

7.19. Characterization of Niobium Chloride, Stanley S. Yamamura

Niobium trichloride, prepared by hydrogen reduction of niobium pentachloride, is nonionic and is therefore insoluble in water and dilute nonoxidizing acids. Because of this, the primary problem in analysis is that of converting the sample into a form suitable for the determination of chloride and niobium by conventional procedures.

Solubility studies showed that niobium trichloride dissolved readily in hot concentrated sulfuric acid. Because of the volatility of chloride under these conditions, the sample was dissolved in 30-ml screw-cap tubes which were immersed in a glycerine bath maintained at about 200°C. After the dissolution was complete, the chloride was "fixed" in a nonvolatile form by contacting the sample solution with sodium hydroxide suspended in a small test tube above the sample.

Chloride was determined by titration with silver(I) after redissolution in dilute sulfuric and hydrofluoric acids. A glass-silver wire electrode system was used to detect the equivalence point.

Niobium was determined on a separate sample by measuring the absorbance of the yellow peroxy complex at 360 mμ. Repeated analysis of the sample, presumed to be niobium trichloride, gave a chloride to niobium mole ratio of 2.67 to 1. The presence in the sample of various oxyniobium compounds has been suggested. Numerous studies with known portions of pure sodium chloride gave chloride recoveries of 100 ±1%.

Alternative approaches, such as pyrohydrolysis, and permanganate oxidation and volatilization of chloride as chlorine, were not reliable.

Details of the potentiometric chloride procedure are described in Appendix II, Method Cl-2.

7.20. Determination of Micro Amounts of Tributylphosphate, Stanley S. Yamamura, George J. Curtis, Robert M. Abernathey

The radiochemical determination of TBP, with tagged phosphorous-32, between the kerosene scrub phase and the uranium-nitric acid aqueous phase in a mixer-settler simulating the plant process is described in Section 5.17.

Various other approaches were unsuccessfully considered. These included:

1. Extraction of the uranyl-TBP complex into hexone and an indirect determination based on a fluorophotometric measurement of the uranium.
2. Extraction of aqueous phases with organic solvents and infrared analysis.
3. Total phosphate determination after conversion of TBP to orthophosphate by fuming with a mixture of nitric and perchloric acids.

In the first approach, a direct relationship was not obtained and the data were badly scattered. The infrared method was not sufficiently sensitive. High phosphate blanks in the water and reagents used to make up solutions prevented use of the third approach.

7.21. Determination of Aluminum in Samples Containing Calcium, Zirconium, Fluoride, and Nitrate, George J. Curtis

In a routine titrimetric method for the determination of aluminum, the hydroxyl ions released by the complexing of aluminum at high pH with fluoride are titrated with standard acid. According to the reaction: $\text{AlO}_2^- + 6\text{F}^- + 2\text{H}_2\text{O} \rightleftharpoons \text{AlF}_6^{3-} + 4\text{OH}^-$: four hydroxyls per aluminum are released.

Fluoride must be absent before converting to aluminate and the calcium hydroxide that forms carries aluminum causing low recovery. Modifications were developed to tolerate these diverse ions. Fluoride is first removed by perchloric acid fuming. Oxalate is added prior to conversion of the aluminum(III) to aluminate. Apparently calcium oxalate does not carry aluminum.

Sample aliquots containing 0.25 mmole of Al, 2.5 mmoles of Ca, 2.5 mmoles of Zr, 25 mmoles of HF, and 10 mmoles of HNO_3 were analyzed with slightly high biases ranging from 1 to 5 relative per cent.

7.22. Separation of Lithium from Lithium-Aluminum Alloys, Stanley S. Yamamura, John H. Sikes

Various schemes were studied for the separation of lithium from aluminum-5% lithium alloys. Precipitation of the aluminum with ammonia carried all the lithium. Formation of lithium aluminate and reaction with excess magnesium oxide gave complete release of lithium (as the hydroxide) with micro levels, but only 20% with 1-gram amounts. The volume of acetylacetone required for extraction of aluminum was beyond practicality.

Two successful procedures were evolved. In the first, aluminum hydroxide was precipitated three times at pH 6 with ammonia, evaporating the supernatant solution each time. The combined supernatant fraction was evaporated to a small volume and adjusted to pH 10 to

precipitate aluminum hydroxide which was filtered off. The filtrate was evaporated with nitric acid to volatilize the ammonium salts and the lithium was converted to lithium chloride by evaporating with hydrochloric acid.

The second procedure was superior. Bromine was added to the alloy in a nitrogen atmosphere and aluminum bromide was sublimed. Residual aluminum was precipitated with ammonia at pH 6 and filtered. Ammonium bromide was removed by nitric acid fuming and the lithium was converted to lithium chloride by three hydrochloric acid evaporations.

7.23. Determination of Uranium in Aluminum Alloys, Fred W. Dykes

As discussed last year, neither nitric acid nor hydrochloric acid dissolution was compatible to the mercury cathode, Jones reductor, cerium titrimetric method. Nitric acid could not be fumed off due to hold up in the copious aluminum salts. Hydrochloric acid resulted in copious evolution of chlorine in the mercury cathode.

Caustic dissolution also was not satisfactory; the uranium was partially attacked.

A mixture of sulfuric acid and hydrogen peroxide containing a trace of hydrochloric acid finally was adopted. One disadvantage is that the large volume required to keep the aluminum in solution reduces the efficiency of the mercury cathode. Even with fresh mercury, iron was incompletely electrolyzed. An iron analysis and correction was thus required. Also, an evaporation after the mercury cathode step was necessary to obtain manageable volumes for the Jones reductor and titration steps.

Though this method gave results that agreed with those of ORNL and New Brunswick on interchange samples, it has not been adopted for routine use because of its complexity.

7.24. General Dynamics (Fort Worth) Field Release Test III - Analysis of Total Effluent Samples, Fred W. Dykes

This project involved the dissolution of filters employed to trap particulate matter released by the melting of irradiated fuel elements. The filters were contained in plastic-lined, lead-filled, steel casks which were specially designed to permit dissolution in place. Aqua regia was used for the dissolution; close surveillance was required to maintain the reaction under control and still proceeding at a satisfactory rate. An insoluble filter medium (glass wool) in the casks resulted in the plugging of the processing system after the filter retainers had dissolved.

7.25. Remote Apparatus Development, Fred W. Dykes

7.25.1. Model B Pipetter

Teflon diaphragms for the valves proved unsatisfactory, and polyethylene was once more employed.

Minor revisions in the drawings were completed by the Design Engineering Group, and authorization was obtained to purchase three units for the replacement of badly worn units in service in the RAF. The low bid for these pipetters was \$1719.00 each; the high bid was \$2394.00. However, the units received from the low bidder were not operable; the extent of fabrication deficiencies is being determined.

7.25.2 Model B Specific Gravity Apparatus

The prototype, described last year, operated satisfactorily during the year. Minor modifications, based on the suggestions of operating personnel, were made to improve its performance.

The use of a single reference liquid proved satisfactory for the specific gravity range from 1.0 to 1.4. The Design Engineering Group is preparing drawings for a final model with a single reference tube position. The preparation of a report covering details of this apparatus has been deferred until completion of this design.

7.25.3. Facility for Analysis of Alpha-Beta Gamma Active Samples

This facility was constructed in Cell X of the ICPP. The facility consists primarily of a 4-inch lead shielded cave connected to a train of stainless steel glove boxes. Construction was completed on August 15. Several months have been spent in testing, modifying, and improving the facility. Samples of high alpha activity have been successfully processed in the glove boxes; the cave has handled high levels of beta-gamma activity.

Details of this facility will be presented in a separate report.

7.26. Determination of Burnup of Fissionable Isotopes

The need for reliable methods for the determination of burnup is becoming increasingly important. Burnup is a fundamental effect used to evaluate the testing of proposed nuclear fuels, and on a broader scale is of economic importance to the civilian reactor program.

The overall objective is the development of reliable methods for the determination of burnup in all fuel types at all burnup levels. The fissionable isotopes and mixtures that will be considered are low enrichment (power reactor) uranium, high enrichment uranium, plutonium, uranium-plutonium mixtures, and uranium-thorium mixtures.

The program will be undertaken jointly with the General Electric Vallecitos Laboratory. The work there is under the direction of Benjamin F. Rider.

The following briefly outlines the program as conceived at this time.

I. In-Pile Fission Counting, Warren H. Burgus, Lowell Miller,
MTR Physics

This is proposed as the means for primary calibration. An in-pile fission counter to be installed in the MTR is being designed. The planned order of irradiation is uranium-235, plutonium-239, and uranium-233.

II. Evaluation of Indicators to Differentiate Fissionable Isotopes, William J. Maeck, S. Fredric Marsh

The differentiation occurs in the light yield peak with a shifting toward higher masses with an increasing atomic weight of the fissionable isotope. Thus, the measurement of the ratio of the abundance of one nuclide on the light shoulder and another of the heavy shoulder of the light peak offers promise as a differentiating indicator.

III. Effect of Neutron Spectra on Fission Yield Distributions, Warren H. Burgus, MTR Physics

The fission yield of the promising nuclides will be measured as a function of neutron energy spectrum for the three fissionable isotopes. In the General Electric irradiations, neutrons spectra will be evaluated with cobalt and cadmium detectors. Experiments by Phillips are being considered in which the in-pile fission counter will be wrapped in cadmium.

IV. Development of Methods for Selected Fission Product Nuclides, William J. Maeck, Paul Goris, S. Fredric Marsh, Maxine E. Kussy

The determination of stable nuclides by mass spectrometer isotope dilution analysis will receive greatest attention. General Electric has started this program by measuring the neutron cross section of selected nuclides (an ideal characteristic is low parasitic neutron capture).

Radiochemical methods still will be required, for such cases as low burnup samples and the determination of selected nuclides on the shoulders of the light peak. Specific radiochemical methods will be developed for selected nuclides.

V. Mass Spectrometric Determination of Heavy Element Transformation, Thomas D. Morgan, Paul Goris

The often-used technique, mass isotopic analysis of uranium followed by the calculation of burnup based upon stoichiometric relationships, is accurate only for high burnup-highly enriched uranium. Because of such complicating factors as fissioning of plutonium-239, plutonium-241, and perhaps other transuranic nuclides, it appears that this technique will not serve as an independent means for determining burnup. An indispensable use will be the determination of total uranium and plutonium in irradiated samples.

VI. Development of a Universal Spike Standard, William J. Maeck,
Maxine E. Kussy

The use of a solution of added spike isotopes of uranium, plutonium, and selected fission product elements on the light peak, valley, and heavy peak coupled with mass analysis appears to be the ideal method of burnup analysis.

Both quantitative sampling and yield determination are bypassed as only ratios are determined.

Both General Electric and Phillips will prepare standard solutions and will engage in a cross analysis program for highly precise standardization.

VII. Chemical Determination of Burnup, Stanley S. Yamamura, Wayne B. Holbrook

All the aforementioned are designed to produce highly accurate means of determining burnup. It is obvious that expensive equipment and highly trained personnel would be required for the techniques discussed.

The reactor operator and the small processing plant with limited funds cannot afford such expenditures. The combination of chemical analysis for total uranium and plutonium and for selected total fission product elements (stable plus long life isotopes) will be evaluated.

8. QUALITY CONTROL AND STANDARDS LABORATORY

James E. Rein, Group Leader, Glenn L. Booman, Assistant Group Ldr.

8.1. Quality Control Program, George J. Curtis, John H. Sikes

The comprehensive quality control program on routine 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 Shift Laboratory's training and testing program, (4) the maintenance of "bench" standards and control charts, and (5) the surveillance of control data. "Bench" standards of known values are processed prior to samples to prevent the use of faulty apparatus or reagents.

The statisticians (Gail Cordes and Robert Finch) now supply regression equations, fitted from control data, that provide the means for the rapid computation of precision and accuracy for routine methods. The equations are presented as two plots, one of corrected result vs. uncorrected analysis, the other of precision vs. uncorrected analysis. Analytical results are reported corrected for bias and with precision limits.

Table 8.1. is a summary of the precision data for routine methods for 1961.

TABLE 8.1. PRECISION OF ROUTINE ANALYTICAL METHODS

<u>Methods</u>	<u>Range and Units</u> ^(a)	<u>Precision</u> ^(b)
<u>Acid</u> , Visual Indicator, Titrimetric	0.5 to 4.5 meq	0.16 meq
<u>Acid</u> , Oxalate, pH Titrimetric	1.2 meq base to 2 meq acid	0.03 meq
<u>Aluminum</u> , Fluoride Complexing, Titrimetric	5 to 11 mg	0.24 mg
<u>Beta Activity</u> , Gross	45 to 360 d/m/ml	37 relative %
<u>Chromium</u> , Redox Titrimetric	2 to 15 mg	0.20 mg.
<u>Chromium</u> , Colorimetric Diphenylcarbazide	0.005 to 0.05 mg	0.0027 mg
<u>Fluoride</u> , Pyrolysis, Ce(III) Titrimetric	6 to 40 mg	0.58 mg
<u>Iron</u> , Hydroxide Precipitation, Redox Titrimetric	50 to 150 mg	2.0 mg

<u>Methods</u>	<u>Range and Units</u> ^(a)	<u>Precision</u> ^(b)
<u>Mercury</u> , Titrimetric, Hg(II) with KSCN	160 to 500 mg Hg(NO ₃) ₂ $\frac{1}{2}$ H ₂ O	4.8 mg
<u>Nickel</u> , Colorimetric Dimethylglyoxime	0.01 to 0.1 mg	0.0030 mg
<u>Nickel</u> , Dimethylglyoxime Precipitation, EDTA Titrimetric	2 to 28 mg	0.59 mg
<u>Nitrate</u> , Devarda Reduction, Distillation, Titrimetric	0.25 to 4.5 millimoles	0.076 millimoles
<u>Specific Gravity</u> , Westphal	1.0 to 1.4 Sp. Gr. Units	0.0014 Sp. Gr. Unit.
<u>Specific Gravity</u> , Falling Drop Remote	1.0 to 1.4 Sp. Gr. Units	0.0046 Sp. Gr. Unit
<u>Uranium</u> , Extraction Spectrophotometric	0.8 to 18 mg	0.26 mg
<u>Uranium</u> , Mass Isotopic Distribution	1.2% 234 89.65% 235 3.01% 236 6.13% 238	0.064% 0.164% 0.023% 0.061%
<u>Uranium</u> , Isotope Dilution Mass Spectrometric	0.885 mg	0.0046 mg
<u>Uranium</u> , Pellet Fluorophotometric	2.5x10 ⁻⁶ to 5x10 ⁻³ mg. on pellet	24.5%
<u>Zirconium</u> , Cupferron Amperometric	0.01 to 0.1 millimole	0.002 millimole

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

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

8.2. Standards and Reagents

8.2.1. Routine, John H. Sikes, George J. Curtis

The number of standard solution, reagents, and quality control samples prepared during the year are summarized in Table 3.4.

8.2.2. Special Programs

8.2.2.1. Preparation of Uranium Standard Solution, George J. Curtis

Standard solutions were prepared from NBS standard sample 950 (normal uranium as U_3O_8) and from purified, fully enriched metal on a weight per volume basis in dilute nitric acid. Mass spectrometric-isotope dilution analysis (using uranium-233 as the added isotope) and coulometric analysis (5) gave results agreeing within 0.2% of the made-up values. These solutions were placed in Pyrex dispensing bottles of a design so that the displacement air bubbles through a side arm of the same solution to minimize evaporating loss. With about a quarter of the solutions dispensed over a 2-month period, the concentrations have remained constant.

8.2.2.2. Eta Program, John H. Sikes

Solutions of uranium-233, uranium-235, and plutonium-239 were prepared on a weight basis for MIR Physics for Eta-constant determinations by reactivity measurements.

8.2.2.3. Preparation of Lithium Aluminate, John H. Sikes

Two lithium compounds, lithium aluminate and lithium fluoride, have been considered for the alloying of lithium-6 with aluminum-uranium metallic fuel by powder metallurgical techniques. Lithium aluminate was selected, mainly for its higher stoichiometric factor.

As stated last year, its preparation by ignition of the precipitate resulting by mixing lithium hydroxide and an aluminate solution seemed promising. The product, however, was contaminated with silicon. Also, it was not stoichiometric $Li_2O \cdot 2Al_2O_3$, rather it was $Li_2O \cdot Al_2O_3$, containing excess Al_2O_3 based upon x-ray diffraction data in this laboratory and as indicated by other investigators (17,18).

(17) Hummel, F. A., J. Am. Ceramic Soc. 34, 237 (1951).

(18) Focht, R. L., Winkler, J. M., King, W. R., Bower, F. J., Paper, "The Separation of Lithium from Complex Solutions as the Acid Lithium Aluminate", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1961.

The following procedure was finally evolved for the preparation of stoichiometric $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3$. Equal mole amounts of $\text{LiOH} \cdot \text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed, nitric acid was added, and impurity silica was filtered off. The supernatant solution was transferred to a platinum dish, evaporated to dryness, and ignited at 970°C for 4 hours. The product, analyzed by x-ray diffraction, was essentially $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3$ (a minor number of unidentified lines were observed). Platinum, 0.2 weight per cent, was the only significant contaminant. This product was stable in air at room temperature; after 6 hours exposure, the gain in weight was less than 0.08%.

