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**LOS ALAMOS SCIENTIFIC LABORATORY**  
of the  
**University of California**  
LOS ALAMOS • NEW MEXICO

Methods of Chemical Analysis for  
FBR Uranium-Plutonium Oxide  
Fuel and Source Materials



For Reference

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ATOMIC ENERGY COMMISSION  
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Methods of Chemical Analysis for  
FBR Uranium-Plutonium Oxide  
Fuel and Source Materials

Edited by

James E. Rein  
George M. Matlack  
Glenn R. Waterbury  
Robert T. Phelps  
Charles F. Metz



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METHODS OF CHEMICAL ANALYSIS FOR FBR URANIUM-PLUTONIUM  
OXIDE FUEL AND SOURCE MATERIALS

Edited by

James E. Rein, George M. Matlack, Glenn R. Waterbury,  
Robert T. Phelps, and Charles F. Metz

ABSTRACT

Twenty-four methods are given for the chemical specification analysis of FBR uranium-plutonium mixed oxide fuel and uranium dioxide insulator pellets, and for the source materials of ceramic grade uranium dioxide and plutonium dioxide used for their manufacture. The methods include dissolution procedures, uranium and plutonium assay, uranium and plutonium isotopic abundances, metal and non-metal impurities, and other specifications relating to total gas, water, and the oxygen-to-metal ratio.

INTRODUCTION

This report provides methods for the chemical analysis of materials that are used in the manufacture of uranium-plutonium mixed oxide fuel for fast breeder reactors (FBRs). The work represented in this report was sponsored by the AEC Division of Reactor Development and Technology (DRDT) in support of the development of mixed oxide fuels for FBRs. More specifically, it directly supports the analytical chemistry development program for the characterization of mixed oxide fuels for the AEC's LMFBR/FFTF Project which is under the management of the WADCO Corporation at Richland, Washington.

Table I summarizes the current chemical specifications for the fuel and source materials of the LMFBR/FFTF. [1-4] The methods presented in this report have been applied to materials having these specifications. In general, these methods also apply to the chemical specification analysis of uranyl nitrate solution [5] and plutonium nitrate solution, [6] two possible source mate-

rials that may be used in the manufacture of FBR mixed oxide fuel.

The special calibration materials discussed in the methods are available only to those laboratories participating in the LMFBR/FFTF program. Further information concerning these calibration materials is given in Ref. 7.

- [1] RDT Standard E13-1 "Fast Flux Test Facility Ceramic Grade Plutonium Dioxide" (October 1970).
- [2] RDT Standard E13-2 "Fast Flux Test Facility Ceramic Grade Uranium Dioxide" (October 1970).
- [3] RDT Standard E13-6 "Fast Flux Test Facility Driver Fuel Pin Fuel Pellet" (October 1970).
- [4] RDT Standard E13-7 "Fast Flux Test Facility Driver Fuel Pin Insulator Pellet" (October 1970).
- [5] RDT Standard E13-3 "Fast Flux Test Facility Uranyl Nitrate Solution" (October 1970).
- [6] RDT Standard E13-4 "Fast Flux Test Facility Plutonium Nitrate Solution" (October 1970).
- [7] RDT Standard F2-6 "Qualification of Analytical Chemistry Laboratories for FFTF Fuel Analysis" (July 1970).

TABLE I  
CURRENT CHEMICAL SPECIFICATIONS FOR LMFBR/FFTF FUEL MATERIALS [1-4]

Specification	Maximum Values (Unless Otherwise Stated)			
	Ceramic Grade Uranium Dioxide	Ceramic Grade Plutonium Dioxide [a]	Mixed Oxide Fuel Pellets	Insulator Pellets
1. Plutonium Isotopic Composition, wt %	Not applicable			Not applicable
239 + 241		88.0 ± 0.5	88.0 ± 0.5	
241		2.5	2.5	
238		0.15	0.15	
sum of others except 240		0.35	0.35	
240		balance	balance	
2. Uranium Isotopic Composition	Natural; 0.71 ± 0.05 wt % <sup>235</sup> U		Natural; 0.71 ± 0.05 wt % <sup>235</sup> U	Natural; 0.71 ± 0.05 wt % <sup>235</sup> U
3. Total Plutonium Content, wt %	Not applicable	Minimum 85.0 at time of packaging  Minimum 87.5 after heating to 950°C	± 3.5% of nominal value for individual pellets and ± 1.0% of nominal value for lot average	Not applicable
4. Total Uranium Content	Minimum 86.6 wt % on dry basis	2000 µg/g	± 1% relative of actual uranium content	None given
5. Americium, wt % of Plutonium	Not applicable	0.25	0.25	Not applicable
6. Carbon, µg/g	150	200	150	200
7. Chlorine, µg/g	25	50	20	20
8. Fluorine, µg/g	25	25	10	10
9. Nitrogen (as Nitride), µg/g	200	200	200	200
10. Phosphorus, µg/g	50	200	100	100
11. Sulfur, µg/g	300	300	300	300
12. Metal Impurities, µg/g				
Al	500	250	500	500
B	10	10	20	20
Be	20	20	20	20
Ca	100	500	250	250

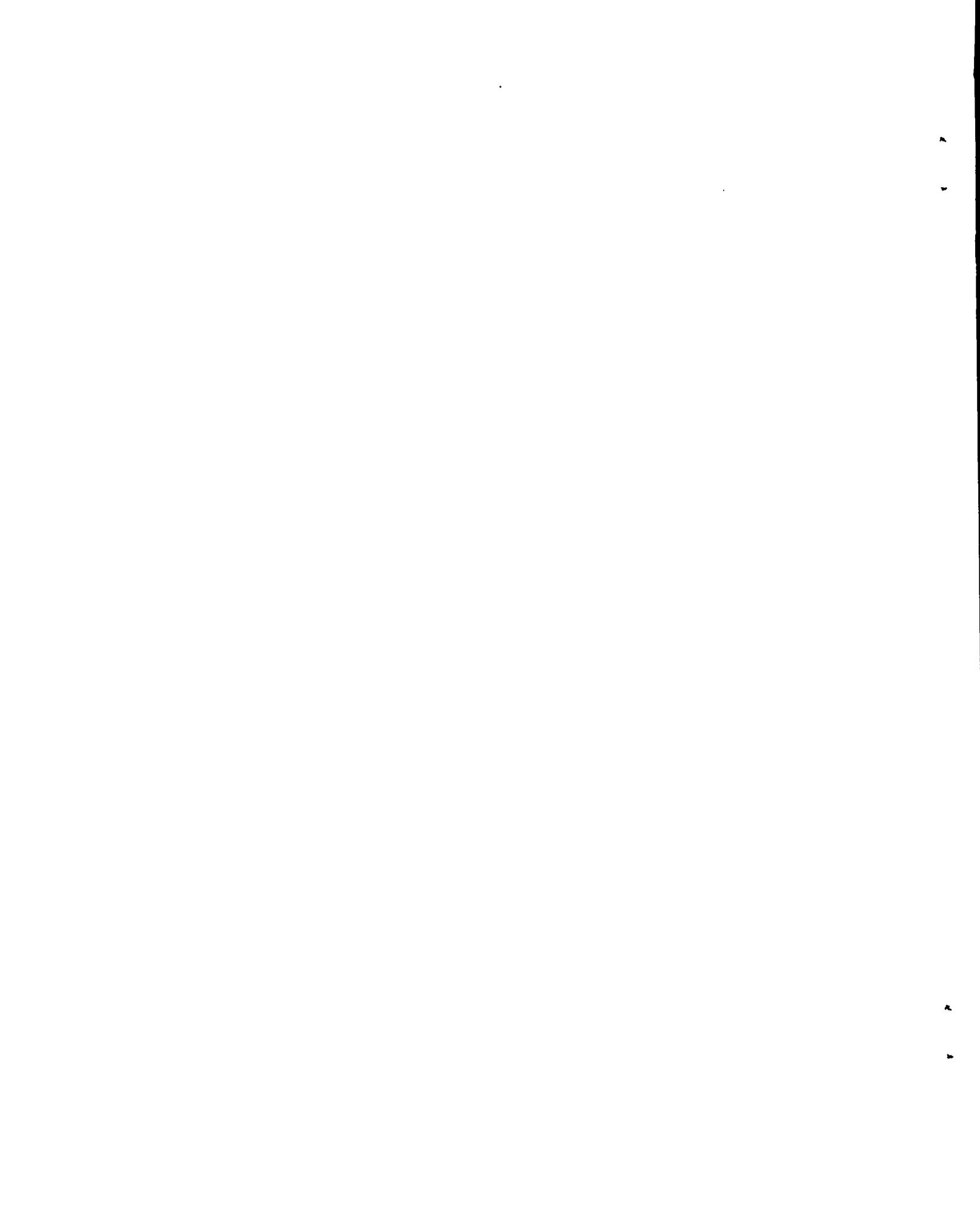
TABLE I

## CURRENT CHEMICAL SPECIFICATIONS FOR LMFBR/FFTF FUEL MATERIALS

Specification	Maximum Values (Unless Otherwise Stated)			
	Ceramic Grade Uranium Dioxide	Ceramic Grade Plutonium Dioxide [a]	Mixed Oxide Fuel Pellets	Insulator Pellets
12. Metal Impurities, $\mu\text{g/g}$				
Cd	20	20	20	20
Co	10	20	20	10
Cr	200	200	250	250
Fe	400	350	500	500
K	200	200	200	200
Li	10	10	10	10
Mg	25	100	25	25
Na	500	300	500	500
Ni	400	300	500	500
Ta	400	400	400	400
W	100	100	100	100
V	400	200	500	500
Sum of Cu, Si, Ti, Zn	800	800	800	800
Sum of Ag, Mn, Mo, Pb, Sn	200	200	200	200
Sum of Dy, Eu, Gd, Sm	100	100	100	100
13. Gas, STP cc/g	None given	None given	0.09	0.09
14. Water, $\mu\text{g/g}$	5000	None given	50 for individual pellets 30 for lot average	50 for individual pellets 30 for lot average
15. Total Volatiles, wt %	None given	2.5	None given	None given
16. Oxygen to Metal (O/M) Ratio	2.00 to 2.25	1.95 to 2.00 [b]	1.95 to 1.99	1.995 to 2.010

[a] All impurity elements are determined after ignition of material at  $950 \pm 25^\circ\text{C}$  to constant weight.

[b] No analysis required for air-calcined oxalate and nitrate source plutonium dioxide powders. See Ref. 1.



# DISSOLUTION OF URANIUM-PLUTONIUM OXIDES BY THE SEALED-TUBE TECHNIQUE

## SUMMARY

Uranium-plutonium oxide samples are dissolved in a hydrochloric acid-perchloric acid mixture by the sealed-tube technique at 310 to 325°C nominally for overnight periods.

## APPLICABILITY

The described method<sup>[1,2]</sup> is applicable to ceramic grade uranium dioxide, ceramic grade plutonium dioxide, uranium-plutonium mixed oxide pellets, and uranium dioxide insulator pellets. It is especially useful for the two plutonium-containing materials which dissolve at much slower rates in nitric acid-hydrofluoric acid mixtures in open containers. Other advantages compared to open-container dissolution are complete retention of the sample constituents and addition only of chloride to the sample. Normally an overnight dissolution is used but one analyst can process about 12 samples in an 8-hr shift.

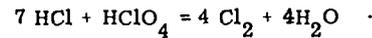
## RELIABILITY

A major source of error in the analysis of the above four materials is incomplete dissolution of samples. This method gives complete dissolution of samples with complete retention of all constituents.

## DISCUSSION OF THE METHOD

The more complete dissolution of samples obtained by the sealed-tube technique results from the higher temperature and pressure of the reaction than is obtained in open containers. The higher temperature and pressure effectively produce a higher concentration

of reactants and the higher temperature increases the dissolution rate. With a hydrochloric acid-perchloric acid mixture as used in this method, the sealed-tube technique conditions establish an equilibrium mixture according to the equation



The chlorine acts as a powerful oxidant and excess hydrochloric acid, present in equilibrium amounts as gaseous hydrogen chloride, acts to metathesize the nominally insoluble oxides to soluble chlorides.

The pressure in the sealed tube is as high as 4000 psi. The sealed tube, therefore, is enclosed in a steel shell along with a measured amount of solid carbon dioxide. At the operating temperature, the external carbon dioxide pressure compensates for the internal pressure to minimize tube ruptures.

The recommended acid mixture for the dissolution of the four oxide materials analyzed in this method is 12M HCl with several drops of 12M HClO<sub>4</sub>; the recommended temperature is 310 to 325°C. Oxidants other than perchloric acid can be used including nitric acid, sodium chlorate, chlorine gas (from a cylinder), and hydrogen peroxide. Perchloric acid is most conveniently used at reaction temperatures above 250°C. Below this temperature, the reaction rate is too slow.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

This technique involves high-pressure operation and should be used only by trained personnel with approval of supervision. A dangerous condition may result from a faulty seal which may leave a minute capillary orifice in the silica tube through which carbon dioxide can flow into the tube. Later in the reaction, the orifice may become plugged with reaction products to produce an extra high internal pressure. The tube then may shatter upon its removal from the shell or when it is opened. For this reason, operational directions must be rigidly followed

[1] C. L. Gordon, W. G. Schlect, and E. Wichers, J. Res. Natl. Bur. Standards 33, 457 (1944).

[2] C. F. Metz and G. R. Waterbury, USAEC Report LA-3554 (1966).

with no exceptions unless approved by supervision.

#### APPARATUS

Dewar flask, 1-l., for dry ice.

Electric oven, adjustable to  $\pm 5^{\circ}\text{C}$  within the range 100 to  $350^{\circ}\text{C}$ .

Hand torch, oxygen-gas, for sealing silica reaction tubes.

Shield, safety glass.

Shell (Figure 1). The shell and nut are machined from 1-3/8-in. mild steel, hexagonal, bar stock. The 1-in.-diam chamber in the shell has a tapered bottom and should be centered to  $\pm 0.002$  in. to avoid thin areas along the walls. The lip of the shell is machined with  $45^{\circ}$  inside and outside chamfers to provide a  $90^{\circ}$  angle that will compress a groove in the copper gasket when the nut is tightened. The centering plug, machined from mild steel, holds the copper gasket in place when the nut is tightened. Additional items required are a support for holding the shell in a rigid vertical position and an 18-in.-long wrench to tighten the steel nut.

Special accessories for the shell (Fig. 2).

- Pellet can assembly. Place 5 g of granular sodium carbonate in a thin-wall brass or copper can, 5/8-in. high x 7/8-in. diam, and cover with a brass or copper lid. The sodium carbonate will neutralize the acid released from a ruptured reaction tube.
- Metal cup, thin-wall brass or copper, 1-in. long, 7/8-in. i. d., flared to a 15/16-in. i. d. top, and having a perforated bottom. Do not use soft solder in the construction of either the pellet can or the metal cup because it will melt at the temperature reached during the dissolution process. This cup holds the reaction tube in the shell.
- Copper gasket, 1-1/4-in. o. d., 1-in. i. d., 1/8-in. thick. Anneal before use by heating with a torch to a cherry red color and quench in 95% ethyl alcohol to room temperature. This treatment removes work-hardening strains so that good seals are obtained.
- Plastic tube, Lucite or equivalent, 7/8-in. o. d., 1/8-in. wall thickness. Seal the top end and make an in-

side bevel at the bottom end. The bevel allows the plastic tube to slip easily over the reaction tube. The plastic tube fits snugly into the metal cup that supports the reaction tube when it is removed from the shell.

Tube glass, 34-cm long, 16- to 18-mm i. d. with one end sealed. This tube is used to hold and prevent contamination of the silica tube during addition of the sample and acid.

Tube, reaction, heavy-wall silica approximately 8-mm bore, 2-mm wall thickness, 38-cm long, one end sealed. The maximum length of a tube after sealing is about 30 cm.

#### REAGENTS

Calcium carbonate, fine powder.

Carbon dioxide, solid, ground.

Hydrochloric acid, 12M (37%), 6M.

Perchloric acid, 12M (70%).

#### PROCEDURE

##### Blank

A blank is not required. When a blank is specifically called for in an analytical method for a sample component, use the same quantities of the same dissolution reagents for the blank as are used for the sample, without carrying them through the sealed-tube dissolution procedure.

##### Calibration

A calibration is not required.

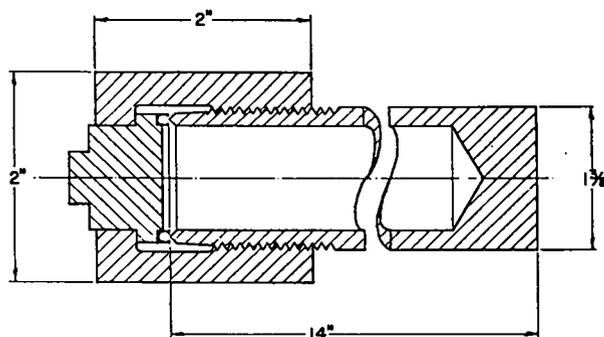


Figure 1. Steel shell and nut.

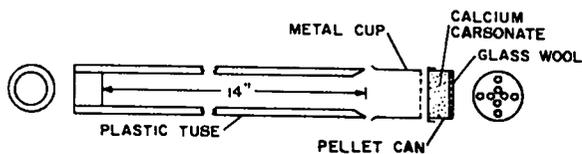


Figure 2. Special accessories for the steel shell.

### Sample Dissolution

1. Crush pellet samples in a glove box.
2. Place a silica reaction tube inside a glass tube and wrap the exposed wall of the reaction tube and the top of the glass tube with masking tape.  
The masking tape prevents contamination by plutonium of the reaction tube external surface.
3. Place the reaction tube assembly in a glove box and transfer a weighed quantity of sample into the reaction tube.  
The weight of sample can be as large as 2.5 g. Weigh to  $\pm 0.2$  mg.
4. Add 7 ml of  $12M$  HCl and 3 to 4 drops of  $12M$   $HClO_4$  to the reaction tube.  
Add the  $12M$  HCl slowly at a rate so that any reaction is controllable.  
The volume of acid added should not exceed 40% of that of the reaction tube.
5. Remove the masking tape from the reaction tube and then remove the reaction tube from the glass tube.  
Avoid contaminating the outer surface of the reaction tube when removing the masking tape.
6. Hold the reaction tube with a clean glove and cover the open end with clean masking tape.
7. Monitor the outer surface for alpha activity and, if uncontaminated, transfer the reaction tube to an uncontaminated glove box containing the gas-oxygen torch.

If the outer surface of the tube is contaminated, hold it in a vertical position, clean the surface with  $12M$  HCl, rinse it with water, and dry it.

Repeat this decontamination process until the outer surface is uncontaminated.

If decontaminated is not attained, discard the reaction tube to salvage and repeat steps 1 through 7.

8. Place the uncontaminated reaction tube in an upright position in a 1-quart carton, fill the space around the tube with dry ice, and seal the tube with the gas-oxygen flame about 3 in. from the taped end.

An experienced person should make the seal in a manner to prevent the formation of a capillary leak.

Test for possible small leaks with moistened acid-indicator paper.

9. Examine the steel shell and related apparatus for proper fit and operation as follows:
  - a. Coat the threads and gasket surface with Aqua-dag to prevent galling or freezing when the nut is tightened.
  - b. Use a new copper gasket.
  - c. Place an encapsulated calcium carbonate pellet and metal cup into position in the bottom of the shell.

The examination and treatment are necessary so that the shell can be sealed immediately after adding dry ice to it in the next step.
10. After the reaction tube cools, carefully insert it into the shell, add 40 g of dry ice to the shell, and immediately seal the shell.  
Make sure the copper gasket is positioned properly before sealing the shell.  
This quantity of dry ice is correct for a tube and shell having the dimensions as given in this method.
11. Immerse the sealed shell in water to test for leaks; if gas bubbles are observed, immediately tighten the nut.  
If a gastight seal is not obtained before an appreciable amount of carbon dioxide escapes, open the shell as directed in steps 14, 15, and 16 and start over at step 9, making sure a new copper gasket is used.
12. Place the loaded shell in a horizontal position in the oven, rock the shell several times to distribute

the sample along the length of the reaction tube, and heat at 310 to 325°C for about 8 hr.

13. Remove the shell from the oven and allow it to cool to room temperature.

The oven should be in a glove box or be fastened to a support which allows the oven door to open directly into a glove box

The glove box should contain a vise for grasping the shell when it is opened.

14. Loosen the nut just sufficiently to let the carbon dioxide escape slowly.

Test for alpha contamination immediately as the carbon dioxide escapes to determine whether the reaction tube has broken

If contamination is detected, immediately re-seal the shell and notify supervision.

15. After the carbon dioxide has completely escaped, support the shell in a vertical position and remove the nut.

16. Insert the open end of the plastic tube into the shell and press it firmly into the metal cup.

The inside bevel of the open end of the plastic tube lets it slip readily over the reaction tube.

Point the open end of the shell away from you during this entire operation.

17. Withdraw the plastic tube containing the reaction tube supported by the metal cup and inspect the contents of the reaction tube for complete dissolution.

If the sample is dissolved completely, proceed to the next step. If not, reinsert the reaction tube into the shell as described in step 10 and repeat steps 10 through 17.

18. Remove the metal cup from the end of the plastic tube and reinsert it into the shell.

19. Hold the plastic tube in a horizontal position, insert it into a 1-quart carton also held in a horizontal position and, with the bottom of the reaction tube held against the bottom of the carton, slowly rotate the carton to a vertical position.

20. Fill the carton with dry ice and slowly withdraw the plastic tube from the reaction tube.

21. Allow the reaction tube to remain in the dry ice for 30 min; keep the carton filled with dry ice.

This chills the sample (and may even freeze it) so that the internal pressure should be no greater than atmospheric pressure. This low pressure must be obtained before proceeding to the next step.

22. Withdraw the reaction tube from the dry ice, score it with a file about 3 or 4 in. from the top end, and snap the tube into two pieces while holding it in an upright position.

Insert the open ends of the two tube sections under the surface of about 2 ml of water in the beaker, and hold in that position until the contents melt and run down into the beaker.

23. Quantitatively transfer the dissolved sample to a beaker with the aid of water rinses.

This transfer must be quantitative because the quantity of dissolved sample is taken to be the sample weight initially placed in the reaction tube.

DETERMINATION OF THE ISOTOPIC DISTRIBUTION  
OF URANIUM IN URANIUM DIOXIDE BY MASS  
SPECTROMETRY

SUMMARY

The isotopic abundances of  $^{235}\text{U}$  and  $^{238}\text{U}$  are directly determined by thermal ionization mass spectrometry on samples of uranium dioxide dissolved in nitric acid.

APPLICABILITY

This method is applicable to samples of ceramic grade uranium dioxide and the sintered uranium dioxide insulator pellets. The method measures the isotopic abundance of  $^{235}\text{U}$  for natural uranium for which the specification value is  $0.71 \pm 0.05$  wt %.

After dissolution of the sample, an analysis takes about 45 min on a thermal ionization mass spectrometer equipped with a vacuum lock.

RELIABILITY

The standard deviation for a single measurement of the isotopic abundance of  $^{235}\text{U}$  by thermal ionization mass spectrometry is 0.01 absolute percent at approximately the level of  $^{235}\text{U}$  in natural uranium. [1]

DISCUSSION OF THE METHOD

At the specification limits for the impurities in the two uranium dioxide materials, there is no interference effect in the direct measurement of the  $^{235}\text{U}$  (and  $^{238}\text{U}$ ) isotopic abundance. A chemical purification of the uranium prior to the mass spectrometric measurement is therefore not necessary.

Other techniques for the measurement of  $^{235}\text{U}$ , including alpha pulse height spectrometry and emission spectroscopy, are not as precise as mass spectrometry and would require a more extensive effort for routine use to meet the specification of  $0.71 \pm 0.05$  wt %.

[1] M. W. Lerner, USAEC Report NBL-231 (1966).

They are recommended only for laboratories not equipped with nor having access to a thermal ionization mass spectrometer.

Although the mass spectrometric measurement in this method is done directly on samples with no chemical separation, care must still be taken to prevent contamination pickup of natural uranium and cross-contamination of samples. The latter is particularly important for mass spectrometry laboratories that also analyze enriched uranium samples.

OPERATING INSTRUCTIONS

SAFETY PRECAUTIONS

Special care must be taken when handling the strong acids used in this method. As a minimum precaution, rubber gloves should be worn.

Mass spectrometers have high-voltage circuits. Consult the manufacturer's manual before opening any instrument panel doors or latches.

APPARATUS

Disposable pipets. Prepare these by drawing 7-mm borosilicate glass tubing to about 0.040-in. o. d. for a length of 3 in. A similar length of Teflon thin-walled tubing of such diameter as to fit over a standard hypodermic needle also may be used. (This tubing is obtainable from Chemplast, Inc., 150 Dey Road, Wayne, N. J. 07470). Use these pipets only once and discard them.

Infrared heating lamp.

Mass spectrometer. The instrument shall have minimum characteristics as follows:

Source: thermal ionization with single or multiple filaments. The latter is recommended to obtain the unoxxygenated uranium spectrum which facilitates calculations. A vacuum lock is recommended to maintain analyzer vacuum which increases sample throughput.

Analyzer: an analyzer and vacuum system capable of producing a resolving power of at least 400

and an abundance sensitivity at mass 238 of at least 20,000. Resolving power is defined as  $M/\Delta M$ , where  $\Delta M$  is the width, in atomic mass units, of a peak at mass  $M$  at 5% of its height. Abundance sensitivity is defined as the ratio of total ion current at mass  $M$  to its contribution at mass  $M-1$ , customarily measured at masses 238 and 237 for a spectrum produced from a filament loading of natural uranium.

Detector: A system consisting of a Faraday cup and an electron multiplier, externally selectable, followed by an electrometer amplifier and a potentiometric recorder. Pulse counting systems using an electron multiplier or a scintillator-photo-multiplier, as well as automatic data acquisition apparatus, also may be used.

Several commercially available mass spectrometers meet or exceed all the above requirements.

#### Mass Spectrometer Accessories

Filaments may be made from tantalum, rhenium, or tungsten ribbon, nominally 0.001 x 0.030 in. Filaments should not be handled with bare hands. They should be prepared and stored so as to minimize contamination by uranium.

Filament forming jigs are used to form the filaments into the configuration required by the mass spectrometer and to hold the filaments in place for welding.

A spot welder is used to weld the filament ribbons to the support posts. Welds must be made carefully to ensure good electrical contact necessary for beam stability.

Sample loading unit. A power supply consisting of a Variac, 6.3-V filament transformer, ammeter, and suitable electrical contacts may be used to heat the filament to evaporate sample solution. A heat lamp or heating block also may be used.

Filament bakeout chamber. A bench-top vacuum system with a 12-in. bell jar is satisfactory. A 5-V or 6.3-V, 10-A, filament transformer with the primary controlled

by a Variac supplies the necessary current. Apply current gradually so that the pressure does not exceed  $10^{-6}$  Torr. Bakeout is complete after 1 hr at 2000°C. Up to 20 filaments can be degassed simultaneously without exceeding the heat dissipation capability of the system.

#### REAGENTS

Nitric acid, 8M, 1M.

Uranium calibration solutions. Prepare three calibration solutions by dissolving 12 mg each of NBS U-010, U-500, and U-930 uranium isotopic standards in minimum amounts of 8M  $\text{HNO}_3$ . Dilute to 100 ml with 1M  $\text{HNO}_3$  to give concentrations of  $1 \mu\text{g}/10 \mu\text{l}$ . Store these solutions in plastic bottles.

#### PROCEDURE

##### Blank

A blank measurement is not routinely required in this method. However, because the samples normally consist of natural uranium, the 8M  $\text{HNO}_3$  sample dissolution reagent can become sufficiently contaminated to affect the results without immediate detection by a quality control program. For this reason, uranium contamination in this reagent shall be checked at least once a month by carrying an aliquot of the sample dissolution reagent entirely through the procedure used by a laboratory for samples. The level of uranium in this reagent blank shall be less than 1 ng on the mass spectrometer filament based on the observed ion currents.

##### Calibration

##### Calibration of Detection System

Calibrate the detection system at startup, at least every three months, and following any alteration which could affect performance, as follows:

##### a. Sensitivity scale factors

1. Connect a precision potentiometer in series with the feedback loop of the amplifier and short out the galvanometer.

2. Set the amplifier on the 10-mV scale and apply 10 mV from the potentiometer. Record the deflection.

3. Repeat step 2 for each amplifier sensitivity setting and the corresponding potentiometer voltage.

4. Determine exact scale factors from the ratios of applied voltage/recorder deflection for each sensitivity setting. Use these factors in subsequent determinations.

b. Recorder linearity:

1. Connect a precision potentiometer as in step a-1 above.
2. Set the amplifier on the 1-V scale and apply voltage in increments of 0.1 V up to 1 V. Record the recorder deflection for each increment.
3. Find the cause for and correct any non-linearity greater than 0.25% of full scale.

- c. Grid resistor linearity and ratio determination: If a standard <sup>[2]</sup> current source is available, the test described in TID-7029 is advisable.

#### Calibration of Complete System

Calibrate the complete mass spectrometer at startup, at least every three months, and following any alteration, as follows:

- a. Determine the mass discrimination bias both for the electron multiplier and the Faraday cup by measuring the <sup>235</sup>U/<sup>238</sup>U ratio on at least three separate filament loadings of the NBS U-500 standard for each detector. Average the results and calculate the respective bias correction factors by:

$$B = \frac{\frac{\bar{R}_o}{R_s} - 1}{3}$$

where B = mass discrimination bias factor per amu in the U-Pu mass range,

$$\bar{R}_o = \text{average of observed atom ratio } ^{235}\text{U}/^{238}\text{U},$$

$$R_s = \text{NBS stated atom ratio } ^{235}\text{U}/^{238}\text{U} = 1.0003.$$

Apply these bias corrections to subsequent determinations.

- b. Establish the linear range of both detection systems by measuring the <sup>234</sup>U/<sup>235</sup>U ratio on separate filament loadings of the NBS U-930 standard for each system over a wide range of ion currents at increments corresponding to the amplifier scale factors. To aid interpretation, plot the observed ratio vs the <sup>235</sup>U ion current on semilog paper. Analyze samples only within the linear range.

#### Daily Verification of Mass Spectrometer Stability

Verify the stability of each mass spectrometer used in any 8-hr working shift with the NBS U-010 uranium isotopic standard when uranium samples are analyzed during that shift. Maintain a control chart for each instrument for the ratio of <sup>235</sup>U/<sup>238</sup>U. When the value of this ratio changes at the .05 significance level, do not analyze samples until the cause is corrected. Possible sources of instability are a deterioration of the electron multiplier, low gain in the electrometer amplifier, electrical or mechanical malfunctions in the recorder, and inadequate regulation in the filament power supply.