9. ANALYTICAL START-UP FOR EOCR

T. D. Morgan, Coordinator

Analytical service for EOCR Operations and Technical Groups will be provided by the Analytical Section located at CPP. All of the known required analyses were outlined and a program was initiated to assemble equipment and carry out the necessary development of methods, calibration and testing. The progress on each method is summarized. During the month of December, people at the Phillips Research Center in Bartlesville were consulted concerning analytical problems. The procedures learned and calibration materials obtained will aid the analytical program materially.

9.1. Total Ash, Marvin A. Wade, Stanley S. Yamamura

A serious problem arising from the use of organic coolants is the loss in efficiency resulting from the deposition of a coating on the fuel element surfaces. Because of the apparent importance of iron and other inorganic substances in the fouling mechanism, methods for the determination of total ash and iron are being investigated.

Ash, defined as the residue remaining after ignition, currently is being determined by a procedure originally developed at the CPP Shift Laboratory. The volatile components of the sample are sublimed by heating from beneath with a hot plate and from above with a heat lamp. The residue is carefully charred over a flame then ignited in a furnace at 900°C for 12 to 24 hours, with the difference between the final gross weight and the original tare weight being the weight of ash. This method though satisfactory for high levels of ash is not adequate at the very low levels because the weight loss of the platinum dish during the ignition process becomes significant. Another disadvantage is that platinum dishes weighing 20 grams or more are used to weigh between 0.5 and 10 mg of ash. Studies to date indicate that the ash can be transferred to a tared filter paper with a volatile solvent such as hexane. The weight of the ash plus filter paper is measured and the ash is obtained by difference. Careful studies with 1" diameter Whatman 542 filter paper indicate no significant weight changes during the transfer, drying and weighing process.

One possible hazard of the present procedure is the accumulation of combustible terphenyl coolant on the walls and ducts of the hood. Controlled sublimations and combustion of the volatile components will be considered.

9.2. Iron by X-Ray, G. Vernon Wheeler, Walter A. Ryder

Vacuum x-ray spectrographic equipment was obtained and installed. The sensitivity for iron in coolant was lowered from 12 ppm to about 2 ppm due mostly to improved optics rather than the vacuum path. Comparison of calibration data for measurement of iron in Santowax with data from the Bartlesville laboratory indicated that our sensitivity and iron background are comparable.

9.3. Flash Point, Dale G. Olson

Equipment for flash point determination is available and ASTM methods will be used.

9.4. Viscosity, Dale G. Olson

Particulate matter in coolant samples leads to errors in viscosity measurement. To eliminate this problem, the sample is melted and filtered at 180°C through a coarse porosity glass fritted filter.

9.5. Water, Robert E. Foster

During studies of the Karl Fischer method, several problems were discovered. Improvements in equipment and purification of chloroform are indicated requirements. A French delegation, sponsored by Euratom, visited Bartlesville and claimed to be able to measure 0.15 ug H₂O per 100 grams of sample by the Karl Fischer method and 100 ppm H₂O by direct infrared. In the Karl Fischer method, they preferred coulometric generation of iodine. A copy of their method has been requested.

9.6. Chromatography, Robert M. Abernathey

An F & M model 500-B linear programmed high temperature gas chromatograph like the ones in use at Bartlesville was obtained and set up. Experience has been gained in the fabrication of columns packed with LiCl on firebrick and in the operation of the instrument. Precision of peak area sensitivities between consecutive runs is 3 to 4%. Resolution has not been as good as is usually obtained in Bartlesville, possibly on account of differences in column packing material.

9.7. High Boiler Content by Sublimation, John H. Sikes, Stanley S. Yamamura

The primary coolant of the EOCR facility will be monitored and reprocessed continuously to maintain the high boiler content at less than 5%. A gravimetric procedure, based on the weight of residue remaining after controlled sublimation, is being investigated. Previous studies at Bartlesville have shown that in practice, some high boiler components sublime with the low boiler fraction and some low boiler components remain with the high boiler fraction. Therefore, the results are "correct" only when the weight of the foreign components in the two phases are equal. The proper conditions for achieving this state of equality can be obtained by controlling such variables as sample size, sublimation time, temperature, and pressure. Unfortunately, these conditions vary with samples of different high boiler content.

A "cold finger" sublimation technique is currently being used to prepare a high boiler fraction free of low boilers. Appropriate mixtures of this high boiler and pure terphenyls will then be used to establish the proper conditions for the sublimation method. Gas chromatographic analyses of the sublimate and residue fraction will also be used.

On numerous occasions, samples have been lost through excessive foaming or spattering. A Vibra-Tool equipped with a rubber eraser, held against the sublimation flask, has been used effectively to minimize these losses.

9.8. Molecular Weight, John H. Sikes, Stanley S. Yamamura

The volatility difference between a pure solvent and a solution of a solute dissolved in the solvent causes a temperature difference which results in a difference in resistance between thermistors located in the solvent and sample.

The Mechrolab Osmometer has a block maintained at 37°C. The sample syringe is introduced into the instrument and allowed to equilibrate for seven minutes before the sample is delivered and measured. Small variations which may be introduced through minor differences in the solvent itself can be prevented by using the same batch of solvent for both calibration and measurement.

The instrument was calibrated with solutions of o-terphenyl in benzene. Each of the standards ranging from 0.01 to 0.1M was determined a total of six times. The calibration data are shown in Table 9.1. The standard deviation based on the 36 determinations is 0.098 ohm. The standard deviations and percent standard deviations for the six values at each level are also presented.

9.9. Distillation, Jack L. Teague

Apparatus was fabricated and used to obtain samples of o-, m-, and p-terphenyls and of high boilers.

9.10. Acid Number, James E. Baker

The ASTM method D-644-54 entitled "Neutralization Value by Potentiometric Titration" was chosen. The apparatus was assembled and the method checked out on Santowax, with extremely low acid numbers resulting. The method was further checked by addition of strong and weak acids to sample aliquot. Distinct inflections were observed on the spiked samples where none were present previously.

9.11. Carbon-Hydrogen Ratio, Ronald E. Ohlin

Carbon-hydrogen apparatus is available in this laboratory. Check out of the method will be made upon arrival of a microbalance.

9.12. Density Measurements of Coolant, Fred O. Cartan

A 4-cc pyrex dilatometer operating in an air thermostat is proposed for density measurement of mixed terphenyls at 300°F and 500°F. A commercial oven, modified by the addition of windows and access ports, will serve as a thermostat. Temperature measurement will be made with thermocouples. The expected accuracy is 0.001 density unit.

TABLE 9.1. VAPOR PRESSURE OSMOMETER CALIBRATION DATA

of <u>o</u> -terphenyl ^a	Average R ^b	Standard ohms	Deviation %
0.0102	4.59	0.050	1.09
0.0284	12.96	0.082	0.63
0.0484	22.09	0.062	0.28
0.0648	29.17	0.125	0.43
0.0820	36.93	0.125	0.34
0.1001	45.16	0.116	0.26

^a Solutions of o-terphenyl in benzene were used to calibrate the instrument.

^b Average of 6 determinations.

APPENDIX I

PUBLICATIONS, REPORTS, AND PAPERS

JOURNAL PUBLICATIONS

1. Maeck, W. J., Kussy, M. E., and Rein, J. E., "Solvent Extraction Method for the Radiochemical Determination of Zinc", Anal. Chem. 33, 235 (1961).
2. Maeck, W. J., Kussy, M. E., and Rein, J. E., "Radiochemical Determination of Molybdenum by Solvent Extraction", Anal. Chem. 33, 237 (1961).
3. Marsh, S. F., Maeck, W. J., Booman, G. L., Rein, J. E., "Improved 2-Thenoyltrifluoroacetone Extraction Method for Radiozirconium", Anal. Chem. 33, 870 (1961).
4. Maeck W. J., Kussy, M. E., Booman, G., Rein, J. E., "Spectrophotometric Extraction Method Specific for Plutonium", Anal. Chem. 33, 998 (1961).
5. Maeck, W. J., Booman, G. L., Kussy, M. E., and Rein, J. E., "Extraction of the Elements as Quaternary (Propyl, Butyl, and Hexyl) Amine Complexes", Anal. Chem. 33, 1775 (1961).
6. Yamamura, S. S., Kussy, M. E., and Rein, J. E., "Complexometric Determination of Fluoride with Cerium(III)", Anal. Chem. 33, 1655 (1961).

U. S. ATOMIC ENERGY COMMISSION REPORTS

1. Goris, P., Morgan, T. D., Nielsen, R. A., "Comparative Boron Isotopic Analysis" IDO-14549, April, 1961.
2. Ginther, B. E., Wheeler, G. V., "Spectrographic Determination of Impurities in Hafnium" IDO-14558, August, 1961.
3. Huff, G. A., Doggett, I. L., Fletcher, R. D., Jacobson, M. E., "Remote Dissolution and Analytical Program for Irradiated Thorium," IDO-14557, July, 1961.
4. Maeck W. J., Kussy, M. E., Morgan, R. T., Rein, J. E., and Laug, M. T., "Simultaneous Mass Spectrometric Determination of Plutonium and Uranium by the Isotope Dilution Technique: Application to Power Reactor Fuel Dissolver Samples", TID-7615, pp. 78-89 (1961).

PAPERS PRESENTED

1. Abernathey*, R. M., Morgan, T. D., "Heavy Water Purity Analysis by Infrared Absorption," Intermountain Section, Society for Applied Spectroscopy, Idaho Falls, January, 1961.
2. Arnold*, K. R., Wheeler, G. V., "Spectrochemical Analysis of Impurities in Uranium Fuel Materials by the Rotating Disc Spark Technique", Intermountain Section, Society for Applied Spectroscopy, Idaho Falls, January, 1961
3. Ginther*, B. E., "Spectrographic Analysis of Impurities in Hafnium", Intermountain Section, Society for Applied Spectroscopy, Idaho Falls, January, 1961.
4. Wheeler, G. V., Ryder*, W. A., "Analysis of Air Samples for Beryllium by the Rotating Platform Spectrographic Technique", Intermountain Section, Society for Applied Spectroscopy, Idaho Falls, January, 1961.
5. Marsh*, S. F., Maeck, W. J., Booman, G. L., and Rein, J. E., "Improved Extraction Method for Radiozirconium", 15th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1961.
6. Goris*, P., "Improved Sample Bonding and Emission from Surface Ionization Filaments," ASTM Mass Spectrometer Meeting, Chicago, June, 1961.
7. Maeck, W. J., Kussy, M. E., Morgan, T. D., Rein*, J. E., Laug, M. T., "Simultaneous Mass Spectrometric Determination of Plutonium and Uranium by the Isotopic Dilution Technique", 1961 AEC Contractor Meeting, Denver, Color., June 15-16, 1961.
8. Wheeler, G. V., Ryder*, W. A., Arnold, K. R., "Analysis of Air Samples for Beryllium by the Rotating Platform Spectrographic Technique", Conferences on X-Ray and Emission Spectroscopy, Denver, August, 1961.
9. Booman*, G. L., "Instrumentation in Electroanalytical Chemistry", Invited paper to Symposium on Electroanalytical Methods, Division of Analytical Chemistry, 140th American Chemical Society Meeting, Chicago, September 3-8, 1961.
10. Maeck*, W. J., Booman, G. L., Kussy, M. E., and Rein, J. E., "Extraction of the Elements as Quaternary (Propyl, Butyl, and Hexyl) Amine Complexes", Division of Analytical Chemistry, 140th American Chemical Society Meeting, Chicago, September 3-8, 1961.

11. Abernathey*, R. M., Morgan, T. D., "Determination of Heavy Water Purity by Infrared Absorption", Conference on Analytical Chemistry, Gatlinburg, October, 1961.
12. Huff*, G. A., Doggett, I. L., Fletcher, R. D., Jacobson, M. E., "Remote Dissolution and Analytical Program for Irradiated Thorium", Fifth Conference on Analytical Chemistry in Tenn., October, 1961.

*Presented paper.

MEASUREMENT EVALUATION SEMINAR

The following are members of various sections of the U. S. Atomic Energy Commission Measurement Evaluation Seminar and attended scheduled meetings during the year:

Booman, G. L., Uranium Sub Section
Maeck, W. J., Radiochemistry Sub Section
Morgan, T. D., Mass Spectrometry Sub Section
Rein, J. E., Main Committee and Plutonium Sub Section
Wheeler, G. V., Emission Spectroscopy Sub Section

MISCELLANEOUS

R. C. Shank is a member of:

1. ASTM Committee D-19, Subcommittee IX on Methods for Radiochemical Analysis of Industrial Water and Industrial Waste Water.
2. ASTM Committee E-10, Subcommittee V on Dosimetry. The particular interest is this Subcommittee is the Task Force on Fuel Burnup.

APPENDIX II

METHODS ADDED TO ICPP ANALYTICAL MANUAL IN 1961

<u>Method Designation</u>	<u>Title</u>	<u>Page</u>
Density and Screen-1	Bulk Density and Screen Analysis of ICPP Calciner Product	71
Density, Solid-4	Solids Density by Air Displacement . .	75
Cl-2	Potentiometric Chloride Deter- mination	78
Cr-3, Mod-2	Volumetric Chromium Determination . .	85
Co-1	Colorimetric Cobalt Determination . .	89
Cu-1	Colorimetric Copper Determination . .	95
Kr-1	Radiometric Krypton-85 Deter- mination	98
Nb-1	Colorimetric Niobium Determination . .	101
Sn-1, Mod-2	Colorimetric Tin Determination	108
W-1	Separation and Gravimetric Tungsten Determination	113
U-Coul-1	Coulometric Uranium Determination . .	117
Zr-3	Extraction-Spectrophotometric Zirconium Determination	120

BULK DENSITY AND SCREEN ANALYSIS OF ICPP CALCINER PRODUCT

ABSTRACT

Methods for the routine measurement of bulk density and particle size distribution of ICPP Waste Calciner Product are described.

APPLICABILITY

These methods are generally applicable to particulate solids. They are based on methods devised and used at the pilot plant.

DISCUSSION

Density is that property of a material equal to the ratio of its weight to its volume. For bulk density, the volume includes not only the actual volume of the solid but the volumes of the unoccupied spaces in and between the particles. Bulk density is dependent on factors such as particle density, degree of packing, and particle size and shape. Packing is the more variable factor so, in order to have reproducible measurements, a constant, arbitrary handling procedure has been adopted.

Particle size distribution is obtained by screening. The results are reported as weight per cent. The nine screens routinely used cover the size range from 1190 microns to 74 microns. Coarser or intermediate screens are used if needed. A common problem with screens is "blinding" or plugging of the screen openings. Screens 48 and 65 are especially liable to this behavior. An arbitrary limit of 100 grams per screen has been set to reduce this problem.

SPECIAL SAFETY PRECAUTIONS

None

APPARATUS

1. Graduate, 500-ml., with tare (Graduate is cut off at the 500-ml. mark and fire polished).
2. Large spatula.
3. Double pan trip balance, readable to 0.1 gram.
4. Set of weights (100 to 1000 grams).
5. Weighing pan, with tare weight.
6. Sample splitter and cleaning brush.
7. Catch pans and trays.
8. Set of standard screens, to include the following sizes Tyler numbers, 6,8,10,14,20,24,28,32,35,42,48,60,65,80,100,150, and 200.
9. Ringstand, ring, and large funnel.
10. Tyler Rotap screening machine, with timer.
11. Fiber and suede (fine brass wire) screen cleaning brushes.

PROCEDURE

1. Make out a worksheet duplicating the example at the end of this procedure.

A. Bulk Density

2. Obtain a sample of from 550 to 800 cc. Use the sample splitter if necessary (Note 1).
3. Mix the sample if it appears inhomogeneous.
4. Place the metal funnel in the ring stand in a catch tray. Place the graduate so it is directly underneath the funnel.
5. Pour the sample rapidly and completely into the graduated cylinder. Let the excess overflow into the catch tray. Be careful not to jar the cylinder.
6. Cut off the excess solids by drawing the blade of the spatula across the top of the graduate. Tap the cylinder gently to pack the contents.
7. Weigh the cylinder and contents, using the proper tare, to the nearest 0.1 gram. Be sure that the 10 gram weight is seated in one of the beam notches. Record the weight on the Worksheet.

B. Screen Analysis

8. Obtain a 250- to 400-gram sample. Use the sample splitter if needed.
9. Weigh the sample to 0.1 gram using a weighing pan and proper tare. Record this weight on the Worksheet.
10. Obtain the following standard screens: Tyler 14, 20, 28, 35, 48, 65, 100, 150 and 200, pan and lid. Examine the screens for solids. If needed, clean them (Note 2). Stack them on the pan so the finer screens are at the bottom. The screen numbers will decrease coming up the stack.
11. Pour the sample into the upper screen. Fit the brass lid on the stack. Cover with the cast iron protective cover. Place the combination on the Rotap screening apparatus. Be sure that the stack is properly centered inside the spring catch at the bottom of the screen platform.
12. Set the timer for 5 minutes operation of the apparatus. When the machine stops, remove the stack of screens from the apparatus, remove cover and lid (Note 3).
13. Gently separate the top screen. Pour its contents into a weighing pan. Brush the remaining particles from the screen into the weighing pan. Do these operations over a catch tray so that solids will not be lost.
14. Weigh the solids to the nearest 0.1 gram (Note 4). Record this weight on the Worksheet opposite the screen number. Place the weighed solids in a catch pan.
15. Repeat steps 13 and 14 for each of the following screens and the pan.

C. Calculations

16. Calculate the bulk density as follows:

$$\text{Bulk density} = \text{wt. in graduate} / 500 = 0.002 \text{ (wt. in graduate).}$$

Record the calculated bulk density on the worksheet.