#### Sample Analysis

1. Dissolve 1 mg of the uranium dioxide sample in 0.5 ml of 8M HNO<sub>3</sub> in a 10-ml beaker with the aid of moderate heating, dilute to 5 ml with water, and mix.

The sample weight and reagent volumes need not be quantitative because only isotopic abundances are to be measured. If a whole insulator pellet has been dissolved, dilute an aliquot of the solution to a uranium concentration of 0.2 μg/ml with 1M HNO<sub>3</sub>.

[2] R. J. Jones, Ed., Method 2.500, "Selected Measurement Methods for Uranium and Plutonium in the Nuclear Fuel Cycle," USAEC Report TID-7029 (1963).

- Transfer 5  $\mu$ l of the diluted solution to the sample filaments of a triple-filament assembly mounted in the sample loading unit, and evaporate slowly to dryness.

Use a new, disposable pipet. With filament loadings of 1  $\mu$ g of uranium, prebaked filaments are not required.

- Introduce the loaded filament assembly into the ion source, using the procedure recommended by the instrument manufacturer.
- When the source pressure drops to  $2 \times 10^{-7}$  Torr, begin degassing by passing 3 A of current through the ionizing filament.
- When the source pressure is below  $10^{-6}$  Torr with the ionizing filament heated, turn on the high voltage and adjust the high voltage and magnet to bring in m/e 238.

Focus on the major isotope:  $^{238}\text{U}$  in most cases,  $^{235}\text{U}$  in the case of NBS U-930.

- Increase the ionizing filament current to  $\sim 4.5$  A, then slowly increase the sample filament currents until an ion beam is detected.
- Adjust focus controls and mechanical alignment for maximum beam intensity.
- Increase the sample filament currents until the  $^{238}\text{U}$  ion current is in the range of  $10^{-13}$  A when the electron multiplier is used, or  $10^{-11}$  A when the Faraday cage is used.

The Faraday cage is preferred because it is essentially free from mass discrimination.

It may be necessary to experiment with different combinations of filament currents to achieve a stable beam of the desired intensity.

- Scan the spectrum repeatedly in both directions over the mass range of interest until at least nine spectra have been recorded. Use scale settings that will cause each peak to be recorded on the top half of the strip chart.

Magnetic field scanning is preferred.

Collect data only when the ion beam intensity is essentially constant.

- Reduce the sample filament currents to zero, record zero readings for each scale setting used, and remove the chart for calculation.

#### Calculations

Relative ion beam intensities, proportional to atom abundances, are measured by interpolating between peak tops and making all measurements of individual isotopes for one set of ratios at one point on the x-axis (one common time) to remove the effect of changes in beam intensity with time. Readings can be made at any point after the completion of the first single sweep and before the beginning of the last sweep. The preferred procedure is to take a reading of all isotopes each time the sweep direction is changed (turnaround). Measurements should be made in pairs. One reading at the high-mass turnaround and one at the adjacent low-mass turnaround constitute a pair. To obtain N pairs of consecutive readings,  $2N + 1$  single sweeps in alternate directions are required.

- Draw lines on the chart connecting the tops of the consecutive peaks of the same isotope for each isotope to be measured.
- Draw vertical lines on the chart at or near the turnaround points corresponding to each change in sweep direction.
- Read the interpolated peak height of each isotope at the intersection of each vertical line with the interpolating lines.
- Make zero corrections where required, using the zero readings taken for each scale setting.
- Combine the zero-corrected peak height readings in pairs. Add these readings for each isotope at the first high-mass turnaround to the corresponding readings at the first low-mass turnaround. Repeat for the second, third, and fourth pairs.
- Determine the agreement among the four paired measurements. Divide each of the four  $^{238}\text{U}$  measurements by the corresponding  $^{235}\text{U}$  measurement. The

range of the four ratios thus obtained shall not exceed 5%. If this range is exceeded, record additional spectra until agreement is obtained.

7. Calculate  $\Sigma$  peak height for each isotope by summing the eight zero-corrected interpolated readings.
8. Calculate the true peak heights ( $MASS_{true}$ ) by multiplying each peak height sum by the exact scale factor for the scale setting used to record that isotope peak.
9. Calculate the bias-corrected peak heights ( $MASS_{corr}$ ) by:

$${}^{234}_{corr} = {}^{234}_{true} (1 - B) ,$$

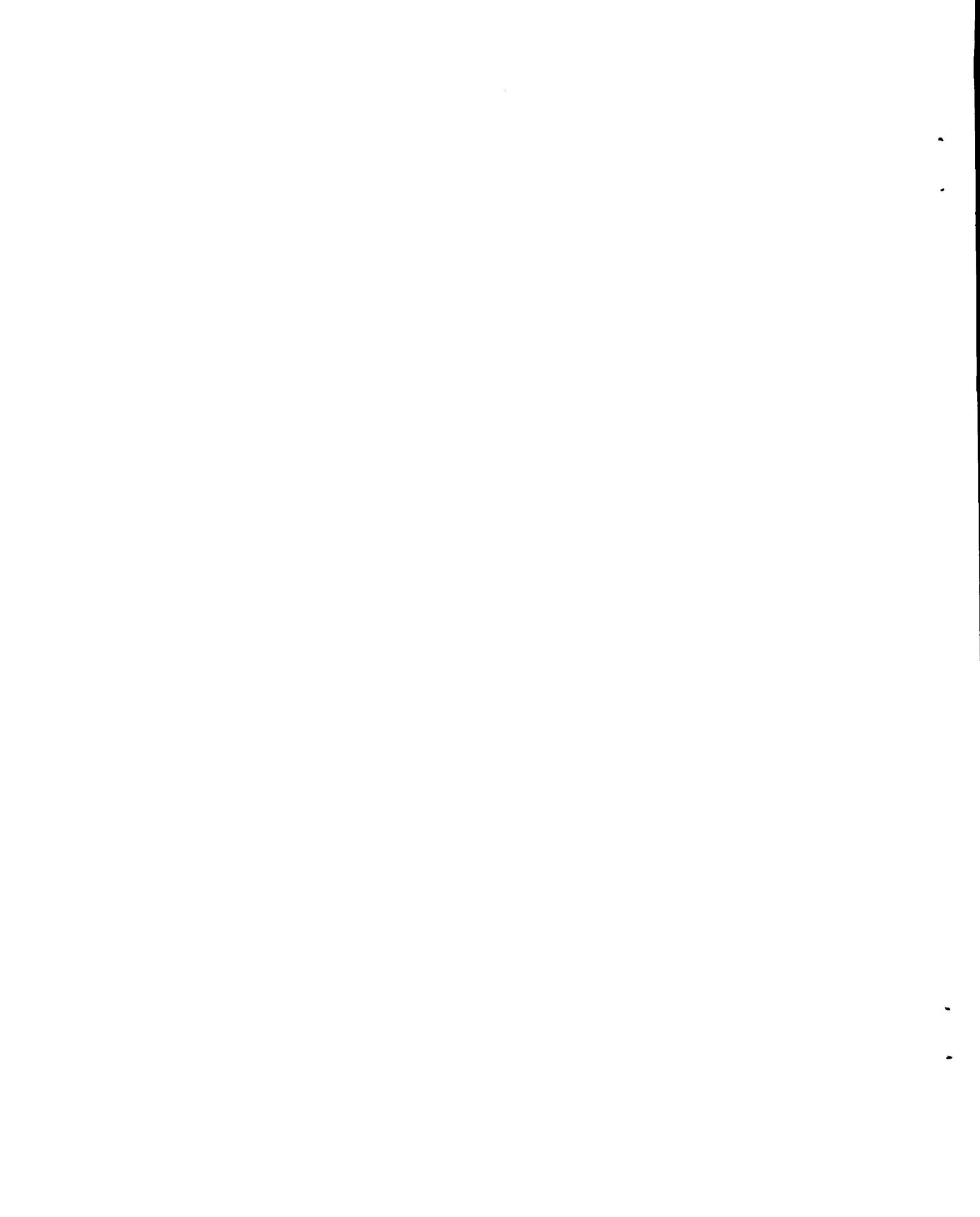
$${}^{235}_{corr} = {}^{235}_{true} ,$$

$${}^{236}_{corr} = {}^{236}_{true} (1 + B) ,$$

$${}^{238}_{corr} = {}^{238}_{true} (1 + 3B) ,$$

where B = the previously determined bias correction factor per atomic mass unit.

10. Convert from atom to weight basis by multiplying each corrected peak height by the corresponding atomic mass (whole number accuracy is adequate).
11. Calculate the weight percent of each isotope by dividing its weight basis peak height by the sum of the weight basis peak heights. For natural uranium samples, only the  ${}^{235}\text{U}$  and  ${}^{238}\text{U}$  peaks need be recorded and calculated.



DETERMINATION OF THE ISOTOPIC DISTRIBUTION  
OF PLUTONIUM IN PLUTONIUM DIOXIDE BY MASS  
SPECTROMETRY FOLLOWING ION EXCHANGE  
PURIFICATION

SUMMARY

Plutonium is separated from americium and impurity uranium on an anion exchange column and the plutonium isotope abundances are determined by thermal ionization mass spectrometry. The decontamination factors for americium and uranium are amply high to permit the isotopic abundance measurements of  $^{241}\text{Pu}$  and  $^{238}\text{Pu}$  along with the  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{242}\text{Pu}$ .

APPLICABILITY

This method <sup>[1]</sup> is applicable to samples of ceramic grade plutonium dioxide. It is similar to the method described on pp. 23 to 32 for the determination of plutonium isotopic abundances in mixed oxide pellets by mass spectrometry following ion exchange purification.

The measurement of the abundances of plutonium isotopes by thermal ionization mass spectrometry is highly reliable over the range of 0.01 to 100%, with extension to lower values provided that mass interferences are not present and that the chemical separation steps are carefully done to minimize contamination.

A single analysis including the chemical separation and mass spectrometric measurement takes about 1 - 1/4 hr for the chemical separation and 45 min for the mass spectrometric measurement. The latter time is for a mass spectrometer equipped with a vacuum lock at the source.

RELIABILITY

The pooled data <sup>[2]</sup> obtained by seven laboratories for the abundances of the plutonium isotopes 239, 240,

241, and 242 on mixed oxide samples are given below. At least this degree of reliability should be obtainable for samples of ceramic grade plutonium oxide.

<u>Isotope</u>	<u>Average of all Labs</u>	<u>Within-Lab Std Dev</u>	<u>Between-Lab Std Dev</u>
239	86.84	0.029	0.017
240	11.56	0.024	0.010
241	1.45	0.007	0.003
242	0.13	0.0017	negligible

These precisions substantially agree with the results obtained by 12 laboratories on a series of plutonium materials in which the within-laboratory absolute percent standard deviations ranged from ~ 0.0004 at an isotopic abundance of 0.01% to ~ 0.02 at isotopic abundances above 90%. <sup>[3]</sup>

DISCUSSION OF THE METHOD

The purification of plutonium in this method is based on its absorption as the chloride complex of Pu(VI) on an anion exchange resin. An aliquot of the dissolved plutonium dioxide sample containing about 100  $\mu\text{g}$  of plutonium is fumed with perchloric acid to oxidize plutonium to the (VI) oxidation state and the solution is transferred in 12M HCl to a highly cross-linked (10X) anion exchange resin column. Plutonium(VI) remains absorbed on the column as a negatively charged chloride complex; while americium and impurity elements are eluted with 12M HCl. Plutonium is then eluted with a 12M HCl-0.1M HI mixture in which the plutonium reduces to the nonabsorbed (III) oxidation state. Any impurity uranium remains absorbed on the resin in the (VI) oxidation state. A small portion of the separated plutonium fraction is analyzed for the 238, 239, 240, 241, and 242 isotope abundances by thermal ionization mass spectrometry as described later in this section. The remaining portion of the separated plutonium fraction can be reserved for the alternate determination of  $^{238}\text{Pu}$  by alpha spectrometry for those laboratories desiring to use this technique. See method entitled "Determination of  $^{238}\text{Pu}$  Isotopic Abundance by Alpha Spectrometry," p. 43.

[1] G. M. Matlack, R. M. Abernathy, and J. E. Rein, Los Alamos Scientific Laboratory, Private Communication (September 1970).

[2] C. F. Metz, R. G. Bryan, and R. K. Zeigler, LASL Report CMB-1-861 (November 1968).

[3] M. W. Lerner, USAEC Report NBL-231(1966).

The separation factors that are obtained in this procedure are 300 for americium and  $> 10^5$  for uranium. With these factors, the  $^{241}\text{Am}$  and  $^{238}\text{U}$  levels in the separated plutonium fraction do not significantly affect the mass spectrometric measurement of the  $^{241}\text{Pu}$  and  $^{238}\text{Pu}$  isotope abundances. At the specification limit of  $\sim 0.24\%$   $^{241}\text{Am}$  ( $\sim 2400 \mu\text{g } ^{241}\text{Am}$  per gram of plutonium) for ceramic grade plutonium dioxide, [4] the ratio of  $^{241}\text{Am}$  to the stated precision of 0.014 absolute percent standard deviation required for the  $^{241}\text{Pu}$  isotope abundance measurement [5] is 17. The separation factor of 300 exceeds this ratio by  $\sim 18$ . Similarly, at the specification limit of 0.23% natural uranium (equivalent to the stated value of  $2000 \mu\text{g}$  of uranium per gram of plutonium dioxide) [4] based on elemental plutonium, the ratio of  $^{238}\text{U}$  to the stated precision of 0.005 absolute percent standard deviation required for the  $^{238}\text{Pu}$  isotope abundance measurement [5] is  $\sim 50$ . The separation factor of  $10^5$  is 2000 times this ratio.

The measurement of  $^{238}\text{Pu}$  isotopic abundance is more precise by alpha spectrometry at the low  $^{238}\text{Pu}$  levels characteristic of ceramic grade plutonium dioxide. As previously mentioned, a portion of the separated plutonium fraction obtained in this method can be used conveniently for the alpha spectrometric measurement when desired.

The mass spectrometric measurement of plutonium is done directly on the separated fraction from the ion exchange column. An aliquot containing  $\sim 0.5 \mu\text{g}$  of plutonium is evaporated on sample filaments of a triple filament source of a thermal ionization mass spectrometer for these measurements.

A major factor governing the attainment of satisfactory analyses is fastidious operation, necessary to preclude sample cross-contamination. Inexpensive glassware, including ion exchange columns, that can be discarded after use for one sample is stipulated, and working areas must be kept scrupulously clean. Purified re-

agents are not necessary because plutonium is not a natural contaminant; however, the contamination of reagents from samples must be avoided. Inasmuch as the measurement is for isotopic abundances only, the recovery of plutonium need not be quantitative.

The recommended mode of mass spectrometer operation includes a triple filament source, magnetic scanning, and a Faraday cup detector. The amount of plutonium loaded on the sample filaments is  $\sim 500 \text{ ng}$  to permit use of the Faraday cup. A secondary advantage of this relatively high filament loading is to minimize any effects of small sample cross-contamination that may occur in the separation procedure or filament loading operation.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Special care must be taken when handling the concentrated acids used in this method. At the minimum, rubber gloves should be worn. Mass spectrometers have high-voltage circuits. Consult the manufacturer's manual before opening any instrument panel doors or latches.

### APPARATUS

Disposable pipets. Prepare these by drawing 7-mm borosilicate glass tubing to about 0.040-in. o.d. for a length of 3 in. A similar length of Teflon thin-walled tubing of such diameter as to fit over a standard hypodermic needle also may be used. (This tubing is obtainable from Chemplast, Inc., 150 Dey Road, Wayne, N. J. 07470.) Use these pipets only once and discard them.

Ion exchange column. Glass, 3-mm i. d., 4-cm long, with a drip tip at the bottom and a 3-ml reservoir at the top. Place a glass wool plug in the tip of the column. Prepare a distilled water slurry of the anion exchange resin (see REAGENTS) and transfer this slurry to the resin column to form a resin bed with the top just below the reservoir. Wash the resin with at least 4 ml of  $12M$  HCl.

Infrared heating lamp.

[4] RDT Standard E13-1 "Fast Flux Facility-Ceramic Grade Plutonium Dioxide" (November 1970).

[5] RDT Standard F2-6 "Program for the Qualification of Analytical Chemistry Laboratories for FFTF Fuel Analysis" (August 1970).

Medicine droppers, 1-ml.

Mass spectrometer. The instrument shall have minimum characteristics as follows:

Source: thermal ionization with multiple filaments. (A single-filament source is satisfactory when an electron multiplier is used as the detector). A vacuum lock is recommended to maintain analyzer vacuum which increases sample throughput.

Analyzer: an analyzer and vacuum system capable of producing a resolving power of at least 400 and an abundance sensitivity at mass 238 of at least 20,000. Resolving power is defined as  $M/\Delta M$ , where  $\Delta M$  is the width, in atomic mass units, of a peak at mass  $M$  at 5% of its height. Abundance sensitivity is defined as the ratio of total ion current at mass  $M$  to its contribution at mass  $M-1$ , customarily measured at masses 238 and 237 for a spectrum produced from a filament loading of natural uranium.

Detector: a system consisting of a Faraday cup and an electron multiplier, externally selectable, followed by an electrometer amplifier and a potentiometric recorder. Pulse counting systems using an electron multiplier or a scintillation-photomultiplier, as well as automatic data acquisition apparatus, also may be used.

Several commercially available mass spectrometers meet or exceed all the above requirements.

#### Mass Spectrometer Accessories.

Filaments may be made from tantalum, rhenium, or tungsten ribbon, nominally 0.001 x 0.030 in. Filaments should not be handled with bare hands. They should be prepared and stored so as to minimize contamination.

Filament forming jigs are used to form the filaments into the configuration required by the mass spectrometer and to hold the filaments in place for welding.

A spot welder is used to weld the filament ribbons to the support posts. Welds must be made carefully to ensure good electrical contact necessary for beam stability.

Sample loading unit. A power supply consisting of a Variac, 6.3-V filament transformer, ammeter, and suitable electrical contacts may be used to heat the filament to evaporate sample solution. A heat lamp or heating block also may be used.

Filament bakeout chamber. A bench-top vacuum system with a 12-in. bell jar is satisfactory. A 5-V or 6.3-V, 10-A filament transformer with the primary controlled by a Variac supplies the necessary current. Apply current gradually so that the pressure does not exceed  $10^{-6}$  Torr. Bakeout is complete after 1 hr at 2000°C. Up to 20 filaments can be degassed simultaneously without exceeding the heat dissipation capability of the system.

#### REAGENTS

Anion exchange resin. AG-1-X10, 50 to 100 mesh, chloride form, Bio-Rad Laboratories, Richmond, Calif., or equivalent.

Hydrochloric acid, 12M (37%), 6M, 2M.

Hydrochloric acid-hydriodic acid mixture, 12M HCl-0. 1M HI. Prepare a new batch each 8-hr shift.

Hydrofluoric acid, 3M.

Nitric acid, 15. 6M (70%).

Perchloric acid, 1M.

Plutonium calibration solution. Dissolve the contents of one ampoule of the NBS 948 plutonium isotopic standard in 6M HCl. Dilute to 500 ml with 2M HCl for a concentration of 0.5 mg Pu/ml. Dilute 1 ml to 10 ml with 2M HCl to give a concentration of 0.5  $\mu\text{g}$  Pu/10  $\mu\text{l}$ . Store this solution in a plastic bottle.

#### PROCEDURE

##### Blank

A blank measurement is not routinely required in this method. However, because the isotopic abundances of the plutonium may change only slightly from sample to sample, reagents can become contaminated and affect the results without immediate detection by a quality control

program. For this reason, plutonium contamination in reagents shall be checked at least once a month by carrying an aliquot of the dissolution reagent used to dissolve ceramic grade plutonium dioxide samples entirely through the procedure that is used for the samples. The level of plutonium in the blank shall be less than 1 ng of plutonium on the mass spectrometer filament based on the obtained ion currents.

### Calibration

#### Calibration of Detection System

Calibrate the detection system at startup, at least every three months, and following any alteration which could affect performance, as follows:

- a. Sensitivity scale factors
  1. Connect a precision potentiometer in series with the feedback loop of the amplifier and short out the galvanometer.
  2. Set the amplifier on the 10-mV scale and apply 10 mV from the potentiometer. Record the deflection.
  3. Repeat step 2 for each amplifier sensitivity setting and the corresponding potentiometer voltage.
  4. Determine exact scale factors from the ratios of applied voltage/recorder deflection for each sensitivity setting. Use these factors in subsequent determinations.
- b. Recorder linearity:
  1. Connect a precision potentiometer as in step a-1 above.
  2. Set the amplifier on the 1-V scale and apply voltage in increments of 0.1 V up to 1 V. Record the recorder deflection for each increment.
  3. Find the cause for and correct any non-linearity greater than 0.25% of full scale.

- c. Grid resistor linearity and ratio determination:

If a standard current source is available, the test described in TID-7029<sup>[6]</sup> is advisable.

#### Calibration of Complete System

Calibrate the complete mass spectrometer at startup, at least every three months and following any alteration, as follows:

- a. Determine the mass discrimination bias for the Faraday cup and the electron multiplier, if used, by measuring the  $^{235}\text{U}/^{238}\text{U}$  ratio on at least three separate filament loadings of the NBS U-500 standard for each detector. Average the results and calculate the respective bias correction factors by

$$B = \frac{\frac{\bar{R}_o}{R_s} - 1}{3},$$

in which

- B = mass discrimination bias factor per amu in the U-Pu mass range,  
 $\bar{R}_o$  = average of observed atom ratio  $^{235}\text{U}/^{238}\text{U}$ ,  
 $R_s$  = NBS stated atom ratio  $^{235}\text{U}/^{238}\text{U} = 1.0003$ .

Apply these bias corrections to subsequent measurements.

- b. Establish the linear range of both detection systems by measuring the  $^{234}\text{U}/^{235}\text{U}$  ratio on separate filament loadings of the NBS U-930 standard for each system over a wide range of ion currents at increments corresponding to the amplifier scale factors. To aid interpretation, plot the observed ratio vs the  $^{235}\text{U}$  ion current on semilog paper. Analyze samples only within the linear range.

[6] R. J. Jones, Ed., Method 2.500, Selected Measurement Methods for Uranium and Plutonium in the Nuclear Fuel Cycle, USAEC Report TID-7029 (1963).

### Daily Verification of Mass Spectrometer Stability

Verify the stability of each mass spectrometer used in any 8-hr working shift with the NBS 948 plutonium isotopic standard when plutonium samples are analyzed during that shift. Maintain a control chart for each instrument by plotting the measured  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio as a function of time. When the value of the ratio significantly changes at the .05 significance level, do not analyze samples until the cause is corrected. Possible sources of instability are a deterioration of the electron multiplier, low gain in the electrometer amplifier, electrical or mechanical malfunctions in the recorder, and inadequate regulation in the filament power supply.

### Sample Analysis

#### Dissolution and Separation of Plutonium

1. Dissolve 0.1 mg of the ceramic grade plutonium dioxide sample in 100  $\mu\text{l}$  of 15.6M  $\text{HNO}_3$  and 10  $\mu\text{l}$  of 3M HF in a 5-ml beaker with the aid of moderate heating.

The sample weight and reagent volumes need not be quantitative because only isotope abundances are to be measured. The sealed tube hydrochloric acid dissolution technique, described on p. 5, also may be used for sample dissolution.

2. Add 2 drops of 1M  $\text{HClO}_4$  to the sample solution and fume to near dryness.

Do not contaminate the perchloric acid dropper with the sample. Lower oxidation states of plutonium oxidize to the (VI) oxidation state. Americium and uranium remain at the (III) and (VI) oxidation states respectively.

3. After the beaker and contents cool to room temperature, add 1 ml of 12M HCl, and mix.

Use a medicine dropper to mix the solution, and for the transfer in the next step.

4. Transfer the solution to a new ion exchange column containing the 12M HCl-equilibrated anion exchange resin and discard the effluent.

Plutonium absorbs on the resin as the chloride complex of Pu(VI), americium and most impurity elements elute from the column.

5. After the original sample solution descends to the top of the resin bed, pass 3 ml of 12M HCl through the column in 15 approximately equal 200- $\mu\text{l}$  additions, and discard the effluent.

Wait between each addition until the previous addition descends to the top of the resin bed. Add the elutant in a manner to wash down the walls of the reservoir. This step elutes the americium and impurity element tailings.

6. Pass 2 ml of freshly prepared 12M HCl-0.1M HI through the column and collect the effluent in a clean small vial with either a plastic screw cap or a plastic stopper and mix the contents.

Plutonium reduces to the (III) oxidation state which elutes from the column. Uranium impurity remains absorbed on the column as the U(VI) complex.

7. With a clean disposable pipet (see APPARATUS), transfer  $\sim 10 \mu\text{l}$  of the eluted plutonium fraction to the sample filaments of a triple filament assembly which is mounted in the sample loading unit and evaporate slowly to dryness.

The amount of plutonium transferred to the sample filaments is  $\sim 0.5 \mu\text{g}$ , about ideal when a Faraday cup collector is used.

8. Restopper the vial and reserve it for the  $^{238}\text{Pu}$  measurement by alpha spectrometry, if desired.

About 90  $\mu\text{g}$  of plutonium is in this tube.

#### Mass Spectrometric Analysis of Plutonium

1. Introduce the loaded filament assembly into the ion source using the procedure recommended by the instrument manufacturer.
2. When the source pressure drops to  $2 \times 10^{-7}$  Torr, begin degassing by passing 3 A of current through the ionizing filament.
3. When the source pressure is below  $10^{-6}$  Torr with the ionizing filament heating, turn on the high voltage and adjust the high voltage and magnet to bring in m/e 239.
4. Increase the ionizing filament current to  $\sim 4.5$  A, then slowly increase the sample filament current until an ion beam is detected.

5. Adjust focus controls and mechanical alignment for maximum beam intensity.

6. Increase the sample filament currents until the  $^{239}\text{Pu}$  ion current is in the range of  $10^{-11}$  A.

With an electron multiplier, the desired  $^{239}\text{Pu}$  ion current is  $\sim 10^{-13}$  A. It may be necessary to experiment with different combinations of filament currents to achieve a stable beam of the desired intensity.

7. Scan the spectrum repeatedly in both directions over the mass range of 239 through 242 until at least nine spectra have been recorded. Use scale settings that will cause each peak to be recorded on the top half of the strip chart.

Magnetic field scanning is preferred.

Collect data only when the ion beam is essentially constant.

8. Reduce the sample filament currents to zero, record the zero readings for each scale setting used, and remove the chart for calculations.

#### Calculations

Relative ion beam intensities, proportional to atom abundances, are measured by interpolating between peak tops and making all measurements of individual isotopes for one set of ratios at one point on the x-axis (one common time) to remove the effect of changes in beam intensity with time. Readings can be made at any point after the completion of the first single sweep and before the beginning of the last sweep. The preferred procedure is to take a reading of all isotopes at each time the sweep direction is changed (turnaround). Measurements should be made in pairs. One reading at the high-mass turnaround and one at the adjacent low-mass turnaround constitute a pair. To obtain  $N$  pairs of consecutive readings,  $2N + 1$  single sweeps in alternate directions are required.

1. Draw lines on the chart connecting the tops of the consecutive peaks of the same isotope for each isotope to be measured.
2. Draw vertical lines on the chart at or near the turnaround points corresponding to each change in sweep

direction.

3. Read the interpolated peak height of each isotope at the intersection of each vertical line with the interpolating lines.
4. Make zero corrections where required, using the zero readings taken for each scale setting.
5. Combine the zero-corrected peak height readings in pairs. Add these readings for each isotope at the first high-mass turnaround to the corresponding readings at the first low-mass turnaround. Repeat for the second, third, and fourth pairs.
6. Determine the agreement among the four paired measurements.

Divide each of the four  $^{239}\text{Pu}$  readings by the corresponding  $^{241}\text{Pu}$  reading. The range of the four ratios thus obtained shall not exceed 0.6% relative. Divide each of the four  $^{239}\text{Pu}$  readings by the corresponding  $^{241}\text{Pu}$  reading. The range of these four ratios shall not exceed 3% relative. If either range is exceeded, collect additional data until agreement is obtained.