17. Total the weights of the screened fractions. If there is more than 3 grams variation from the measured total weight, check the tares and the weight accumulated in the catch pan in order to find the error.
18. Calculate the wt. percentages of the screened fractions as follows:

$$\text{Wt. \%} = \frac{100 \text{ (wt. in screen)}}{\text{(meas. total wt.)}}$$

Calculate the wt. percent for each screen. Record this result on the Worksheet opposite the corresponding screen number.

19. Add the collected wt. percentages. They should give a total close to 100%. If not check the calculations.
20. Record the bulk density, the screen sizes used, and the corresponding wt. percentages on the front of the Worksheet.
21. Place the sample in its original container. If no other analyses are to be made, discard it.

NOTES

1. The sample splitter is designed to permit breaking a large sample into a number of smaller representative samples. To use it, place one or more catch pans under each side and pour the sample through the chutes. Move the stream of sample rapidly back and forth across the chutes so that sample falls into all chutes. The fractions obtained can be recombined so that almost any fraction desired can be obtained.
2. Only the large screens should be cleaned with the suede (wire) brush. Use the fiber brush for the finer screens (Tyler 48 and higher number). Never poke lodged particles free with a pointed instrument. This ruins the calibration of the screen. Try to clean screens as they are used so that they are ready for the next measurement.
3. If there are more than a few grams of solid in the upper screen, this material will have to be screened with coarser screens. Pour the sample from the top screen into a clean pan. Get out the next two or three coarser screens. Stack them on the top screen. Hand screen the solids through them over a catch pan. Record the screen numbers on the Worksheet. Then follow steps 13 and 14 for each screen.

Calciner Product 1:4

4. There is an arbitrary load limit of 100 grams on any pan. If there are more than 100 grams on a pan, there is danger that the screening was incomplete. With sample loads less than 400 grams, this will rarely occur. The screening should be repeated, with the addition of the screen intermediate in size between the loaded screen and its preceding screen. This should be done for each overloaded screen. Additional room on the apparatus can be had by eliminating empty upper screens or by moving the lower platform downward with the special tool. The numbers of the screens added should be placed on the Worksheet in their numerical order. Dump all solids into a catch pan and begin with step 11.

F. O. Cartan
4/18/61

SOLIDS DENSITY BY AIR DISPLACEMENT

ABSTRACT

A method for the measurement of the density of solids using the Beckman No. 930 Air Displacement Pycnometer is described. A standard deviation of 0.028 density units is obtainable for typical calciner product.

APPLICABILITY

This method is suitable for the rapid measurement of the density of solids. It is generally applicable. Wet solids or those producing corrosive fumes should not be measured. The maximum sample volume is 50 cc. Results from this method are comparable to those obtained by the carbon tetrachloride displacement method (Method Density Solid-1).

DISCUSSION

In this method, the mass of the sample is determined by weighing and its volume by air displacement with an air pycnometer. In the case of porous solids, the measured volume includes bubbles and closed pores.

The air pycnometer consists of two equal volume chambers fitted with pistons. The chambers are connected by a differential pressure gage. With no sample in either chamber, the gage reads zero with equal piston strokes. In use, a sample is placed in one chamber with both pistons in their "out" positions. The piston in the other chamber is moved a fixed stroke, then the piston in the sample chamber is moved until the differential pressure gage reads zero. The difference between the two piston positions is read as the sample volume from a mechanical counter attached to the sample piston.

Leaks or a temperature difference between the sample and pycnometer are the most common causes of error.

APPARATUS

1. Beckman No. 930 Air Comparison Pycnometer, with sample cup, calibrating spheres, and cup tare.
2. Balance, readable to 0.1 gram.
3. Funnel and scoopula or spatula.

PROCEDURE

A zero check should be made at the start of a series of measurements. The procedures used for the zero check, calibration, and density measurement are identical except for the contents of the sample cup and the weighing steps.

1. Prepare a worksheet as shown.

A. Zero Check

2. Inspect the sample cup. If necessary, clean it with acetone. Do not use abrasive cleaners.
3. Open the valve on top of the instrument. Rotate both handwheels counterclockwise until they rest against their stops. This rotation must be gentle as jamming easily occurs.
4. Turn the measuring handwheel (the one nearest the counter) clockwise until the counter indicates the instrument starting number.
5. Move sample holder handle upwards and place the empty sample cup firmly against the compartment backstop. Lock the sample cup in place by firmly pressing the handle down.
6. Wait 30 seconds for temperature equalization. Then close the valve on top.
7. Turn the reference and measuring handwheels clockwise simultaneously until the reference handwheel rests against its stop. During the rotation, watch the needle of the differential pressure indicator and keep it on scale. Wait 30 seconds and make the final adjustment. Turn the measuring handwheel in a clockwise direction until the gage needle reads zero.
8. Slowly open the valve, watching the gage needle while doing so. If the needle did not move from the zero position, record the counter reading on the worksheet. The first 3 digits read in cc.'s, the fourth digit in 1/10 cc.'s and the vernier in 1/100 cc. units. If the counter passed zero, record the difference as a negative number. If the needle did move, complete step 9, then repeat the procedure starting with step 3.
9. Be sure the valve on top is open. Rotate both handwheels counterclockwise as far as they will go. Remove the sample cup.
10. Obtain a duplicate zero reading by repeating the procedure.

B. Calibration

Two steel spheres are supplied as volume standards. It is advisable to measure their volume occasionally as a means of checking the instrument. Follow steps 3 through 9, placing the sphere in the cup used in step 5. The volume read in step 8

should be; 1-inch diameter sphere (8.58 ± 0.15 cc.) and 1.5-inch diameter sphere (28.96 ± 0.15 cc.).

C. Density Measurements

11. If needed, mix the sample until it is homogeneous.
12. Add sample until the cup is approximately $\frac{4}{5}$ full. Wipe the cup rim clean. Weigh the sample to the nearest 0.1 gram. Record the weight on the worksheet.
13. Repeat steps 3 through 9 except that the filled cup is used in step 5 and the counter reading obtained in step 8 is the uncorrected sample volume.
14. Return the sample to its original container.
15. Repeat steps 11 through 14 to obtain a duplicate value.

CALCULATIONS

16. Average the two zero check readings. Record the value on the worksheet. If this measurement is part of a series, use the average value obtained from the zero check made at the start of the series.
17. Subtract this average zero reading from each of the uncorrected volume readings to give the corrected volumes. Record on the worksheet.
18. Calculate the densities as follows:

$$\text{density (gram/cc.)} = \frac{\text{Weight}}{\text{Corr. Volume}}$$

Record the results on the worksheet. Average the calculated densities and record this average on the front of the worksheet.

Report results to 2 decimal places.

Fred Cartan
4/25/61

POTENTIOMETRIC CHLORIDE DETERMINATION

ABSTRACT

A method is described for the direct titration of milligram quantities of chloride with silver(I). The equivalence point is determined potentiometrically using a glass-silver wire electrode system.

APPLICABILITY

This method was specifically developed for determining chloride in chloro-niobium compounds which were soluble only in hot concentrated sulfuric acid. Under these conditions, chloride is volatilized as hydrogen chloride gas. The dissolution is therefore performed in a sealed screw-cap test tube containing also a small test tube of sodium hydroxide which fixes the chloride as non-volatile sodium chloride (See Figure 1).

Known anionic interferences are bromide, iodide, and other anions precipitated by silver(I). Metallic ions such as Cr(III), Hg(I,II), Nb(V), Tl(I), and other cations which form stable chloride complexes or precipitates or which affect the electrode system interfere. Interference from cations such as Cr(III) and Nb(V) is avoided by the addition of fluoride which release the chloride bound to these metal ions.

The range of the method is 0.025 to 0.45 millimole (about 1 to 15 mg.) of chloride.

SAFETY PRECAUTIONS

Rapid mixing of concentrated sulfuric acid and concentrated sodium hydroxide may generate sufficient pressure in the form of steam to rupture the sealed test tube. Always cool the tube in an ice bath before contacting the base with the acid.

APPARATUS AND REAGENTS

A. Apparatus

1. Leeds and Northrup pH meter equipped with a glass-silver wire electrode system. The glass electrode must be of the large type (L & N item no: STD. 1199-30). A Beckman glass electrode (no. 4990-80) equipped with an L & N glass electrode lead may also be used. The silver electrode is shown in Figure 2.
2. Beakers, 100-ml.
3. Buret, 10-ml., calibrated in 0.02-ml. divisions
4. Magnetic stirrer and stirring bars.

Figure 1. Apparatus for Dissolving Samples

Figure 2. Silver Electrode

5. Glycerine bath, $200 \pm 10^{\circ}\text{C}$.
6. Ice bath
7. Screw-cap test tubes, 30-ml, equipped with Teflon-lined screw caps.
8. Graduated cylinders, assorted sizes.
9. Pipets, assorted sizes.

B. Reagents

All reagents are made from Analytical Reagent Grade chemicals. Distilled water is used throughout.

1. Sodium chloride calibration and bench standard, 0.900M (3.191mg Cl/ml). Dissolve 5.2609 grams of sodium chloride in water and dilute to 1 liter.
2. Silver nitrate solution, 0.05M. Dissolve 8.5 grams of silver nitrate in water and dilute to 1 liter. Store in the dark in a dark colored bottle. Standardize according to Section B - "Standardization and Bench Standard".
3. Sulfuric acid, concentrated and 50% ($\frac{V}{V}$).
4. Sodium Hydroxide, carbonate free, saturated.
5. Hydrofluoric Acid, 0.1 M. Dilute 2 ml of 48% sulfuric acid to 500 ml with water. Store in a polyethylene bottle.
6. Nitric acid, 8M.
7. Acetone
8. Glycerine

PROCEDURE

- A. Special Instruction for using the L & N pH meter for potentiometric titrations.

Note: Read the directions on the face of the pH meter.

1. Set the temperature selector knob at the 700-mv. range.
2. Insert the silver electrode equipped with the needle or calomel type lead into the small electrode receptacle.
3. Insert the glass electrode into its proper receptacle.

4. In the titration of chloride with silver ions, the meter pointer moves from left to right. Because all readings taken during the titration are used only to calculate the equivalence point, any of the scales may be used. In the course of the titration, the pointer movement covers nearly a half of the scale. Consequently, at the start of the titration, adjust the position of the pointer by means of the standardization knob to the left hand end of the scale.

B. Standardization and Bench Standard

Run a pair of standards with each set of samples; however, one standardization per day is sufficient. To 2.0 ml. and 4.0 ml. of the chloride standard, add 25 ml. of water, 25 ml. of acetone, and 0.5 ml. of 50% sulfuric acid. Process these according to E. Calculate the molarity of silver nitrate.

$$\underline{M} = \frac{(\text{ml. of NaCl std.})(M \text{ of NaCl})}{\text{ml. of AgNO}_3}$$

If the two values do not agree within limits set by the Quality Control Laboratory, process another pair of standards. Contact your supervisor if agreement is still not obtained.

C. Blank

Run a reagent blank with each set of samples.

D. Procedure for Dissolution of the Sample in Sealed Tubes

Note: The screw-cap tube and the small test tube for the sodium hydroxide are shown in Figure 2.

1. Weigh a sample containing between 1 and 15 mg. of chloride into the bottom of the screw-cap tube.
2. Add 0.5 ml. of concentrated sulfuric acid.
3. Quickly place the small tube containing 1.25 ml. of saturated sodium hydroxide above the sample. Screw the cap on tightly.
4. Immerse the sample tube in a glycerine bath maintained at $200 \pm 10^\circ\text{C}$. until dissolution is complete.
5. Cool the whole tube in water, then chill in an ice bath.
6. Invert the tube repeatedly to contact the base with the sulfuric acid.
7. Open the tube and add 10 ml. of 0.1 M hydrofluoric acid and 0.5 ml. of 50% sulfuric acid. Re-cap and mix to redissolve the solids.

8. Transfer quantitatively to a 100-ml. beaker containing 25 ml. of acetone. Use 15 to 20 ml. of water for the transfer.

9. Continue on according to E.

E. Potentiometric Titration of the Chloride

1. Insert the electrodes into the sample solution. Raise the zero button and turn the standardization knob to adjust the meter pointer to the left hand end of the scale.
2. Titrate the chloride with the silver nitrate solution. Near the equivalence point, add the titrant in 0.05-ml. increments and record the scale reading after each increment.

Note: When working with more than a few milligrams of chloride, the silver chloride produced tends to adhere to the silver electrode causing sluggish response. Tap the silver electrode gently with a clean glass rod to dislodge the silver chloride precipitate.

Take at least 3 readings on either side of the region of maximum change.

3. Calculate the equivalence point according to the following example.

Example

<u>ml.</u>	<u>reading</u>	<u>$\Delta 1$</u>	<u>$\Delta 2$</u>	
5.60	430			
5.65	✓445			
5.70	✓490	45		
Equiv. pt. → region	5.75	120	75	$\Delta 2A$
	✓610	80	40	$\Delta 2B$
5.80	✓690			
5.85	720			
5.90	735			

Equiv. pt. = $5.70 \pm 0.05 \left(\frac{75}{75 + 40} \right)$
= 5.733 ml.

DIRECTIONS

- Upon inspection the region of maximum change as indicated by the arrow is between 5.70 and 5.75 ml.

- B. Take the 2 readings immediately before and after the arrow. The 4 readings used in the calculation are indicated by checks (✓).
- C. Obtain the difference ($\Delta 1$) between the 4 readings: 490-445, 610-490, and 690-610.
- D. Obtain the difference ($\Delta 2$) between the 3 $\Delta 1$ values.
- E. Equivalence point =
- $$5.70 + 0.05 \times \left(\frac{\Delta 2A}{\Delta 2A + \Delta 2B} \right) = 5.733 \text{ ml.}$$
- Buret reading immediately preceding the arrow Volume of increments added

CALCULATIONS

Record the data on the work sheet as follows:

Column

A	Volume of chloride standard used, ml.
B	Volume of silver nitrate used to titrate the standards, ml. = B' and B''
C	Molarity of silver nitrate according to procedure B,
	$C' = 2 \left(\frac{0.0900}{B'} \right)$
	$C'' = 4 \left(\frac{0.0900}{B''} \right)$
D	Average molarity
	$D = \frac{C' + C''}{2}$
E	Weight of sample in grams
F	Volume of silver nitrate required to titrate sample, in ml.
G	Millimoles chloride titrated
	$G = DF$
H	Result, millimoles chloride per gram of sample
	$H = \frac{G}{E} = \frac{DF}{E}$

Report to 3 significant figures as 15.5, 1.55, and 0.155 millimoles per gram.

REFERENCES

1. Yamamura, S. S., IDO Notebook No. U-455, pp. 121-142.

VOLUMETRIC DETERMINATION OF CHROMIUM

ABSTRACT

A method is described for the determination of total chromium. A reduction is first made with hydrogen peroxide in a sulfuric acid-nitric acid media. After heating to fumes of sulfur trioxide, the sample is oxidized with ammonium persulfate and silver ion. The chromium (VI) is then titrated with iron (II) using ferroin as an internal indicator.

APPLICABILITY

This method is applicable to stainless steel type samples dissolved in various acid mixtures. The hydrogen peroxide prereduction prevents loss of volatile chromyl chloride and is required for samples that contain chloride. As written, the range of the method of 0.03 to 0.3 millimole of chromium. By using larger burets and more ammonium persulfate and silver (I) the upper range can be extended. The stated amount of ammonium persulfate, assuming a twofold excess is required for complete oxidation, is sufficient for 4 millimoles of chromium.

Ions that are oxidized by persulfate and silver (I) and reduced by iron (II) interfere.

APPARATUS AND REAGENTS

A. Apparatus

1. Buret, 10-ml., graduated in 0.05-ml. increments.
2. Beakers, Griffin low form, 250-ml.
3. Graduate, 25-ml., pharmaceutical.
4. Pipets, volumetric, assorted sizes.
5. Magnetic stirring apparatus.
6. Teflon stirring bars.
7. Cover glasses, speedy-vap.

B. Reagents

Note: All reagents are made from C.P. or Analytical Reagent Grade Stock. Use distilled or deionized water throughout the procedure.

1. Potassium dichromate solution, standard, 0.1N.
2. Ferrous ammonium sulfate solution, 0.1N, standardize daily.
3. Ferroin indicator, 0.025M.
4. Sulfuric acid, concentrated.
5. Nitric acid, concentrated.
6. Phosphoric acid, 1:1 v/v.
7. Hydrogen peroxide, 30%.
8. Ammonium persulfate.
9. Silver nitrate, 10 grams per liter.
10. Sulfuric acid, 1:1 v/v.

SPECIAL PRECAUTIONS

A. Safety

1. Sulfuric acid tends to spatter in step 5. Wash spattered areas with copious quantities of cold water.
2. Samples must be cooled to room temperature before adding sulfuric acid in D, step 12.

B. Procedure

1. The excess persulfate must be completely destroyed in D, step 10 or high results will be obtained.
2. For highest accuracy, the small indicator blank should be determined.

PROCEDURE

A. Standardization of Iron (II)

Note: Do in duplicate each shift. Duplicate difference limits are 0.03 ml.

1. Pipet 5 ml. of the standard dichromate solution into a 250-ml. beaker.
2. Add 50 ml. of water.
3. Add 25 ml. of 1:1 v/v sulfuric method.
4. Add 10 ml. of 1:1 v/v phosphoric acid.
5. Add 1 drop of 0.025M Ferroin indicator.
6. Titrate with iron (II) until the indicator changes from blue-green to orange.
7. Calculate the normality of the iron (II) solution by $N_{Fe} = (5) (N_{Cr}) (\text{ml. titer} - \text{ml. blank})$.