7. Calculate  $\Sigma$  peak height for each isotope by summing the eight zero-corrected interpolated readings.
8. Calculate the true peak heights ( $\text{MASS}_{\text{true}}$ ) by multiplying each peak height sum by the exact scale factor for the scale setting used to record that isotope peak.
9. Calculate the bias-corrected peak heights ( $\text{MASS}_{\text{corr}}$ ) by

$$^{238}_{\text{corr}} = (^{238}_{\text{true}}) (1 - B) ,$$

$$^{239}_{\text{corr}} = (^{239}_{\text{true}}) ,$$

$$^{240}_{\text{corr}} = (^{240}_{\text{true}}) (1 + B) ,$$

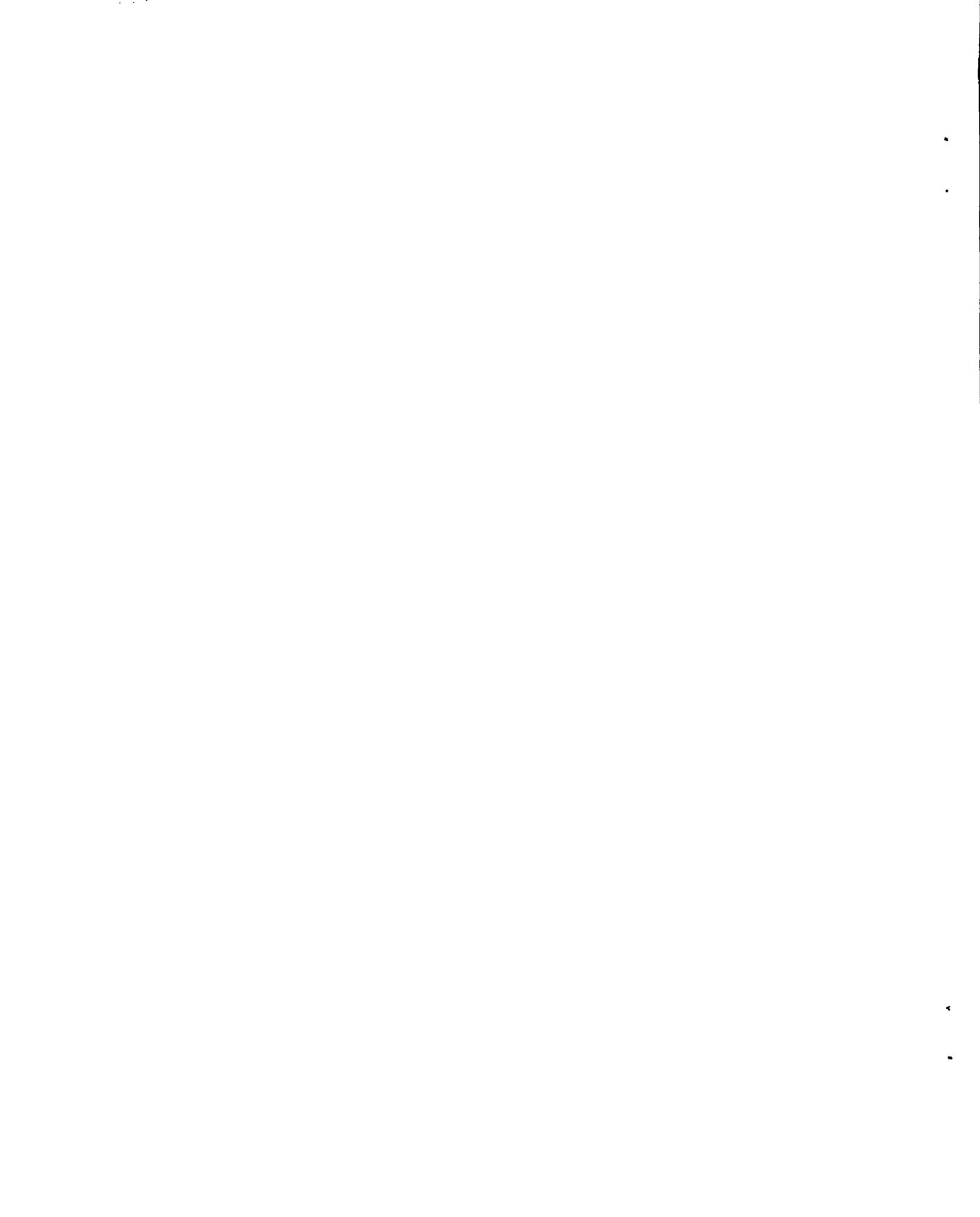
$$^{241}_{\text{corr}} = (^{241}_{\text{true}}) (1 + 2B) ,$$

$$^{242}_{\text{corr}} = (^{242}_{\text{true}}) (1 + 3B) ,$$

where  $B$  = the previously determined bias correction factor per atomic mass unit.

10. Convert from atom to weight basis by multiplying corrected peak heights by the corresponding atomic mass (whole number accuracy is adequate).

11. Calculate the weight percent of each isotope by dividing its weight basis peak height by the sum of the weight basis peak heights, and multiplying by 100.



DETERMINATION OF THE ISOTOPIC DISTRIBUTION  
OF URANIUM AND PLUTONIUM IN MIXED-OXIDE  
PELLETS BY MASS SPECTROMETRY FOLLOWING  
SEQUENTIAL ION EXCHANGE SEPARATION

SUMMARY

Plutonium and uranium are sequentially separated on a single anion exchange column and the separated fractions are individually analyzed for isotopic abundances by thermal ionization mass spectrometry. The decontamination factor for uranium in the separated plutonium fraction is amply high to permit the isotopic abundance measurement of  $^{238}\text{Pu}$  by mass spectrometry with a precision that satisfies the specification requirements for mixed oxide fuel.

APPLICABILITY

This method<sup>[1]</sup> is applicable to samples of mixed oxide pellets. An alternative mass spectrometric method, which is based on a liquid-liquid extraction, is given on p. 33 for use by laboratories that prefer liquid-liquid extraction techniques.

The measurement of the abundances of plutonium and uranium by thermal ionization mass spectrometry, as described in this method, is highly reliable over the range of 0.01 to 100% with extension to lower values provided that mass interferences are not present and that the chemical preparation steps are carefully done to minimize contamination.

A single analysis including the chemical separation and the mass spectrometric measurement both of uranium and plutonium takes about 2 hr, 0.5 hr for the chemical separation and 45 min for each mass spectrometric measurement. The latter time is for a mass spectrometer equipped with a vacuum lock at the source.

RELIABILITY

The pooled data obtained by seven laboratories for the abundances of the plutonium isotopes 239, 240, 241, and 242 in mixed oxide fuel pellets with a uranium to plutonium ratio of 3 to 1 were:<sup>[2]</sup>

<u>Pu Isotope</u>	<u>Average of all Labs</u>	<u>Within-Lab Std Dev</u>	<u>Between-Lab Std Dev</u>
239	86.84	0.029	0.017
240	11.56	0.024	0.010
241	1.45	0.007	0.008
242	0.13	0.0017	negligible

These precisions substantially agree with those obtained by laboratories on a series of uranium and plutonium materials analyzed on thermal ionization mass spectrometers using both single and triple filament sources.<sup>[3]</sup> In general, the absolute precision is a function of the level of the abundance of an isotope and not of the isotopic mass. The within-laboratory absolute percent standard deviations ranged from ~ 0.0004 at an isotopic abundance of 0.01% to ~ 0.02 at isotopic abundances greater than 90%.

DISCUSSION OF THE METHOD

The separation of plutonium and uranium in this method is based on the absorption of the chloride complexes of plutonium and uranium, both in the (VI) oxidation state, on an anion exchange resin followed by their sequential elution. An aliquot of the dissolved mixed oxide fuel pellet containing about 100  $\mu\text{g}$  of plutonium and 300  $\mu\text{g}$  of uranium is fumed with perchloric acid to oxidize plutonium to the (VI) oxidation state and the solution is transferred in 12M HCl to a highly cross-linked (10X) anion exchange resin column. Plutonium(VI) and U(VI) remain absorbed on the column as negatively charged chloride complexes while americium and impurity elements are eluted with 12M HCl. Plutonium is eluted with a 12M HCl-0.1M HI mixture in which the plutonium reduces to the nonab-

[1] G. M. Matlack, R. M. Abernathy, and J. E. Rein, Los Alamos Scientific Laboratory, Private Communication, (September 1970).

[2] C. F. Metz, R. G. Bryan, and R. K. Zeigler, LASL Report CMB-1-861 (November 1968).

[3] M. W. Lerner, USAEC Report NBL-231 (1966).

sorbed (III) oxidation state. After a 12M HCl-0.1M HI rinse is applied to the column to remove plutonium tailings, uranium is eluted with 0.1M HCl. Small portions of the separated plutonium and uranium fractions are separately analyzed for isotope abundances by thermal ionization mass spectrometry as described more fully later in this section. The remaining portion of the separated plutonium fraction can be reserved for the alternative determination of  $^{238}\text{Pu}$  by alpha spectrometry for those laboratories desiring to use this technique. See method entitled "Determination of  $^{238}\text{Pu}$  Isotopic Abundance by Alpha Spectrometry," p. 43.

The important separation factors in this procedure are 300 for americium and  $> 1 \times 10^5$  for uranium in the plutonium fraction, and  $> 1 \times 10^4$  for americium and 150 for plutonium in the uranium fraction. This separation factor for americium in the plutonium fraction reduces the  $^{241}\text{Am}$  level so that it does not significantly affect the mass spectrometric measurement of the  $^{241}\text{Pu}$  isotopic abundance. At the maximum specification limit of  $\sim 2400 \mu\text{g } ^{241}\text{Am}$  per gram of plutonium and a  $^{241}\text{Pu}$  isotopic abundance of 1.5% in the mixed oxide fuel, the ratio of  $^{241}\text{Am}/^{241}\text{Pu}$  in the separated plutonium fraction is  $< 1 \times 10^{-3}$  at a separation factor of 300.

In a mixed oxide fuel in which the ratio of uranium (natural) to plutonium is 3 to 1, the  $^{238}\text{U}/^{238}\text{Pu}$  ratio is almost 2000 to 1 at the specification limit of 0.15% for the  $^{238}\text{Pu}$  abundance in mixed oxide fuel. The more important factor governing the separation factor required for uranium in the separated plutonium fraction is the precision with which the  $^{238}\text{Pu}$  isotopic abundance is to be measured. The standard deviation stated to be required is 0.005 absolute abundance percent. This demands a separation factor of at least  $6 \times 10^4$ . The separation factor of  $> 1 \times 10^5$  obtainable in the method meets this demand. Laboratories are cautioned, however, to evaluate each lot of ion exchange resin by processing  $^{233}\text{U}$  through the plutonium separation stage of the separation procedure followed by gross alpha counting of the various fractions to ensure that the resin will give satisfactory re-

[4] RDT Standard F2-6 "Qualification of Analytical Chemistry Laboratories for FFTF Fuel Analysis" (August 1970).

sults. Some resin lots have been found not to be satisfactory.

The measurement of  $^{238}\text{Pu}$  isotopic abundance is more precise by alpha spectrometry at the low  $^{238}\text{Pu}$  levels characteristic of LMFBR/FFTF mixed oxide fuel. As previously mentioned, a portion of the separated plutonium fraction obtained in this method can be used conveniently for the alpha spectrometric measurement when desired.

The mass spectrometric measurements for plutonium and uranium are done directly on the respective separated fractions. Aliquots containing  $\sim 0.5 \mu\text{g}$  of plutonium and  $\sim 1 \mu\text{g}$  of uranium are evaporated on sample filaments of a triple-filament source of a thermal ionization mass spectrometer for these measurements.

A major factor governing the attainment of satisfactory analyses is fastidious operation, necessary to preclude sample cross-contamination, and especially in the case of uranium, natural uranium contamination.

Purified reagents, especially acids, stored in plastic or quartz bottles are stipulated, and inexpensive glassware and plastic ware that can be discarded after use for one sample are strongly recommended. In addition, the working areas must be kept scrupulously clean. Inasmuch as the measurement is for isotopic abundances only, the operations need not be quantitative.

The recommended mode of mass spectrometer operation in addition to a triple-filament source includes magnetic scanning and a Faraday cup detector. The use of the Faraday cup requires sample loadings of  $\sim 0.5$  to  $1 \mu\text{g}$ . A secondary advantage of this relatively high level of filament loadings is to minimize the effects of small sample cross contamination and natural uranium contamination that may occur in the separation procedure or filament loading operations.

The selection of the two methods presented here and on p 33 for the determination of the isotopic abundances of uranium and plutonium in mixed oxide fuels was based on their proven capability for these analyses. The ASTM ion exchange method, [5] designed for irradiated fuel

[5] ASTM Standards, Part 30, Method E267-67T, American Society for Testing and Materials, Philadelphia, 1969.

samples with a very high preirradiated ratio of uranium to plutonium and containing fission products, is relatively long and does not give a plutonium fraction sufficiently free of uranium to permit the reliable measurement of the  $^{238}\text{Pu}$  isotopic abundance. The only method presented in the USAEC Manual [6] applicable to uranium-plutonium fuels is based on a liquid-liquid extraction that gives a combined uranium-plutonium fraction for simultaneous analysis in a triple-filament source, thermal ionization mass spectrometer. This method is not recommended because the precision of the measured isotopic abundance values both of uranium and plutonium is about twice poorer than the precision obtained when separated uranium and plutonium fractions are independently analyzed [3] and because  $^{238}\text{Pu}$  cannot be measured in the presence of  $^{238}\text{U}$ .

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Special care must be taken when handling the concentrated acids used in this method. As a minimum precaution, rubber gloves should be worn.

Mass spectrometers have high-voltage circuits. Consult the manufacturer's manual before opening any instrument panel doors or latches.

### APPARATUS

Disposable pipets. Prepare these by drawing 7-mm borosilicate glass tubing to about 0.040-in. o.d. for a length of 3 in. A similar length of Teflon thin-walled tubing of such diameter as to fit over a standard hypodermic needle also may be used. (This tubing is obtainable from Chemplast, Inc., 150 Dey Road, Wayne, N. J. 07470). Use these pipets only once and discard them.

Ion exchange column. Glass, 3-mm i.d., 4-cm long, with a drip tip at the bottom and a 3-ml reservoir at the top. Place a glass wool plug in the column tip. Prepare

[6] R. J. Jones, Ed., Method 4.502, Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle, USAEC Report TID-7029 (1963).

a distilled water slurry of the anion exchange resin (see REAGENTS) and transfer this slurry to the resin column to form a resin bed with the top just below the reservoir. Wash the resin with at least 4 ml of 12M HCl.

Infrared heating lamp.

Medicine droppers, 1-ml.

Mass spectrometer. The instrument shall have minimum characteristics as follows:

Source: thermal ionization with multiple filaments. (A single-filament source is satisfactory when an electron multiplier is used as the detector). A vacuum lock is recommended to maintain analyzer vacuum which increases sample throughput.

Analyzer: an analyzer and vacuum system capable of producing a resolving power of at least 400 and an abundance sensitivity at mass 238 of at least 20,000. Resolving power is defined as  $M/\Delta M$ , where  $\Delta M$  is the width, in atomic mass units, of a peak at mass  $M$  at 5% of its height. Abundance sensitivity is defined as the ratio of total ion current at mass  $M$  to its contribution at mass  $M-1$ , customarily measured at masses 238 and 237 for a spectrum produced from a filament loading of natural uranium.

Detector: a system consisting of a Faraday cup and an electron multiplier, externally selectable, followed by an electrometer amplifier and a potentiometric recorder. Pulse counting systems using an electron multiplier or a scintillator-photomultiplier, as well as automatic data acquisition apparatus, also may be used.

Several commercially available mass spectrometers meet or exceed all the above requirements.

Mass Spectrometer Accessories.

Filaments may be made from tantalum, rhenium, or tungsten ribbon, nominally  $0.001 \times 0.030$  in. Filaments should not be handled by bare hands. They should be prepared and stored so as to minimize contamination.

Filament forming jigs are used to form the filaments into the configuration required by the mass spectrometer and to hold the filaments in place for welding.

A spot welder is used to weld the filament ribbons to the support posts. Welds must be made carefully to ensure good electrical contact which is necessary for beam stability.

Sample loading unit. A power supply consisting of a Variac, 6.3-V filament transformer, ammeter, and suitable electrical contacts may be used to heat the filament to evaporate sample solution. A heat lamp or heating block also may be used.

Filament bakeout chamber. A bench-top vacuum system with a 12-in. bell jar is satisfactory. A 5-V or 6.3-V, 10-A, filament transformer with the primary controlled by a Variac supplies the necessary current. Apply current gradually so that the pressure does not exceed  $10^{-6}$  Torr. Bakeout is complete after 1 hr at  $2000^{\circ}\text{C}$ . Up to 20 filaments can be degassed simultaneously without exceeding the heat dissipation capability of the system.

## REAGENTS

Anion exchange resin. AG 1-X10, 50 to 100 mesh, chloride form, Bio-Rad Laboratories, Richmond, Calif.; or equivalent.

Hydrochloric acid,  $12\text{M}$  (37%),  $6\text{M}$ ,  $2\text{M}$ ,  $0.1\text{M}$ .

Hydrochloric acid-hydrionic acid mixture,  $12\text{M}$  HCl- $0.1\text{M}$  HI. Prepare a new batch each 8-hr shift.

Hydrofluoric acid,  $28\text{M}$  (48%).

Nitric acid,  $15.6\text{M}$  (70%),  $8\text{M}$ ,  $1\text{M}$ .

Perchloric acid,  $1\text{M}$ .

Plutonium calibration solution. Dissolve the contents of one ampoule of the NBS 948 plutonium isotopic standard in  $6\text{M}$  HCl. Dilute to 500 ml with  $2\text{M}$  HCl for a concentration of 0.5 mg Pu/ml. Dilute 1 ml to 10 ml with  $2\text{M}$  HCl to give a concentration of 0.5  $\mu\text{g}$  Pu/10  $\mu\text{l}$ . Store this solution in a plastic bottle.

Uranium calibration solutions. Prepare three calibration solutions by dissolving 12 mg each of NBS U-010, U-500, and U-930 uranium isotopic standards in minimum amounts of  $8\text{M}$   $\text{HNO}_3$ . Dilute to 100 ml with  $1\text{M}$   $\text{HNO}_3$  to give concentrations of 1  $\mu\text{g}$  U/10  $\mu\text{l}$ . Store these solutions in plastic bottles.

## PROCEDURE

### Blank

A blank measurement is not routinely required in this method. However, reagents can become sufficiently contaminated to affect the results without immediate detection by a quality control program because the samples contain natural uranium and plutonium whose isotopic abundances may change slightly from sample to sample. For this reason, uranium and plutonium contamination in reagents shall be checked at least once a month by carrying an aliquot of the mixed oxide dissolution reagents entirely through the procedure used by a laboratory for samples. The levels of uranium and plutonium in this reagent blank shall be less than 1 ng of both elements on the mass spectrometer filament based on the observed ion currents.

### Calibration

#### Calibration of Detection System

Calibrate the detection system at startup, at least every three months, and following any alteration which could affect performance, as follows:

- a. Sensitivity scale factors
  1. Connect a precision potentiometer in series with the feedback loop of the amplifier and short out the galvanometer.
  2. Set the amplifier on the 10-mV scale and apply 10 mV from the potentiometer. Record the deflection.
  3. Repeat step 2 for each amplifier sensitivity setting and the corresponding potentiometer voltage.
  4. Determine exact scale factors from the ratios of applied voltage/recorder

deflection for each sensitivity setting. Use these factors in subsequent determinations.

b. Recorder linearity:

1. Connect a precision potentiometer as in a-1 above.
2. Set the amplifier on the 1-V scale and apply voltage in increments of 0.1 V up to 1 V. Record the recorder deflection for each increment.
3. Find the cause for and correct any non-linearity greater than 0.25% of full scale.

c. Grid resistor linearity and ratio determination:

If a standard current source is available, the test described in TID-7029<sup>[7]</sup> is advisable.

Calibration of Complete System

Calibrate the complete mass spectrometer at startup, at least every three months, and following any alteration, as follows:

- a. Determine the mass discrimination bias for the Faraday cup and the electron multiplier, if used, by measuring the  $^{235}\text{U}/^{238}\text{U}$  ratio on at least three separate filament loadings of the NBS-500 standard for each detector. Average the results and calculate the respective bias correction factors by

$$B = \frac{\frac{\bar{R}_o}{\bar{R}_s} - 1}{3}$$

in which

B = mass discrimination bias factor per amu in the U-Pu mass range,

[7] R. J. Jones, Ed., Method 2.500, Selected Measurement Methods for Uranium and Plutonium in the Nuclear Fuel Cycle, USAEC Report TID-7029 (1963).

$\bar{R}_o$  = average of observed atom ratio  $^{235}\text{U}/^{238}\text{U}$ ,

$\bar{R}_s$  = NBS stated atom ratio  $^{235}\text{U}/^{238}\text{U} = 1.0003$ .

Apply these bias corrections to subsequent measurements.

- b. Establish the linear range of both detection systems by measuring the  $^{234}\text{U}/^{235}\text{U}$  ratio on separate filament loadings of the NBS U-930 standards for each system over a wide range of ion currents at increments corresponding to the amplifier scale factors. To aid interpretation, plot the observed ratio vs the  $^{235}\text{U}$  ion current on semilog paper. Analyze samples only within the linear range.

Daily Verification of Mass Spectrometer Stability

Verify the stability of each mass spectrometer used in any 8-hr working shift with the NBS 948 plutonium isotopic standard when plutonium samples are analyzed during that shift and with the NBS U-010 uranium isotopic standard when uranium samples are analyzed during that shift. Maintain control charts for each standard by plotting the ratio of  $^{240}\text{Pu}/^{239}\text{Pu}$  for NBS-948 and the ratio of  $^{235}\text{U}/^{238}\text{U}$  for NBS-010 as functions of time. When the value of either ratio significantly changes at the .05 significance level, do not analyze samples until the cause is corrected. Possible sources of instability are a deterioration of the electron multiplier, low gain in the electrometer amplifier, electrical or mechanical malfunctions in the recorder, and inadequate regulation in the filament power supply.

Sample Analysis

Dissolution

1. Dissolve a weighed, whole mixed oxide pellet in 5 to 10 ml of 15.6M  $\text{HNO}_3$  in a 50-ml beaker or a 30-ml platinum dish with covers and with the aid of heat.

A pellet weighed to  $\pm 0.2$  mg is recommended because aliquots of the dissolved solution also can be used for the determination of uranium and plutonium concentrations by the appropriate method on p. 47. If a pellet is used only

for the isotopic abundance measurements, this step need not be quantitative.

Use platinum dishes if the dissolution reagent is 15.6M  $\text{HNO}_3$ -0.01M HF. This acid mixture gives faster dissolution rates. In this case, omit step 3

The sealed-tube technique described on p. 5 also may be used for the dissolution.

2. Repeat the additions of 5 to 10 ml of 15.6M  $\text{HNO}_3$  and heating until dissolution is apparently complete.

Again use simmering heat to speed the dissolution and use covers to prevent spattering loss.

3. With the last addition of 15.6M  $\text{HNO}_3$  or when the dissolution reaction is complete, add 1 drop of 1M HF and sufficient 15.6M  $\text{HNO}_3$  to give a total volume of 5 to 10 ml. Continue the heating until complete solubility is obtained.

4. Transfer the solution quantitatively with the aid of at least five 5-ml rinses of 1M  $\text{HNO}_3$  to a tared, preferably heavy-walled polyethylene container having an airtight cap, and weigh to  $\pm 1$  mg.

Weighed aliquots of this solution can serve also for various other analyses, including measurements of uranium and plutonium contents and iron.

A heavy-walled polyethylene container minimizes changes in concentration caused by transpiration of water vapor through the walls.

#### Separation of Plutonium and Uranium

1. Transfer a  $\sim 20$ - $\mu\text{l}$  aliquot of the dissolved mixed oxide pellet solution into a 5-ml beaker.

This aliquot, which need not be quantitative, should contain  $\sim 100$   $\mu\text{g}$  of plutonium and  $\sim 300$   $\mu\text{g}$  of uranium. Use a disposable pipet and deliver the solution to the bottom of the beaker without placing any on the walls.

2. Add 2 drops of 1M  $\text{HClO}_4$  to the sample solution and fume to near dryness.

Do not contaminate the perchloric acid dropper with the sample.

Lower oxidation states of plutonium oxidize to the (VI) oxidation state. Americium and uranium remain at the (III) and (VI) oxidation states, respectively.

3. After the beaker and contents cool to room temperature, add 1 ml of 12M HCl, and mix.

Use a new medicine dropper to mix the solution and for the transfer in the next step.

4. Transfer the solution to a new ion exchange column containing the 12M HCl-equilibrated anion exchange resin and discard the effluent.

Plutonium and uranium absorb on the resin as chloride complexes of Pu(VI) and U(VI), americium and most impurity elements elute from the column.

5. After the original sample solution descends to the top of the resin bed, pass 3 ml of 12M HCl through the column in 15 approximately equal 200- $\mu\text{l}$  additions, and discard the effluent.

Wait between each addition until the previous addition descends to the top of the resin bed. Add the elutant in a manner to wash down the walls of the reservoir. This step elutes the americium and impurity element tailings.

6. Pass 2 ml of freshly prepared 12M HCl-0.1M HI through the column and collect the effluent in a clean small vial with either a plastic screw cap or a plastic stopper and mix the contents.

Plutonium reduces to the (III) oxidation state which elutes from the column. Uranium remains absorbed on the resin column.

7. With a clean disposable pipet (see APPARATUS), transfer  $\sim 10$   $\mu\text{l}$  of the eluted plutonium fraction to the sample filaments of a triple filament assembly which is mounted in the sample loading unit and evaporate slowly to dryness.

The amount of plutonium transferred to the sample filaments is  $\sim 0.5$   $\mu\text{g}$ , about ideal when a Faraday cup collector is used.

8. Restopper the vial and reserve it for the  $^{238}\text{Pu}$  measurement by alpha spectrometry, if desired.

About 100  $\mu\text{g}$  of plutonium is in this tube.

9. Pass 4 ml of 12M HCl-0.1M HI through the column and discard the effluent.

Plutonium tailings elute from the column. Additional 12M HCl-0.1M HI may be passed through if a higher plutonium separation factor is desired. Uranium does not significantly migrate down the highly cross-linked resin.

10. Pass 2 ml of 0.1M HCl through the column in 10 approximately equal 200- $\mu\text{l}$  additions and collect

the effluent in a clean small vial with either a plastic screw cap or a plastic stopper and mix the contents.

Wait between each addition until the previous addition descends to the top of the resin bed. Add the elutant in a manner to wash down the walls of the reservoir. Uranium elutes from the column.

11. With a clean disposable pipet (see APPARATUS), transfer 5 to 10  $\mu\text{l}$  of the eluted uranium fraction to the sample filaments of a triple-filament assembly which is mounted in the sample loading unit and evaporate slowly to dryness.

The amount of uranium transferred to the sample filaments is 0.75 to 1.5  $\mu\text{g}$ , about ideal when a Faraday cup collector is used.

#### Mass Spectrometric Analysis of Plutonium

1. Introduce the loaded filament assembly into the ion source using the procedure recommended by the instrument manufacturer.
2. When the source pressure drops to  $2 \times 10^{-7}$  Torr, begin degassing by passing a 3-A current through the ionizing filament.
3. When the source pressure is below  $10^{-6}$  Torr with the ionizing filament heated, turn on the high voltage and adjust the high voltage and magnet to bring in m/e 239.
4. Increase the ionizing filament current to  $\sim 4.5\text{A}$ , then slowly increase the sample filament currents until an ion beam is detected.
5. Adjust focus controls and mechanical alignment for maximum beam intensity.
6. Increase the sample filament currents until the  $^{239}\text{Pu}$  ion current is the range of  $10^{-11}$  A.  
With an electron multiplier, the desired  $^{239}\text{Pu}$  ion current is  $\sim 10^{-13}$  A. It may be necessary to experiment with different combinations of filament currents to achieve a stable beam of the desired intensity.
7. Scan the spectrum repeatedly in both directions over the mass range of 239 through 242 until at least nine spectra have been recorded. Use scale settings that will cause each peak to be recorded on the top half of the strip chart.

Magnetic field scanning is preferred.

Collect data only when the ion beam is essentially constant.

8. Reduce the sample filament currents to zero, record the zero readings for each scale setting used, and remove the chart for calculations.

#### Mass Spectrometric Analysis of Uranium

1. Introduce the loaded filament assembly into the ion source, using the procedure recommended by the instrument manufacturer.
2. When the source pressure drops to  $2 \times 10^{-7}$  Torr, begin degassing by passing a 3-A current through the ionizing filament.
3. When the source pressure is below  $10^{-6}$  Torr with the ionizing filament heated, turn on the high voltage and adjust the high voltage and magnet to bring in m/e 238.  
Focus on the major isotope -  $^{238}\text{U}$  in most cases;  $^{235}\text{U}$  in the case of NBS U-930.
4. Increase the ionizing filament current to 4.5 A, then slowly increase the sample filament currents until an ion beam is detected.

If no ion beam is detected with sample filament currents of 2 A, reduce the currents to 1 A and focus on the ion beam of the ionizing filament material, then go back to the uranium beam.

5. Adjust focus controls and mechanical alignment for maximum beam intensity.
6. Increase the sample filament currents until the  $^{238}\text{U}$  ion current is in the range of  $10^{-11}$  A.  
With an electron multiplier, the desired  $^{238}\text{U}$  ion current is  $\sim 10^{-13}$  A. It may be necessary to experiment with different combinations of filament currents to achieve a stable beam of the desired intensity.
7. Scan the spectrum repeatedly in both directions over the range of interest until at least nine spectra have been recorded. Use scale settings that will cause each peak to be recorded on the top half of the strip chart.

Magnetic field scanning is preferred.

Collect data only when the ion beam intensity is essentially constant.

8. Reduce the sample filament currents to zero, record zero readings for each scale setting used, and remove the chart for calculations.

### Calculations

#### Plutonium

Relative ion beam intensities, proportional to atom abundances, are measured by interpolating between peak tops and making all measurements of individual isotopes for one set of ratios at one point on the x-axis (one common time) to remove the effect of changes in beam intensity with time. Readings can be made at any point after the completion of the first single sweep and before the beginning of the last sweep. The preferred procedure is to take a reading of all isotopes at each time the sweep direction is changed (turnaround). Measurements should be made in pairs. One reading at the high-mass turnaround and one at the adjacent low-mass turnaround constitute a pair. To obtain N pairs of consecutive readings, 2N + 1 single sweeps in alternate directions are required.

1. Draw lines on the chart connecting the tops of the consecutive peaks of the same isotope for each isotope to be measured.
2. Draw vertical lines on the chart at or near the turnaround points corresponding to each change in sweep direction.
3. Read the interpolated peak height of each isotope at the intersection of each vertical line with the interpolating lines.
4. Make zero corrections where required, using the zero readings taken for each scale setting.
5. Combine the zero-corrected peak height readings in pairs. Add these readings for each isotope at the first high-mass turnaround to the corresponding readings at the first low-mass turnaround. Repeat for the second, third, and fourth pairs.
6. Determine the agreement among the four paired measurements. Divide each of the four  $^{239}\text{Pu}$  readings by the corresponding  $^{240}\text{Pu}$  reading. The range of the four ratios thus obtained shall not exceed 0.6%

relative. Divide each of the four  $^{239}\text{Pu}$  readings by the corresponding  $^{241}\text{Pu}$  reading. The range of these four ratios shall not exceed 3% relative. If either range is exceeded, collect additional data until agreement is obtained.

7. Calculate  $\Sigma$  Peak Height for each isotope by summing the eight zero-corrected interpolated readings.
8. Calculate the true peak heights ( $\text{MASS}_{\text{true}}$ ) by multiplying each peak height sum by the exact scale factor for the scale setting used to record that isotope peak.
9. Calculate the bias-corrected peak heights ( $\text{MASS}_{\text{corr}}$ ) by:

$$^{238}_{\text{corr}} = ^{238}_{\text{true}}(1 - B),$$

$$^{239}_{\text{corr}} = ^{239}_{\text{true}},$$

$$^{240}_{\text{corr}} = (^{240}_{\text{true}})(1 + B),$$

$$^{241}_{\text{corr}} = (^{241}_{\text{true}})(1 + 2B),$$

$$^{242}_{\text{corr}} = (^{242}_{\text{true}})(1 + 3B),$$

where B = the previously determined bias correction factor per atomic mass unit.

10. Convert from atom to weight basis by multiplying corrected peak heights by the corresponding atomic mass (whole number accuracy is adequate).
11. Calculate the weight percent of each isotope by dividing its weight basis peak height by the sum of the weight basis peak heights, and multiplying by 100.

#### Uranium

Relative ion beam intensities, proportional to atom abundances, are measured by interpolating between peak tops and making all measurements of individual isotopes for one set of ratios at one point on the x-axis (one common time) to remove the effect of changes in beam intensity with time. Readings can be made at any point after the completion of the first single sweep and before the beginning of the last sweep. The preferred procedure is to take a reading of all isotopes at each time the sweep direction is changed (turnaround). Measurements should be made in pairs. One reading at the high-mass turnaround and one at the adjacent low-mass turnaround con-

stitute a pair. To obtain N pairs of consecutive readings, 2N + 1 single sweeps in alternate directions are required.

1. Draw lines on the chart connecting the tops of the consecutive peaks of the same isotope for each isotope to be measured.
2. Draw vertical lines on the chart at or near the turnaround points corresponding to each change in sweep direction.
3. Read the interpolated peak height of each isotope at the intersection of each vertical line with the interpolating lines.
4. Make zero corrections where required, using the zero readings taken for each scale setting.
5. Combine the zero-corrected peak height readings in pairs. Add these readings for each isotope at the first high-mass turnaround to the corresponding readings at the first low-mass turnaround. Repeat for the second, third, and fourth pairs.
6. Determine the agreement among the four paired measurements. Divide each of the four  $^{238}\text{U}$  measurements by the corresponding  $^{235}\text{U}$  measurement. The range of the four ratios thus obtained shall not exceed 5%. If this range is exceeded, record additional spectra until agreement is obtained.
7. Calculate  $\Sigma$  peak height for each isotope by summing the eight zero-corrected interpolated readings.
8. Calculate the true peak heights ( $\text{MASS}_{\text{true}}$ ) by multiplying each peak height sum by the exact scale factor for the scale setting used to record that isotope peak.
9. Calculate the bias-corrected peak heights

( $\text{MASS}_{\text{corr}}$ ) by:

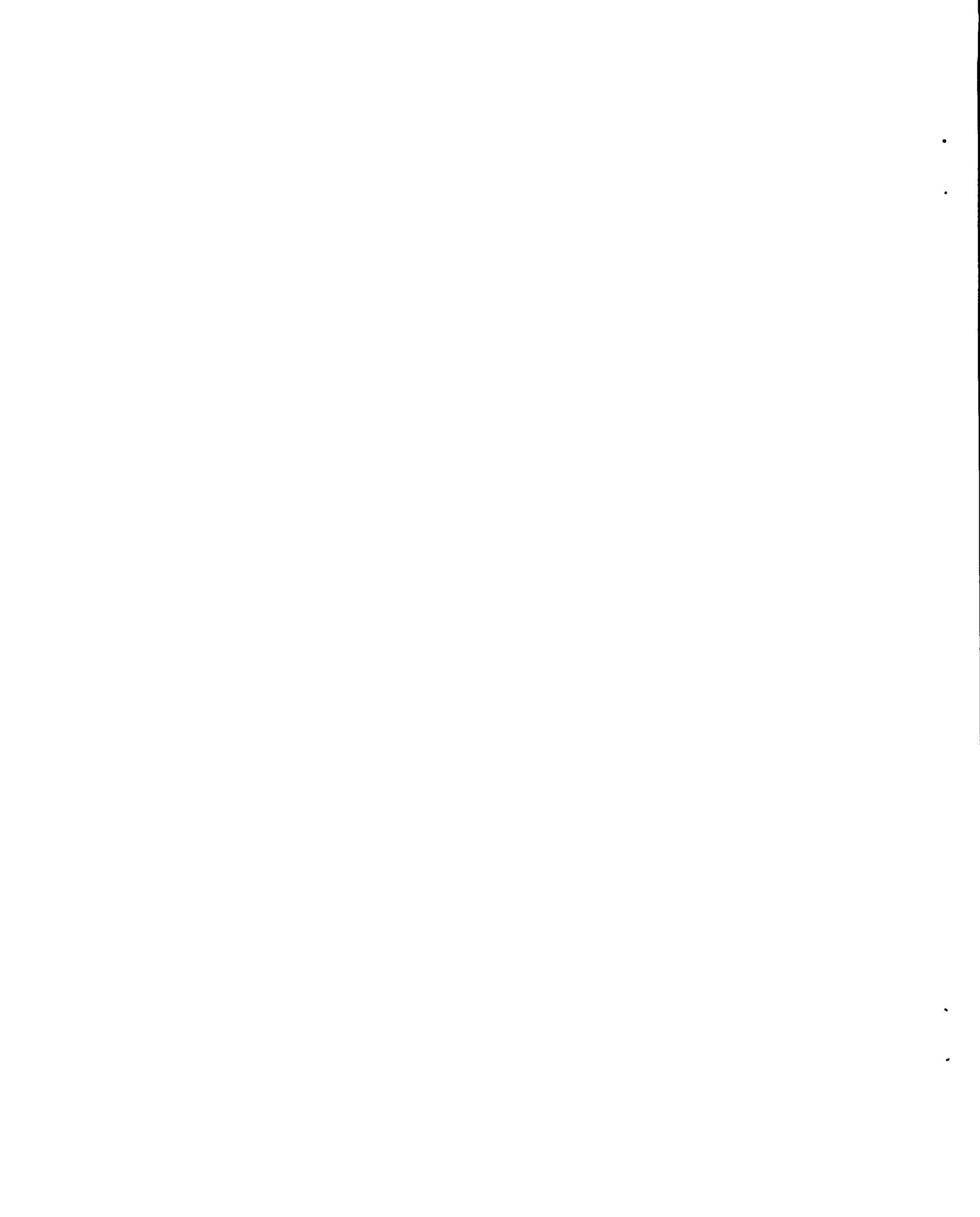
$$^{234}_{\text{corr}} = ^{234}_{\text{true}}(1 - B) ,$$

$$^{235}_{\text{corr}} = ^{234}_{\text{true}} ,$$

$$^{236}_{\text{corr}} = ^{236}_{\text{true}}(1 + B) ,$$

$$^{238}_{\text{corr}} = ^{238}_{\text{true}}(1 + 3B) .$$

10. Convert from atom to weight basis by multiplying each corrected peak height by the corresponding atomic mass (whole number accuracy is adequate).
11. Calculate the weight percent of each isotope by dividing its weight basis peak height by the sum of the weight basis peak heights. For natural uranium samples, only the  $^{235}\text{U}$  and  $^{238}\text{U}$  peaks need be recorded and calculated.



DETERMINATION OF THE ISOTOPIC DISTRIBUTION OF URANIUM AND PLUTONIUM IN MIXED-OXIDE PELLETS BY MASS SPECTROMETRY FOLLOWING LIQUID-LIQUID EXTRACTION SEPARATION

SUMMARY

Plutonium and uranium are sequentially separated by a two-cycle thenoyltrifluoroacetone (TTA)-xylene extraction procedure and the separated fractions are individually analyzed for isotopic abundances by thermal ionization mass spectrometry. The mass spectrometric conditions for the plutonium analysis are designed to minimize the ionization of uranium that carries through with the plutonium, thereby providing results for the isotopic abundance of  $^{238}\text{Pu}$  as well as the higher mass plutonium isotopes.

APPLICABILITY

This method<sup>[1]</sup> is applicable to the determination of the isotopic distributions of uranium and plutonium in mixed oxide fuel pellets. It is an alternative to the mass spectrometric method based on an ion exchange separation scheme given on p. 23 for mixed oxide fuel pellets. Although the ion exchange separation is faster, this liquid-liquid extraction method is included for those laboratories that prefer to use it.

The measurement of the abundances of uranium and plutonium isotopes by thermal ionization mass spectrometry, as described in this method, is highly reliable over the range of 0.01 to 100% with extension to lower values provided that mass interferences are not present and that the chemical preparation steps are carefully done to minimize contamination. A single analysis including the chemical separation and the mass spectrometry both of uranium and plutonium takes about 2.5 hr; 1 hr for the chemical separation and 45 min for each mass spectrometric measurement. This time is for a mass spectrometer equipped with a vacuum lock on the source.

[1] A. C. Leaf and M. W. Goheen, Methods 10.2 and 10.5, USAEC Report WHAN-IR-5 (August 1970).

The average time per sample for the chemical separation decreases to about 30 min when a group of samples is analyzed.

RELIABILITY

The pooled data obtained by seven laboratories for the abundances of the plutonium isotopes 239, 240, 241, and 242 in mixed oxide fuel pellets with a uranium to plutonium ratio of 3 to 1 were:<sup>[2]</sup>

Pu Isotope	Average of all Labs	Within-Lab Std Dev	Between-Lab Std Dev
239	86.84	0.029	0.017
240	11.56	0.024	0.010
241	1.45	0.007	0.008
242	0.13	0.0017	negligible

These precisions substantially agree with those obtained by 12 laboratories on a series of uranium and plutonium materials analyzed on thermal ionization mass spectrometers using both single and triple filament sources.<sup>[3]</sup> In general, the absolute precision is a function of the level of the abundance of an isotope and not of the isotopic mass. The absolute within-laboratory standard deviations ranged from ~ 0.0004% at an isotopic abundance of 0.01 to ~ 0.02% at isotopic abundances greater than 90%.

DISCUSSION OF THE METHOD

The separation of uranium and plutonium in this method is based on a sequential two-cycle extraction of plutonium and uranium into TTA-xylene. An aliquot of the dissolved mixed oxide fuel, containing ~ 10  $\mu\text{g}$  of uranium and ~ 3  $\mu\text{g}$  of plutonium, is evaporated to dryness, dissolved in 2M HCl, and the plutonium is reduced to the (III) oxidation state with ferrous sulfamate and hydroxylamine hydrochloride. An initial TTA extraction is made to scavenge extractable impurities, if necessary. Plutonium is oxidized to the (IV) oxidation state with nitrite

[2] C. F. Metz, R. G. Bryan, and R. K. Zeigler, LASL Report CMB-1-861 (November 1968).

[3] M. W. Lerner, USAEC Report NBL-231 (1966).

and extracted into TTA-xylene. This TTA-xylene extract is scrubbed with 1M  $\text{HNO}_3$ , the plutonium is back-extracted into 8M  $\text{HNO}_3$ , evaporated to dryness, and dissolved in dilute nitric acid for the mass spectrometric analysis. The aqueous phase remaining from the extraction of the plutonium, which contains the unextracted uranium, is first treated with hydroxylamine hydrochloride to reduce any residual plutonium to the nonextractable (III) oxidation state. To further hinder extraction of plutonium, EDTA is added. The solution is adjusted to ~ pH 2 (basic side of methyl violet) by the addition of sodium hydroxide and the uranium is extracted into TTA-xylene. The uranium then is back-extracted into 1M  $\text{HNO}_3$ , fumed with perchloric acid, and dissolved in dilute nitric acid for the mass spectrometric analysis.

The most difficult nuclide to determine in mixed oxide fuels by mass spectrometry is  $^{238}\text{Pu}$ . The specification for the  $^{238}\text{Pu}$  isotopic abundance in the plutonium of LMFBR/FFTF fuel is a maximum 0.15%. In a mixed oxide pellet in which the uranium (natural) to plutonium ratio is 3 to 1, the  $^{238}\text{U}/^{238}\text{Pu}$  ratio at this specification limit is almost 2000 to 1 and increases proportional to a decrease in the  $^{238}\text{Pu}$  content. With equal ionization efficiency of the uranium and plutonium from a mass spectrometer filament, a separation factor of about 60,000 for uranium in the plutonium fraction would be required to determine the  $^{238}\text{Pu}$  isotopic abundance with a standard deviation of 0.005 absolute abundance percent. Because this degree of separation is not always attained in this liquid-liquid extraction procedure, the mass spectrometer conditions are designed to preclude the ionization of uranium in the plutonium analysis. These conditions are the loading of a small amount of sample (containing 1 to 10 ng of plutonium) onto a single filament source and the addition of sucrose to the evaporated sample on the filament. The small amount of uranium is not significantly volatilized and ionized from the filament under these conditions and a satisfactory volatilization and ionization of the plutonium is obtained. This small amount of sample requires an electron multiplier as the detector. In the alternative (ion exchange separation) method on p. 23, microgram amounts

of plutonium are loaded to permit the use of a Faraday cup collector. Compared to the electron multiplier, the Faraday cup requires essentially no mass discrimination corrections and has a more linear response.

A major factor governing the attainment of satisfactory analyses is fastidious operation, necessary to preclude natural uranium contamination and sample cross-contamination. Purified reagents, especially acids, stored in plastic or quartz bottles are stipulated, inexpensive glassware and plastic ware that are discarded after use for one sample are strongly recommended, and the working areas must be scrupulously clean. Inasmuch as the measurement is for isotopic abundances only, the operations need not be quantitative.

The selection of the two methods presented here and on p. 23 was based on their proven capability for mixed oxide fuel samples. The ASTM ion exchange method, [4] designed for irradiated fuel samples with a very high preirradiated ratio of uranium to plutonium and containing fission products, is relatively long and does not give a plutonium fraction sufficiently free of uranium to permit the reliable measurement of the  $^{238}\text{Pu}$  isotopic abundance. The only method presented in the USAEC Manual [5] that is applicable to uranium-plutonium fuels is based on a liquid-liquid extraction that gives a combined uranium-plutonium fraction for simultaneous analysis in a triple-filament source, thermal ionization mass spectrometer. This method is not recommended because the precision of the measured isotopic abundance values both of uranium and plutonium is about twice poorer than the precision obtained when separated uranium and plutonium fractions are independently analyzed [3] and because  $^{238}\text{Pu}$  cannot be measured in the presence of  $^{238}\text{U}$ .

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[4] ASTM Standards, Part 30, Method E267-67T, American Society for Testing and Materials, Philadelphia (1969).

[5] R. J. Jones, Ed., Method 4.502, Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle, USAEC Report TID-7029 (1963).

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Special care must be taken when handling the concentrated acids used in this method. As a minimum precaution, rubber gloves should be worn.

Mass spectrometers have high-voltage circuits. Consult the manufacturer's manual before opening any instrument panel doors or latches.

### APPARATUS

Centrifuge. International Clinical, or equivalent.

Disposable pipets. Prepare these by drawing 7-mm borosilicate glass tubing to about 0.040-in. o. d. for a length of 3 in. A similar length of Teflon thin-walled tubing of such diameter as to fit over a standard hypodermic needle also may be used. (This tubing is obtainable from Chemplast, Inc., 150 Dey Road, Wayne, N. J. 07470). Use these pipets once and discard them.

Extraction equipment. The various aqueous-organic extractions are conveniently done in test tubes or centrifuge tubes with polyethylene stoppers. The desired phase is removed with a syringe-operated disposable pipet. Phase mixing is efficiently accomplished with a vortex mixer.

Medicine droppers, 1-ml.

Infrared heating lamp.

Mass spectrometer. The instrument shall have minimum characteristics as follows:

Source: thermal ionization with single filament. (A triple-filament source also is satisfactory for plutonium). A vacuum lock is recommended to maintain analyzer vacuum which increases sample throughput.

Analyzer: an analyzer and vacuum system capable of producing a resolving power of at least 400 and an abundance sensitivity at mass 238 of at least 20,000.

Resolving power is defined as  $M/\Delta M$ , where  $\Delta M$  is the width, in atomic mass units, of a peak at mass  $M$  at 5% of its height. Abundance sensitivity is defined as the ratio of total ion current at mass  $M$  to its contribution at mass  $M-1$ , customarily measured at masses

238 and 237 for a spectrum produced from a filament loading of natural uranium.

Detector: a system consisting of a Faraday cup and an electron multiplier, externally selectable, followed by an electrometer amplifier and a potentiometric recorder. Pulse counting systems using an electron multiplier or a scintillator-photomultiplier, as well as automatic data acquisition apparatus, also may be used.

Several commercially available mass spectrometers meet or exceed all the above requirements.

### Mass Spectrometer Accessories.

Filaments may be made from tantalum, rhenium, or tungsten ribbon, nominally 0.001 x 0.030 in. Filaments should not be handled by bare hands. They should be prepared and stored so as to minimize contamination by uranium.

Filament forming jigs are used to form the filaments into the configuration required by the mass spectrometer and to hold the filaments in place for welding.

A spot welder is used to weld the filament ribbons to the support posts. Welds must be made carefully to ensure good electrical contact which is necessary for beam stability.

Sample loading unit. A power supply consisting of a Variac, 6.3-V filament transformer, ammeter, and suitable electrical contacts may be used to heat the filament to evaporate sample solution. A heat lamp or heating block also may be used.

Filament bakeout chamber. A bench-top vacuum system with a 12-in. bell jar is satisfactory. A 5-V or 6.3-V, 10-A, filament transformer with the primary controlled by a Variac supplies the necessary current. Apply current gradually so that the pressure does not exceed  $10^{-6}$  Torr. Bakeout is complete after 1 hr at 2000°C. Up to 20 filaments can be degassed simultaneously without exceeding the heat dissipation capability of the system.

## REAGENTS

EDTA, 0.03M, adjusted to pH 7 with NaOH.

Ferrous sulfamate, 3.2M.

Hydrochloric acid, 6M, 2M, 1M.

Hydrofluoric acid, 28M (48%).

Hydroxylamine hydrochloride, 5M.

Methyl violet, 0.05% in water.

Nitric acid, 15.6M (70%), 8M, 1M.

Plutonium calibration solution. Dissolve the contents of one ampoule of the NBS 948 plutonium isotope standard in 6M HCl. Dilute to 500 ml with 2M HCl for a concentration of 0.5 mg Pu/ml. Dilute 1 ml to 10 ml with 2M HCl to give a concentration of 0.5 µg/10µl. Store this solution in a plastic bottle.

Sodium hydroxide, 4M.

Sodium nitrite, 2M.

Sucrose, 0.04M.

TTA, 0.5M in xylene.

Uranium calibration solutions. Prepare three calibration solutions by dissolving 12 mg each of NBS U-010, U-500, and U-930 uranium isotopic standards in minimum amounts of 8M HNO<sub>3</sub>. Dilute to 100 ml with 1M HNO<sub>3</sub> to give concentrations of 1 µg U/10 µl. Store these solutions in plastic bottles.

## PROCEDURE

### Blank

A blank measurement is not routinely required in this method. However, reagents can become sufficiently contaminated to affect the results without immediate detection by a quality control program because the samples contain natural uranium and plutonium whose isotopic abundances may change slightly from sample to sample. For this reason, uranium and plutonium contamination in reagents shall be checked at least once a month by carrying an aliquot of the mixed oxide dissolution reagents entirely through the procedure used by a laboratory for samples. The levels of uranium and plu-

tonium in this reagent blank shall be less than 1 ng of both elements on the mass spectrometer filament based on the observed ion currents.

### Calibration

#### Calibration of Detection System

Calibrate the detection system at startup, at least every three months, and following any alteration which could affect performance, as follows:

##### a. Sensitivity scale factors

1. Connect a precision potentiometer in series with the feedback loop of the amplifier and short out the galvanometer.
2. Set the amplifier on the 10-mV scale and apply 10 mV from the potentiometer. Record the deflection.
3. Repeat step 2 for each amplifier sensitivity setting and the corresponding potentiometer voltage.
4. Determine exact scale factors from the ratios of applied voltage/recorder deflection for each sensitivity setting. Use these factors in subsequent determinations.

##### b. Recorder linearity:

1. Connect a precision potentiometer as in step a-1 above.
2. Set the amplifier on the 1-V scale and apply voltage in increments of 0.1 V up to 1 V. Record the recorder deflection for each increment.
3. Find the cause for and correct any non-linearity greater than 0.25% of full scale.

##### c. Grid resistor linearity and ratio determination:

If a standard current source is available, the test described in TID-7029<sup>[6]</sup> is advisable.

#### Calibration of Complete System

Calibrate the complete mass spectrometer at startup, at least every three months, and following any

[6] R. J. Jones, Ed., Method 2.500, Selected Measurement Methods for Uranium and Plutonium in the Nuclear Fuel Cycle, USAEC Report TID-7029 (1963).

alteration, as follows:

- a. Determine the mass discrimination bias both for the electron multiplier and the Faraday cup by measuring the  $^{235}\text{U}/^{238}\text{U}$  ratio on at least three separate filament loadings of the NBS U-500 standard for each detector. Average the results and calculate the respective bias correction factors by:

$$B = \frac{\frac{\bar{R}_O}{R_s} - 1}{3},$$

where B = mass discrimination bias factor per amu in the U-Pu mass range,

$\bar{R}_O$  = average of observed atom ratio  $^{235}\text{U}/^{238}\text{U}$ ,

$R_s$  = NBS stated atom ratio  $^{235}\text{U}/^{238}\text{U} = 1.0003$ .

Apply these bias corrections to subsequent determinations.

- b. Establish the linear range of both detection systems by measuring the  $^{234}\text{U}/^{235}\text{U}$  ratio on separate filament loadings of the NBS U-930 standard for each system over a wide range of ion currents at increments corresponding to the amplifier scale factors. To aid interpretation, plot the observed ratio vs the  $^{235}\text{U}$  ion current on semilog paper. Analyze samples only within the linear range.

#### Daily Verification of Mass Spectrometer Stability

Verify the stability of each mass spectrometer used in any 8-hr working shift with the NBS 948 plutonium isotopic standard when plutonium samples are analyzed and with the NBS U-010 uranium isotopic standard when uranium samples are analyzed during that shift. Maintain control charts for each instrument for each standard as follows: ratio of  $^{235}\text{U}/^{238}\text{U}$  for NBS U-010 and ratio of  $^{240}\text{Pu}/^{239}\text{Pu}$  for NBS 948. When the value of either ratio changes at the .05 significance level, do not analyze samples until the cause is corrected. Possible sources of instability are a deterioration of the electron multiplier, low gain in the electrometer amplifier, electrical or mechanical malfunctions in the

recorder, and inadequate regulation in the filament power supply.

### Sample Analysis

#### Dissolution

1. Dissolve a weighed, whole, mixed oxide pellet in 5 to 10 ml of 15.6M  $\text{HNO}_3$  in a 50-ml beaker or a 30-ml platinum dish with covers and with the aid of simmering heat.

These dissolution conditions are the same as described for method "Determination of Uranium or Plutonium by Controlled Potential Coulometry," p. 47.

Weigh all samples to  $\pm 0.2$  mg.

A 15.6M  $\text{HNO}_3$  - 0.01M HF mixture may be used for dissolution with platinum dishes. This mixture gives faster dissolution rates. If this mixture is used, omit step 3.

Rapid dissolution rates may be obtained with the sealed-tube technique described on p. 5.

2. Repeat the additions of 5 to 10 ml of 15.6M  $\text{HNO}_3$  and heating as necessary until dissolution is apparently complete.
3. With the last addition of 15.6M  $\text{HNO}_3$  or when the dissolution reaction is complete, add 1 drop of 1M HF and sufficient 15.6M  $\text{HNO}_3$  to give a total volume of 5 to 10 ml. Continue heating until the sample is completely dissolved.
4. Transfer the solution quantitatively with the aid of at least five 5-ml rinses of 1M  $\text{HNO}_3$  to a tared, preferably heavy-walled polyethylene container having an airtight cap, and weigh to  $\pm 1$  mg.

A heavy-walled polyethylene container minimizes changes in concentration caused by transpiration of water vapor through the walls.

#### Separation of Uranium and Plutonium

1. Transfer a 50- $\mu\text{l}$  aliquot of the dissolved mixed oxide pellet solution into a small vial or tube, dilute to 1 ml with 2M HCl, and mix.  
Use a disposable pipet for this transfer. This step need not be quantitative.
2. Transfer 10  $\mu\text{l}$  of the diluted solution to a 13- x 100-mm test tube.

Use a disposable pipet. This aliquot, which need not be quantitative, should contain ~ 10 µg of uranium and ~ 3 µg of plutonium.

3. Add 2 ml of 2M HCl and mix.
4. Add 10 µl of 3.2M ferrous sulfamate and 50 µl of 5M hydroxylamine hydrochloride and heat just below boiling for 5 min.

Higher oxidation states of plutonium reduce to Pu(III). Uranium remains in the (VI) oxidation state.

5. Add 2 ml of 0.5M TTA-xylene and place a polyethylene stopper in the tube.
6. Mix for 2 min and then centrifuge at 3/4 speed for 1 min.

A vortex mixer is recommended for mixing in this and all subsequent steps. Extractable impurities are extracted in this step. With "pure" mixed oxide samples, experience may show that this step, step 5, and step 7 are not necessary.

7. Transfer the aqueous phase to a clean 13- x 100-mm test tube. Discard the TTA phase.

Insert a disposable medicine dropper with a drawout tip through the top TTA-xylene phase while maintaining positive pressure on the syringe so as not to take any of the top phase.

8. Add 0.5 ml of 2M sodium nitrite and heat just below boiling for 5 min.

Plutonium (III) oxidizes to the (IV) oxidation state which extracts into TTA-xylene. Uranium remains in the nonextractable (VI) oxidation state.

9. Add 2 ml of 0.5M TTA-xylene and place a polyethylene stopper in the tube.
10. Mix for 2 min and then centrifuge at 3/4 speed for 1 min.

Plutonium (IV) extracts into the TTA-xylene phase; U(VI) extracts only slightly.

11. Transfer the TTA-xylene phase to a clean 13- x 100-mm test tube and reserve the aqueous phase for separation of the unextracted uranium starting at step 18.

Use a disposable medicine dropper for the transfer.

12. Add 2 ml of 1M HNO<sub>3</sub> to the TTA-xylene phase containing the extracted plutonium, and place a poly-

ethylene stopper in the tube.

13. Mix for 2 min and then centrifuge at 3/4 speed for 1 min.

Extracted uranium is back-extracted into the 1M HNO<sub>3</sub> phase.

14. Transfer the TTA-xylene phase to a clean 13- x 100-mm test tube. Discard the aqueous phase.

Use a disposable medicine dropper for the transfer.

15. Add 1 ml of 8M HNO<sub>3</sub> to the transferred TTA-xylene phase and place a polyethylene stopper in the tube.

16. Mix for 2 min and then centrifuge at 3/4 speed for 1 min.

Plutonium back-extracts into the 8M HNO<sub>3</sub>.

17. Transfer the 8M HNO<sub>3</sub> phase to a clean 10- x 75-mm test tube, place a polyethylene stopper in the tube, and reserve it for the mass spectrometric measurement of plutonium isotope abundances.

Insert a disposable medicine dropper with a drawout tip through the top TTA-xylene phase while maintaining positive pressure on the syringe so as not to take any of the top phase. Inscribe the sample number and the words "plutonium fraction" on the tube.

18. Remove the last traces of the TTA-xylene phase from the aqueous phase containing the uranium from step 11 and discard these traces.

To more effectively separate the plutonium, also remove a small portion of the aqueous phase.

19. Add 0.2 ml of 5M hydroxylamine hydrochloride and heat just below boiling for 5 min.

Any residual plutonium reduces to the (III) oxidation state.

20. Add 1 ml of 0.03M EDTA adjusted to pH 7.

EDTA forms a stable complex with Pu(III) which greatly decreases its extraction into TTA-xylene in step 23.

21. Add 1 drop of 0.05% methyl violet.

22. Dropwise add 4M NaOH while gently mixing the contents of the tube until the solution turns blue, then add one more drop of 4M NaOH.

The pH of the solution is now about 2 at which value U(VI) extracts into TTA-xylene.

23. Add 2 ml of 0.5M TTA-xylene and place in a polyethylene stopper in the tube.
24. Mix for 2 min and then centrifuge at 3/4 speed for 1 min.

Uranium extracts into the TTA-xylene phase; plutonium only slightly extracts.

25. Transfer the TTA-xylene phase to a clean 13- x 100-mm test tube.

Use a disposable medicine dropper for the transfer.

26. Add 1 ml of 1M HNO<sub>3</sub> to the transferred TTA-xylene phase and place a polyethylene stopper in the tube.

27. Mix for 2 min and then centrifuge at 3/4 speed for 1 min.

Uranium back-extracts into the 1M HNO<sub>3</sub>.

28. Transfer the 1M HNO<sub>3</sub> phase to a clean 13- x 100-mm test tube, place a polyethylene stopper in the tube, and reserve it for the mass spectrometric measurement of uranium isotope abundances.

Insert a disposable medicine dropper with a drawnout tip through the top TTA-xylene phase while maintaining positive pressure on the syringe so as not to take any of the top phase. Inscribe the sample number and the words "uranium fraction" on the tube.

#### Mass Spectrometric Analysis of Plutonium

1. Evaporate the 8M HNO<sub>3</sub> solution, containing ~ 3 μg of plutonium, from step 17 in the previous subsection, to dryness.

Do not boil the solution as spattering will contaminate the environs. The combination of a heat lamp and a filtered air jet will give fast evaporation with no bumping of the solution. Do not bake the residue because plutonium dioxide that may form is not readily soluble in 1M HNO<sub>3</sub> used in the next step.

2. Add 1 ml of 1M HNO<sub>3</sub> and heat gently until solution is complete.
3. Using a new disposable pipet, transfer 3 to 5 μl of the solution to a prebaked single filament which is

mounted in the sample loading unit and evaporate slowly to dryness.

Do not let the solution spatter as this will contaminate the environs. The low surface tension of the clean baked filament may make loading quite difficult.

4. Slowly add 5 μl of 0.04M sucrose with a new disposable pipet and heat until the sucrose chars.

Adding the sucrose and charring first tends to keep the plutonium near the center of the filament.

5. Introduce the loaded filament assembly into the ion source using the procedure recommended by the instrument manufacturer.
6. When the source pressure is  $2 \times 10^{-7}$  Torr or lower, pass current through the filament until it becomes barely red from heating.

This degasses the sample residue and filament.

7. When the source pressure is below  $10^{-6}$  Torr with the filament heated, turn on the high voltage and adjust the high voltage and magnet to bring in m/e 239.
8. Beginning at 2.5 A, increase the filament current in steps of 0.1 A scanning about 1% in each direction between steps. When an ion beam is detected, adjust focus controls and mechanical alignment for maximum beam intensity.
9. Increase the filament current until the <sup>239</sup>Pu ion current is  $\sim 10^{-13}$  A.
10. Scan the spectrum over m/e 238 through 242 in both directions repeatedly until at least nine spectra have been recorded, using scale settings that will cause each peak to be recorded on the top half of the chart.