B. Determination of Indicator Blank

Note: A single determination is satisfactory.

1. Repeat steps 2-6 of section A.

C. Bench Standard

Run a single determination according to D. Limits will be specified by the Quality Control Laboratory.

D. Samples

1. Pipet an aliquot of sample containing 0.03-0.3 millimole of chromium into a 250-ml. beaker.
2. Carefully add 5 ml. of concentrated sulfuric acid and cool in a cold water bath to room temperature.

3. Add 10 ml. of 30% hydrogen peroxide.
4. Add 2 ml. of concentrated nitric acid.
5. Heat on hot plate to voluminous white fumes of sulfur trioxide. Do not mistake condensing water vapor which is a white mist for sulfur trioxide.
6. Cool to room temperature in a cold water bath.
7. Add 50 ml. of water.
8. Add 3 grams of ammonium persulfate and stir sample until the added reagent is dissolved.
9. Add 5 ml. of silver nitrate solution.
10. Heat on a hot plate until excess persulfate is destroyed. This may be determined by a change in boiling characteristics from copious small oxygen bubbles to fewer and fewer large bubbles.
11. Cool to room temperature in a cold water bath.
12. Add 15 ml. of 1:1 v/v sulfuric acid.
13. Add 10 ml. of 1:1 v/v phosphoric acid.
14. Add 1 drop of 0.025M ferroin indicator.
15. Titrate with the standardized iron(II) solution to the blue-green to orange endpoint.
16. Calculate the chromium concentration of the sample according to the section on Calculations.

CALCULATIONS

1. Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Volume of sample, in ml.
B	Volume of iron(II) solution used, in ml.
C	Normality of iron(II) solution.
D	Indicator blank, in ml.
E	Volume of iron(II) corrected for indicator blank, (E=B-D)
F	Result, mg. chromium per ml. of sample.

2. Calculate the mg. chromium per ml. of sample by

$$F = \frac{17.34 C E}{A}$$

3. Report results to 0.5% accuracy.

REFERENCES

1. American Society for Testing Materials, "ASTM Methods Chemical Analysis of Metals, p. 105-106, 1950.
2. Smith, G. F., and Richter, F. P., "Phenanthroline and Substituted Phenanthroline Indicators", The G. Frederick Smith Chemical Co., 1944.
3. Walton, H. F., "Principles and Methods of Chemical Analysis", p. 331-336, Prentice-Hall Inc., 1952.
4. Henry, R. W., IDO Notebook U-268, (1959).

January, 1961

COLORIMETRIC COBALT DETERMINATION

ABSTRACT

Cobalt (III) reacts with nitroso-R salt (sodium 1-nitroso-2-naphthol-3,6-disulfonate) to form a soluble red complex anion which is stable in acid solution. The solution is passed through an alumina column, on which the cobalt complex and unreacted nitroso-R salt are adsorbed. Successive elution, first of excess reagent, and then of the cobalt complex enables the cobalt to be isolated and measured spectrophotometrically at 500 mμ. Combination of the ion exchange technique with the usual colorimetric procedure renders nitroso-R salt a specific reagent for cobalt, and the usual interference from copper, chromium, nickel, and iron is eliminated.

APPLICABILITY

The procedure is applicable to all varieties of steels and cast irons, and to copper and nickel base alloys without prior separation. Large quantities of anions which are volatilized by fuming perchloric acid do not interfere.

The sample aliquot should contain between 50 μg and 250 μg of cobalt.

DISCUSSION

The position of an organic sulfonate ion apparently lies intermediate between nitrate and perchlorate in the order of anion affinity on an acid alumina column. Both the cobalt complex and the excess nitroso-R salt readily adsorb on a perchloric acid-washed alumina column. The excess reagent is eluted with hot 1M nitric acid, while only a slight bleeding (migration down the column) of the cobalt complex is observed. Evidently it is more probable that at least one of the six possible sulfonate groups of the complex will remain adsorbed at any instant in the presence of nitrate ions, although the reagent with only two sulfonate groups is easily displaced. Severe bleeding of the cobalt during this step indicates that the nitric acid is either too hot or stronger than 1M.

The reason for preparing a column in the perchloric acid form, when a nitric acid wash will follow, is that cobalt forms a very narrow band in a perchlorate medium. Subsequent treatment with nitrate ions causes only slight bleeding, whereas if the band is formed in the presence of nitrate ion, excessive bleeding occurs due to the slight difference in exchange ability of the two ions.

Ferrous ion forms a more stable complex with nitroso-R than does cobalt. For this reason it is imperative that all iron salts be oxidized during or after the dissolution of the sample. Hydrogen peroxide accomplishes this, as well as the reduction of dichromate and permanganate to non-interfering forms.

The cobalt complex is eluted with 1M sulfuric acid, which must in turn be replaced by hydroxide ion before regenerating the column in the perchlorate form.

APPARATUS AND REAGENTS

A. Apparatus

1. Spectrophotometer, Beckman, Model B or DU.
2. Absorption cells, Corex, 1-cm.
3. pH meter, Leeds and Northrup, with glass-calomel electrodes.
4. Chromatographic exchange column, 1.5 to 2.0-cm. diameter with reservoir, (typical lead or silver reductor column).
5. Flasks, volumetric, 100-ml.
6. Pipets, volumetric, assorted sizes.
7. Pipets, micro, assorted sizes, with control syringe.
8. Hotplate, capable of maintaining solution at 70 to 80°C.
9. Beakers, 250-ml
10. Coverglasses, Speedyvap, 3.5-inch diameter..

B. Reagents

Note: All reagents are prepared from C. P. or Analytical Reagent Grade Stock.

1. Cobalt standard solution, 250 µg./ml. Dissolve 250 mg. of high purity cobalt metal in a minimum of perchloric acid. Add an 8-ml. excess of 12M perchloric acid and dilute to 1 liter with distilled water.
2. Sodium acetate solution, 4M. Dissolve 544 grams of sodium acetate trihydrate in distilled water and dilute to 1 liter.
3. Nitroso-R salt, 1% aqueous solution. Dissolve 10 grams of sodium 1-nitroso-2-naphthol-3,6-disulfonate in distilled water. Dilute to 1 liter. The pure reagent is golden yellow in color. A greenish tint indicates the presence of ferrous iron impurity which, in small amounts, can be tolerated. If an aqueous solution of the reagent is dark green in color, the reagent should not be used.
4. Alumina, activated, Woelm anionotropic form or equivalent high purity grade, 50-100 mesh.
5. Hydrogen peroxide, 30% solution.
6. Hydrochloric acid, concentrated.
7. Perchloric acid, 12M and 1M solution by diluting 85 ml. of 12M acid to 1 liter with distilled water.

8. Nitric acid, concentrated and 1M. Prepare the 1M solution by diluting 63 ml. of concentrated acid to 1 liter with distilled water.
9. Sulfuric acid, 1M. Add 56 ml. of concentrated acid slowly to 500 ml. of distilled water. Dilute to 1 liter.
10. Ammonium hydroxide, 1M. Dilute 68 ml. of concentrated reagent to 1 liter with distilled water.

PREPARATION OF AN ACID-ALUMINA COLUMN

Treat the alumina column with 1M perchloric acid until the effluent liquid is distinctly acid, then wash with several portions of distilled water to remove excess acid.

To recharge the column, pass 1M ammonium hydroxide through the column until the effluent is distinctly basic. Wash with distilled water and recharge with perchloric acid as described above. Ignore any yellowish material which is eluted by the base. This contains no cobalt, but is either an impurity in the reagent or is a decomposition product formed during step 3 of the procedure.

PROCEDURE

A. Special instructions for Use of Model B Instrument

1. Turn instrument on at least 1 hour before making first reading.
2. Prevent parallax error by viewing the meter needle at right angles.
3. Set SENSITIVITY multiplier knob on position 1 for all readings. Turn to STAND BY when not in use.
4. (a) Set the wavelength at 500 mμ. approaching from the low wavelength side to prevent backlash error.
(b) At this wavelength, the blue-sensitive phototube, RCA type 935, should be used. The Beckman 12216 filter is not used.
5. (a) Adjust the DARK CURRENT knob to align the meter needle with the SET DK-CUR position before and after every absorbance reading. Correct readings are obtained only when there is no dark current drift.
(b) Adjust the slit width to give absorbance readings of 0.000 on the reagent blank with the red line on the Shutter Control Switch set at the OPEN position.

- (c) After making the above adjustments immediately make readings on cells containing samples.

B. Matching of Cells:

Cells should be matched or correction factors determined to within 0.002 absorbance units. To do this, fill them with the higher calibration standard carried through procedure D and compare in the spectrophotometer at 500 m μ . Rinsing with alcohol followed by acetone rinses is recommended for cleaning of cells.

C. Calibration and Bench Standards

A separate calibration is required for each set of samples. Use 500 λ and 1000 λ of the standard cobalt solution. Process these according to D. Record the absorbance for each of the standards and divide by the concentration to obtain the conversion factor. If the conversion factors do not agree within limits set by the Quality Control Laboratory, process another pair of standards. Contact your supervisor if agreement is still not obtained.

D. Recommended Procedure

Note: The sample aliquot, in all cases, should be selected to contain 50 to 250 μ g. of cobalt.

1. Solid samples

- a. For cast irons and plain carbon steels, dissolve sample in 5 ml. of 12M perchloric acid plus 10 ml. of distilled water. When dissolution is complete, add 1 ml. of concentrated nitric acid and boil the solution several minutes to oxidize all iron. Continue with 2.
- b. Dissolve stainless steels with the minimum amount of hydrochloric acid. Filter off any free carbon and wash the filter with hot 1% perchloric acid solution. Continue with 2.
- c. Dissolve non-ferrous alloys in a minimum amount of 5M nitric acid. Continue with 2.

2. Liquid samples

If large quantities of chloride or nitrate are present, evaporate the entire solution to fumes of perchloric acid in a covered 250-ml. beaker after any free carbon has been filtered off; add 5 ml. of perchloric acid for this purpose. After fuming, dilute the solution with 20 ml. of distilled water, 0.5 ml. of 30% hydrogen peroxide, and boil several

minutes to reduce any dichromate or permanganate ions, as well as to expel excess peroxide.

3. To a suitable aliquot of the sample, add 5 ml. of 1% nitroso-R solution and sufficient 4M sodium acetate solution to adjust the pH between 5.0 and 5.5. Heat the solution to boiling then add 0.5 ml. of 12M perchloric acid for each 1 ml. of sodium acetate solution added previously. Swirl and continue heating the solution, if necessary, to dissolve any precipitate which may form at this point.
4. Pass the sample through a perchloric acid-washed alumina column at a rapid rate, allowing the individual drops of effluent to be barely discerned. The cobalt nitroso-R complex forms a brilliant red band at the top of the alumina column, while immediately below the diffuse yellow band of the excess nitroso-R salt is seen.
5. Wash the column with hot (70°-80°C.) 1M nitric acid until the excess reagent has been completely eluted and the effluent is colorless when viewed against a white background. Care should be taken to avoid too rapid a flow-rate or too hot a solution as this will cause severe bleeding and possible elution of the cobalt complex.
6. Finally, elute the cobalt complex into a 100-ml. volumetric flask with 1M sulfuric acid at the rate of 5 to 10 ml. per minute until the effluent appears colorless. Pass an additional 10-ml. portion of acid through the column. Dilute to volume with distilled water and measure the absorbance at 500 mμ.

CALCULATION

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Total micrograms cobalt in the calibration standards aliquot.
B	Absorbance of the calibration standards.
C	Conversion Factor. $C = \frac{B}{A}, \quad C' = \frac{B'}{A'}$
D	Average conversion factor. $D = \frac{(C + C')}{2}$

CALCULATION (Con't)

<u>Column</u>	<u>Unit to Record</u>
E	Sample size, in ml. or gram.
F	Sample dilution (decimal fraction of total sample taken).
G	Absorbance reading of sample.
H	Micrograms cobalt in sample dilution aliquot (F). $H = \frac{G}{D}$
I	Result, μ g. of cobalt per ml. (liquid sample) or μ g of cobalt per gram (solid sample). $I = \frac{H}{EF}$

Report results to 1% accuracy.

REFERENCES

Dean, J., Anal. Chem. 23, 1096 (1951)

S. F. Marsh
November, 1961

COLORIMETRIC DETERMINATION OF COPPER WITH NEOCUPROINE

ABSTRACT

Neocuproine (2,9-dimethyl-1,10 phenanthroline) reacts specifically with copper⁽¹⁾ to form a bright orange soluble compound, which is extracted into hexone. The absorbance is measured at 454 mμ. The method is specific for copper and no prior separation is required from other cations. The common anions chloride, sulfate, nitrate, perchlorate, tartrate, citrate, and acetate do not interfere.

APPLICABILITY

The method is applicable to any solution of copper. Luke and Campbell found the method to be specific for copper in the presence of 56 different metals. Lead at 400:1 and uranium at 50:1 weight ratio to copper has no effect. The linear range is 10 to 75 μg. of copper.

APPARATUS AND REAGENTS

A. Apparatus

1. Spectrophotometer, Beckman Model B or DU.
2. Absorption cells, corex, 1.000-cm., matched set.
3. Flasks, volumetric, assorted sizes.
4. Pipets, volumetric, assorted sizes.
5. Pipets, micro, assorted sizes, with control syringe.
6. Graduated cylinders, 10-ml.
7. Culture tubes, screw cap with polyethylene liners, 50-ml. The tubes must not leak when shaken with hexone.

B. Reagents

NOTE: All reagents are made from C.P. or Analytical Reagent Grade stock. Distilled water is used throughout.

1. Neocuproine solution. Dissolve 1 gram of 2,9-dimethyl-1,10 phenanthroline (G. F. Smith Chemical Co., Item No. 154) in 1 liter of hexone.
2. Hydroxylammonium chloride solution, 10% w/v. Dissolve 50 grams of hydroxylamine hydrochloride in distilled water and dilute to 500 ml. Transfer to a separatory funnel and add 1 ml. of neocuproine solution. Extract with 50-ml. portions of chloroform until a colorless extract is obtained.
3. Sodium citrate solution, 30%, w/v. Dissolve 150 grams of sodium citrate, dihydrate in water and dilute to 500 ml. Transfer to a separatory funnel and add 2 ml. of hydroxylammonium chloride solution, 1 ml. of neocuproine solution,

B. Reagents (Con't)

Cu-1:2

and extract with 50-ml. portions of chloroform until a clear extract is obtained.

4. Standard copper solution, 100 $\mu\text{g.}/\text{ml.}$ Prepare a 1 mg./ml. stock solution of copper by dissolving exactly 1 gram of pure copper in 50 ml. of 2M nitric acid and diluting to 1 liter. Dilute 1 to 10 with water to obtain the 100 $\mu\text{g.}/\text{ml.}$ copper solution.
5. Sodium Acetate.

PROCEDURE

A. Calibration and Bench Standard

Two calibration standards are processed with each series of samples. Use 250 λ and 500 λ of the standard copper solution containing 25 and 50 $\mu\text{g.}$ of copper respectively. Process these according to the directions given in C below. If the two conversion factors do not agree within limits set by the Quality Control Laboratory, process another pair of standards. Contact your supervisor if agreement is still not obtained.

B. Reagent Blank

Use 10 ml. of water carried through the recommended procedure C, beginning with step 2 as the blank.

C. Recommended Procedure

1. Pipet an aliquot of 10 ml. or less of the sample solution containing between 10 and 75 $\mu\text{g.}$ of copper into a 50-ml. culture tube. Dilute to 10 ml. with water.

NOTE: The use of a separatory funnel is permissible. Shake gently to avoid formation of an emulsion. After extraction into hexone, step 5, drain off most of the lower aqueous layer. Transfer the hexone layer to a clean test tube and centrifuge to clear the organic phase.

2. Add 5 ml. of 10% hydroxylamine hydrochloride solution to reduce the copper to the cuprous state.
3. Add 10 ml. of 10% sodium citrate solution. If the amount of iron in the sample is greater than 0.5 gram, add an additional 10 ml. for each additional 0.5 gram of iron present.
4. Add 1 gram of sodium acetate and adjust the pH to between 5 and 6 using a pH meter.

C. Recommended Procedure (Con't)

Cu-1:3

5. Add exactly 10.0 ml. of hexone by means of a transfer pipet. Screw the cap on tightly and shake for 60 seconds.
6. Centrifuge briefly (low speed) to separate the two layers.
7. By means of an eye dropper transfer the hexone layer to a 1-cm. Corex cell and read the absorbance at 454 mμ. against the reagent blank.

CALCULATIONS

Record the data on the work sheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms of copper in the calibration standards
B	Absorbance of calibration standards
C	Conversion factor $C = B/A$, $C^1 = B^1/A^1$
D	Average conversion factor $D = 1/2 (C + C^1)$
E	Absorbance reading of sample
F	Micrograms of copper in the sample aliquot taken $F = E/D$
G	Sample size, in ml.
H	Result, μg. of Cu per ml. of sample F/G

Report results to 1% accuracy.

REFERENCES

1. Diehl, H., Smith, G. F., "The Copper Reagents: Cuproine, Neocuproine, Bathocuproine," p. 23, The G. Frederick Smith Chemical Company, Columbus, Ohio, 1958.
2. Smith, G. F., McCurdy, W., Anal. Chem. 24, 371 (1952).
3. Luke, C. L., Campbell, Anal. Chem. 25, 1588 (1953).
4. Wade, M., IDO Notebook No. U-454, pp. 40-42 (1961).