Magnetic field scanning is preferred because it introduces less mass discrimination than does voltage scanning. Collect data only when the ion beam intensity is essentially constant.

11. Reduce the filament current to zero, record zero readings for each scale factor used, and remove the chart for calculation.

#### Mass Spectrometric Analysis of Uranium

1. Evaporate the 1M HNO<sub>3</sub> solution, containing ~ 10 μg of uranium, from step 28 in the subsection "Separation

of Uranium and Plutonium, " to dryness.

Do not boil the solution as spattering will contaminate the environs. The combination of a heat lamp and a filtered air jet will give fast evaporation with no bumping of the solution.

2. Add 50  $\mu$ l of 1M  $\text{HNO}_3$  with a new disposable pipet and heat gently until solution is complete.
3. With the same pipet used in step 2, transfer  $\sim 5 \mu$ l of the solution to the sample filaments of a triple filament assembly which is mounted in the sample loading unit, and evaporate slowly to dryness.
4. Introduce the loaded filament assembly into the ion source, using the procedure recommended by the instrument manufacturer.
5. When the source pressure drops to  $2 \times 10^{-7}$  Torr, begin degassing by passing 3 A of current through the ionizing filament.
6. When the source pressure is below  $10^{-6}$  Torr with the ionizing filament heated, turn on the high voltage and adjust the high voltage and magnet to bring in m/e 238.  
Focus on the major isotope,  $^{238}\text{U}$  in most cases,  $^{235}\text{U}$  in the case of NBS U-930.
7. Increase the ionizing filament current to 4.5 A, then slowly increase the sample filament currents until an ion beam is detected.  
If no ion beam is detected with sample filament currents of 2 A, reduce the currents to 1 A and focus on the ion beam of the ionizing filament material, then go back to the uranium beam.
8. Adjust controls for maximum beam intensity with symmetrical peak shape.
9. Increase the sample filament currents until the  $^{238}\text{U}$  ion current is in the range of  $10^{-13}$  A when the electron multiplier is used, or  $10^{-11}$  A when the Faraday cage is used.  
It may be necessary to experiment with different combinations of filament currents to achieve a stable beam of the desired intensity.
10. Scan the spectrum repeatedly in both directions over the mass range of interest until at least nine spectra have been recorded. Use scale settings that will

cause each peak to be recorded on the top half of the strip chart.

Magnetic field scanning is preferred.

Collect data only when the ion beam intensity is essentially constant.

11. Reduce the sample filament currents to zero, record zero readings for each scale setting used, and remove the chart for calculation.

### Calculations

#### Plutonium

Relative ion beam intensities, proportional to atom abundances, are measured by interpolating between peak tops and making all measurements of individual isotopes for one set of ratios at one point on the x-axis (one common time) to remove the effect of changes in beam intensity with time. Readings can be made at any point after the completion of the first sweep and before the beginning of the last sweep. The preferred procedure is to take a reading of all isotopes at each time the sweep direction is changed (turnaround). Measurements should be made in pairs. One reading at the high-mass turnaround and one at the adjacent low-mass turnaround constitute a pair. To obtain N pairs of consecutive readings,  $2N + 1$  single sweeps in alternate directions are required.

1. Draw lines on the chart connecting the tops of the consecutive peaks of the same isotope for each isotope to be measured.
2. Draw vertical lines on the chart at or near the turnaround points corresponding to each change in sweep direction.
3. Read the interpolated peak height of each isotope at the intersection of each vertical line with the interpolating lines.
4. Make zero corrections where required, using the zero readings taken for each scale setting.
5. Combine the zero-corrected peak height readings in pairs. Add these readings for each isotope at the first high-mass turnaround to the corresponding readings at the first low-mass turnaround. Repeat for the second, third, and fourth pairs.

6. Determine the agreement among the four paired measurements. Divide each of the four  $^{239}\text{Pu}$  measurements by the corresponding  $^{240}\text{Pu}$  measurements. The range of the four ratios thus obtained shall not exceed 1.5% relative. Divide each of the four  $^{239}\text{Pu}$  measurements by the corresponding  $^{241}\text{Pu}$  measurements. The range of these four ratios shall not exceed 4% relative. If either range is exceeded, collect additional data until agreement is obtained.
7. Calculate  $\Sigma$  peak height for each isotope by summing the eight zero-corrected interpolated readings.
8. Calculate the true peak heights ( $\text{MASS}_{\text{true}}$ ) by multiplying each peak height sum by the exact scale factors for the scale setting used to record that isotope peak.
9. Calculate the bias-corrected peak heights ( $\text{MASS}_{\text{corr}}$ ) by:

$$^{238}_{\text{corr}} = ^{238}_{\text{true}}(1 - B) ,$$

$$^{239}_{\text{corr}} = ^{239}_{\text{true}} ,$$

$$^{240}_{\text{corr}} = (^{240}_{\text{true}})(1 + B) ,$$

$$^{241}_{\text{corr}} = (^{241}_{\text{true}})(1 + 2B) ,$$

$$^{242}_{\text{corr}} = (^{242}_{\text{true}})(1 + 3B) ,$$

where B = the previously determined bias correction factor per atomic mass unit.

10. Convert from atom to weight basis by multiplying corrected peak heights by the corresponding atomic mass (whole number accuracy is adequate).
11. Calculate the weight percent of each isotope by dividing its weight basis peak height by the sum of the weight basis peak heights, and multiplying by 100.

### Uranium

Relative ion beam intensities, proportional to atom abundances, are measured by interpolating between peak tops and making all measurements of individual isotopes for one set of ratios at one point on the x-axis (one common time) to remove the effect of changes in beam

intensity with time. Readings can be made at any point after the completion of the first single sweep and before the beginning of the last sweep. The preferred procedure is to take a reading of all isotopes at each time the sweep direction is changed (turnaround). Measurements should be made in pairs. One reading at the high-mass turnaround and one at the adjacent low-mass turnaround constitute a pair. To obtain N pairs of consecutive readings,  $2N + 1$  single sweeps in alternate directions are required.

1. Draw lines on the chart connecting the tops of the consecutive peaks of the same isotope for each isotope to be measured.
2. Draw vertical lines on the chart at or near the turnaround points corresponding to each change in sweep directions.
3. Read the interpolated peak height of each isotope at the intersection of each vertical line with the interpolating lines.
4. Make zero corrections where required, using the zero readings taken for each scale setting.
5. Combine the zero-corrected peak height readings in pairs. Add these readings for each isotope at the first high-mass turnaround to the corresponding readings at the first low-mass turnaround. Repeat for the second, third, and fourth pairs.
6. Determine the agreement among the four paired measurements. Divide each of the four  $^{238}\text{U}$  measurements by the corresponding  $^{235}\text{U}$  measurement. The range of the four ratios thus obtained shall not exceed 5%. If this range is exceeded, record additional spectra until agreement is obtained.
7. Calculate  $\Sigma$  peak height for each isotope by summing the eight zero-corrected interpolated readings.
8. Calculate the true peak heights ( $\text{MASS}_{\text{true}}$ ) by multiplying each peak height sum by the exact scale factor for the scale setting used to record that isotope peak.

9. Calculate the bias-corrected peak heights ( $MASS_{corr}$ )

by:

$${}^{234}_{corr} = {}^{234}_{true}(1 - B),$$

$${}^{235}_{corr} = {}^{235}_{true},$$

$${}^{236}_{corr} = {}^{236}_{true}(1 + B),$$

$${}^{238}_{corr} = {}^{238}_{true}(1 + 3B).$$

10. Convert from atom to weight basis by multiplying each corrected peak height by the corresponding atomic mass (whole number accuracy is adequate).

11. Calculate the weight percent of each isotope by dividing its weight basis peak height by the sum of the weight basis peak heights. For natural uranium samples, only the  ${}^{235}\text{U}$  and  ${}^{238}\text{U}$  peaks need be recorded and calculated.

# DETERMINATION OF PLUTONIUM-238 ISOTOPIC ABUNDANCE BY ALPHA SPECTROMETRY

## SUMMARY

The  $^{238}\text{Pu}$  alpha particle abundance is measured in a freshly purified plutonium sample with a surface barrier silicon detector and multichannel analyzer. The  $^{238}\text{Pu}$  isotopic abundance is calculated from the alpha spectrum data and from mass spectrometric measurements for major plutonium isotopes on a separate portion of the sample. The relative standard deviation is 2% at a  $^{238}\text{Pu}$  abundance of 0.01 wt %.

## APPLICABILITY

This method is applicable to ceramic grade plutonium dioxide and uranium-plutonium mixed oxide fuel pellets. It is an alternative to the mass spectrometric determination of plutonium isotopic abundances and is especially useful for samples in which the  $^{238}\text{Pu}$  content is too low for a precise mass spectrometric measurement, or for samples in which uranium contamination has interfered with the mass spectrometric determination of  $^{238}\text{Pu}$ .

The measurement of  $^{238}\text{Pu}$  isotopic abundance by alpha particle spectrometry is reliable over the range from 0.001% to 0.5%. Because the measurement is based on a ratio of  $^{238}\text{Pu}$  alpha activity to total plutonium alpha activity, no bias is present provided that  $^{241}\text{Am}$ , which interferes, has been removed according to the specifications of the method.

A single determination requires approximately 30 min for source preparation, and 10 min of counting time.

## RELIABILITY

The precision of the method is 2% relative standard deviation in the  $^{238}\text{Pu}$  isotopic abundance range of 0.01% to the specification limit of 0.15%. This is based on accumulating at least 2500 counts in the  $^{238}\text{Pu}$  alpha particle peak for samples containing 0.01%  $^{238}\text{Pu}$ . A much larger count will be accumulated under this peak for most samples, thus achieving a relative standard

deviation less than 2%. Because an alpha activity ratio is measured, quantitative recovery of the plutonium in the method is not required.

## DISCUSSION OF THE METHOD

This method is based on a procedure for the determination of the  $^{238}\text{Pu}$  alpha activity fraction in high-purity plutonium.<sup>[1]</sup> The principal steps are the preparation of an americium-free plutonium counting source, and the measurement of the  $^{238}\text{Pu}$  alpha activity ratio. The alpha particle source is prepared from a portion of the plutonium fraction purified for isotopic abundance measurements by mass spectrometry. The chemical separation is described in the methods "Determination of the Isotopic Distribution of Uranium and Plutonium in Mixed Oxide Pellets by Mass Spectrometry Following Sequential Ion Exchange Separation," p. 33, and "Determination of the Isotopic Distribution of Plutonium in Plutonium Dioxide by Mass Spectrometry Following Ion Exchange Purification," p. 15.

These chemical purifications yield a plutonium fraction free of nonvolatile substances. Thus, when an aliquot is evaporated to dryness for source preparation, the amount of inert residue is below the level that causes significant alpha absorption giving an undegraded alpha spectrum. If a degraded spectrum is observed, it indicates that inadequately purified reagents were used in the methods referred to above.

Good source preparation also requires an extremely smooth surface for the evaporated plutonium compound. The alpha particle sources are prepared on glass cover slips commonly used for microscopy. The glass surface is consistently smoother than highly polished metal plates, and the slips are so inexpensive that they are discarded after use. Metal plates of polished tantalum or platinum may be used, but stainless steel is unsuitable because the strong hydrochloric acid solution of the plutonium fraction will corrode it.

[1] G. M. Matlack and R. K. Zeigler, USAEC Report TID-7629 (June 1962), p. 185.

The reliable determination of low levels of  $^{238}\text{Pu}$  in plutonium by alpha particle spectrometry is enhanced by the high specific alpha activity of  $^{238}\text{Pu}$  relative to the other alpha-active plutonium isotopes,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{242}\text{Pu}$  that are present. In actual practice, only the  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  isotopes have to be considered, because the alpha activity contributed by the  $^{242}\text{Pu}$  isotope is less than 0.03%. The  $^{241}\text{Pu}$  nuclide, a beta emitter with a very low alpha branching ratio of about  $2 \times 10^{-5}$ , [2] does not contribute significantly to the total alpha activity. Reactor-produced plutonium that contains 0.01 wt %  $^{238}\text{Pu}$  has approximately 2.5%  $^{238}\text{Pu}$  alpha activity. At the specification limit of 0.15%  $^{238}\text{Pu}$ , the  $^{238}\text{Pu}$  alpha activity will be close to 40% of the total plutonium activity.

The measurement of the  $^{238}\text{Pu}$  alpha activity is simple and straightforward because its energy of 5.50 MeV is greater than the 5.16 to 5.17 MeV alpha particle energy of the  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  isotopes. This relationship ensures that the  $^{238}\text{Pu}$  peak is located in a region of the spectrum free of background caused by degraded alpha particles from the other plutonium isotopes, which is especially advantageous for the measurement of low  $^{238}\text{Pu}$  abundances.

There are no interfering elements provided that an americium decontamination factor of 300 is achieved in the plutonium fractions from the two mass spectrometry methods. Growth of  $^{241}\text{Am}$  into the purified fraction should not be significant if the plutonium fraction is analyzed within a reasonable time following purification. Even in plutonium containing 2.5%  $^{241}\text{Pu}$ , the specification limit for that isotope, the  $^{241}\text{Am}$  growth rate is only 3.3  $\mu\text{g/g Pu}$  per day, equivalent to 0.6  $\mu\text{g }^{238}\text{Pu/g Pu}$  per day.

The calculation of the  $^{238}\text{Pu}$  abundance on a weight percent basis requires a knowledge of either the total weight of plutonium in the source that is analyzed or the isotopic abundance of the  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  isotopes

in the material. Since the source is prepared from a separated plutonium fraction also used for the mass spectrometric measurement, the mass spectrometry data provides a very reliable calculational base.

## OPERATING INSTRUCTIONS

### APPARATUS

Cover slip heater. Bore four 3/4-in.-diam holes through a 1/8-in.-thick stainless steel plate, 3-in. square. Place each hole in a corner of the plate, approximately 1/2 in. from the sides of the plate.

Disposable pipets, 50- $\mu\text{l}$ .

Microscope cover slips, 1-in. square, No. 1 thickness.

Multichannel analyzer. This should be an instrument capable of accepting input pulses of 0 to 8 V with widths of 3 to 6  $\mu\text{sec}$ . The conversion gain ratio should be not greater than 8 V per 100 channels.

Surface barrier detector system. The detector should have a minimum surface area of 50  $\text{mm}^2$ , a depletion depth of 60  $\mu\text{m}$ , and a resolution of not greater than 50 keV FWHM. The detector should be used with a suitable power supply and amplifier to give a conversion ratio of 35 keV or less per channel in the multichannel analyzer.

### REAGENTS

No reagents are needed.

### PROCEDURE

#### Blank

A blank measurement is not routinely required.

#### Calibration

Calibration is not routinely required.

#### Sample Analysis

1. Place the cover slip heater on a hot plate set at 150 to 200°C. Center a glass cover slip over a hole on the heater.
2. Transfer about 50  $\mu\text{l}$  of the plutonium solution with a disposable micropipet to the center of the cover slip.

[2] E. K. Hyde, I. Perlman, and G. T. Seaborg, "The Nuclear Properties of the Heavy Elements," vol II, Prentice-Hall, Inc., Englewood Cliffs, N. J. (1964).

The plutonium solution is the unused portion of the purified plutonium fraction from the mass spectrometric methods for fuel materials containing plutonium. The hole in the cover slip heater keeps the center of the cover slip cooler than the edges, to prevent movement of the liquid to the hotter edges with consequent spattering.

3. Allow the liquid to evaporate to complete dryness.
4. Transfer the cover slip to the surface barrier detector.
5. Count the alpha activity in such a way as to accumulate not less than 2500 counts in the 5.50-MeV alpha energy peak.

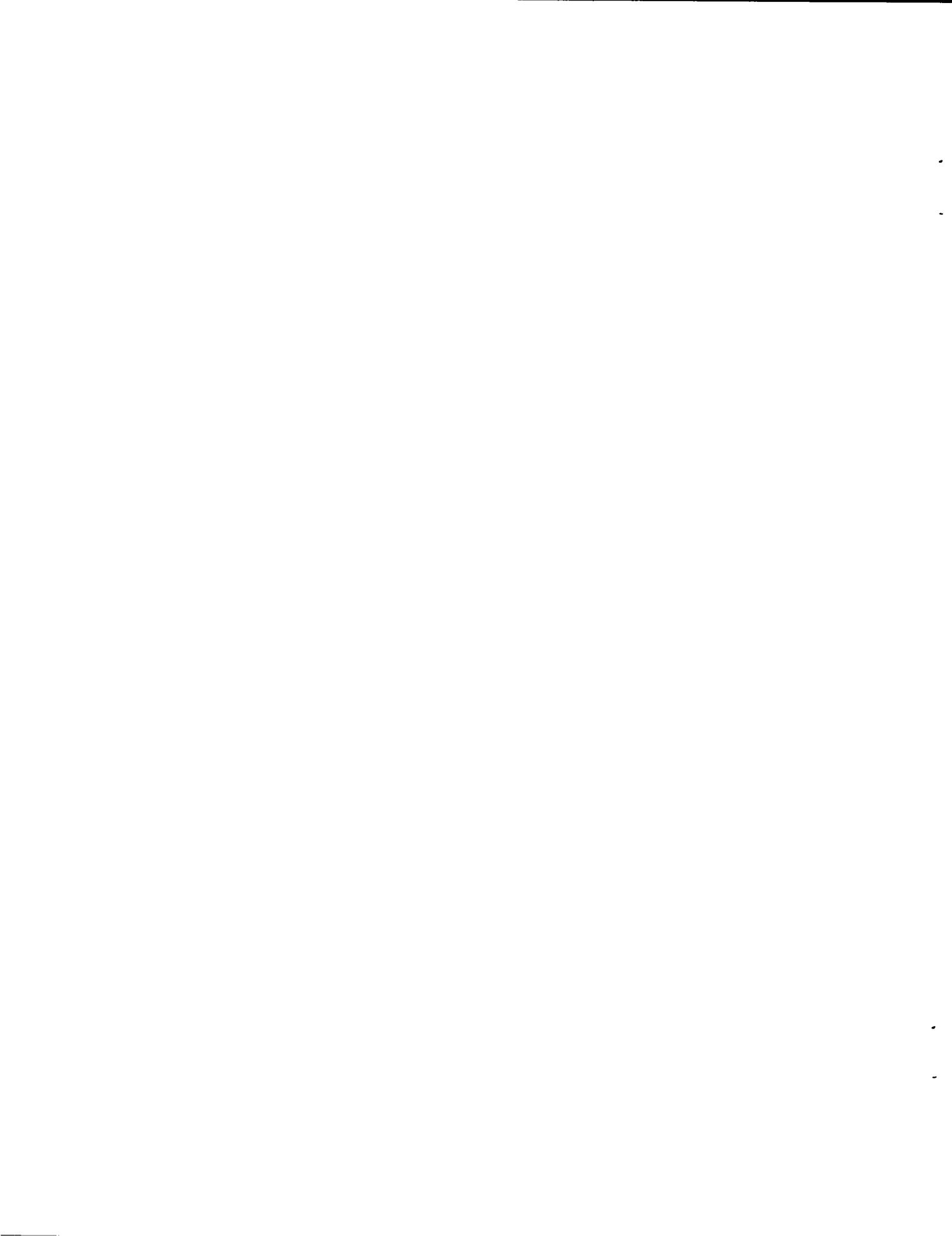
The measurement may be repeated to check the reproducibility of the system.

Calculations

$$\begin{aligned}
 W_8 &= \frac{C_8 T_8}{C_9} \left( \frac{W_9}{T_9} + \frac{W_0}{T_0} \right) \\
 &= \frac{C_8}{C_9} (0.00359W_9 + 0.0133W_0),
 \end{aligned}$$

where

- $W_8$  = weight percent  $^{238}\text{Pu}$ ,
- $W_9$  = weight percent  $^{239}\text{Pu}$ , from mass spectrometry,
- $W_0$  = weight percent  $^{240}\text{Pu}$ , from mass spectrometry,
- $T_8$  = half-life of  $^{238}\text{Pu}$ , 87.5 yr,
- $T_9$  = half-life of  $^{239}\text{Pu}$ , 24,400 yr,
- $T_0$  = half-life of  $^{240}\text{Pu}$ , 6600 yr,
- $C_8$  = observed counts in  $^{238}\text{Pu}$  peak,
- $C_9$  = observed counts in  $^{239}\text{Pu} + ^{240}\text{Pu}$  peak.



## DETERMINATION OF URANIUM OR PLUTONIUM BY CONTROLLED POTENTIAL COULOMETRY

### SUMMARY

Uranium is reduced at a mercury electrode to U(IV) at a controlled potential of -325 mV following a preliminary reduction of plutonium and reducible impurities at + 85 mV. Plutonium is oxidized to Pu(IV) at a platinum electrode at a controlled potential of + 670 mV following reduction to Pu(III) at + 310 mV. The weight of uranium or plutonium is calculated from the number of coulombs required for the reduction or oxidation. Chemical calibration eliminates bias in the method. Relative standard deviations are 0.18% in measuring uranium and 0.07% in measuring plutonium in uranium-plutonium mixed oxide samples.

### APPLICABILITY

This method is applicable to the determination of uranium or plutonium in reactor fuels made from uranium-plutonium mixed oxides, (U, Pu)O<sub>2</sub>. No separation of the two elements is required.<sup>[1]</sup> It may be used for mixed oxide fuels in which the U/Pu weight ratio varies within limits of 0.1 to 10. The method may also be used for the analysis of ceramic grade plutonium dioxide, ceramic grade uranium dioxide, and sintered uranium dioxide insulator pellets.

At the impurity specification limits for the four materials in this program, the only interference is iron which causes a positive bias of 0.214% absolute in the result for plutonium at the iron specification limit of 500 µg/g in mixed oxide fuel or of 0.107% absolute at the iron specification limit of 250 µg/g in plutonium dioxide. The correction for iron should be based on an accurate spectrophotometric determination (see "Determination of Iron by Spectrophotometry," p. 55) when the iron content is greater than 100 µg/g, rather than on the less accurate emission spectroscopy determination.

[1] G. B. Nelson, K. S. Bergstresser, G. R. Waterbury, and C. F. Metz, Paper 13, 12th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 8-10, 1968.

Iron does not interfere with the uranium determination. Organic matter interferes with both determinations by preventing 100% current efficiency.

The recommended quantities for titration are 5 to 10 mg of plutonium and 3 to 5 mg of uranium. A single titration of either uranium or plutonium, excluding dissolution and fuming operations, requires 0.5 to 1 hr. One analyst with two instruments can analyze four samples for uranium and plutonium in 8 hr.

### RELIABILITY

The relative standard deviations obtained by a single laboratory were 0.07% for titrating plutonium and 0.18% for titrating uranium in mixed oxide sintered pellets having a U/Pu ratio of 3/1. The pooled relative standard deviations obtained by six laboratories were 0.15% for plutonium and 0.27% for uranium in these samples.<sup>[2]</sup> The relative standard deviations for the calibration titrations were 0.04% for plutonium and 0.08% for uranium.<sup>[1]</sup>

The recommended calibration materials are NBS plutonium metal (SRM 949) and NBS U<sub>3</sub>O<sub>8</sub> (SRM 950). Electrical calibration has been used by some laboratories. Generally, the latter is biased high by 0.1% for uranium and agrees with the chemical calibration for plutonium. For long-term consistency, chemical calibration is recommended both for uranium and plutonium as used in this method.<sup>[1]</sup>

### DISCUSSION OF THE METHOD

The fundamental concepts of coulometry are set forth in Faraday's laws which state that the weight of a given substance liberated at an electrode is proportional to the coulombs of electricity passed through the system, and also to the chemical equivalent weight of the substance as determined by the electrode reaction. By measuring the number of coulombs required to convert, by electrolysis, one species quantitatively into another, the electrochemical equivalents of the element in question are obtained.

[2] J. E. Rein, R. K. Zeigler, and C. F. Metz, USAEC Report LA-4407 (1970).

Calculation of the amount of material electrolyzed generally is based on the assumption that only one electrochemical reaction, either oxidation or reduction, occurs with the element being measured. Therefore, conditions must be precisely controlled to ensure that all of the current passing through the coulometric cell produces the desired electrochemical reaction. Impurities, including dissolved oxygen and carbonaceous material, that can be electrolytically oxidized or reduced must be removed when they interfere with maintaining 100% current efficiency.

Control of the potential of the working electrode usually limits the electrochemical reaction to the one desired, and greatly reduces the number of other elements that cause interference. As the reaction proceeds and the concentration of the species being titrated decreases, the current through the cell decreases and ultimately approaches zero. The titration is assumed to be complete when the current drops to the level of the background current, generally a few microamperes.

Dissolution of the sample materials may be accomplished in several ways. Uranium oxide, plutonium oxide, and uranium-plutonium mixed oxide, especially when sintered, are not readily soluble, but will dissolve slowly in simmering 15.6M HNO<sub>3</sub>. Hydrofluoric acid at low concentration in the nitric acid accelerates the dissolution especially of the plutonium-containing oxides or samples contaminated with silica. Uranium oxide and the mixed oxides dissolve in a few hours under these conditions, but plutonium oxide may require longer. The sealed-tube method, described on p. 5, is recommended for high-fired plutonium dioxide although prolonged heating with nitric-hydrofluoric acid and repeated fumings with sulfuric acid will bring about solution.

Plutonium can be titrated coulometrically in various mineral acid solutions, including hydrochloric, sulfuric, perchloric, and nitric acids. The nitric-hydrofluoric acid solution obtained in dissolving an oxide material, however, cannot be titrated without addition of a complexant for the fluoride ion, and of sulfamic acid to

eliminate interference by nitrite. Fuming with sulfuric or perchloric acids eliminates the volatile acids and also traces of organic materials, resulting in a solution suitable for titration without such additives. Sulfuric acid is preferred for this purpose because it stabilizes Pu(IV). Perchloric acid oxidizes plutonium to the (VI) oxidation state which reduces very slowly by electrolysis because of the high overpotential of the (VI)/(IV) couple.<sup>[3]</sup>

The  $E_o$  values for  $\text{Pu}^{+3}/\text{Pu}^{+4}$  and  $\text{Fe}^{+2}/\text{Fe}^{+3}$  couples in sulfuric acid are both approximately equal to 490 mV vs sce,<sup>[4]</sup> so that iron is titrated quantitatively with plutonium. A correction for the effect of the iron is obtained by determining the iron spectrophotometrically (see p. 55, "Determination of Iron by Spectrophotometry"); 1 mg of iron is equivalent to 4.28 mg of plutonium. The voltages of + 310 and + 670 mV provide a span of  $E_o \pm 180$  mV, which should ensure quantitative (99.9%) reduction and oxidation, respectively, of the plutonium in the 0.5M H<sub>2</sub>SO<sub>4</sub> medium.<sup>[5]</sup> The titration cell atmosphere is argon to prevent air oxidation of Pu(III).

The electrochemical reduction of uranyl ions at a mercury electrode is an established method for precisely measuring uranium in sulfuric acid solutions.<sup>[4,6]</sup> The generally accepted mechanism is the formation of an unstable  $\text{UO}_2^+$  ion that disproportionates to U(VI) and U(IV). When the electrolysis is carried to completion, all U(VI) is converted to U(IV).<sup>[7]</sup> This reaction is irreversible. Reduction at -325 mV vs sce quantitatively reduces U(VI) to U(IV) without interference from plutonium, iron, and most impurity elements, provided a preliminary reduction is made at + 85 mV vs sce. Electrolysis of uranium in oxide samples at -325 mV gives recoveries that are slightly high relative to the weight of uranium oxide (U<sub>3</sub>O<sub>8</sub>) taken on the basis of an absolute electrical calibration of

[3] W. D. Shults, USAEC Report ORNL-2921 (1960).

[4] G. W. C. Milner, A. J. Wood, G. Phillips, and G. J. Weldrick, Z. Anal. Chem. 224, 346 (1967).

[5] W. D. Shults, Talanta 10, 833 (1963).

[6] W. D. Shults and P. F. Thomason, Anal. Chem. 31, 492 (1959).

[7] I. M. Kolthoff and J. J. Lingane, Polarography, 2nd ed., Interscience, New York, N.Y. (1952), p. 462.

the coulometer. <sup>[1,4,8]</sup> No bias was observed for titrations of uranium solution prepared from high-purity metal. <sup>[4]</sup> Chemical calibration is preferred to electrical calibration. Because dissolved oxygen might be reduced at the potential used to reduce uranium the sample solution is purged with argon prior to the titration.

The success of these coulometric titrations is strongly dependent upon the design of the titrating cells. The cell dimensions, stirring rate, and electrode area and spacing are important parameters in a design which will minimize the time required for titration. The cell volume should be kept small relative to the electrode area to ensure rapid electrolysis, and the stirring should be adequate to bring unreacted ions to the electrode quickly and quantitatively. It is strongly recommended that cells be fabricated that have the design and geometrical dimensions, including electrodes, stated below.

One of the main advantages of the controlled potential coulometric titrations is that a chemical separation of plutonium and uranium is not required. This feature greatly shortens the time for analysis and improves the precision and accuracy. Under ideal conditions, relative standard deviations are in the range between 0.04 and 0.08% for measuring either element, and the method is not biased if chemical calibration is used as specified. The equipment required is relatively inexpensive and commercially available. A titration apparatus, exclusive of glove box containment, costs less than \$5,000.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Special care must be taken when handling the concentrated acids used in this method. At the minimum, rubber gloves should be worn. When preparing dilute sulfuric acid solutions, always carefully add the acid to the water, not water to the acid. Hydrofluoric acid is especially dangerous to the skin and will cause slow-healing ulcerating sores. Consult your laboratory safety manual for further information.

[8] H. C. Jones, W. D. Shults, and J. M. Dale, *Anal. Chem.* **37**, 680 (1965).

## APPARATUS

Battery, mercury. Burgess Mercury Activator, 1.35 V, or equivalent.

Beaker, titration, 42-mm o.d., 40-mm height. Cut off evenly the top portion of a 50-ml borosilicate, low-form beaker and fire-polish the edge.

Differential voltmeter (DVM). John Fluke Manufacturing Company, Model 881A, or equivalent.

Laboratory jack.

Resistor, precision, 150-ohm. Calibrate to  $\pm 0.01$  ohm.

Stopwatch, with 0.2-sec subdivisions.

Controlled potential coulometer. The solid-state instrument for controlled potential electrolysis and coulometry consists of two plug-in modules -- a potentiostat and integrator. A satisfactory instrument, which was designed by the Lawrence Radiation Laboratory, <sup>[9]</sup> is marketed by the M-T Electronics Company, 536-A Lewelling Blvd., San Leandro, California 94579. Other instruments of equal competence may be used. The potentiostat output should be 10 W and  $\pm 24$  V at  $\pm 400$  mA with an impedance of 1 ohm. The control potential should be fully adjustable with a full-scale span from 0.5 to 10 V, and have less than 0.1% change for a 10% change in line voltage and a maximum ripple of 0.02% peak-to-peak. Integrator features should include a range of 1.9 and 19 coulombs full scale, a maximum output of 50 V, an output drift rate adjustable to at least 0.2 mV/15 min, and a long-term stability such that the output drift rate does not change by more than 0.5 mV/15 min in one month.

Uranium titration cell. The titration cell for uranium consists of the titration beaker, Teflon cover, stirrer, electrodes, and inert gas tube (see Figure 1). The Teflon cover has a circular groove to retain securely a 1-11/16-in. o.d. Viton O-ring having a 1/8-in. wall. A small laboratory jack forces the titration beaker up against the O-ring, making an airtight seal.

[9] J. E. Harrar and E. Behrin, *Anal. Chem.* **39**, 1230 (1967).

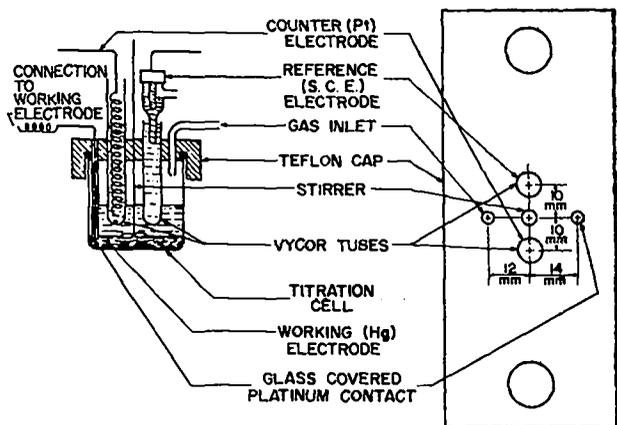


Figure 1. Uranium titration cell and cover.

The stirrer is a  $5.15 \pm 0.05$ -mm glass rod attached to a glass disk 1.5-cm diam,  $2.5 \pm 0.5$  mm thick, and slightly deformed or fluted. The rod is rotated at the mercury-aqueous interface by a 1800-rpm synchronous motor. Magnetic stirring, which simplifies cell design, also is satisfactory. A stirring bar, 13-mm long and 8-mm diam, is recommended for the uranium titration cell, and a bar, 24-mm long and 10-mm diam is recommended for the plutonium titrating cell.

The counter electrode is a spiral about 1-in. long and 3/16-in. diam made from a 6-in. length of No. 18 platinum wire. The spiral is inserted into 0.5M  $H_2SO_4$  contained in an unfired Vycor tube 45 mm in length. The bottom of the Vycor tube is held 2 mm above the mercury working electrode by the Teflon cover.

The reference electrode is a saturated calomel electrode (Beckman No. 39270 or equivalent) inserted into 0.5M  $H_2SO_4$  in an unfired Vycor tube as described above.

The working electrode is 7 ml of triple-distilled mercury with electrical connection made by a platinum wire insulated in a 4-mm glass tube. The mercury is replaced daily or whenever a film or scum is visible on the surface. The gas tube admits oxygen-free argon, saturated with water vapor, at a flow rate of 300 ml/min.

**Titration Cell for Plutonium.** The titration cell for plutonium is similar to the titration cell for uranium except for the position of the counter and reference electrodes

(Figure 2), and the fact that the working electrode is platinum gauze (Figure 3) rather than a mercury pool. The working electrode is made from a 2.25- x 3.25-in. piece of 45-mesh platinum gauze and a 6-in. length of 0.035-in.-diam platinum wire. Three folds are made lengthwise in the gauze to give four layers approximately 0.5-in. wide. The folded gauze is bent around a 1.5-in.-diam mandrel, and is reinforced by spot-welding the 0.035-in.-diam platinum wire entirely around one inner edge. The

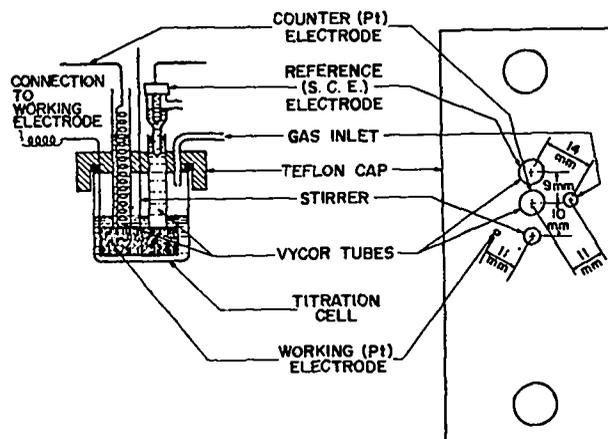


Figure 2. Plutonium titration cell and cover.

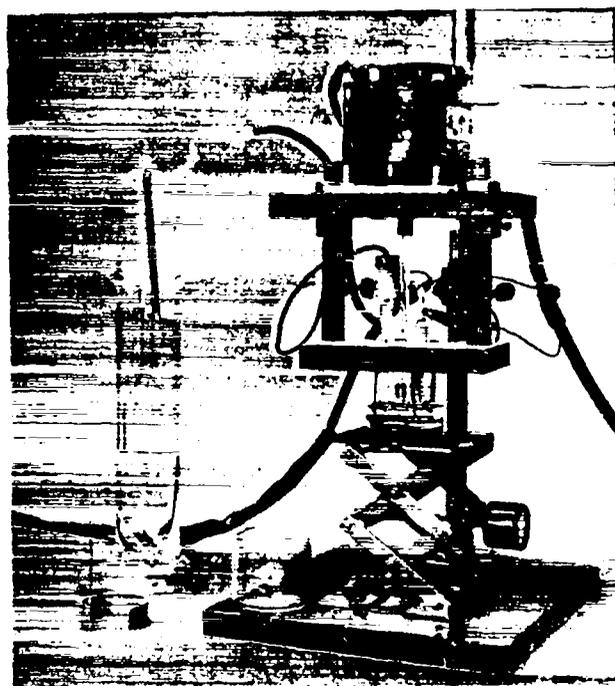


Figure 3. Controlled potential coulometric titration cell and electrodes.

remaining 2.75-in. length of the wire is spot-welded to the reinforcing wire and to one vertical edge to form the vertical support and electrical contact. Store the electrode in  $8M$   $HNO_3$ .

#### REAGENTS

Argon, 99.99% pure.

Hydrochloric acid,  $6M$ .

Hydrofluoric acid,  $28M$  (48%).

Mercury, triple-distilled.

Nitric acid,  $15.6M$  (70%),  $6M$ .

Plutonium calibration solution. Dissolve the entire contents of one 0.5-g ampoule of NBS 949 plutonium metal in a minimum quantity of  $6M$   $HCl$ . Add 10 ml of  $3M$   $H_2SO_4$  and evaporate to copious fumes of  $H_2SO_4$ . Dilute to approximately 50 ml and weigh to 0.02 g precision.

Sulfuric acid,  $18M$  (96%),  $3M$ ,  $0.5M$ .

Uranium calibration solution. Dissolve a weighed 1-g portion of NBS 950  $U_3O_8$  in a minimum volume of  $6M$   $HNO_3$ . Add 10 ml of  $3M$   $H_2SO_4$  and evaporate to copious fumes of  $H_2SO_4$ . Dilute to approximately 200 ml with  $0.5M$   $H_2SO_4$  and weigh the solution to 0.1 g precision.

#### PROCEDURE

##### Blank

A blank measurement is not required in this method.

##### Calibration

Calibrate each titration apparatus used for samples in any 8-hr working shift at the beginning of that shift. For the uranium calibration, use a weighed aliquot of the NBS uranium solution containing 3 to 5 mg of uranium as the sample, starting at step 5 in the subsection "Sample Analysis, Uranium". For the plutonium calibration, use a weighed aliquot of the NBS plutonium solution containing 5 to 10 mg of plutonium as the sample, starting at step 4 in the subsection "Sample Analysis, Plutonium".

Maintain a quality control chart for the uranium and plutonium calibration results obtained each shift. If an individual calibration value disagrees significantly from the average of the previous results on the quality control chart, investigate the cause for the difference and rectify the difficulty before proceeding with further analyses. Unless some other cause is immediately obvious, replacement of the saturated calomel electrode is often one of the first changes to make in determining the difficulty.

##### Sample Analysis

1. Dissolve a weighed, whole, mixed oxide pellet or uranium dioxide insulator pellet, or a weighed 1-g quantity of ceramic grade uranium dioxide or plutonium dioxide powder in 5 to 10 ml of  $15.6M$   $HNO_3$  in a 50-ml beaker or a covered 30-ml platinum dish and with the aid of simmering heat.

Weigh all samples to  $\pm 0.2$  mg.

A  $15.6M$   $HNO_3$ - $0.01M$   $HF$  mixture may be used for dissolution in platinum dishes. This mixture gives faster dissolution rates, especially with plutonium oxide or mixed oxide samples. In this case, omit step 3.

The dissolution time required ranges from a few hours for uranium dioxide samples, somewhat longer for mixed oxide samples, and as long as 12 hr for the higher fired, plutonium oxide samples.

Rapid dissolution rates may be obtained with the sealed-tube technique described on p. 5.

2. Repeat the additions of 5 to 10 ml of  $15.6M$   $HNO_3$  and heating as necessary until dissolution is apparently complete.

Again use simmering heat to speed the dissolution and use covers to prevent spattering loss.

3. With the last addition of  $15.6M$   $HNO_3$  or when the dissolution reaction is complete, add 1 drop of  $1M$   $HF$  and sufficient  $15.6M$   $HNO_3$  to give a total volume of 5 to 10 ml. Continue the heating until complete solubility is obtained.

The addition of hydrofluoric acid is especially effective for plutonium dioxide and mixed oxide

samples or for materials containing silica. It may not be necessary for uranium dioxide samples. When glass beakers are used, early addition of hydrofluoric acid will increase the attack on the glass and introduce more impurities deleterious to subsequent analyses.

4. Transfer the solution quantitatively with the aid of at least five 5-ml rinses of  $1M$   $HNO_3$  to a tared, preferably heavy-walled polyethylene container having an air-tight cap, and weigh to  $\pm 1$  mg.

Weighed aliquots of this solution can serve also for various other analyses, including measurements of iron, americium, uranium in ceramic grade plutonium dioxide, and isotopic abundance measurements.

A heavy-walled polyethylene container minimizes changes in concentration caused by transpiration of water vapor through the walls.

#### Uranium

1. Transfer a weighed aliquot of the sample solution containing 3 to 5 mg of uranium into a 50-ml beaker or a 30-ml platinum dish.

Weigh the aliquot to  $\pm 0.2$  mg.

2. Add 10 ml of  $3M$   $H_2SO_4$  and evaporate to near dryness, or about 0.1 ml.

Evaporate slowly and carefully to avoid spattering.

3. Rinse the uranium titration cell and the outside of the Vycor tubes containing the counter and reference electrodes with  $0.5M$   $H_2SO_4$ .

4. Add 7 ml of triple-distilled mercury to the cell.

Replace the mercury daily or whenever a film or scum is visible on the surface.

5. Quantitatively transfer the evaporated solution obtained in step 2 with the aid of five 1-ml rinses of  $0.5M$   $H_2SO_4$  to the cell.

6. Raise the cell by means of the laboratory jack until the top of the cell snugly fits the O-ring in the Teflon cover.

The cell rim must make a tight seal to assure the exclusion of air.

7. Connect the cell electrodes to the coulometer.
8. Start the argon gas flow at a rate of 300 ml/min.

The argon purges dissolved oxygen from the solution and air from the cell.

9. Set the control potential to + 85 mV.

At a potential of + 85 mV vs sce, plutonium, iron, and extraneous oxidants are reduced but not U(VI).

10. After 5 min of argon gas flow, turn the current on.

11. Turn off the current when it decreases to  $50 \mu A$ .

The current should decrease to the background level which usually is about  $50 \mu A$ . Determine this value by a preliminary titration or by titration of a blank solution.

12. Change the control potential to -325 mV.

13. Turn the current on.

This reduces U(VI) to U(IV).

14. Turn off the current when it decreases to  $50 \mu A$ .

Complete reduction of U(VI) is indicated by the decrease in current to the background level.

15. Record the readout voltage (mg uranium).

This is proportional to the milliequivalents of U(VI) reduced to U(IV). Most instruments may be calibrated to read directly in mg of uranium.

#### Plutonium

1. Transfer a weighed aliquot containing 5 to 10 mg of plutonium into a 50-ml beaker or a 30-ml platinum dish.

Weigh the aliquot to  $\pm 0.2$  mg.

2. Add 10 ml of  $3M$   $H_2SO_4$  and evaporate to near dryness, or about 0.1 ml.

Evaporate slowly and carefully to avoid spattering.

3. Rinse the plutonium titration cell and the outside of the Vycor tubes containing the counter and reference electrodes with  $0.5M$   $H_2SO_4$ .

4. Quantitatively transfer the evaporated solution obtained in step 2 with the aid of five 1-ml rinses of 0.5M  $H_2SO_4$  to the cell.

5. Raise the cell by means of the laboratory jack until the top of the cell snugly fits the O-ring in the Teflon cover.

The cell rim must make a tight seal to assure the exclusion of air.

6. Connect the cell electrodes to the coulometer.

7. Start the argon gas flow at a rate of 300 ml/min.

The argon flow purges air from the cell and prevents air-oxidation of Pu(III).

8. Set the control potential to + 310 mV.

At a potential of + 310 mV vs sce, plutonium is quantitatively reduced to Pu(III). Iron impurity is reduced to Fe(II).

9. After 5 min of argon gas flow, turn the current on.

10. Turn off the current when it decreases to 30  $\mu A$ .

The current should decrease to the background level which usually is about 50  $\mu A$ . Determine this value by a preliminary titration or by titration of a blank solution. Complete reduction of plutonium to Pu(III) is indicated by the decrease in current to the background level.

11. Set the control potential to + 670 mV.

At a potential of + 670 mV, Pu(III) is oxidized only to Pu(IV) in the presence of sulfate which complexes and stabilizes tetravalent plutonium. Fe(II) impurity is oxidized to Fe(III).

12. Turn the current on at a maximum initial level of 30 mA.

13. Turn off the current when it decreases to 30  $\mu A$ .

Complete oxidation of Pu(III) to Pu(IV) is indicated by the decrease in current to the background level.

14. Record the readout voltage (mg plutonium).

This is proportional to the milliequivalents of Pu(III) oxidized to Pu(IV). Most instruments may be calibrated to read directly in mg of plutonium.

Calculations

Uranium

$$C_U = \frac{0.8395 W_{U_3O_8}}{W_{sol}}$$

in which:

$C_U$  = concentration of uranium, mg U/g solution,

0.8395 = the product of the stoichiometric factor of 0.8480 for converting  $U_3O_8$  to U and the recommended purity of 0.9994 of the NBS  $U_3O_8$ ,

$W_{U_3O_8}$  = grams of NBS  $U_3O_8$  dissolved, corrected for air buoyancy,

$W_{sol}$  = final weight, grams, of the calibration solution.

Plutonium

$$C_{Pu} = \frac{0.9999 W_{Pu}}{W_{sol}}$$

in which:

$C_{Pu}$  = concentration of plutonium, mg Pu/g solution,

0.9999 = purity of the NBS plutonium metal,

$W_{Pu}$  = grams of NBS Pu dissolved, corrected for air buoyancy,

$W_{sol}$  = final weight, grams, of the calibration solution.

Calibration Factors

Uranium

$$F_U = \frac{(W_{al})(C_U)}{V_U}$$

in which:

$F_U$  = calibration factor for U, mg U/V,

$W_{al}$  = grams of uranium calibration solution in aliquot,

$C_U$  = concentration of uranium, mg U/g solution of uranium calibration solution,

$V_U$  = readout volts from coulometer DVM.

Plutonium

$$F_{\text{Pu}} = \frac{(W_{\text{al}})(C_{\text{Pu}})}{V_{\text{Pu}}},$$

in which:

- $F_{\text{Pu}}$  = calibration factor for Pu, mg Pu/V ,
- $W_{\text{al}}$  = grams of plutonium calibration solution in aliquot ,
- $C_{\text{Pu}}$  = concentration of plutonium, mg Pu/g solution of uranium calibration solution ,
- $V_{\text{Pu}}$  = readout volts from coulometer DVM .

D = grams of final dissolver solution divided by grams of initial sample ,

W = grams of dissolver solution analyzed .

Sample Results

Uranium

$$U = 100 \frac{(A_{\text{U}})(V_{\text{S}})(F_{\text{U}})(D)}{W},$$

in which:

- U = weight percent uranium in sample ,
- $A_{\text{U}}$  = atomic weight of uranium in sample divided by atomic weight of uranium in NBS  $\text{U}_3\text{O}_8$  (238.03) ,
- $V_{\text{S}}$  = readout volts from coulometer for sample ,
- $F_{\text{U}}$  = calibration factor for uranium ,
- D = grams of final dissolver solution of initial sample divided by grams of initial sample ,
- W = weight in grams of sample aliquot analyzed .

Plutonium

$$\text{Pu} = \frac{(A_{\text{Pu}})(V_{\text{S}})(F_{\text{Pu}})(D)}{W},$$

in which:

- Pu = weight percent plutonium in sample ,
- $A_{\text{Pu}}$  = atomic weight of plutonium in sample divided by atomic weight of plutonium in NBS Pu (239.09) ,
- $V_{\text{S}}$  = readout volts from coulometer for sample ,
- $F_{\text{Pu}}$  = calibration factor for Pu ,

SUMMARY

Iron is measured spectrophotometrically as the Fe(II) o-phenanthroline complex at a wavelength of 508 nm after removal of plutonium by oxalate precipitation. The quantity of iron is calculated from the measured absorbance and the absorbance per microgram of iron obtained for prepared solutions having known iron contents. The relative standard deviation is approximately 1%.

APPLICABILITY

This method is applicable to the determination of iron in the concentration range between 100 and 1000  $\mu\text{g/g}$  of sample in uranium-plutonium mixed oxide pellets and in ceramic grade plutonium oxide. The result is used to correct the interference caused by iron in the coulometric titration of plutonium (see "Determination of Uranium or Plutonium by Controlled Potential Coulometry," p. 47). This method also may be used to determine iron in ceramic grade uranium dioxide and uranium dioxide insulator pellets.

At the impurity specification limits for the four materials in this program, only nickel might interfere in this method. On an equal weight basis to iron, nickel causes a 1.5% high bias.<sup>[1]</sup> The expected bias for any of the four materials, however, is negligible because iron usually is the larger contaminant. The recommended quantity of iron for measurement is between 10 and 40  $\mu\text{g}$ , but as little as 1  $\mu\text{g}$  may be determined with some sacrifice in precision. A single determination, exclusive of dissolution, requires about 3 hr, but eight determinations can be made in 3.5 to 4 hr. Operator time is about 1 hr for a single determination or 1.5 hr to 2 hr for eight determinations.

[1] G. F. Smith and F. P. Richter, "Phenanthroline and Substituted Phenanthroline Indicators," G. R. Smith Chemical Co., Columbus, Ohio (1944), pp. 67-81.

The relative standard deviation is 1% in the range between 125 and 500  $\mu\text{g/g}$  and 2% at 90  $\mu\text{gFe/g}$ . The recommended calibration material is electrolytic iron or ferrous ammonium sulfate hexahydrate.

DISCUSSION OF THE METHOD

The major steps in the procedure are reduction of iron and plutonium to the (II) and (III) oxidation states, respectively, with hydroxylamine hydrochloride; separation of plutonium by its precipitation as the oxalate; formation of the colored Fe(II)-o-phenanthroline complex; and spectrophotometric measurement. The recommended sample is an aliquot of the solution prepared for the coulometric determination of uranium and plutonium (see "Determination of Uranium or Plutonium by Controlled Potential Coulometry," p. 47).

A strongly colored chelate complex of the hexavalent type,  $\text{FePh}_3^{+2}$ , is formed by Fe(II) with o-phenanthroline in weakly acidic, neutral, or weakly alkaline solution. The chelate structure is a five-member ring involving the metal with the cyclic N-C-C-N group. The reagent reacts stoichiometrically and selectively with Fe(II) to form a product having a desirable hue for spectrophotometric measurement.<sup>[2]</sup> The pH in the range between 2 and 9 has little influence on the reaction. A great advantage of o-phenanthroline over some other iron reagents is its use in slightly acid solutions which greatly reduces interference caused by the precipitation of hydroxides or phosphates of several metals.<sup>[2]</sup> At a pH of less than 2, the color develops more slowly and is less intense. The complex is stable, Beer's law is closely followed, and the molar absorptivity under the conditions of this method is 11,100. A stability constant of  $2.5 \times 10^6$  was reported in an investigation of the equilibrium and kinetics of the Fe(II) o-phenanthroline system.<sup>[3]</sup>

[2] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience, New York, N.Y. (1959), pp. 535-40.

[3] I. M. Kolthoff, T. S. Lee, and D. L. Leussing, Anal. Chem. 20, 985 (1948).

Hydroxylamine, hydroquinone, or less preferably, sulfur dioxide, are suitable reductants for Fe(III). Under the slightly acidic conditions used in this method, hydroxylamine is an effective reductant. Following reduction, the color is formed by addition of o-phenanthroline, pH 6 buffer solution, and ammonium hydroxide to bring the pH to 6. This order of addition of reagents is important to ensure complete color development. [4]

Plutonium(III), stabilized by hydroxylamine hydrochloride in this method, at relatively high concentrations absorbs slightly at the wavelength for measuring the iron. One mg of plutonium can be tolerated without separation; larger amounts require separation prior to the color development. Various extraction, ion exchange, and other methods may be used for this purpose, but the precipitation of Pu(III) as the oxalate has the advantages of being fast and of providing a clean separation.

In addition to speed, simplicity, and relative freedom from interferences, this method has the advantages of requiring only small amounts of sample, about 100 mg for iron concentrations between 100 and 500  $\mu\text{g/g}$ , and the use of equipment usually found in a laboratory equipped to analyze plutonium materials spectrophotometrically.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Special care must be taken when handling the concentrated acids used in this method. As a minimum precaution, rubber gloves should be worn. When preparing dilute sulfuric acid solutions, always add the acid carefully to the water and not the reverse. Hydrofluoric acid is especially dangerous to the skin and will cause slow-healing ulcerating sores. Consult your laboratory safety manual for further information.

### APPARATUS

Centrifuge, clinical.

Centrifuge tubes, conical, 15-ml.

[4] N. F. Davis, C. E. Osborne, Jr., and H. A. Nash, *Anal. Chem.* **30**, 2035 (1958).

Spectrophotometer, Beckman, Model DU, with matched 1-cm cells, or equivalent.

## REAGENTS

Ammonium hydroxide, 14.8M (28%).

Hydroxylamine hydrochloride, 20% aqueous solution.

Iron calibration solution, 20  $\mu\text{g}$  Fe/ml. Dissolve 125.0 mg of 99.9 to 100% pure iron wire in 5 ml of 12M HCl. If pure iron wire is not available, dissolve 880 mg of ferrous ammonium sulfate hexahydrate  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$  in water and add 5 ml of 12M HCl. Dilute either solution to 250.0 ml with water. Dilute 4.00 ml to 100.0 ml for use in the calibration steps.

Iron calibration solution in uranium-plutonium matrix. Dissolve 2.500 g of the LASL-supplied uranium-plutonium mixed oxide blend, which has a nominal iron content of 100  $\mu\text{g/g}$ , as described in steps 1 through 3 in the Dis-solution subsection of "Determination of Uranium or Plutonium by Controlled Coulometry," p. 47. Then add 10 ml of 3M  $\text{H}_2\text{SO}_4$  and evaporate to near dryness. Dissolve the residue in 0.5M  $\text{H}_2\text{SO}_4$ , quantitatively transfer the solution to a 50-ml volumetric flask with 0.5M  $\text{H}_2\text{SO}_4$  rinses, and dilute to volume with 0.5M  $\text{H}_2\text{SO}_4$ .

Oxalic acid, 10% aqueous solution.

o-Phenanthroline, 0.5% solution. Dissolve 1 g of o-phenanthroline in 10 ml of 95% ethanol and dilute to 200 ml with water. Discard this solution when it discolors.

Sodium acetate buffer solution. Dissolve 84 g of sodium acetate trihydrate in 20 ml of glacial acetic acid and dilute to 1 l. with water.

Wash solution, 1% oxalic acid in 1M HCl.

## PROCEDURE

Determine the reagent blank in duplicate starting with step 2 in the subsection Sample Analysis and measure the absorbances as described in step 14. If the measured average absorbance is significantly greater than zero at the .05 significance level, replace each reagent individually to determine the source of contamination. Start

with the hydroxylamine hydrochloride, which often is contaminated with iron.

#### Calibration

For the initial calibration of each analysis apparatus, pipet eight 2-ml aliquots of the iron calibration solution in uranium-plutonium matrix into separate 15-ml centrifuge tubes. Pipet duplicate amounts of 0.5, 1.0, and 1.5 ml of the 20  $\mu\text{g}/\text{ml}$  iron calibration solution into six of the tubes giving duplicates of nominal 10, 20, 30, and 40  $\mu\text{g}$  of iron per tube. Carry these entirely through the Sample Analysis subsection starting at step 2. Process the results using least-squares formulas to obtain the linear calibration equation

$$y = Ax + B$$

that best fits the data. In this equation,  $y$  is the absorbance,  $x$  is the micrograms of iron,  $A$  is the slope, and  $B$  is the intercept with the  $y$ -axis.  $B$  should be approximately zero. Prepare a quality control chart for the values of  $A$  and  $B$  obtained for each analysis apparatus.

Once each week during periods that samples are analyzed, verify the calibration by processing duplicate 2-ml aliquots of the iron calibration solution in uranium-plutonium matrix. (The nominal contents of each duplicate are 10  $\mu\text{g}$  of iron and 100 mg of uranium-plutonium mixed oxide). Pipet the aliquots into 15-ml centrifuge cones and start at step 2 in the Sample Analysis subsection. Calculate  $A' = y/x$  and plot it on the quality control chart for  $A$ . If an individual value of  $A'$  disagrees at the .05 significance level with the value of  $A$  from the complete calibration set, investigate the cause and rectify the difficulty before proceeding with the analysis of samples.

#### Sample Analysis

1. Transfer to a 15-ml centrifuge tube an accurately weighed aliquot of the dissolved sample prepared for the coulometric analysis of uranium and plutonium that contains the equivalent of 80 to 100 mg of original oxide sample.

See "Determination of Uranium or Plutonium by Controlled Potential Coulometry," p. 47. The approximate weight of the aliquot, based on an initial 1-g sample and a final weight of 35 g for the dissolved sample solution, is 2.8 to 3.5 g.

If other samples are analyzed, especially nitrate-containing ones, fume them with sulfuric acid and redissolve the residue in not more than 3 ml of 0.5M  $\text{H}_2\text{SO}_4$ .

2. Add 1 ml of 20% hydroxylamine hydrochloride and heat just below boiling for 30 min under an infrared lamp.

Plutonium reduces to Pu(III) and iron to Fe(II).

3. After the solution cools, add 1 ml of 10% oxalic acid and mix.

Plutonium oxalate precipitates. If the precipitate does not settle readily, add more 10% oxalic acid dropwise until no further precipitate forms.

4. Centrifuge for 1 min.

5. Decant the supernatant solution into a 10-ml volumetric flask.

Do not transfer any plutonium oxalate to the flask.

6. Add 0.5 ml of the wash solution to the centrifuge tube and agitate the precipitate until a suspension is obtained.

7. Centrifuge for 1 min.

8. Decant the supernatant solution into the 10-ml volumetric flask.

Do not transfer any plutonium oxalate to the flask.

9. Repeat steps 6 through 8.

10. Add 0.5 ml of 20% hydroxylamine hydrochloride to the flask and heat just below boiling for 30 min under an infrared lamp.

This ensures complete reduction of iron to Fe(II).

11. After the solution cools, add the following reagents, mixing the contents thoroughly between each addition:

(a) 0.2 ml of 0.5% o-phenanthroline

(b) 1 ml of sodium acetate buffer

(c) sufficient 14.8M  $\text{NH}_4\text{OH}$  to increase the pH

to 6 while thoroughly mixing the solution

This order of reagent addition is necessary to obtain complete color development. pH indicator paper is satisfactory to measure the pH.

12. Let the solution stand 30 min.

This waiting period and the period stated in the next step are necessary to obtain complete color development.

13. Dilute to volume with water, mix thoroughly, and let the solution stand 30 min.

14. Measure the absorbance at 508 nm in a 1-cm cell against a reference prepared starting at step 10.

#### Calculations

$$R = \frac{(Y-B)D}{AWI} ,$$

in which:

R = micrograms of iron per gram of initial sample ,

Y = absorbance of sample ,

A, B = constants in the linear calibration equation,

D = weight, grams, of dissolver solution prepared for the coulometric analysis of uranium and plutonium,

I = weight, grams, of initial sample dissolved for the coulometric analysis of uranium and plutonium,

W = weight, grams, of aliquot of dissolver solution taken for the iron analysis .

DETERMINATION OF AMERICIUM BY GAMMA  
COUNTING IN MIXED OXIDE FUEL PELLETS AND  
PLUTONIUM DIOXIDE

SUMMARY

Americium is determined by measuring the gamma activity of the dissolved sample in a well-type NaI(Tl) detector. A chemical separation is not required, because a correction can be made for the slight interference caused by plutonium gamma activity, and uranium does not interfere.

APPLICABILITY

The method is designed for the determination of americium in mixed oxide fuel pellets and in ceramic grade plutonium dioxide. The Pu/U ratio may have any value from pure plutonium to pure uranium. The method cannot be used for materials containing fission products or other high specific-activity gamma emitters.

The recommended quantity of americium in the aliquot that is counted is 1 to 50 ng. A single determination, excluding dissolution of the sample, requires approximately 30 min. With a multiple gamma counter setup, this effort is reduced to 20 min per determination.