March 22, 1961

THE RADIOMETRIC DETERMINATION OF KRYPTON-85

ABSTRACT

A method is described for determining the disintegration rate of krypton-85 in gas sample. It involves sampling a stainless steel bomb or glass collecting tube, dilution of the sample using a special vacuum apparatus, taking a pressure reading on a known volume of gas, and measurement of the beta activity in a beta proportional counter. Conversion of the counting rate to disintegration rate is accomplished with geometry factors obtained from Tl²⁰⁴ calibration.

APPLICABILITY

The following procedure is directly applicable to krypton-85 samples.

APPARATUS AND REAGENTS

A. Apparatus

1. Gas collecting tube, 250-ml.
2. Gas sampling apparatus
3. Gas counting cell
4. RCL Nucleometer proportional counter
5. Special vacuum apparatus
6. Slotted aluminum card, 3-1/4 x 3-1/2 inches

B. Reagents

1. Ethylene, C. P. reagent grade

PROCEDURE

1. Connect the sample bomb, a 250-ml. gas collecting tube, and the gas sampling apparatus (manometer with special sample bomb fittings) in a line in that order.
2. Open both stopcocks of the collecting tube and turn on the vacuum pump. Continue the evacuation until there is no further change in the mercury level on the manometer. Check the system for leaks by turning the vacuum pump off. If the mercury level on the manometer does not change, the system may be considered tight.
3. Introduce sample into the system by carefully opening the valve on the sample bomb. When the manometer indicates approximately an 18-inch change, turn off the valve on the sample bomb and both stopcocks on the collecting tube.

4. Put counting cell, with its stopcock open, in cell filler. Put cover on cell filler and attach to manifold, with filler stopcock to the right ($\vdash$).
5. Attach collecting tube containing the sample to the heavy walled rubber tube on the special vacuum train. Stopcocks 2 and 5 are open, 1, 4 and 7 are closed, 3 is to the right ($\vdash$), and 6 is to the left ($\succ$).
6. Turn on the vacuum pump and slowly open stopcock 1 (to minimize the pressure differential across the counting cell window). If the sample to be analyzed is in a glass tube, purge the plug of the stopcock at the end where the rubber tube is attached, as follows:
 - a. Turn stopcock 3 down ($\top$).
 - b. Momentarily open the stopcock of the sample tube. Then close it. This allows the gas to flow through the plug into the previously evacuated rubber tube.
 - c. Turn stopcock 3 to the right ($\vdash$). Purging the plug is necessary only once, even if the same sample is analyzed more than one time.
7. Pump the entire system down until the sound of the vacuum pump indicates that evacuation is essentially complete (about 1 minute), then close stopcock 5, open 7, and turn 6 down ($\wedge$). Stop the mercury in the center column of the gauge at zero by placing a finger on the capillary extending from 6. Continue pumping on the system until a pressure of not over 0.01 mm. Hg is indicated on the Todd gauge. When this pressure has been attained, close stopcock 1 and lower the mercury in the Todd gauge.
8. Adjust the mercury in the measuring bulb to the desired level, turn stopcock 3 down ($\top$) and momentarily open the stopcock on the sample tube to admit gas to the measuring bulb. Then turn stopcock 3 to the left ($\dashv$), and after a second, close stopcock 2. Measure the pressure of the sample on the Todd gauge, and record the observed reading.
9. Again lower the mercury in the gauge. After about one minute, i.e., when the air has been removed by the pump, close stopcock 7, then open 5. (Caution: Do not reverse this order, or part of the sample will be pumped out).
10. Open stopcock 4 and admit ethylene, controlled by the needle valve on the regulator, until the system has been filled to a pressure of 1 atmosphere, as indicated on the mercury manometer. Close stopcock 4.

11. Condense as much of the gas as possible by immersing the cold finger in liquid nitrogen. Vaporize this by raising a beaker of warm water around this trap. Repeat three more times.
12. Turn filler stopcock down (T), remove from the manifold, remove lid, take out the counting cell and immediately close its stopcock.
13. Place the cell in a slotted aluminum card and count with this card on the fourth shelf of the proportional counter.

CALCULATIONS

Report results as disintegrations per min. per ml. of gas at standard condition.

The brass cells are 1" dia. x 1/2" deep, having a capacity of 3.21 ml. The volume of sample taken may be computed at standard conditions from the general gas law:

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

where: $P_0 = 760$ mm.

$T_0 = 273^\circ\text{K}$

$P_1 =$ pressure observed on Todd gauge, in mm.

$V_1 = 3.21$ ml.

$T_1 =$ room temp. (298°K may be used in all calculations if usual laboratory conditions obtain.)

Solving this for $V_0 = P_1 \times \frac{3.21 \times 273}{760 \times 298}$

$$V_0 = 0.00387 P_1 \text{ ml.}$$

Then, $\text{C/min./ml.} = \frac{\text{Observed C/min.}}{V_0}$

$$\text{d/min./ml.} = \frac{\text{C/min./ml.}}{\text{geometry (0.227)}}$$

REFERENCES

1. Regier, R. B., Anal. Chem. 31, 54 (1959).

I. L. Doggett
October 26, 1961

COLORIMETRIC DETERMINATION OF NIOBIUM

ABSTRACT

A selective method is described for the separation and determination of niobium. The determination is based on the yellow peroxy complex. When necessary, the niobium is separated from interfering ions by extraction as the cupferrate into ethylacetate. The peroxy complex is developed in concentrated sulfuric acid and measured at 360 $m\mu$. A brief discussion of the chemical properties of niobium and its compounds is also included.

APPLICABILITY

This method is applicable to a wide variety of samples including samples originating from the reprocessing of zircaloy-based uranium fuels. ARCO-type samples containing varying levels of the chlorides of cadmium, lead, and zirconium can be analyzed.

In this method, the yellow peroxy niobium complex is formed in 96% sulfuric acid and measured at 360 $m\mu$. Molybdenum, rhenium, titanium, and tungsten interfere by forming peroxy compounds absorbing in the region of niobium (3,5). Interference from molybdenum can be eliminated by separating the niobium as niobic acid from dilute sulfuric acid prior to color development. Interference from cations such as Fe(III) and $UO_2(II)$ which do not react with hydrogen peroxide in strong acid medium but which absorb at 360 $m\mu$ can be corrected by comparing the sample solution against a sample aliquot not treated with peroxide. With this technique, the metals Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Sn, U, Zn, and Zr do not interfere. Metals such as Ba, Pb, and Th which precipitate from strong sulfuric acid also interfere unless separated prior to color development. Niobium can be separated from most di- and trivalent cations but not from cations such as Fe(III), Th(IV), Ti(IV), and Zr(IV) by extraction as the cupferrate (1). In addition, metals of the acid sulfide group can be precipitated with hydrogen sulfide from dilute hydrofluoric acid.

The sample aliquot should contain between 0.2 and 10 mg. of niobium. Lesser amounts can be determined by working with smaller volumes.

DISCUSSION

- A. Chemical Behavior of Niobium and Niobium Compounds. Metallic niobium is dissolved by nitric-sulfuric or nitric-hydrofluoric acid mixtures. Neither nitric acid nor hydrochloric acid has any effect with short periods of contact. Refractory oxides are best dissolved by fusion with potassium pyrosulfate. The melt is subsequently dissolved in sulfuric acid or in an aqueous solution of a suitable complexing agent such as oxalate or fluoride. Non-refractory oxides, oxysalts and simple salts dissolve readily in hydrofluoric acid or hot sulfuric acid. Nitric, perchloric, and hydrochloric acids are generally unsatisfactory because of the tendency of niobium to polymerize and to precipitate as niobic acid when a complexing anion is not present. Solutions of niobium(V)

are best stabilized by complexing with fluoride or oxalate. Fluoride is easily removed by fuming with sulfuric acid. Anhydrous niobium salts are extremely hygroscopic and must be handled in dry boxes and protected from moisture during storage and weighing. Niobium pentachloride, for example, is rapidly converted to the oxide when exposed to moist air. However, niobium trichloride is not hygroscopic.

Niobium is best separated as the cupferrate (1), as the thiocyanate complex (5), and as niobic acid (4). The precipitation of niobic acid is slow, and often incomplete after strong fuming with perchloric acid. Complex mixtures containing Mo, Nb, Ti, and W are best separated by anion exchange chromatography (2).

B. Analysis of ARCO-type Samples

Composition of ARCO-type Samples. The compositions of the various types of niobium samples originating from ARCO studies pertaining to the molten lead chloride dissolution of niobium are given in Table I.

TABLE I. Composition of ARCO-type Niobium Samples

<u>Type of Dissolution</u>	<u>Vapor Phase (Sublimate)</u>	<u>Melt Phase</u>
1. Molten PbCl_2	NbCl_x (high)	PbCl_2 (high)
	PbCl_2 (low)	Pb (high)
		Nb (unreacted coupon)
		Nb (sand)
		NbCl_x (low)
2. Molten PbCl_2 with Cl_2 purge	NbCl_x (high)	PbCl_2 (high)
	PbCl_2 (low)	NbCl_x (low)
		Nb (unreacted coupon)

Analysis of Samples

- A. Vapor Phase from Dissolution Types 1 and 2. Dissolve in dilute hydrofluoric acid and precipitate the lead with hydrogen sulfide. Separate the lead sulfide on a millipore filter paper. Take an aliquot of the filtrate to fumes of sulfuric acid and determine the niobium as the peroxy complex. Transfer the filter

paper and residue to a 150-ml. beaker. Boil first with concentrated hydrochloric acid to expel hydrogen sulfide then with nitric acid. Determine the lead complexometrically by adding a measured excess of EDTA and back titrating with manganese(II) to an Eriochrome Black T end point.

- B. Melt Phase from Dissolution Type 1. Remove the unreacted niobium coupon manually, clean, and weigh. Dissolve successively, lead chloride, lead metal, and niobium metal with respectively, 0.01M nitric acid, concentrated nitric acid, and nitric-sulfuric acid mixture. Isolate the desired fractions by filtrations. Complex the niobium with hydrofluoric acid prior to dilution with water. Determine the lead and niobium as described under A. The NbCl_x compound is converted to precipitates during the dilute nitric acid treatment and accompanies the metallic niobium fractions.
- C. Melt Phase from Dissolution Type 2. Remove the unreacted niobium coupon, clean, and weigh. Dissolve the lead chloride in 0.01M nitric acid. Filter. Digest the filter paper and niobium residue with nitric and sulfuric acids. Determine each constituent as described under A.

APPARATUS AND REAGENTS

A. Apparatus

1. Spectrophotometer, Beckman, Model B or DU.
2. Absorption cells, Corex, 1-cm., matched set of 4.
3. Flasks volumetric, assorted sizes.
4. Beakers, assorted sizes.
5. Separatory funnels, 125-ml. capacity.
6. Pipets, volumetric, assorted sizes.
7. Pipets, micro, assorted sizes.
8. Hot plate.
9. Millipore filtration apparatus, 47-mm. diameter.

B. Reagents

NOTE: All reagents are made from C.P. or Analytical Reagent Grade stock. Distilled water is used throughout.

1. Niobium standard solution, 10 mg. Nb per ml. Dissolve about 5 grams (weighed accurately to ± 0.1 mg.) of niobium in a 400-ml. beaker with 50 ml. of concentrated sulfuric acid and sufficient concentrated nitric acid added 2 ml. at a time. Evaporate to fumes of sulfuric acid, cool, and dilute to 500 ml. with concentrated sulfuric acid.
2. Hydrofluoric acid, 5M. Dilute 20 ml. of 48% hydrofluoric acid to 100 ml. with water.

3. Hydrogen peroxide, 30%.
4. Sulfuric acid.
5. Nitric acid.
6. Perchloric acid.
7. Cupferron, 0.2M. Prepare fresh as needed by dissolving 3.1 grams of cupferron in 100 ml. of water.
8. Ethylacetate.
9. Ammonium tartrate, 10% w/v.

PROCEDURE

- A. Calibration and Bench Standard. A separate calibration is required for each series of samples. Use 400- and 800- λ portions of the niobium standard and process these with the sample by the same procedure used for the sample. Calculate the conversion factor by dividing the absorbance for each of the standards by the concentration. If the two conversion factors do not agree within limits specified by the Quality Control Laboratory, process another pair of standards. Contact your supervisor if agreement is still not obtained.
- B. Blank. All samples are compared against a sample blank. The sample blank is prepared by taking a portion of the sample (equal to the test portion) through the entire procedure omitting the addition of hydrogen peroxide.
- C. Preliminary Treatment of Samples. No detailed comprehensive description of the many possible preliminary approaches is feasible because the choice of the preliminary manipulations depends on the nature of the sample, i.e., the concentration of niobium and the foreign ion content. Read the APPLICABILITY and DISCUSSION sections and consult your supervisor for specific details for sample pretreatment. The following approaches are presented as general guides.
 1. Aqueous samples. In general aqueous solutions of niobium will contain ions such as fluoride or oxalate which are necessary to stabilize the solutions. In the absence of ions which yield interfering peroxy complexes or which precipitate in strong sulfuric acid, heat an aliquot of the sample with a mixture of sulfuric and perchloric acids to fumes of sulfuric acid. Continue with the color development according to D beginning with step 2.
 2. Solid samples. Dissolve in hot concentrated sulfuric acid or molten potassium pyrosulfate. Dissolve the pyrosulfate

melt in sulfuric acid. When the entire sample is to be used for color development and interfering metal ions are absent, continue according to D beginning with step 2. When it is necessary to work with an aliquot of the sample, complex the niobium with fluoride and dilute to volume with water. Treat an aliquot of this sample dilution according to C-1 or C-3.

3. Separation of niobium from cations such as Al(III), Cd(II), Co(II), Cr(III), Cu(II), Hg(II), Mn(II), Ni(II), U(VI), and Zr(II) which may precipitate in 96% sulfuric acid, particularly when present in large amounts. Add 4 ml. of 0.2M cupferron to an aliquot of the sample containing between 0.2 and 10 mg. of niobium. Add 10 ml. of 10% ammonium tartrate and adjust to about 1.5 to 2M in sulfuric acid or 1M in hydrochloric acid. Extract with 30 ml. of ethylacetate for 1 minute. Discard the aqueous phase. Evaporate the ethylacetate layer containing the niobium to near dryness, then digest the sample with 5 ml. of concentrated nitric, 2 ml. of concentrated perchloric, and 5 ml. of concentrated sulfuric acids to sulfuric acid fumes. Continue according to D beginning with step 2. Extraction of niobium is incomplete when the fluoride to niobium molar ratio exceeds 5 to 1. Fume the sample with sulfuric acid to expel fluoride.

D. Recommended Color Development Procedure

1. Pretreat the sample according to C.

NOTE: The resulting sample solution should be a solution of niobium in concentrated sulfuric acid which is free of perchloric acid.

2. Transfer the sample quantitatively to a 100-ml. volumetric flask using concentrated sulfuric acid for the transfer.
3. Add 0.5 ml. of 30% hydrogen peroxide and dilute to volume with sulfuric acid. Mix well by repeated inversion.
4. After 10 minutes, measure the absorbance in 1-cm. cells at 360 mμ against a sample blank solution.

NOTE: Rinse the cells with water and acetone and air dry between different samples.

CALCULATIONS

Record the data on the work sheet as follows:

CALCULATIONS (Continued)

<u>Column</u>	<u>Unit to Record</u>
A	Milligrams niobium in the calibration standard aliquot.
B	Absorbance of the calibration standards.
C	Conversion Factor. $C = \frac{B}{A}, \quad C^1 = \frac{B^1}{A^1}$
D	Average conversion factor. $C = \frac{C + C^1}{2}$
E	Sample size in grams or in ml.
F	Sample dilution in ml.
G	Sample dilution aliquot taken for analysis, in ml.
H	Absorbance reading of sample.
I	Result, milligrams of niobium per ml. or per gram of sample. $I = \frac{FH}{DEG}$ <p>or if the entire sample was used for color development</p> $I = \frac{H}{DE}$

Report results to three significant figures as 606, 60.6, 6.06, and 0.606 mg. Nb/ml.

REFERENCES

1. Furman, N. H., Mason, W. B., Pekola, J. S., Anal. Chem. 21, 1325 (1949).

REFERENCES (Continued)

2. Hague, J. L., Brown, E. D., Bright, H. A., J. Research Natl. Bur. Standards 53, 2542 (1959).
3. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., Hoffman, J. I., "Applied Inorganic Analysis", 2nd ed., pp. 588-610, John Wiley, New York, 1953.
4. Puphal, K. W., IDO-notebook No. U-213, 1957.
5. Sandell, E. B., "Colorimetric Determination of Traces of Metals", Vol. III, 3rd ed., pp. 683-698, Interscience Publishers, New York, 1959.
6. Yamamura, S. S., IDO-Notebook No. U-256, pp. 169-181, 1961.

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COLORIMETRIC DETERMINATION OF TIN

ABSTRACT

A sensitive colorimetric procedure is described for the determination of tin (IV) with pyrocatechol violet. The blue 1:2 tin (IV)-pyrocatechol violet complex is developed in a medium buffered at $\text{pH } 2.75 \pm 0.25$ with monochloroacetic acid. Gelatin is used as a dispersing agent. The absorbance is measured at 638 m μ . Interference from most metal ions is avoided by a preliminary distillation as tin tetrabromide. Sensitivity is increased by a lanthanum hydroxide carrier precipitation prior to color development. The reliability over the range, 15 to 100 $\mu\text{g.}$ of tin, is $\pm 2.0\%$ relative standard deviation.