RELIABILITY

The pooled relative standard deviation for several hundred plutonium samples was less than 1% when the counted aliquot contained more than 5 ng of americium. For aliquots containing 1 ng or less, the relative standard deviation was 2 to 5%. The expected concentration range of americium in the plutonium dioxide to be used for LMFBR/FFTF fuel is 500 to  $\sim 2400 \mu\text{g/g}$ , so an aliquot containing at least 5 ng is obtained easily. Recommended calibration materials are NBS  $\text{U}_3\text{O}_8$  (SRM 950), NBS plutonium metal (SRM 949), and americium oxide containing less than 10 wt % plutonium. NBS americium is not yet available. When the calibration materials are properly used, the method is not biased.

DISCUSSION OF THE METHOD

The method is based on measuring the gamma activity of  $^{241}\text{Am}$  which is large relative to all plutonium and uranium isotopes present in the samples. Under the conditions of the method, the conversion factor for  $^{241}\text{Am}$  is  $2 \times 10^6$  cpm/ $\mu\text{g}$  and for plutonium and natural uranium are  $\sim 80$  cpm/ $\mu\text{g}$  and 0.2 cpm/ $\mu\text{g}$ , respectively. At these high ratios, corrections for the gamma contributions of plutonium and uranium are accurately made, especially when the aliquot taken for the americium determination is from the same solution from which aliquots are taken for the uranium and plutonium determinations.

A well-type NaI(Tl) scintillation detector is used to measure the gamma activity of the sample aliquot because it offers a high counting efficiency for the 59.6-keV gamma ray, which is the most abundant photon in  $^{241}\text{Am}$  decay. The high voltage for the detector is set at a 30-keV cutoff to eliminate counting of the lower energy L x-rays from plutonium. A 2-ml, 1M  $\text{HNO}_3$  aliquot of the dissolved sample containing  $\sim 25 \mu\text{g}$  of plutonium is counted for a time sufficient to accumulate  $\sim 10^5$  counts, equivalent to a counting error of 0.3% relative standard deviation. At the expected lower limit of 500  $\mu\text{g}$  of  $^{241}\text{Am}$  per gram of plutonium, this period is  $\sim 4$  min.

The method is adversely affected by gamma emitters other than plutonium and uranium, especially fission products. The levels of such interferences, however, are normally insignificant in ceramic grade plutonium dioxide and mixed oxide fuel pellets.

The proper high-voltage setting for the detector is established in a manner similar to that usually done to obtain a counting plateau for an alpha or beta proportional counter. Using an americium sample, a series of count rates is measured at voltage intervals of 5 or 10 V, depending on the sensitivity of the scaler, starting at a point well below the plateau. Instead of plotting the observed count rates, however, the differences between adjacent count rates are plotted as a function of the voltage, to give a differential curve similar to a gamma pulse height analysis. Table I and Figure 1 give examples of a typical set of data and the resulting differential curve.

The peak corresponds to the 59.6-keV photo peak from  $^{241}\text{Am}$  with photon energy increasing to the right. The proper operating voltage is at the bottom right-hand side of the peak and corresponds to a lower discrimination level of 30 or 40 keV, thus preventing the detection of gamma or x rays below this level.

Comparison of the results obtained by this method with other methods has demonstrated its accuracy for alpha pulse height analysis and its superiority to methods based on a chemical separation of the americium from the plutonium. [1] Its advantage over pulse height analysis is that no correction is necessary for  $^{238}\text{Pu}$ , whose alpha particle energy of 5.50 MeV cannot be readily resolved from the  $^{241}\text{Am}$  alpha particle energy of 5.49 MeV, and that the errors caused by alpha particle absorption by inert material in the sample are eliminated. This advantage is due to the fact that in the gamma counting method, americium is the principal activity

Table I  
VOLTAGE PLATEAU DATA FOR A DIFFERENTIAL  
COUNT CURVE

Volts	Count Rate, c/m	Differential Count Rate
950	511	-
960	817	306
970	7065	6248
980	11732	4667
990	21672	9940
1000	25212	3540
1010	27577	2365
1020	28005	428
1030	28188	183
1040	28712	524
1050	29405	693
1060	29806	401
1070	30442	636
1080	31189	747
1090	31475	286
1100	31998	523

[1] J. Bubernak, M. S. Lew, and G. M. Matlack, Anal. Chem. 30, 1759 (1958).

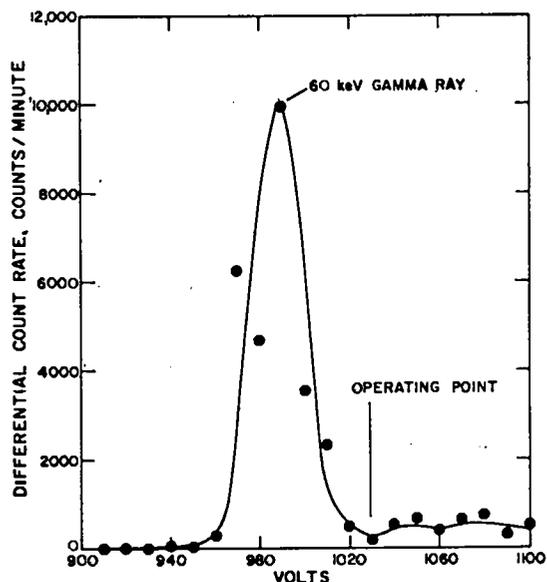


Figure 1.  $^{241}\text{Am}$  gamma spectrum from differential counting data.

counted, whereas in alpha pulse height analysis, the americium activity is a minor fraction of the total alpha activity.

### OPERATING INSTRUCTIONS

#### APPARATUS

Gamma Counter. The recommended gamma detector is a well-type  $\text{NaI(Tl)}$  crystal, 5.1-cm diam with a 1.7-cm-diam x 4-cm-deep well, coupled to a 2-in.-diam multiplier phototube. This easily accommodates a 13- x 100-mm test tube, which fills to a depth of 2 cm with 2 ml of solution. The detector, with its associated power supply, should be connected to an amplifier and scaler capable of accepting count rates of 100,000 cpm with a coincidence loss of less than 2%. To achieve low background count rates, the detector should be surrounded by at least 5 cm of lead shielding.

Test tubes. 13- x 100-mm.

#### REAGENTS

Americium calibration solution. Dissolve an accurately known weight of  $^{241}\text{Am O}_2$  in a minimum quantity of 8M  $\text{HNO}_3$ , with the aid of heat. Dilute accurately with 1M  $\text{HNO}_3$  to give approximately 5 ng of  $^{241}\text{Am}$  per ml. The americium oxide may be obtained from the Isotopes Sales Division, Oak Ridge, Tenn.

Nitric acid, 8M, 1M.

Plutonium calibration solution. Obtain a portion of freshly purified plutonium prepared for mass spectrometric analysis from a ceramic grade plutonium dioxide sample (see "Determination of Isotopic Distribution of Plutonium in Plutonium Dioxide by Mass Spectrometry Following Ion Exchange Purification," p. 15). Dilute with 1M  $\text{HNO}_3$  to give a plutonium concentration of approximately 100  $\mu\text{g/ml}$ . Count the plutonium calibration sample within 6 hr after purification to avoid errors caused by the growth of  $^{241}\text{Am}$ .

#### PROCEDURE

##### Blank

A blank measurement is not required.

##### Calibration

1. Transfer 2.00 ml of the  $^{241}\text{Am}$  calibration sample into a 13- x 100-mm test tube and cork the tube.

The cork prevents evaporation during the calibration procedure and protects against accidental spillage of the sample.

2. Place the tube in the detector well.
3. With the counter turned on, adjust the high voltage to the point where the count rate begins to increase rapidly with increasing voltage.

This is done by observing the scaler; it is not necessary to record the count rates at this point.

4. Count the calibration sample for 10 min and record the count rate.
5. Increase the high voltage by 10 V, and repeat step 4.
6. Repeat steps 4 and 5 until the count rate remains constant for 5 to 10 successive voltage points.

Ten successive points are recommended until you become familiar with the procedure.

7. Prepare a graph from the counting data by plotting the difference between successive count rates (y-

coordinate) against the voltage (x-coordinate).

This gives a crude pulse height analysis with a clearly defined peak corresponding to the 59.6-keV gamma ray of  $^{241}\text{Am}$ .

8. Locate the voltage on the graph, on the higher voltage side of the peak, at which the successive differences are small. Record this as the operating voltage and adjust the power supply to this voltage.

This voltage corresponds to a discrimination level that accepts 59.6-keV pulses but rejects those less than 30 to 40 keV, thus eliminating interference from plutonium L x rays at 17 keV.

9. Transfer 2.00 ml of the plutonium calibration sample into a 13- x 100-mm test tube and seal the tube with a cork.
10. Place the test tube in the detector well.

11. Count the plutonium calibration sample at the operating voltage determined in step 8 and after subtracting the detector background, record the net count rate as  $R_{\text{Pu}}$ .

Obtain at least  $10^4$  counts to ensure a counting precision of 1% relative standard deviation.

12. Count the americium calibration sample at the operating voltage determined in step 8. After subtracting the detector background, record the net count rate as  $R_{\text{Am}}$ .

Obtain at least  $10^6$  counts to ensure a counting precision of 0.1% relative standard deviation.

Calibrate each americium gamma counter with the americium calibration sample at the beginning of each 8-hr shift in which the counter will be used. Use the same calibration sample and tube that was prepared for the initial calibration. Then seal the top of the test tube with a hot flame, instead of closing the tube with a cork.

It is not necessary to repeat the initial calibration procedure for each shift calibration. It is sufficient to count the calibration sample and to readjust the operating voltage slightly to reproduce the count rate obtained in step 12.

Calibration with a plutonium calibration sample is not necessary for each 8-hr shift, because this value is not likely to change significantly with slight variations in operating voltage. When the isotopic distribution of the plutonium in the samples changes, a plutonium calibration sample from the new material must be purified and counted within 6 hr, or within a time during which the gamma count rate will not increase by more than 1% due to  $^{241}\text{Am}$  growth.

Maintain a quality control chart for the americium shift calibrations for each counter. Use the chart to determine when significant changes or trends are noted in the operating voltage. These changes should be investigated and the trouble corrected before using the counter for further americium determinations.

### Sample Analysis

#### Dissolution

1. Dissolve a weighed, whole, mixed oxide pellet or a weighed 1-g quantity of ceramic grade plutonium dioxide in 5 to 10 ml of 15.6M  $\text{HNO}_3$  in a 50-ml beaker or a covered 30-ml platinum dish and with the aid of simmering heat.

These dissolution conditions are the same as described for "Determination of Uranium or Plutonium by Controlled Potential Coulometry," p. 47

Weigh all samples to  $\pm 0.2$  mg.

A 15.6M  $\text{HNO}_3$ -0.01M HF mixture may be used for dissolution with platinum dishes. This mixture gives faster dissolution rates. If this mixture is used, omit step 3.

Rapid dissolution rates may be obtained with the sealed-tube technique described on p. 5.

2. Repeat the additions of 5 to 10 ml of 15.6M  $\text{HNO}_3$  and heat as necessary until dissolution is apparently complete.

Use simmering heat to speed the dissolution and use covers to prevent spattering loss.

3. With the last addition of 15.6M  $\text{HNO}_3$  or when the dissolution reaction is complete, add 1 drop of 1M HF and sufficient 15.6M  $\text{HNO}_3$  to give a total volume

of 5 to 10 ml. Continue the heating until complete solubility is obtained.

4. Transfer the solution quantitatively with the aid of at least five 5-ml rinses of 1M  $\text{HNO}_3$  to a tared, preferably heavy-walled polyethylene container having an airtight cap, and weigh to  $\pm 1$  mg.

Weighed aliquots of this solution can serve also for various other analyses, including measurements of plutonium, uranium, iron, and isotope abundance measurements.

A heavy-walled polyethylene container minimizes changes in concentration caused by transpiration of water vapor through the walls.

#### Counting

1. Dilute a 25-mg weight aliquot of the dissolved sample solution obtained in step 4 of the previous subsection to 50 ml with 1M  $\text{HNO}_3$  and mix until the solution is homogeneous.

This aliquot weight is based on a weight of 35 g for the dissolved sample solution. Select the aliquot weight proportional to this basis.

2. Pipet 2.00 ml of the diluted solution into a new 13-x 100-mm test tube and cork the tube.
3. Place the tube in the gamma detector and count until a total of at least  $10^5$  counts are accumulated.

Record the count rate as  $R_s$  after correcting for background.

#### Calculations

##### Americium Calibration Factor

$$F_A = \frac{R_{Am}}{W_A},$$

in which:

$$F_A = \text{cpm}/\mu\text{g Am},$$

$$R_{Am} = \text{cpm of calibration sample},$$

$$W_A = \text{weight, } \mu\text{g, of americium in calibration sample.}$$

##### Plutonium Calibration Factor

$$F_P = \frac{R_{Pu}}{W_P},$$

in which:

$$F_P = \text{cpm}/\mu\text{g Pu} ,$$

$$R_{Pu} = \text{cpm of calibration sample} ,$$

$$W_P = \text{weight, } \mu\text{g, of plutonium in calibration sample.}$$

#### Sample Results

$$R = 10^6 \frac{R_S - (F_P W_S)}{F_A W_S} ,$$

in which:

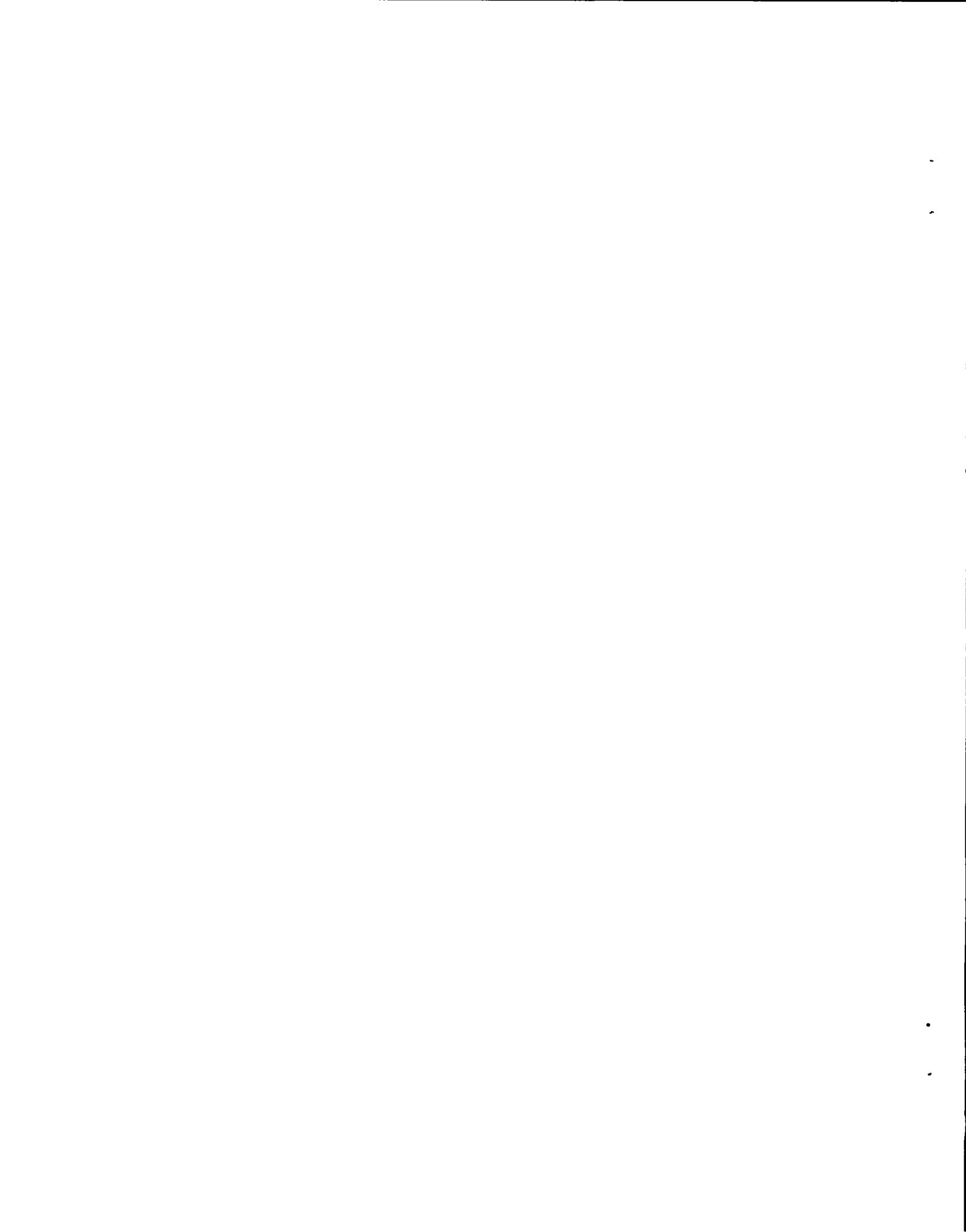
$$R = \mu\text{g Am/g Pu} ,$$

$$R_S = \text{cpm of sample} ,$$

$$F_P = \text{plutonium calibration factor} ,$$

$$F_A = \text{americium calibration factor} ,$$

$$W_S = \text{weight, } \mu\text{g, of plutonium in sample counting tube.}$$



## DISCUSSION OF METHODS FOR CARBON

Two methods are given for the determination of carbon in the four materials, ceramic grade uranium dioxide, ceramic grade plutonium dioxide, sintered uranium-plutonium mixed oxide pellets, and sintered uranium dioxide insulator pellets. The methods are similar in that the sample is heated in an oxygen stream to produce carbon dioxide. They differ in the way the carbon dioxide is measured. In the first method, the carbon dioxide is condensed in a capillary trap at liquid nitrogen temperature, the trap is warmed, and the carbon dioxide pressure is measured in a calibrated manometer. In the second method, the carbon dioxide is adsorbed on a molecular sieve trap, then measured in a gas chromatograph equipped with a thermal conductivity detector. Both measurement techniques have adequate reliability, are fast, and avoid high-vacuum problems. The equipment for the first method is less expensive.

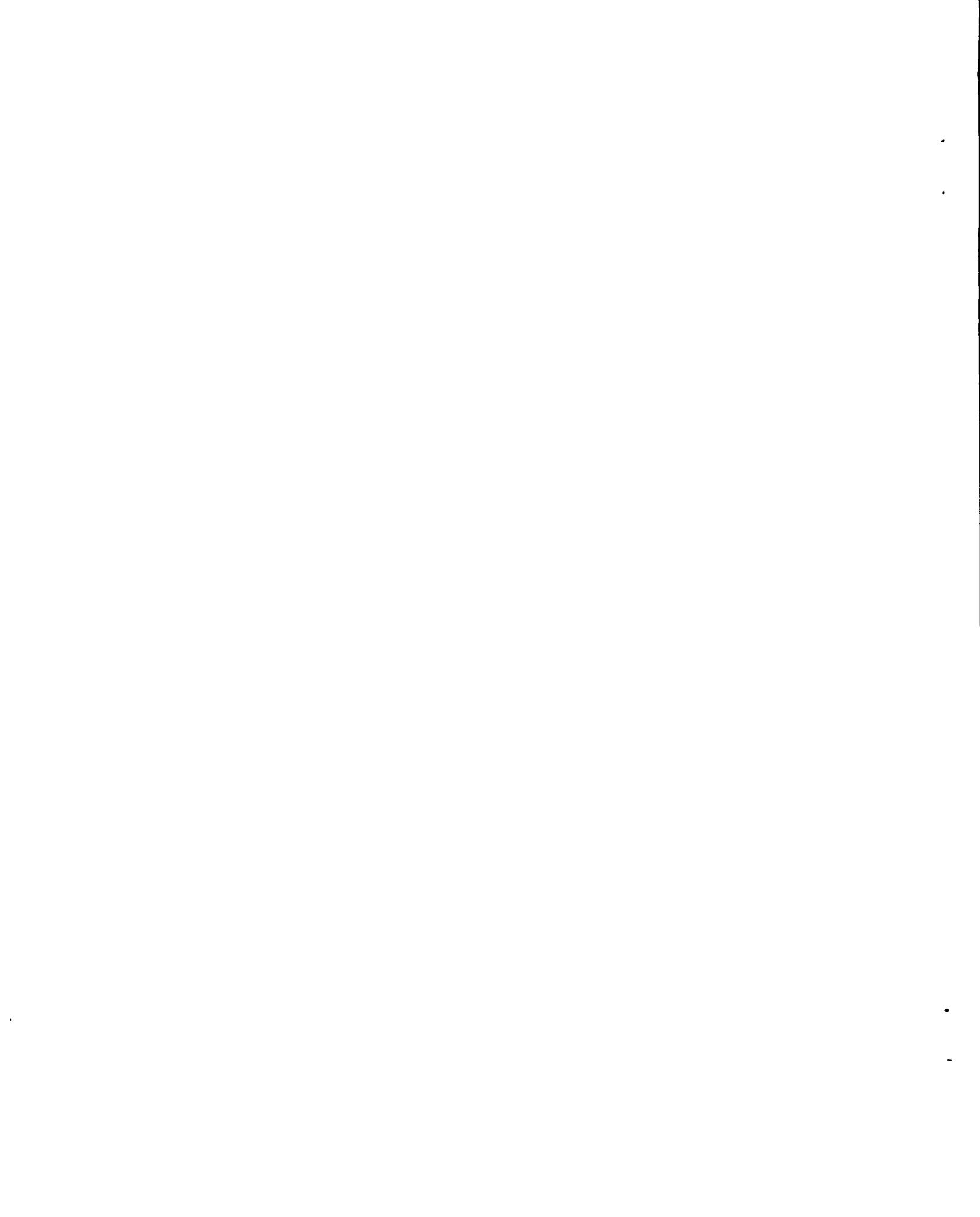
The major factors that control the success of these methods are the conditions of the combustion. A thorough evaluation of the conditions required for complete conversion of the total carbon in a sample to carbon dioxide has not been possible because reference materials have not been available with exactly known carbon contents and which match the samples in composition. One important and necessary condition is that the pellets be pulverized to assure complete oxidation of the carbon in the sample to carbon dioxide. This requirement was first reported by LASL<sup>[1]</sup> in a study of pellets analyzed both with and without conversion to powder. The results from the powder samples were a factor of two and more greater than those from the unpulverized samples. The same effect was reflected in the Phase II evaluation of analytical methods<sup>[2]</sup> in which six laboratories reported results on samples of pellets randomly selected from a batch considered to be homogeneous. Each laboratory used its own analytical method with

differing combustion conditions; the only statistically significant effect was that the two laboratories that did not first pulverize the samples reported low results.

The temperature and duration of the combustion in the two methods have been different. In the manometric method, a temperature of about 1200°C and a combustion time of 10 min are used. The second method uses a higher temperature of 1300 to 1600°C and a shorter combustion time, which are characteristic of commercial carbon analyzers designed for the analysis of metal samples, particularly steels, that actually ignite to give a rapid conversion of the free and combined carbon to carbon dioxide. For refractory samples, such as uranium and plutonium oxides, a combustion period of 4 min is recommended to guarantee complete conversion.

[1] C. S. MacDougall and M. E. Smith, USAEC Report LA-4284-MS (1969), p. 18.

[2] J. E. Rein, R. K. Zeigler, and C. F. Metz, USAEC Report LA-4407 (1970).



DETERMINATION OF CARBON BY COMBUSTION TO  
CARBON DIOXIDE AND ITS MANOMETRIC  
MEASUREMENT

SUMMARY

Carbon is determined by measuring the volume of carbon dioxide produced by heating the pulverized sample at 1000°C for 10 min in a stream of oxygen. The carbon dioxide volume is calculated from PVT measurements in a calibrated manometer.

APPLICABILITY

This method is applicable to all four materials analyzed in this program, ceramic grade uranium dioxide, ceramic grade plutonium dioxide, sintered uranium-plutonium mixed oxide pellets, and sintered uranium dioxide insulator pellets. With 100-mg samples, the nominal lower limit of the method is 25 µg C/g. This limit can be lowered by using larger samples. With one apparatus setup, an analyst can analyze eight samples per 8-hr shift.

RELIABILITY

For a 100-mg sample, the relative standard deviation is 5% for carbon contents of 60 µg/g and 100 µg/g. The relative standard deviation can be improved by using larger samples.

DISCUSSION OF THE METHOD

The method is patterned after that developed by Smiley<sup>[1]</sup> for the determination of oxygen in plutonium metal. Pellet samples are pulverized immediately before analysis. Weighed portions of the four sample types in powder form, usually 0.1 g for the range of ~ 25 to 500 µg C/g, are wrapped in aluminum foil and transferred to the apparatus. As shown in Figure 1, the powder sample is dropped into a tube furnace operating at 1000°C. The oxygen stream is first passed through a

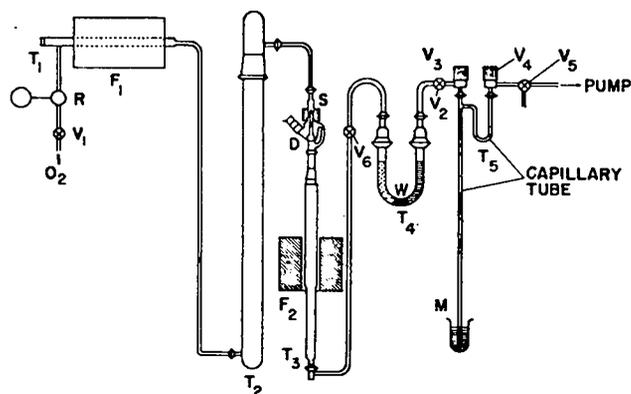


Figure 1. Apparatus for determination of carbon by combustion to carbon dioxide and its manometric measurement. R, oxygen flow regulator; T<sub>1</sub>, preoxidation tube; T<sub>2</sub>, oxygen purification trap; S, solenoid; D, sample dropper; T<sub>3</sub>, combustion tube; T<sub>4</sub>, gas purification trap; T<sub>5</sub>, carbon dioxide trap; M, mercury manometer; V<sub>1</sub> through V<sub>5</sub>, bellows valves.

tube furnace containing cupric oxide at 800°C to oxidize any traces of carbon monoxide, through a purification trap containing magnesium perchlorate-Ascarite to remove water vapor and carbon dioxide, then through the furnace containing the sample. The unreacted oxygen and gases evolved from the reaction flow through a trap of manganese dioxide and magnesium perchlorate that removes oxides of nitrogen, phosphorus, and sulfur. The oxygen and carbon dioxide continue through a capillary trap immersed in liquid nitrogen in which the carbon dioxide is quantitatively condensed. At the system operating pressure of ~ 50 Torr, no oxygen condenses in the trap. After a 10-min combustion, the capillary trap and connected capillary manometer are isolated, the trap is allowed to warm to room temperature, and the amount of carbon dioxide is calculated from the pressure-volume-temperature relationship in the manometer.

Precautions necessary to obtain highly reliable results include careful calibration of the capillary trap and manometer, operation at a maximum oxygen pressure of 7 in. of water to obtain quantitative condensation of carbon dioxide, and the pulverization of samples that are not in powder form.

[1] W. G. Smiley, *Anal. Chem.* **27**, 1098 (1955).

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Handle liquid nitrogen in a manner prescribed by your Laboratory Safety Manual to prevent contact with the skin. Take the necessary precautions in the design and operation of the furnace sections of the apparatus to prevent burns to personnel and to dry box gloves.

### APPARATUS

Gas combustion and manometric measurement apparatus (Figure 1).

Note: The components are assembled using Apiezon W wax to seal unheated ball joints, high-vacuum grease to seal heated ball joints, and solder for 1/4-in. soft-drawn copper lines.

R. Oxygen flow regulator. Range of 0 to 50 in. of water, Nullmatic No. 40-2, Moore Products, Inc., or equivalent.

T<sub>1</sub>. Preoxidation tube. Nickel, 1-in. diam x 18-in. length, filled with wire-form cupric oxide held in place by copper wool plugs, with a brass screw cap sealed with a lead gasket. This tube is heated at 800°C with a 750-W resistance furnace, 1.25-in. bore x 12-in. length, Hevi Duty Electric Co., or equivalent.

T<sub>2</sub>. Oxygen purification trap. Glass, 5-cm diam x 75-cm length, filled with Ascarite and magnesium perchlorate separated by a plug of glass wool.

D. Sample dropper. This component, described by Smiley, [1] is connected to the combustion tube, T<sub>3</sub>, by a standard-taper adapter which is cemented with sodium silicate into the ground end of the combustion tube. Samples are introduced into a side arm fitted with a standard-taper glass cap. The solenoid, S, lifts the plunger allowing the sample to drop into the combustion tube. Power to the solenoid is controlled through a rheostat to lift and seat the plunger gently.

T<sub>3</sub>. Combustion tube. Alundum or zirconia, 1 1/4-in. o.d. x 18-in. length, double reduced, cut off at the larger end, Burrell Corp., or equivalent. The ends are tapered to fit a 12/30 outer joint and a 19/38 inner joint. The tube is packed to half its height with broken fused silica chips or with Alundum chips supported on a glass wool plug to retain all particles of uranium and plutonium oxide. This tube is heated at 1000°C with a 500-W resistance furnace, 1 1/4-in. bore x 8-in. length, Hevi Duty Electric Co., or equivalent. See Figure 2 for details of the combustion tube.

T<sub>4</sub>. Gas purification tube. Glass U-tube, 6-in. height, 28/12 outer semiball joints on each end, filled with manganese dioxide and magnesium perchlorate separated by a glass wool plug. The joints are connected to the gas lines with adapters made by joining a 28/12 inner semiball joint and a 12/5 outer semiball joint.

T<sub>5</sub>. Carbon dioxide trap. Glass, with dimensions as detailed in Figure 3.

M. Mercury manometer. Glass capillary tube immersed in a glass reservoir containing mercury. The reservoir is held in a cylindrical brass container with screw adjustment to provide zero correction for changing atmospheric pressure.

V<sub>1</sub> through V<sub>5</sub>. Bellows valves, Hoke, No. 482,

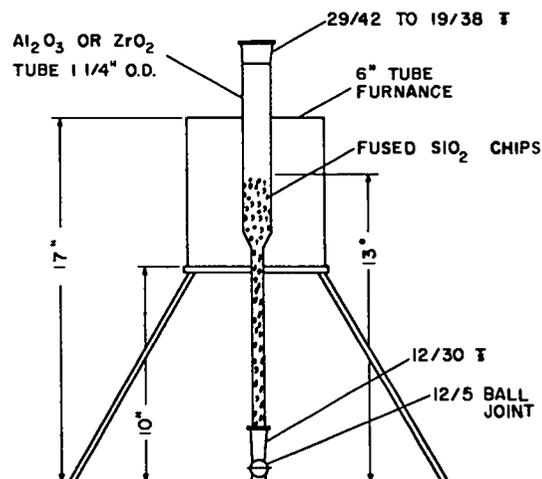


Figure 2. Details of combustion tube.