APPLICABILITY

The sample taken for analysis should contain between 15 and 100 $\mu\text{g.}$ of tin.

Most metals with the exception of arsenic, germanium, antimony, selenium, tellurium, and molybdenum are separated during distillation. Of the metals which distill, germanium, antimony, and selenium interfere seriously. Volatile anions which strongly complex tin, such as fluoride, citrate, tartrate, oxalate, and thiosulfate interfere by bleaching the tin (IV)-pyrocatechol violet complex. Large amounts of nitrate should be avoided. Both nitric and fluoride are removed prior to distillation by evaporating to sulfuric acid fumes in the presence of phosphoric acid.

Because of a negative intercept value on the absorbance axis, a reference curve or regression equation must be used rather than processing calibration standards with each set of sample.

APPARATUS AND REAGENTS

A. Apparatus

1. Spectrophotometer, Beckman, Model B, or DU
2. Absorption cells, Corex, matched set of 3
3. Arsenic distillation flask with water cooled condenser (Figure 1).
4. Beakers, 100 and 150-ml.
5. Flasks, volumetric, 50-ml.
6. Pipets, volumetric, assorted sizes
7. Pipets, micro, assorted sizes, with control syringe
8. Clinical centrifuge
9. Glass centrifuge tubes, 50-ml.
10. Bunsen burner
11. Magnetic stirrer and stirring bars

B. Reagents

Note: All reagents are made from C. P. or Analytical Reagent Grade chemicals and distilled water.

1. Standard tin solution, 100 ug. of tin per ml. Dissolve 0.1000 gram of spectrographically pure tin metal in 300 ml. of concentrated hydrochloric acid and dilute to 1 liter with water.
2. Pyrocatechol violet solution, 0.05% w/v. Dissolve 0.50 - 0.01 gram of the reagent (obtainable from J. T. Baker Chemical Co.) in water and dilute to 1 liter. This solution is stable for 2 months.
3. Gelatin solution, 0.5%. Suspend 0.25 gram of gelatin in 15 ml. of water and add 30 ml. of boiling water. Dissolve by swirling and dilute to 50 ml. with water. This solution should be prepared fresh daily.
4. Hydroxylamine hydrochloride, 1M. Dissolve 69.5 grams of hydroxylamine hydrochloride in water and dilute to 1 liter with water.
5. Monochloroacetic acid solution, 2M. Dissolve 189 grams of monochloroacetic acid in water and dilute to 1 liter with water.
6. Lanthanum nitrate solution, 25 mg. of lanthanum per ml. Dissolve 39 grams of lanthanum nitrate hexahydrate in water. Add 2 drops of concentrated nitric acid and dilute to 500 ml. with water.
7. Hydrochloric-hydrobromic acid mixture. Mix 3 volumes of concentrated hydrochloric acid and 1 volume of concentrated hydrobromic acid.
8. Ammonium hydroxide.

PROCEDURE

A. Special Instructions for Use of Instrument

1. Turn instrument on at least 1 hour before making first reading.
2. Prevent parallax error by viewing the meter needle at right angles.
3. Set SENSITIVITY multiplier knob on position 1 for all readings. Turn to STAND BY when not in use.
4. (a) Set the wave length at 638 mμ. approaching from the low wave length side to prevent backlash error.
5. (a) Adjust the DARK CURRENT knob to align the meter needle with the SET DK-CUR position before and after every absorbance reading. Correct readings are obtained only when there is no dark current drift.
- (b) Adjust slit width to give absorbance readings of 0.000 on the reagent blank with the red line on the Shutter Control Switch set at the OPEN position.
- (c) After making the above adjustments immediately make readings on cells containing samples.

B. Cell Matching

1. Fill four clean cells with a processed bench standard and place in the spectrophotometer set at 638 mμ.

2. Designate the cell with the lowest absorbance reading as the reference cell.
3. Adjust the instrument to 0.000 absorbance reading with the reference cell in position.
4. Determine the absorbance for each of the other three cells.
5. A correction for the cells is applied when this value is equal to or greater than 1% of the absorbance value of the sample.
6. Redetermine these correction factors each time samples are run.
7. Be sure that cells of the same path length, within 0.005 cm., are used.
8. Because the pyrocatechol violet - tin chelate plates out on the cells it is necessary to rinse once with 6M hydrochloric acid and three times with distilled water between readings.

C. Blank

Run a blank in the same manner as the samples, substituting water for sample.

D. Calibration

1. Distill 0.15, 0.25, 0.50, 0.75, and 1.0 ml. portions of the 100 µg./ml. tin standard into five 150-ml. beakers according to procedure F.
2. Precipitate according to procedure G.
3. Develop color according to procedure H.
4. Submit the resultant data in at least duplicates to the Quality Control Laboratory for preparation of the calibration equation and necessary control data.

E. Bench Standard

Run a single determination on the provided bench standard according to F, G, and H. Limits will be specified by the Quality Control Laboratory.

F. Distillation Procedure

1. Immerse the tip of the condenser into a 150-ml. beaker containing 25 ml. of distilled water. Immerse the beaker in an ice bath.
2. Transfer the sample containing between 15 and 100 µg. of tin into the distillation flask through A shown on Figure 1. Connect the reservoir assembly to the distillation flask.

Note: If samples contain nitrate and/or fluoride, pipet the sample into a 100-ml. quartz beaker or platinum dish.

Add 5 ml. of 85% phosphoric acid and 5 ml. of concentrated sulfuric acid and evaporate to fumes of sulfuric acid. Transfer to the distillation flask using 20 ml. of concentrated sulfuric acid. Continue with step 3 omitting step 4.

3. Adjust the air flow to about 2 bubbles per second and start cooling water through the condenser.
4. Introduce 25 ml. of concentrated sulfuric acid to the reservoir. Drain the sulfuric acid slowly into the distilling flask.
5. Introduce 25 ml. of the 3:1 HCl-HBr mixture to the reservoir and drain 5 ml. into the distilling flask.
6. Heat rapidly to 200°C. Admit the HCl-HBr mixture over a period of 25 minutes maintaining the temperature at 200 to 220°C.
7. Rinse the condenser and condenser tip with water adding it to the distillate.

G. Precipitation Procedure

1. Add 1 ml. of the lanthanum solution to the condensate in a 150-ml. beaker.
2. Precipitate by adding concentrated ammonium hydroxide while stirring. (Approximately 27 ml. of ammonium hydroxide.)
3. Place a cover glass on the beakers and digest on a hot plate at low heat for 10 minutes, maintaining the pH between 7.0 and 8.0. (pH paper)
4. Cool. Transfer portions to a centrifuge tube, centrifuge and carefully decant the supernatant solution each time until the entire volume in the beaker has been centrifuged.
5. Dissolve the precipitate with 2 ml. of the HCl-HBr mixture.

H. Color Development

1. Add 3 ml. of 1M hydroxylamine hydrochloride solution and 1 ml. of 0.5% gelatin solution.
2. Pipet 3.0 ml. of 0.5% pyrocatechol violet solution and place on a magnetic stirrer.
3. Add 3 ml. of 2M monochloroacetic acid buffer solution, dilute to approximately 35 ml. with water, and adjust to pH 2.75 - 0.25 with ammonium hydroxide.
4. Transfer quantitatively to a 50-ml. volumetric flask, and dilute to 50-ml. with distilled water. Mix well.
5. After 5 minutes, transfer to a clean absorption cell, and read the absorbance against the blank at 638 mμ.

CALCULATION

Record the data on the worksheet as follows:

Column
A

Volume of sample, in ml.

Column

- B. Absorbance of sample after cell correction
- $C = \frac{B-b}{Aa}$, from the equation of the straight line
- $y = ax + b$ where y = absorbance of sample x =
microgram tin in sample
- a = slope
- b = y intercept
- C. Result, micrograms tin per ml. of sample
- Report the results to 2% accuracy

REFERENCES

1. Smith, G. F., Mixed Perchloric, Sulphuric, and Phosphoric Acids and their Application in Analysis, 2nd Ed., G. Frederick Smith Chemical Company, Columbus, Ohio, 1942.

R. E. Foster
October 25, 1961

W-1:1

SEPARATION AND GRAVIMETRIC DETERMINATION OF TUNGSTEN
IN TUNGSTEN-ALUMINUM ALLOYS

ABSTRACT

A gravimetric method is described for the determination of tungsten in tungsten-aluminum alloys. The tungsten is precipitated as tungstic acid from a strong hydrochloric acid medium with the aid of cinchonine. Because of aluminum contamination, the crude tungstic acid is redissolved in sodium hydroxide and reprecipitated before ignition to the oxide. This separation scheme on a larger scale can be used to recover natural or enriched tungsten in aluminum.

APPLICABILITY

This method was developed specifically for the separation and determination of tungsten in tungsten-aluminum alloys containing negligible amounts of other acid-insoluble elements such as niobium, silicon, and tin. For best results, samples taken for analysis should contain greater than 50 mg. of tungsten equivalent to 63 mg. of tungstic oxide.

APPARATUS AND REAGENTS

A. Apparatus

1. Balance
2. Beakers, assorted sizes
3. Crucibles, platinum, 15- or 30-ml.
4. Evaporating dishes, platinum, 100-ml.
5. Millipore filter apparatus, 47-mm. diameter, and 0.45 μ filter paper.

B. Reagents

1. Cinchonine solution. Dissolve 62.5 grams of cinchonine in 500 ml. of 50% ($\frac{V}{V}$) hydrochloric acid.
2. Cinchonine wash solution. Add 30 ml. of concentrated hydrochloric acid to 25 ml. of the cinchonine solution and dilute to 1 liter with water.
3. Hydrochloric acid, concentrated and 9M.
4. Nitric acid, concentrated.
5. Sodium hydroxide, 1M. Dissolve 40 grams of sodium hydroxide in water and dilute to 1 liter.
6. Sodium carbonate, anhydrous.
7. Sodium nitrate, anhydrous.

PROCEDURE

A. Recovery of Normal or Enriched Tungsten

NOTE: This procedure is used to recover enriched tungsten isotopes which have been alloyed with aluminum. Because of the high cost of producing these isotopes, quantitative recovery of the tungsten is desirable. Whenever possible, guard against sample loss through unexpected bumping or foaming by placing the sample container in a larger container. Check all filtrates for completeness of precipitation before discarding.

1. Dissolve the sample in 9M hydrochloric acid. If the sample is large, control the rate of reaction by adding the hydrochloric acid a little at a time or by adding the sample in small portions.
2. Filter through a 0.45 μ Millipore filter paper.
3. Treatment of residue.
 - a. Transfer the filter paper and residue to a 400-ml. beaker and add 5 ml. of concentrated nitric acid. Heat to destroy the filter paper then carefully add 10 ml. of concentrated hydrochloric acid. Cover with a solid watch glass and digest slowly to dissolve the residue and convert the tungsten to yellow tungstic acid. Use more aqua regia if necessary.
 - b. Combine the tungstic acid precipitate and the supernatant solution with the filtrate from step 2.
4. Transfer the filtrate from step 2 to a beaker large enough to hold also the tungstic acid precipitate and supernatant solution from step 3. Add 10 ml. of concentrated nitric acid and digest for 1 hour on a steam bath or hot plate set at low.
5. Add cinchonine reagent and digest for 2 hours or if possible over night.

NOTE: The volume of cinchonine reagent added depends on the sample size and the amount of tungsten present. For small samples, 5 ml. of the reagent is sufficient; but for samples greater than 50 grams, use 25 ml. of the reagent.

6. Filter through a 0.45 μ filter paper. It may be necessary to use several filter papers and filter a portion at a time to expedite filtration and washing. Use the cinchonine wash solution for the transfer. Add 5 ml. of cinchonine solution

to the filtrate and digest further to check for completeness of precipitation. Discard when additional precipitation is not observed.

7. Dissolve the tungstic acid precipitate on the filter paper and on the walls of the filter funnel with 1M sodium hydroxide. The residual cinchonine will precipitate as a white flocculant material.
8. Dilute slightly with water and filter through a 0.45 μ filter paper. Wash the residue thoroughly with water.
9. Treatment of the residue.

Discard the residue if it appears white or nearly so. If the residue appears dark, ignite the filter paper and residue in a zirconium crucible. Cool. Add 10 pellets of sodium hydroxide and 0.5 grams of sodium nitrate and fuse. Dissolve the melt in warm water and filter.

10. Transfer the combined filtrates of steps 8 and 9 quantitatively to a beaker containing 25 ml. of concentrated hydrochloric acid and 25 ml. of water. Add sufficient cinchonine reagent and digest for several hours.
11. Filter the precipitate on a 0.45 μ filter paper.
12. Transfer the precipitate and filter paper to a platinum crucible or dish. Use portions of a Whatman No. 41 ashless filter paper to wipe off the tungstic acid adhering to the walls of the filter funnel.
13. Char carefully, then ignite to the oxide in a muffle furnace set at 800° C.

B. Gravimetric Determination of Tungsten

1. Weigh a sample containing between 50 and 500 mg. of tungsten into a suitable beaker.
2. Separate the tungsten and convert to the oxide as described under A. Use a tared platinum crucible for the ignition.
3. Obtain the weight of the crucible plus tungstic oxide and determine the weight of the oxide by difference.

CALCULATIONS

Record the data on the work sheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Weight of sample in grams
B	Crucible weight in grams
C	Weight of crucible plus tungstic oxide in grams.
D	Weight of tungstic oxide in grams
	$D = C - B$
E	Result in weight per cent
	$E = \frac{(100)(0.793)(D)}{A} = 79.3 \frac{D}{A}$

Report results to three significant figures as 10.1 and 1.01%.

REFERENCES

1. Hillebrand, W. F., Lundell, G. E. F., Bright, M. S., Hoffman, J. I., "Applied Inorganic Analysis", Wiley, New York, 1953.
2. Yamamura, S. S., IDO-Notebooks U-256 pp. 153-162, and U-455, pp. 107-120.

THE COULOMETRIC DETERMINATION OF URANIUM

ABSTRACT

A method is described for the determination of total uranium in solutions by controlled-potential coulometry. A clean-up extraction and fusion is employed to remove interfering ions when they are present.

APPLICABILITY

This method is applicable to samples containing from 1 to 6 mg. of uranium. The clean-up extraction and fusion will remove known interferences from solutions containing fission products and fuel element cladding materials. For information concerning this extraction procedure see U-Sep-1.

APPARATUS AND REAGENTS

A. Apparatus

1. Multipurpose coulometer
2. Gas scrubbing apparatus
3. Coulometer cell apparatus
4. Coulometer cells
5. Pipets, macro, assorted sizes.
6. Pipets, micro, assorted sizes, with control syringes.
7. Meker burner
8. Hot air evaporator

B. Reagents

Note: All reagents are made from C. P. or Analytical Reagent Grade Stock.

1. Sulfuric acid solution, 1N
2. Salting solution, $2N^b$ - $2.8M$ $Al(NO_3)_3$ - $0.025M$ TPAN, pre-treated for removal of trace uranium by extraction with hexone. (TPAN must then be readded.)
3. Hexone, equilibrated with distilled water.
4. Potassium pyrosulfate
5. Uranium standard solutions, to be furnished by the Quality Control Laboratory
6. Mercury metal, freshly distilled

CALIBRATION STANDARDS

Each cell must be individually calibrated. A minimum of 4 standard NBS normal uranium samples, 2 at a level of 2.5 mg./gram and 2 at a level of 5 mg./gram, is recommended. Also 2 blanks are required. These standards must be carried through the entire procedure starting with the extraction. The pipets used for all the reagents for these standards are the same as used for samples. The calibration units are in volts per mg. of uranium (normal) corrected for blank.

Every fifth sample analyzed should be a control sample submitted by the Quality Control Laboratory. The results will be plotted as a percent difference of "reported-known" and will serve in lieu of bench standards.

PROCEDURE

Notes:

1. Use the same pipets for all reagent additions (and for uranium if a volume aliquot is delivered) as used for the calibration standards.
 2. A blank is to be run with every other control. Substitute 1 ml. of distilled water for the sample.
1. Weigh or pipet a sample containing from 1 to 6 mg. of uranium into a 15x125 mm. test tube. The volume of this sample should not be greater than 1.0 ml. If the volume is less than 1.0 ml. it should be made up to 1.0 ± 0.1 ml. with distilled water.
 2. Add 8.0 ml. of salting solution.
 3. Add 4.0 ml. of hexone.
 4. Mix by repeatedly inverting the test tube or in the rotating mixer for 5 minutes. Use a polyethylene stopper.
 5. Allow the phases to separate for 5 minutes or centrifuge. Whichever is used, do the same for standards and samples.
 6. Pipet 3.0 ml. of the organic phase to a coulometer cell.
 7. Evaporate the organic phase to dryness using a hot air jet.
 8. Add 0.5 ± 0.005 gram of potassium pyrosulfate to the coulometer cell.
 9. Heat over a burner until the uranium dissolves into the melt and SO_3 fumes are copiously emitted.
 10. Cool to room temperature.
 11. Add 5.0 ml. of 1N sulfuric acid to the coulometer cell.
 12. Gently heat over the burner until the sulfate melt is dissolved.
 13. Cool to room temperature.
 14. Add the specified volume of freshly distilled mercury to the cell.
 15. Position the coulometer cell in the cell holder.
 16. Deaerate the sample for 15 minutes.
 17. Reduce the sample at -0.296 volt for 15 minutes.
 18. Make a background correction for 3 minutes.
 19. Record the readout voltage.

CALCULATIONS

A. Standardization

$$F = \frac{(A-B)}{(0.75)(C)(D)}$$

A = readout voltage result D = mg. of uranium per
 B = blank readout voltage gram of uranium standard
 C = Grams of uranium standard F = volts per mg. of uranium

B. Samples

1. Record on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Readout voltage of sample
B	Blank readout voltage
C	Weight of sample in grams or volume in ml.
D	Volts per mg. of uranium (standardization)
E	Sample average atomic weight
F	Standard average atomic weight
G	Result in mg. U per gram or mg. U per ml. of sample.

2. Calculate concentration of uranium by:

$$G = \frac{(A-B)(E)}{(0.75)(C)(D)(F)}$$

F = 238.04 for normal uranium

3. Report results to three decimal places.

REFERENCES

1. Booman, G. L., Holbrook, W. B., Rein, J. E., "Coulometric Determination of Uranium (VI) at Controlled Potential", Anal. Chem. 29, 219 (1957).
2. Booman, G. L., Holbrook, W. B., "Extraction Controlled-Potential Coulometric Method Specific for Uranium (VI)", Anal. Chem. 31, 10 (1959).
3. Holbrook, W. B., IDO Notebook No. 47, 1956.
4. Holbrook, W. B., IDO Notebook No. 203, 1957.

May 22, 1961

EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM

ABSTRACT

A sensitive method is described for the determination of zirconium with pyrocatechol violet (PCV). Zirconium is first separated from interfering cations by complexing with thenoyltrifluoroacetone (TTA) and extracting from a 6 M HCl-H₂O₂ solution into xylene. Following acid-peroxide digestion of the organic phase, zirconium is determined spectrophotometrically by measuring the absorbance of the blue Zr-PCV complex. Absorbance readings are made in an acetate media buffered at pH 5.2. The wave length of maximum absorbance is 650 mu.

APPLICABILITY

The method is applicable to the analysis of zirconium solution containing the following metals at a 100 to 1 molar ratio to zirconium: Al, Bi, Cd, Co, Cr, Cu, Fe, Hg, La, Mn, Mo, Ni, Pb, Sn, Th, Y. Niobium, titanium, and tungsten at 10 to 1 and scandium at 1 to 1 molar ratios are also tolerated by the method. Other metals are not expected to cause any interference.

The sample aliquot taken for analysis must not contain more than 1 mmole of sulfate. Phosphate, which complexes zirconium, interferes. The common anions, nitrate, chloride, and perchlorate, do not interfere. Fluoride, and organic complexing ions such as citrate, are removed during the perchloric acid fuming step.

DISCUSSION

The blue Zr-PCV complex is very sensitive but is not specific for zirconium. Specificity of the method is obtained through the TTA-xylene extraction. Because of the high sensitivity and the low specificity of the PCV complex, great care must be exercised to prevent contamination of the samples after the TTA-xylene extraction. It is recommended that special glassware be reserved for this procedure and that it be acid washed before each analysis.

Hydrochloric acid is used in the extraction procedure to minimize the extraction of Fe(III) into the organic phase. A small amount of Fe(III) distributes into the xylene phase even in the presence of high chloride system. This residual iron interference is effectively masked by adding mercaptoacetic acid to the sample just prior to color development. In the presence of mercaptoacetic acid the blue Zr-PCV complex is unstable and must be read between 30 and 60 minutes after color development.

In water or weak acid solutions, zirconium has a tendency to form polymers that do not extract in the TTA-xylene system. It is necessary to break up these polymers by the addition of hydrofluoric acid to the samples. The hydrofluoric acid is then removed by fuming with perchloric acid.

The low tolerance to titanium, niobium and tungsten is attributed to their insolubility in perchloric and hydrochloric acids. These metals, if present in greater than 10 to 1 molar ratio to zirconium, cause low recovery of zirconium.

REAGENTS AND APPARATUS

A. REAGENTS

Note: All reagents are C.P. or Analytical Grade Stock. Use distilled water for preparation of all reagents and throughout the procedure.

1. Standard zirconium stock solution, 1 mg./ml. Dissolve 0.5 ± 0.0001 gram of pure zirconium in 10 ml. of concentrated hydrofluoric acid using a platinum dish. Add 30 ml. of concentrated sulfuric acid and heat to strong fumes until all the hydrofluoric acid is removed. Dilute to volume in a 500-ml. volumetric flask with water. The resulting solution should be about 1 M in sulfate.
2. Zirconium bench standard, 200 $\mu\text{g.}/\text{ml.}$ Pipet 100.0 ml. of the stock standard zirconium solution into a 500-ml. volumetric flask. Add 20 ml. of concentrated sulfuric acid and dilute to volume with water. The resulting solution should be about 0.90 M in sulfate.
3. Pyrocatechol violet (PCV), 0.05%. Dissolve 0.5 ± 0.01 gram of PCV in 1 liter of water.
4. Acetic acid, concentrated.
5. Phenol
6. Gelatin, Knox unflavored, U. S. P.
7. Composite Color Reagent. To a 1-liter flask, add 200 ml. of the PCV solution and about 300 ml. of water. Add 60 ml. of acetic acid followed by 1.6 grams of gelatine dissolved in about 200 ml. of water. Add 3.2 grams of phenol dissolved in about 100 ml. of water, mix, and dilute to volume. This reagent is stable for at least 2 weeks.
8. Mercaptoacetic Acid, 80%.
9. Hydrogen peroxide, 30%.
10. Sulfuric acid, concentrated.
11. Hydrochloric acid, concentrated.

12. Thenoyltrifluoroacetone (TTA)-xylene solution, 0.5M.
Dissolve 111 grams of TTA in xylene and dilute to 1 liter.
Store in a glass-stoppered bottle.
13. Hydrofluoric acid, 1 M.
14. Perchloric acid, concentrated.

B. APPARATUS

1. Beckman Model DU or Beckman Model B spectrophotometer.
2. Matched corex cells, 1 cm.
3. pH meter and electrodes.
4. Pipets, macro, assorted sizes.
5. Pipets, micro, assorted sizes.
6. Beakers, Griffen, assorted sizes.
7. Volumetric flasks, 50-ml.
8. Screw cap test tube, 30 ml.; caps to have teflon liners.
Mark at the 10 ml. level.
9. "Wheel of Fortune" extraction apparatus.
10. Centrifuge tubes, 50-ml.

PROCEDURE

A. MATCHING OF CELLS

Cells should be matched or correction factors determined to within 0.002 absorbance unit. To do this, fill them with the higher calibration standard carried through procedure E and compare in the spectrophotometer at 650 mμ.

B. CALIBRATION

Prepare a calibration curve by taking 0, 0.2, 0.4, 0.6, 0.8, and 1.0- ml. aliquots of the bench standard, corresponding to 40, 80, 120, 160, and 200 μg of zirconium, through procedure E starting with step 2. The above values of zirconium must be divided by 2 before calculating the regression equation because only one-half of the organic phase is taken for analysis. Submit this data to the Quality Control Laboratory for calculation of the regression equation and necessary control data.

A new calibration curve should be prepared for each new batch of composite reagent.

C. BENCH STANDARD

Run a single determination on 0.5 ml. of the bench standard according to procedure E starting with step 2. Limits will be specified by the Quality Control Laboratory.

D. BLANK

A blank is prepared by going through procedure E starting with step 2.

E. SAMPLES

1. Pipet an aliquot of the sample containing 20 to 200 μ g. of zirconium into a platinum dish. Add 10 drops of 1 M hydrofluoric acid and 4 ml. of concentrated perchloric acid. Heat to strong fumes of perchloric acid to remove the fluoride. Fume to a volume of about 1 ml. A precipitate may form but will dissolve during step 2.

(Note: If the sample contains organic matter, nitric acid must also be used to prevent an explosion. Contact your supervisor if you suspect the presence of organic material.)

2. Transfer the sample to a screw cap test tube. Rinse with 5 ml. of concentrated hydrochloric acid followed by water and dilute to the 10-ml. mark. (The sample is now 6 M HCl.)
3. Add 4 drops of 30% hydrogen peroxide.
4. Pipet exactly 10.0 ml. of TTA-xylene solution into the sample. Fasten screw cap securely and extract on the "wheel of fortune" for 30 minutes.
5. Transfer exactly 5.0 ml. of the organic phase to a 50-ml. centrifuge tube and evaporate on an oscillating hot plate at medium heat. Rate of evaporation can be increased by drawing air over the samples with the vacuum line. All traces of xylene must be removed before proceeding.
6. Add 5 drops (0.25 ml.) of concentrated sulfuric acid and allow to cool.
7. Add 2 to 4 drops of hydrogen peroxide and heat over a flame. Heat slowly at first until the foaming stops, then increase the rate of heating until all the peroxide is removed and strong fumes of sulfuric acid emerge from the tube. If oxidation is not complete, as evidenced by coloration of the sulfuric acid, cool, and add more peroxide. Repeat the heating. Total digestion time will take about 30 to 60 seconds per sample.

8. Transfer the sample to a 100-ml. beaker using about 10 ml. of water.
9. Add 1 drop of mercaptoacetic acid followed by 15.0 ml. of the composite color reagent. Adjust the pH to $5.2 \pm .02$ with a pH meter by addition of ammonium hydroxide.
10. Transfer the solution to a 50-ml. volumetric flask and dilute to a volume with water.
11. Read the absorbance against a reagent blank at 650 mμ. Take the readings 30 minutes after color development.

(Note: The color can be read between 15 to 60 minutes after the color is developed but for best results, the time should be held constant between samples and standards.)

CALCULATIONS

Record the data on the work sheet as follows:

<u>COLUMN</u>	<u>UNIT TO RECORD</u>
A	Volume of original sample taken for analysis, ml.
B	Absorbance of the sample.
C	Concentration, microgram Zr in sample aliquot.

$$C = 2 \frac{B-b}{a}$$

from the regression equation

$$y = ax + b$$

where

y = absorbance of sample
 x = concentration, μg Zr
 a = slope
 b = intercept

D Result, microgram Zr per ml. of sample

$$D = C/A$$

Report the results to 1 relative %.

REFERENCES

1. Morrison, G. H., Freiser, H., "Solvent Extraction in Analytical Chemistry", Wiley, New York, 1957.
2. More, F. L., Anal. Chem. 28, 997 (1956).
3. Wish, Leon, Anal. Chem. 31, 327 (1959).
4. Yamamura, S. S., IDO NOTEBOOK U-251, 1958.
5. Wade, M. A., IDO NOTEBOOK U-666, 1961.

M. A. Wade
October, 1961

APPENDIX III

METHODS ADDED TO ICPP ANALYTICAL RADIOCHEMICAL MANUAL IN 1961

<u>Element</u>	<u>Applicable to Samples of</u>	<u>Type of Separation</u>	<u>Page</u>
Cerium	Aqueous	Extraction, TPAN-nitroethane	127
Cesium	Aqueous	Precipitation, as perchlorate	129
Chromium	Aqueous	Extraction, TPAN-hexone	131
Cobalt	Aqueous, high activity	Extraction, ammonium thio- cyanate-hexone	133
Gamma Spectral Analysis	Variable	Instrumental	135
Molybdenum	Aqueous	Extraction, benzoinoxime- ethylacetate	136
Rare Earths	Aqueous	Precipitation, oxalate	139
Sodium	Aqueous	Ion Exchange	141
Strontium	3/4" diam. mount	Beta absorption for Sr ⁸⁹ / Sr ⁹⁰	142

Element Separated	- Cerium
Type of Separation	- Solvent Extraction
Type of Sample	- Aqueous
Time for Separation	- 1 hour
Yield	- ~ 80%

Procedure:

1. a. Chloride-containing samples. Pipet 1 to 5 ml. of the sample into a 50-ml. test tube. Add 1 ml. of cerium carrier and a volume of concentrated nitric acid equal to the sample aliquot. Fume over a burner until evolution of NO_2 ceases. Continue fuming, if necessary, to a final volume of 1 ml. Transfer to a 30-ml. separatory funnel and continue with Step 2.
- b. Other aqueous samples. Pipet 1 ml. of the sample into a 30-ml. separatory funnel. Add 0.5 ml. of concentrated nitric acid. If the sample contains fluoride, add 1 ml. of saturated aluminum nitrate solution for each 3 millimoles of fluoride present. Add 1 ml. of cerium carrier and continue with Step 2.
2. Add a small excess of the solid silver monoxide. (A dark color will persist when an excess is present.)
3. Add 10 ml. of the tetrapropylammonium nitrate (TPAN) reagent. A muddy brown precipitate will form at this point. (Note 1).
4. Add 10 ml. of 9:1 nitroethane:n-hexane and extract by gentle inversion or swirling until both phases are clear. Vigorous shaking causes emulsion, delaying the phase separation. Discard the aqueous phase.
5. Add 5 ml. of the TPAN reagent and scrub the organic phase for 30 seconds, discarding the aqueous phase. Repeat.
6. Add 3 ml. of 2M hydrochloric acid and 1 drop of 30% hydrogen peroxide. Mix until both phases are colorless.
7. Drain the aqueous phase into a 50-ml. test tube, add 10 ml. of water, and heat to near boiling. Add 15 ml. of saturated oxalic acid and cool in an ice bath for 5 minutes.
8. Filter the precipitate on a tared glass-fiber filter. Wash with water, ethanol, and diethyl ether. Dry in a vacuum desiccator for 5 minutes and weigh as $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ (38.7% cerium).

Preparation of Tetrapropylammonium Nitrate (TPAN) Reagent

Add 78 ml. of concentrated nitric acid to 500 ml. of 10% (0.5M) tetra-n-propylammonium hydroxide (Eastman Kodak) and dilute to 1 liter with distilled water.

Preparation and Standardization of Cerium Carrier

Dissolve 33 grams of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 1 liter of 0.01M HNO_3 . Pipet an aliquot into a 250 ml. beaker and dilute to 150 ml. with water. Add 1 ml. of pyridine, 2 drops of 0.2% cresol red indicator, and sufficient 1:100 arseneazo:sodium chloride salt mixture to give a reddish-purple color to the solution. Titrate with standard 0.05M EDTA to the yellow-red end point.

Note 1. The precipitate is an ion association complex of $\text{Ce}(\text{IV})$ and the tetrapropylammonium ion. Complete extraction is indicated by disappearance of the precipitate.

S. F. Marsh
W. J. Maeck
5/16/61

Element Separated	- Cesium
Type of Separation	- Precipitation
Type of Sample	- Aqueous
Time for Separation	- 2 - 2 1/2 hours

Note: If excessive (more than 0.5 g) potassium, ammonium, or sodium ions are present treat the sample as outlined in Note 1.

Procedure:

1. Pipet the sample into a 50-ml. centrifuge tube and add cesium carrier.
2. Add 5 ml. of 70% HClO_4 , evaporate until dense white fumes are evolved.
3. Cool, place the tube in an ice bath and when chilled, cautiously add 15 ml. of absolute alcohol.
4. Stir for 1-2 minutes, centrifuge and wash the precipitate with 10 ml. absolute alcohol.
5. Dissolve the cesium perchlorate in 10 ml. of water, add 5 mg. of iron holdback (Note 2) and 6M ammonia dropwise until the $\text{Fe}(\text{OH})_3$ precipitate coagulates.
6. Centrifuge, decant the supernatant solution to a clean tube, and repeat the iron scavenge.
7. Add 5 drops of 6M NaOH and boil down to about 5 ml.
8. Add 4 ml. 70% HClO_4 and evaporate to dense fumes.
9. Cool, place the tube in an ice bath and when chilled, cautiously add 15 ml. of absolute alcohol. Centrifuge and discard the supernatant solution. A voluminous precipitate indicates the presence of sodium perchlorate. Dissolve it by adding portions of absolute alcohol and stirring. Centrifuge and discard solutions.
10. Suspend the cesium perchlorate in absolute alcohol and filter onto a weighed 1-inch piece of Whatman #542 filter paper.
11. Wash 3 times with 5 ml. portions of absolute alcohol.
12. Dry in a vacuum desiccator, determine yield and mount for scanning.
13. Gamma scan and calculate the d/m/ml of Cs^{137} . (Remove Cs^{134} contribution using the instrumental complement nullification technique. The combined branching ratio and internal conversion correction for the 0.660 mev photopeak is 0.82.

Note 1. Add 2 ml. cesium carrier and 20 ml. of 6M HCl to the sample in a 50-ml. centrifuge tube. Add 1 ml. 0.13M silicotungstic acid and let stand for 5 minutes. Centrifuge and wash the precipitate twice with 10 ml. of 6M HCl. Dissolve the precipitate in 1 ml. of 6M NaOH. Carefully add 5 ml. of 70% HClO₄, evaporate to fumes, then boil 2 minutes. Cool, dilute to 10 ml., centrifuge and transfer the supernatant to a clean tube. Treat this solution by the regular procedure omitting the addition of carrier.

Note 2. Prepare iron carrier by adding sufficient Fe(NO₃)₃ to make about 10 mg. iron per ml. in 0.015M HNO₃.

Note 3. Preparation and Standardization of Carrier:

Dissolve 12.5 g CsCl (C-24, Fisher Chemical Co. purified) in 1 liter of distilled water.

Pipet 2 ml. carrier solution into a 50-ml. centrifuge tube and add a known amount of Cs¹³⁷ tracer. Precipitate as CsClO₄ in the normal manner and filter on a weighed filter paper. Rinse 3 times with denatured alcohol and dry in an oven at 110°C. for 30 minutes. Cool and reweigh. Count samples and correct for chemical losses. Duplicate samples should agree within 2 per cent.

D. G. Olson
8/15/61

Element Separated	- Chromium
Type of Separation	- Solvent Extraction
Types of Samples	- Aqueous
Time for Separation	- 1 hour
Yield	- 80%

Procedure:

1. Place an aliquot of sample into a 50-ml. centrifuge tube containing 5 mg. of chromium carrier as dichromate.
2. Acidify with nitric acid and add 6 drops of 1M sodium bisulfite.
3. Add 2 drops of phenolphthalein followed by ammonium hydroxide just before the transition point (Note 1).
4. Heat to coagulate the precipitate, centrifuge, and decant the supernatant liquid.
5. Wash the precipitate with water, centrifuge, and again decant.
6. Dissolve the precipitate in 1 ml. of concentrated perchloric acid and 0.5 ml. of sulfuric acid. Fume to a deep red dichromate color (Note 2).
7. Add 15 ml. of 1M hydrochloric acid and transfer to a 125-ml. separatory funnel.
8. Add 5 ml. of 0.5M tetrabutylammonium hydroxide and 25 ml. of hexone.
9. Extract for 2 minutes. Discard the aqueous phase.
10. Scrub for 3 minutes with 15 ml. of 1M hydrochloric acid. Discard the aqueous phase.
11. Add 20 ml. of 2M sodium hydroxide - 3M ammonium chloride and strip until the organic phase is colorless. Drain the aqueous phase into a 50-ml. centrifuge tube.
12. Add 10 mg. of iron as iron scavenger solution, heat, and centrifuge.
13. Filter into a 25-ml. volumetric flask and dilute to volume with the strip reagent.
14. Transfer a 250 aliquot into a 10-ml. volumetric flask and dilute to volume with the strip reagent.
15. Transfer to a 1-cm. cell and measure the absorbance at 370 mu.
16. Rinse the remaining portion of the sample in the 25-ml. volumetric flask into a 50-ml. plastic counting tube and gamma scan.

Note 1. The ammonium hydroxide addition should be stopped just before the solution turns pink. Chromium is amphoteric and will redissolve in excess base.

Note 2. After the first appearance of the red color, stop heating, the reaction will continue on its own. Do not heat to dryness because chromium(VI) may be reduced.

Preparation of Carrier

Dissolve 14.135 grams of potassium dichromate in water and dilute to 1 liter. (Equivalent to 5 mg. Cr/ml.)

Standardization of Carrier

Prepare a working curve by removing a series of aliquots of the carrier solution and processing through steps 13-15.

M. E. Kussy
W. J. Maeck
8/4/61

Element Separated	- Cobalt
Type of Separation	- Solvent Extraction
Type of Sample	- Aqueous High Activity
Time for Separation	- 1 hour
Yield	- 75%

Procedure:

1. Place an aliquot of sample in a 50-ml. centrifuge tube containing 1 ml. of cobalt carrier. Add sufficient sodium hydroxide to completely precipitate $\text{Co}(\text{OH})_2$. Centrifuge and discard the supernatant solution.
2. Dissolve the precipitate in a minimum (~2 drops) of sulfuric acid. Heat, if necessary, until dissolution is complete and the cobalt red color appears. Cool, add 2 ml. of concentrated ammonium hydroxide, and dilute to 10 ml. with water.
3. Slowly add 10 drops of 10 mg./ml. iron holdback while vigorously swirling the solution. Centrifuge and decant (or filter) into a 125-ml. separatory funnel.
4. Add 2 ml. of glacial acetic acid, 20 ml. of 25% ammonium thiocyanate solution, and 10 ml. of hexone. Extract for 1 minute. Discard the aqueous phase.
5. Add 20 ml. of 25% ammonium thiocyanate solution and scrub the organic phase for 1 minute. Discard the aqueous phase. Repeat.
6. Strip the cobalt with 5 ml. of water for 30 seconds. Drain the aqueous phase into a clean 50-ml. centrifuge tube. Repeat the strip with an additional 5 ml. of water, combining the aqueous portions.
7. Heat to near boiling. Add concentrated hydrochloric acid dropwise to dissolve the precipitate which may form and add 1 ml. of ammonium tetrathiocyanomercurate reagent. Swirl until precipitation of the blue cobalt tetrathiocyanomercurate is complete.
8. Cool in an ice bath (this may be done while filters are being tared) and filter onto a tared glass-fiber filter. Wash with water, alcohol, and ether. Dry for 5 minutes in a vacuum desiccator and weigh as $\text{CoHg}(\text{SCN})_4$. This precipitate is 11.98% cobalt.
9. For low activity samples, the counting geometry may be improved by dissolving the precipitate in sulfuric acid and counting in a well crystal.

Preparation of Cobalt Carrier

Dissolve about 10 grams of accurately weighed, high purity cobalt metal in 32 ml. of concentrated nitric acid. Dilute to 1 liter with distilled water.

Preparation of Ammonium Tetrathiocyanomercurate

Dissolve 190 grams of mercuric nitrate and 213 grams of ammonium thiocyanate in 250 ml. of distilled water.

Preparation of Ammonium Thiocyanate Solution

Dissolve 250 grams of ammonium thiocyanate and 35 grams of monobasic sodium phosphate in distilled water. Adjust pH to 7.0 with sodium hydroxide and dilute to 1 liter with water.

References:

1. Sporek, K. F., Anal. Chem. 33, 754-758 (1961).
2. Korenman, M., Sheyanova, F. R., and Baryshnikova, M. N., J. Gen. Chem. (USSR) 26, 387-391 (1956).

S. F. Marsh
W. J. Maeck
6/21/61

Element Separated	Gamma Spectral
Type of Separation	Instrumental
Type of Sample	Variable
Time for Separation - 10 min./nuclide	

Procedure:

Note: Standard sources should be available for each nuclide present in the sample. These standards must be identical in physical configuration to the sample being analyzed.

1. Scan the sample at a fixed distance for a known time.
2. Assume four nuclides are present "A", "B", "C", and "D", with gamma-ray energies increasing from "A" to "D".
3. Complement the information in the analyzer.
4. Replace the sample with a standard mount of nuclide "D" and determine the time required to remove the photopeak.
5. Remove the photopeaks from nuclides "C", "B", and "A" by the same process.
6. Calculate the disintegration rate of each nuclide by the following equation:

$$\frac{\text{removal time}}{\text{accumulate time}} \times d/m \text{ of standard} = d/m \text{ of sample}$$

D. G. Olson
9/7/61

Element Separated	- Molybdenum
Type of Separation	- Extraction
Type of Samples	- Aqueous
Time of Separation	- 1-1/2 hours
Average Yield	- 75%

Procedure:

1.

a. Low Activity Water Samples

Transfer 200 ml. of sample to a 400-ml. beaker. Add molybdenum carrier (equivalent to ~ 35 mg. of PbMoO_4), 1 ml. of iodine holdback carrier (10 mg./ml. KI), 5 ml. of 0.05M KMnO_4 , 10 mg. of zirconium scavenger, 2 ml. of concentrated hydrofluoric acid, heat to boiling, and transfer to a 250-ml. centrifuge tube. Add 2N sodium hydroxide to precipitate the zirconium and manganese. Centrifuge and filter through coarse paper into another tube. Add a few drops of methyl red indicator and make just acid with nitric acid. Add 3 ml. of $\text{Pb}(\text{NO}_3)_2$ (50 mg./ml.) and make the solution just alkaline to methyl red. Add 1 ml. of glacial acetic acid. Centrifuge and discard the supernatant liquid. Dissolve the precipitate in 5 ml. of 10N hydrochloric acid and dilute to 25 ml. with water. Continue with step 3 (note the omission).

b. High Activity Fission Product Samples

Transfer a suitable aliquot of the sample to a 50-ml. centrifuge tube. Add molybdenum carrier (equivalent to ~ 35 mg. of PbMoO_4), 1 ml. of iodine holdback carrier (10 mg./ml. KI), 1 ml. of 0.05M KMnO_4 , 10 mg. of zirconium scavenger, 1 ml. of concentrated hydrofluoric acid, dilute to 20 ml. and heat.

2. Add 2N sodium hydroxide to precipitate the zirconium and manganese. Centrifuge.
3. Decant or filter into a 125-ml. separatory funnel and add 5 ml. of 10N hydrochloric acid. (Omit the acid addition if continuing from step 1-a.)
4. Add 10 ml. of α benzoin oxime (2% in 95% EtOH), 30 ml. of ethyl acetate, and extract for 2 minutes.
5. Discard the aqueous phase and scrub for 2 minutes with 25 ml. of 1N hydrochloric acid. Discard the aqueous phase.
6. Add 15 ml. of 4N ammonium hydroxide and shake for 5 minutes or until the organic phase is clear.
7. Drain the aqueous strip into another 125-ml. separatory funnel and add 10 ml. of 10N hydrochloric acid.

8. Repeat steps 4 through 6.
9. Drain the aqueous strip into a 50-ml. centrifuge tube, add 5 ml. of concentrated nitric acid, cool, and add 3 ml. of $\text{Pb}(\text{NO}_3)_2$ (50 mg./ml. solution). If the strip solution is not clear after being acidified, it should be filtered before the lead nitrate addition is made.
10. Either adjust the pH to 4.5 or add a few drops of methyl red indicator and then ammonium hydroxide until just yellow. Add 1 ml. of glacial acetic acid.
11. Centrifuge and decant the supernatant liquid. Wash the precipitate with water and filter on a 1-inch tared glass fiber filter. Wash with water followed by alcohol and ether. Dry in a vacuum desiccator.
12. Reweigh the filter and precipitate to determine the yield. Mount and count. See the following section for counting technique.

Counting:

The Mo-99 content may be determined by either gross beta counting or scanning on the gamma spectrometer.

1. Beta Counting - The plate should be gamma scanned to verify purity of separation from other gamma emitters. Additional verification of separation from beta emitters is obtained by following the half life for a period of 12 to 15 days. Counting immediately after separation will minimize the small beta contribution from 6 hr. $\text{Tc}^{99\text{m}}$.
2. Gamma Spectrometry - The area under the 740-760 kev photopeak may be determined any time after separation. The branching ratio through this level is 16.25% (as determined by MTR Physics). After a period of 48 hours, the 140 kev photopeak may be measured to check the purity of the 740-760 peak. The peak height ratio (140-740-760) should be approximately 40/1 at equilibrium. Because the contribution of the Mo^{99} 180 kev gamma to the area under the 140 kev peak is not accurately known, errors can result in using the 140 kev $\text{Tc}^{99\text{m}}$ photopeak as an analysis peak.

Preparation of Carrier

Dissolve 18.4 grams of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 100 ml. of water. Add 1 ml. of 0.5M NaBrO_3 . Dilute to 1 liter with 6M HCl . (This solution is equivalent to 100 mg./ml. of Mo or 38.2 mg. of PbMoO_4).

Standardization of Carrier

The solution is standardized by adding 5 ml. of the carrier solution to a 250-ml. beaker containing 50 ml. of water and 25 ml. of 50% ammonium acetate. The solution is heated to boiling and the $\text{Pb}(\text{NO}_3)_2$

(50 mg./ml.) solution added dropwise until the precipitation is complete. Boil for 2 to 3 minutes and check for complete precipitation by adding more $\text{Pb}(\text{NO}_3)_2$. Adjust to a pH of 4.5 and quantitatively filter through a tared medium porosity crucible. Transfer and wash with 15 ml. of 3% ammonium nitrate. Wash with water followed by alcohol and ether. Dry to constant weight in a vacuum desiccator.

M. E. Kussy

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8/4/61

Element Separated	- Rare Earth Method
Type of Separation	- Precipitation
Type of Sample	- Aqueous
Time for Separation	- 2 hours
Yield	- 60 - 80%

Procedure:

1. To a measured amount of sample in a lusteroid centrifuge tube add 2 ml. of cerium carrier, 2 ml. of zirconium holdback carrier and 1 drop of 30% H_2O_2 . Add 1 ml. of HCl and 2 ml. of conc. HF, mix well, and centrifuge. Wash with 10 ml. of 1M HF acid.
2. Dissolve the precipitate in 1 ml. of saturated H_3BO_3 and 1 ml. of conc. HNO_3 . Add 2 ml. of zirconium holdback carrier and dilute to 10 ml. with water. Add 2 ml. of conc. HF, mix well, centrifuge, and wash with 10 ml. of 1M HF.
3. Dissolve the precipitate in 1 ml. of saturated H_3BO_3 and 1 ml. of HNO_3 . Transfer to a glass centrifuge tube and dilute to about 10 ml. using the dilution water to transfer the sample. Bring the solution to a pH of about 10 by dropwise addition of 19M NaOH (indicator paper). Centrifuge and wash the precipitate with 10 ml. of water.
4. Dissolve the hydroxide precipitate with 8 ml. of conc. HNO_3 . Add 1 drop of 30% H_2O_2 and 0.5 ml. of zirconium holdback carrier. Add 15 ml. of 0.35M HIO_3 , centrifuge, and transfer the supernatant solution to a clean glass centrifuge tube (discard the precipitate).
5. Cautiously add an excess of 19M NaOH (about 9 ml.), mix carefully, centrifuge, and decant. Dissolve the precipitate in 1 ml. of 6M HCl. Add 1 ml. each of barium and strontium holdback carriers, dilute to 15 ml., and precipitate the cerium with 1 ml. of conc. carbonate-free NH_4OH . Centrifuge and wash the precipitate with 10 ml. of water.
6. Dissolve the precipitate with 1 ml. of 6M HCl and dilute to 15 ml. Precipitate with 1 ml. of conc. carbonate-free NH_4OH . Centrifuge and wash with 10 ml. of water.
7. Dissolve the hydroxide precipitate in 1 ml. of 6M HCl, add 15 ml. of water, heat to near boiling, and add 15 ml. of saturated $H_2C_2O_4$ slowly with stirring. Cool in an ice bath for 10 minutes after precipitation has started. Filter through a weighed 24-mm. circle of filter paper on the fritted-glass filtrator and rinse with three 5-ml. portions of water, three 5-ml. portions of alcohol, and three 5-ml. portions of ether. Place in a vacuum desiccator and dry. Weigh, mount, and beta count the sample. Use the geometry value listed for 0.80 mev gammas.

Preparation of Carrier: Dissolve 12 grams of $Ce(NO_3)_3 \cdot 6H_2O$ in distilled water and dilute to 1 liter.

Standardize the cerium carrier as follows: Pipet 50 ml. of the carrier solution into a beaker and add 20 ml. of water. Heat to boiling and add 15 ml. of saturated $\text{H}_2\text{C}_2\text{O}_4$ solution with stirring. Precipitation from a hot solution causes the formation of a fine crystalline precipitate in which the co-precipitation of oxalic acid is reduced. Cool in an ice bath for 7-8 minutes. Filter the precipitate with suction through a tared, fine sintered-glass crucible. Wash with three 5-ml. portions of water, three 5-ml. portions of 95% alcohol and three 5-ml. portions of anhydrous ether. Wipe the outside of the crucible dry with absorbent tissue, place it in a vacuum desiccator and dry. Weigh, dessicate and reweigh until duplicate weighings agree within 0.2 mg. Weigh as $\text{Ce}_2(\text{C}_2\text{O}_4) \cdot 10\text{H}_2\text{O}$.

Reference

1. Regier, R. B., U. S. Atomic Energy Commission Report IDO-14315, 1955.

D. G. Olson
8/15/61

Element Separated - Sodium
Type of Separation - Ion Exchange
Type of Sample - Aqueous
Yield - 100%

Procedure:

1. A 5 cm. x 0.2 cm² column of Dowex 50W x 8 (100-200 mesh) resin is used with a flow rate of 3 minutes per ml. The sample, in 0.1N HCl is placed on the column.
2. Rinse the column with 2 ml. of 0.1N HCl.
3. Pass 5 ml. of 0.125M sodium dichromate through the column and discard the effluent.
4. Pass 8 ml. of 0.125M sodium dichromate through the column. The effluent, containing the separated sodium is collected and counted.

References:

1. Wish, L, U. S. Naval Radiological Defense Laboratory Report, USNRDL-TR-485 (1960).

S. F. Marsh
May, 1961

Element Separated - Strontium
Type of Separation - Beta Absorption
Type of Sample - 3/4" diam. mount
Time of Separation - 1.5 hours
Yield

Procedure:

Note: This analysis must be made during the 1.5 hours following the strontium and yttrium separation. Counting is to be done with absorbers on the second shelf.

1. Make a beta absorption analysis on the separated strontium sample beginning with the heavy absorbers. (Use the list of absorbers found in the lid of the absorber box marked for this determination).
2. Plot the data on 3 cycle semilog paper with the horizontal layout as shown on the plastic Sr⁸⁹ curve template.
3. Draw the best curve through the plotted points.
4. Fit the Sr⁸⁹ curve so that it conforms as closely as possible to the unknown curve. (Because the Sr⁸⁹ beta is nearly three times as energetic as Sr⁹⁰ the heavy absorber points should be used in the fitting).
5. Draw the Sr⁸⁹ curve.
6. Extrapolate the unknown curve back to -2.5 mg. absorber (allowance for air absorption).
7. Read the Sr⁸⁹ plus Sr⁹⁰ from the unknown curve, then the Sr⁸⁹ from the fitted curve both at the -2.5 mg. cm⁻² absorber point.
8. Obtain the per cent Sr⁸⁹ by dividing the value found for Sr⁸⁹ by the value found for Sr⁸⁹ + Sr⁹⁰.

References:

1. L. J. Beaufait Jr., U. S. Atomic Energy Commission Report NP- 5056.

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8/21/61

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