Using the initial pressure in the system, H, and the pressure after expansion,  $H - X_2 + X_1$ , apply Boyle's law according to the following equations to calculate the volume, V, of the trap above the zero mark.

$$VH = (V + SX_1)(H - X_2 + X_1) \quad (1)$$

$$V = SX_1 (H - X_2 + X_1) / (X_2 - X_1) \quad (2)$$

Repeat the determination of V until four successive determinations agree within a range of 1%.

Insert the values obtained above for V and S into the following equation for the weight, W, of carbon,

$$W = 12 X(V + SX) / RT, \quad (3)$$

in which X is the manometer reading.

To obtain the weight of carbon in micrograms, express the linear dimensions in millimeters and take the temperature as  $25^\circ\text{C}$  to convert Eq. (3) to Eq. (4).

$$W = 0.00065(VX + SX^2) \quad (4)$$

#### Blank

At the beginning of each 8-hr shift, determine the blank. Proceed according to the Sample Analysis subsection starting at step 2 without an aluminum foil or sample. The blank must be less than the equivalent of  $0.5 \mu\text{g}$  of carbon, equivalent to  $5 \mu\text{g/g}$  for a 0.1-g sample, before samples can be analyzed. If the blank exceeds this value, rectify the difficulty before proceeding.

After each sample analysis, redetermine the blank. Again the blank must be less than the equivalent of  $0.5 \mu\text{g}$  of carbon before proceeding with another analysis.

#### Calibration

For the initial calibration of each analysis apparatus, analyze the appropriate set of calibration materials provided. One set consists of five blends of a metal carbide blended into a uranium-plutonium mixed oxide matrix for the analysis of ceramic grade plutonium dioxide and uranium-plutonium mixed oxide pellets. The

other set consists of five blends of a metal carbide blended into a uranium oxide matrix for the analysis of ceramic grade uranium dioxide and uranium dioxide insulator pellets. Process each of the five blends in the appropriate set in duplicate starting with step 1 under Sample Analysis. Process the results using least-squares formulas to obtain the values of A and B in the equation

$$y = Ax + B \quad (5)$$

that best fit the data. In this equation, y is the measured carbon content in  $\mu\text{g/g}$ , x is the blend value in the same units, and A and B are the slope and intercept values, respectively. B should be approximately zero. Maintain a quality control chart for the values of A and B obtained for each calibration.

Once each week, verify the calibration by analyzing one blend in duplicate starting with step 1, Sample Analysis. For these weekly verifications, assume that B is zero. If an individual value for A disagrees significantly at the .05 confidence level, investigate the cause for the difference and rectify the difficulty before proceeding with further analyses.

#### Sample Analysis

1. Pulverize a whole pellet for 2 to 5 min in a mixer-mill with stainless steel balls.

Minimize the exposure of the ground sample to air by proceeding quickly to step 2 and thence to the analysis.

2. Weigh a 0.1-g aliquot of the pulverized sample into a 15- x 15-mm aluminum foil and wrap the sample tightly.

This aliquot weight is recommended for the determination of carbon in the range of 25 to  $500 \mu\text{g/g}$ . A larger sample, up to 1 g, may be used, and is recommended for expected low levels of carbon.

3. Transfer the sample to the glove box where the apparatus is installed.
4. Adjust the oxygen pressure with regulator (R) to 7 in. of water, close valve  $V_3$ , and verify that the furnaces are at their proper operating temperatures.

In this and subsequent steps, refer to Figure 1

for identification of the components.

The oxygen pressure should not be greater than 7 in. of water because at larger pressures all the carbon dioxide may not be retained in trap T<sub>5</sub> due to the increased flow rate.

5. Remove the sample dropper cap (D) and introduce the sample.

The positive oxygen pressure prevents air from entering the apparatus while the cap is removed.

6. Replace the cap and flush the sample dropper thoroughly with oxygen before seating it.

7. With valves V<sub>3</sub> and V<sub>4</sub> open to the pump, adjust V<sub>2</sub> to give a manometer reading of about 50 Torr.

This pressure corresponds to a flow rate of 100 ml/min.

8. Immerse trap T<sub>5</sub> in liquid nitrogen.

Keep the Dewar flask full of liquid nitrogen throughout the analysis.

9. After the liquid nitrogen ceases boiling, drop the sample into the combustion tube by activating solenoid D.

Premature dropping of the sample before trap T<sub>5</sub> is sufficiently cold will cause loss of carbon dioxide.

10. After 10 min, sequentially close V<sub>3</sub> and V<sub>4</sub>, remove the Dewar flask, immerse the trap in warm water for a few seconds, then wipe the trap dry.

11. Record the manometer reading to the nearest 0.5 mm after tapping it gently with a short length of rubber tube to free the meniscus.

#### Calculations

$$R = \frac{W_1 - W_2 - W_3 - B}{AW_4} ,$$

in which

R =  $\mu$ g C/g sample ,

W<sub>1</sub> = micrograms of carbon calculated by equation (4) for sample ,

W<sub>2</sub> = micrograms of carbon calculated by equation (4) for average of blanks before and after sample (see subsection Blank),

W<sub>3</sub> = micrograms of carbon calculated by equation (4) for the aluminum foil sample container.

This value is the product of the foil weight and its determined carbon concentration (see section REAGENTS AND MATERIALS),

W<sub>4</sub> = weight, g, of sample analyzed ,

A ,B = constants of calibration equation (5) for the appropriate LASL blends (see subsection Calibration).



DETERMINATION OF CARBON BY COMBUSTION TO  
CARBON DIOXIDE AND ITS CHROMATOGRAPHIC  
MEASUREMENT

SUMMARY

Pulverized samples are heated at approximately 1200°C for 4 minutes in a stream of oxygen. The produced carbon dioxide is absorbed on a molecular sieve trap, the trap is warmed to 70°C and flushed with helium, and the desorbed carbon dioxide is separated on a silica gel chromatographic column and measured in a thermal conductivity cell.

APPLICABILITY

This method<sup>[1]</sup> is applicable to all four materials analyzed in this program: ceramic grade uranium dioxide, ceramic grade plutonium dioxide, uranium-plutonium mixed oxide pellets, and uranium dioxide insulator pellets. The combination of a trap to remove oxides of sulfur from the gas produced in the combustion and the silica gel chromatographic column eliminates interference from all impurity elements that may be present in the materials. With the recommended sample size of 1 g, the nominal lower limit of the method is 10 µg C/g. With one apparatus setup, an analyst can analyze 25 samples per 8-hr shift.

RELIABILITY

The reliability of the method has not been reported unequivocally for uranium-plutonium oxide materials. This statement is especially true concerning accuracy because such materials containing known amounts of carbon that also match the analyzed materials in composition have not been available. The standard deviation obtained for a batch of uranium dioxide powder was 3.4 µg C/g at an average level of 34 µg C/g, corresponding to a relative precision of 10%.<sup>[1]</sup> It is expected that the relative precision will improve at higher levels of carbon. It also is expected that this degree of precision can be attained for samples of plutonium dioxide and uranium-plutonium mixed oxide.

DISCUSSION OF THE METHOD

The commercial equipment used is designed primarily for the determination of carbon in steel samples. In discussing equipment, neither approval nor disapproval of specific equipment is implied or intended.

Pellet samples are pulverized immediately prior to the analysis. Exposure of the pulverized sample to air must be minimum to prevent adsorption of carbon dioxide. A weighed portion of the powder sample, 1 g for the range of 25 to 500 µg C/g, is added to a low-carbon ceramic crucible, and mixed with 1 g of low-carbon iron chips, 2 g of tin, and a 1-g copper ring. A low-carbon ceramic crucible cover is placed on the crucible which is transferred to the combustion furnace where the sample is heated to approximately 1200°C in a stream of purified oxygen for 4 min. The unreacted oxygen and the gases evolved from the combustion flow successively through a particulate filter, a trap containing manganese dioxide to absorb oxides of sulfur, a heated cupric oxide bed to oxidize any carbon monoxide to carbon dioxide, a magnesium perchlorate bed to remove water, and then into the analyzer to a column of molecular sieve 4A that traps the carbon dioxide and other combustion product gases. This column then is eluted with a stream of helium to a silica gel chromatographic column for separation of carbon dioxide from other gases. The effluent from the silica gel column flows through a dual compartment thermal conductivity detector connected to an integrator that measures the amount of carbon dioxide relative to helium.

The commercial equipment used for this analysis is an integral unit with all of the components listed in the previous paragraph. The normal readout component is a digital voltmeter. A strip chart recorder can be substituted or added.<sup>[2]</sup>

The importance of having the sample in a finely divided condition cannot be overemphasized. Pellet samples must be pulverized before analysis. Otherwise,

[1] A. Zerwekh, B. H. Baca, and W. H. Ashley, LASL unpublished data (February 1970).

[2] D. H. Schmitt, Babcock & Wilcox Report BAW-4088-1 (1969).

combustion is incomplete with consequent low results.

The other factor controlling complete recovery is the duration of the combustion time. Experience at LASL with various metal samples, particularly NBS Steel Standard Reference Materials, has shown that the short combustion time of 1 to 2 min used by many laboratories equipped with commercial equipment similar to that described in this method is not sufficient to always convert the carbon present in the sample quantitatively to carbon dioxide. Repeated analyses of NBS steels have shown that quantitative combustion of the carbon to carbon dioxide is achieved using a 4-min combustion time. Results with a 2-min combustion time averaged about 5% lower. These analyses were done with 1 g of sample, 1 g of iron chips, 2 g of tin accelerator, and a copper ring combustion starter. Over a 3-yr period, approximately 100 portions of NBS Steel SRM 81 have been burned as standards to calibrate the LECO Low Carbon Analyzer in use at LASL. Repeated analyses of this material with a 4-min combustion time consistently have given an average value of 770  $\mu\text{g/g}$  with a relative standard deviation of 5%. The range reported for this material by NBS, for seven different analysts, is 720 to 810  $\mu\text{g/g}$ . Based on this experience, a 4-min combustion time is routinely used at LASL for metal samples.

The combustion time for refractory materials such as uranium-plutonium oxides is even more critical than it is for steel samples. To determine the best combustion time, 1-g samples of two uranium dioxide materials were analyzed by the method described below in Sample Analysis; combustion times varied from 2 to 5 min. The same materials also were analyzed by a classical gravimetric method in which 5-g samples were burned for 35 min at 1350°C in oxygen using sillimanite combustion tubes and zirconium silicate boats. The released carbon dioxide was absorbed in Ascarite and weighed. Table I summarizes the results from these experiments.

Statistical analyses of those data show that the 4-min results for both uranium dioxide materials are not significantly different from the gravimetric results, but

are significantly higher than the results obtained for 2-, 3-, and 5-min combustion periods. The low results for the 5-min combustion time are thought to be caused by loss of carbon dioxide somewhere in the automated equipment. Each laboratory should establish the minimum and maximum combustion periods for complete combustion and recovery of carbon when using commercial equipment.

Other accelerator and flux materials have been used with 1-g samples. The Babcock & Wilcox laboratory<sup>[2]</sup> uses only 1.5 g of low-carbon iron chips, and the WADCO laboratory<sup>[3]</sup> uses 4 g of tin powder and 2 g of copper powder. The use of these materials was not investigated at LASL.

Because commercial equipment is used in this method for which manufacturers provide detailed operating instructions, the Sample Analysis subsection has only general instruction steps.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Observe the necessary precautions as outlined in the manufacturer's manuals, especially those concerning the high-voltage components of the equipment. During operation avoid burns to personnel and containment gloves when handling hot components. Operate the equipment only when all components are properly sealed.

### APPARATUS

Combustion-analyzer apparatus. LECO Low Carbon Analyzer Model 734-300 (Laboratory Equipment Company, St. Joseph, Mich.) or equivalent. The apparatus should include a purification train for oxygen in which the sequential flow is wire-form copper oxide at 700°C, Ascarite, Anhydrone, 95%  $\text{H}_2\text{SO}_4$ , Anhydrone, and Ascarite.

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[3] M. W. Urie, Method 20.3, Report WHAN-IR-5 (1970).

TABLE I  
RESULTS FOR TWO URANIUM DIOXIDE MATERIALS

<u>Material</u>	<u>Gravimetric Method</u>	<u>Combustion Time for Commercial Equipment</u>			
		<u>2 Min</u>	<u>3 Min</u>	<u>4 Min</u>	<u>5 Min</u>
1. LASL Uranium Dioxide					
Av $\mu\text{g C/g}$	35.8	23.8	20.3	33.5	22.2
No. of Analyses	6	6	6	6	6
Std Dev	6.6	3.6	3.2	3.4	5.5
2. Pulverized Uranium Dioxide					
Insulator Pellets					
Av $\mu\text{g C/g}$	11.7	7.6	No data	11.4	No data
No. of Analyses	6	8		8	
Std Dev	4.1	2.0		2.7	

Crucibles and covers, low-carbon, LECO 528-35 and 538-42, or equivalent.

Micro-mill, Spex, Model 8000 II, or equivalent, with stainless steel capsule and balls for pulverizing pellet samples.

#### REAGENTS

Copper ring, low-carbon, LECO 550-184, or equivalent.

Helium, high-purity.

Iron chips, low-carbon, LECO 501-77, or equivalent.

Magnesium perchlorate, anhydrous.

Manganese dioxide, LECO 501-60 "Specially Prepared"  $\text{MnO}_2$ , or equivalent.

Oxygen, high-purity.

Tin, granulated metal accelerator, low-carbon, LECO 501-76, or equivalent.

#### PROCEDURE

##### Blank

At the beginning of each 8-hr shift, determine the overall blank in duplicate. Proceed according to the Sample Analysis subsection starting at step 2 without sample. The allowable difference in the duplicate blank measurements is 10  $\mu\text{g}$  of carbon. Repeat the blank

measurement, if necessary, until a consistent blank value is obtained.

##### Calibration

The primary calibration materials are the two sets of blends prepared by LASL. One set consists of five blends of a metal carbide blended into a uranium-plutonium mixed oxide matrix for the analysis of ceramic grade plutonium dioxide and uranium-plutonium mixed oxide pellets. The other set consists of five blends of a metal carbide blended into a uranium oxide matrix for the analysis of ceramic grade uranium dioxide and uranium dioxide insulator pellets. Process each of the five blends in the appropriate set in duplicate, starting with step 1 under Sample Analysis. Process the results by least-squares formulas to obtain the values of A and B in the equation

$$y = Ax + B$$

that best fit the data. In this equation, y is the measured carbon content in  $\mu\text{g/g}$ , x is the blend value in the same units, and A and B are the slope and intercept values, respectively. B should be approximately zero. Maintain a quality control chart for the values of A and B obtained for each calibration.

Once each week, verify the calibration by

analyzing one blend in duplicate starting with step 1, Sample Analysis. For these weekly verifications, assume that B is zero. If an individual value for A disagrees at the .05 significance level, investigate the cause for the difference and rectify the difficulty before proceeding with further analyses.

#### Sample Analysis

1. Pulverize a uranium-plutonium mixed oxide pellet or a uranium dioxide insulator pellet for 2 to 5 min in a mixer-mill with a stainless steel capsule and ball.

Minimize the exposure of the ground sample to air by proceeding quickly with its analysis.

Ceramic grade uranium dioxide or plutonium dioxide are powders and do not require pulverization.

2. Weigh a crucible to  $\pm 0.01$  g.
3. Transfer 1 g of powder sample to the crucible and weigh to  $\pm 0.01$  g.

This sample weight is recommended for the determination of carbon in the range of 25 to 500  $\mu\text{g/g}$ .

4. Add 1 g of iron chips, 2 g of tin, mix them, and place a 1-g copper ring on top of the mixture.
5. Place a lid on the crucible, position the crucible on the pedestal within the combustion tube, and lock it in position.

Clean the combustion tube at least once each day with a wire brush. Errors can be caused by partial plugging of the outlet end of the tube and by extraneous material falling into the heated zone during a sample combustion.

6. Flush the furnace system for 1 min with oxygen.
7. Flow the helium carrier gas into the chromatograph section of the apparatus and establish baseline equilibrium.

Leave the helium flow on continuously. It may be reduced to a low flow rate over long periods between sample analyses.

8. Heat the crucible and sample at approximately  $1200^{\circ}\text{C}$  for 4 min.
9. Record the analyzer reading.

#### Calculations

$$R = \frac{(S - b) - B}{AW}$$

in which:

- R =  $\mu\text{g C}$  per g of sample ,  
S = analyzer reading,  $\mu\text{g C}$ , for sample,  
b = analyzer reading,  $\mu\text{g C}$ , for blank,  
A, B = constants of calibration equation for the appropriate set of LASL calibration blends (see subsection Calibration),  
W = weight, g, of sample .

## DETERMINATION OF FLUORIDE AND CHLORIDE

### SUMMARY

Fluoride and chloride are jointly separated by pyrohydrolysis and separately measured in the distillate. Fluoride is measured in a relatively small aliquot of the distillate with a fluoride specific ion electrode; chloride in the remainder of the distillate is determined spectrophotometrically by reaction with mercuric thiocyanate and iron(III) to form the intense red ferric thiocyanate complex. The relative standard deviation is better than 10% for the measurement of both halides over the ranges of 0.9 to 50  $\mu\text{g F/g}$  and 4 to 50  $\mu\text{g Cl/g}$ .

### APPLICABILITY

This method<sup>[1]</sup> is applicable to samples of ceramic grade uranium dioxide, ceramic grade plutonium dioxide, uranium-plutonium mixed oxide pellets, and uranium dioxide insulator pellets. For 1-g samples, the concentration ranges covered by the method are 0.9 to 50  $\mu\text{g F/g}$  and 4 to 50  $\mu\text{g Cl/g}$ . With specification limits of 10  $\mu\text{g F/g}$  and 20  $\mu\text{g Cl/g}$  for the two types of pellets, and 25  $\mu\text{g F/g}$  and 25 to 50  $\mu\text{g Cl/g}$  for the two ceramic grade materials, the 1-g sample is near optimum.

At the impurity specification limits for the four materials in this program, none of the impurities interfere with either determination.

Four samples can be separated by pyrohydrolysis and analyzed for both fluoride and chloride by one analyst in an 8-hr shift.

### RELIABILITY

The relative standard deviations for the measurement of fluoride are approximately 7% for the concentration range of 5 to 50  $\mu\text{g/g}$  and 10% for the range of 0.9 to 5  $\mu\text{g/g}$ . The relative standard deviations for the measurement of chloride are approximately 5% for the concentration range of 6 to 50  $\mu\text{g/g}$  and 10% at the lower limit of 4  $\mu\text{g/g}$ . The above precisions were obtained

[1] T. K. Marshall and N. L. Koski, LASL, unpublished work (1970).

using 1-g samples as recommended in the method.

To obtain minimum between-laboratory differences, LASL-prepared blends are used for overall calibration of the method both for the measurements of fluoride and chloride. Solutions prepared with hydrofluoric acid and sodium chloride are used to calibrate the fluoride-specific-ion electrode and chloride spectrophotometric measurement, respectively.

### DISCUSSION OF THE METHOD

The two pellet-type samples are pulverized to powder before analysis. The two ceramic grade raw materials are analyzed as received. A 1-g sample in a nickel boat is heated at 1000°C in a nickel tube furnace in a water-saturated argon-flowing atmosphere. Hydrogen fluoride and hydrogen chloride, formed by pyrohydrolysis, are collected in three sequential 8-ml distillate fractions. Each fraction is analyzed for fluoride and chloride. Fluoride is directly determined by a specific ion electrode in 1-ml aliquots of the distillates, and chloride is determined in the remaining distillate volumes by a spectrophotometric method based on a reaction with a mixture of mercuric thiocyanate and iron(III) to form the intense red ferric thiocyanate complex.

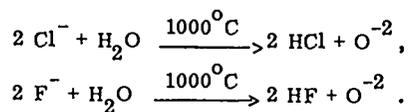
The analytical aspects of pyrohydrolysis were explored over 20 yr ago by Warf<sup>[2]</sup> and later by Warf, Cline, and Tevebaugh<sup>[3]</sup> for separating halides from salts and oxides of uranium and other metals. This method proved to be rapid and quantitative for separating the halides, except iodide, without introducing the problems associated with sample dissolution. Gahler and Porter<sup>[4]</sup> were among the first to use a nickel pyrohydrolysis tube and boat to obtain quantitative separation and recovery of chloride from titanium sponge samples. An all-nickel apparatus was found best also for recovery

[2] J. C. Warf, "Analytical Chemistry of the Manhattan Project," National Nuclear Energy Series, 1st ed., Div. VIII, vol. 1, McGraw-Hill, New York, N. Y. (1950), pp. 728 ff.

[3] J. C. Warf, W. D. Cline, and R. D. Tevebaugh, Anal. Chem. **26**, 342 (1954).

[4] A. R. Gahler and G. Porter, Anal. Chem. **29**, 296 (1957).

of fluoride from uranium oxide, plutonium oxide, and mixed uranium-plutonium oxide. [5] Essentially complete separation of microgram quantities of fluoride and chloride from the ground oxide materials was obtained by heating the sample at 1000°C in a nickel boat in a nickel tube through which a stream of moist argon was swept. Moisture is introduced by bubbling the argon through boiling water before the gas passes through the heated pyrohydrolysis tube. The pyrohydrolysis converts the halides to hydrogen chloride and hydrogen fluoride according to the following equations:



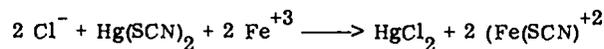
The evolved hydrogen halides are carried by the stream of moist argon through a water-cooled condenser into a water trap.

The concentration of fluoride is measured using a fluoride-specific-ion electrode [6] in conjunction with a saturated calomel reference electrode. A small aliquot of the distillate is placed in a microsample dish, the tips of the electrodes are immersed, and the millivolt reading obtained on a high-sensitivity pH meter is compared to the values on a previously prepared calibration curve to determine the fluoride concentration. For an initial 1-g sample and the volume of distillate and aliquots specified in the method, the fluoride concentration range determined is 0.9 to 50 µg/g.

Determinations of fluoride by measurement of the corresponding hydrogen ion and by microtitration with thorium nitrate [7] are also reliable, but the fluoride-specific-ion electrode offers a more convenient and rapid method of determining fluoride without altering the nature of the solution. The electrode, which is constructed from a single crystal section of rare-earth fluorides,

shows high selectivity for fluoride ion over other anions and responds to fluoride ion activities over a range of more than five orders of magnitude. The electrode has varied applications [8] and has been used to measure fluoride in volumes as small as 50 µl. [9] In addition to measurements of fluoride ion activities, another application has been the detection of the end points of titrations. [10]

The chloride concentration is measured in the distillate remaining after removal of the aliquot for fluoride determination. Nitric acid, mercuric thiocyanate, and ferric sulfate are added to the distillate to form an equivalent amount of red colored ferric thiocyanate complex:



More than one complex can be formed depending upon the thiocyanate concentration, but at low thiocyanate concentrations  $[\text{Fe}(\text{CNS})]^{+2}$  is the predominant colored species. [11] All of these complexes are red, with a shift in maximum absorption toward shorter wavelengths with decreasing thiocyanate concentration. The absorbance of the complex is measured spectrophotometrically at a wavelength of 460 nm in this method. Time and temperature also affect the complex formation so that the spectrophotometric measurement must be made after a fixed reaction time at a constant temperature. Under the conditions used in this method, the molar absorptivity of the complex is 3090. With the 1-g sample and the volume of distillate stipulated in the method, the chloride concentration range is 4 to 50 µg/g.

The normally excellent separation achieved by pyrohydrolysis eliminates ions, such as iodide, cyanide, and thiosulfate, that would interfere with the chloride

[5] T. K. Marshall and G. R. Waterbury, USAEC Report LA-4284-MS (1969), pp. 16-17.

[6] M. S. Frant and J. W. Ross, Jr., *Science* **154**, 1553 (1966).

[7] J. E. Lee, Jr., J. H. Edgerton, and M. T. Kelly, *Anal. Chem.* **28**, 1441 (1956).

[8] J. D. Neefus, J. Cholak, and B. E. Saltzman, *Amer. Ind. Hyg. Ass. J.* **31**, 96 (1970).

[9] R. A. Durt and J. K. Taylor, *Anal. Chem.* **39**, 1483 (1967).

[10] W. Krijgaman, J. F. Mansveld, and B. F. A. Griepink, *Fresenius' Z. Anal. Chem.* **249**, 368 (1970).

[11] C. E. Crouthamel and C. E. Johnson, *Anal. Chem.* **24**, 1780 (1952); **26**, 1284 (1954).

spectrophotometric method. The most common source of interference is accidental contamination of the sample with extraneous chloride-containing materials, especially sodium chloride or ammonium chloride.

In combination with the pyrohydrolytic separation, this method of measuring chloride offers a simple and rapid alternative to argentometric titration or micro-distillation. [12]

### OPERATING INSTRUCTIONS

#### SAFETY PRECAUTIONS

Special care must be taken when handling the concentrated acids used in this method. As a minimum precaution, rubber gloves should be worn. Hydrofluoric acid is especially dangerous to the skin and will cause slow-healing ulcerating sores. Consult your laboratory safety manual for further information.

#### APPARATUS

Boat transfer unit, nickel, for rapid and safe transfer of the sample boat into the reaction tube. Prepare two units by cutting in half, lengthwise, an 8-in. length of 0.75-in. o.d. nickel tube having a wall thickness of 0.035 in. Bend in one end of each half-tube to form a lip that can be grasped with a pair of tongs.

Centrifuge tubes, conical, polyethylene, 15-ml. Pipet 8.5 ml of water into each tube and mark it at the meniscus.

Electrode, fluoride-ion-specific, Orion Model 94-09, or equivalent.

Electrode, reference, saturated calomel.

Flowmeter, Fischer and Porter Co., Catalog No. 448-100, or equivalent.

Furnace, Hevi Duty Electric Co., Multiple Unit Type 122H-2, or equivalent.

Microsample dish, Orion Catalog No. 94-00-14, or equivalent.

[12] H. N. Elsheimer, A. L. Johnston, and R. L. Kochen, *Anal. Chem.* **38**, 1684 (1966).

Mixer-mill, Spex Industries, Model 8000, or equivalent, with a tungsten carbide capsule and ball.

pH meter, Beckman Expandomatic Model SS-2, or equivalent.

Pyrohydrolytic tube and condenser, nickel (see Figure 1). Weld the nickel parts of this apparatus with pure nickel under an inert atmosphere. Silver solder the brass or stainless steel water jacket to the nickel tube. Insert a suitable length of polyethylene or Tygon tubing that is drawn down to a fine tip into the end of the condenser (see Figure 2). Position the reaction tube and condenser in the tube furnace with the condenser tube within 0.5 in. of the outer vertical surface of the furnace (see Figure 2).

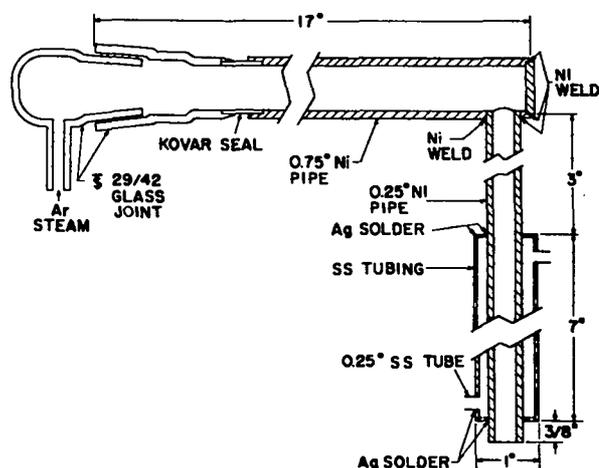


Figure 1. Pyrohydrolysis tube and condenser.

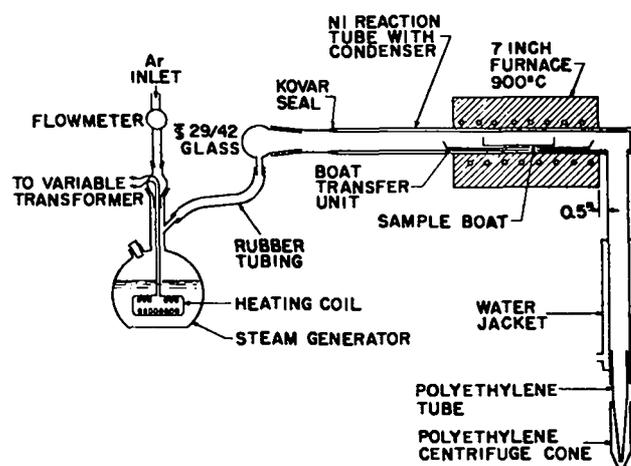


Figure 2. Pyrohydrolysis apparatus.

Sample boat, nickel, fabricated from a 1- x 3-in. piece of 3-mil thick sheet. Make right-angle bends about 3/16 in. from each 3-in. edge to form sides 3/16-in. high.

Spectrophotometer, Beckman Model DU, or equivalent, with matched 1-cm cells.

Volumetric flasks, 10-ml. Pipet 9.0 ml of water into each flask and mark it at the meniscus.

Water heater, borosilicate glass, made from a 1-l. flask (see Figure 2). Prepare a 5-ohm resistance coil by winding a 21-ft length of No. 26 nichrome wire over a 5/16-in.-diam mandrel, and assemble as shown. Adjust the variable transformer to 75 V to maintain the water at its boiling point.

#### REAGENTS

Argon gas, cylinder gas without purification.

Chloride stock solution, 250  $\mu\text{g Cl/ml}$ . Dissolve 206.1 mg of sodium chloride in a final volume of 500 ml of distilled water.

Chloride calibration solution, 10  $\mu\text{g Cl/ml}$ . Dilute 4 ml of the stock solution to 100 ml with distilled water.

Ferric ammonium sulfate, 0.25M in 9M  $\text{HNO}_3$ . Dissolve 12 g of  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$  in 58 ml of 15.6M (70%)  $\text{HNO}_3$  and dilute to 100 ml with distilled water.

Fluoride stock solution, 640  $\mu\text{g F/ml}$ . Dilute 700 mg of 28M (48%) HF to 500 ml with distilled water.

Fluoride calibration solutions, 64  $\mu\text{g F/ml}$  and 0.64  $\mu\text{g F/ml}$ . Dilute 10 ml of the stock solution to 100 ml with distilled water to prepare calibration solution I containing 64  $\mu\text{g F/ml}$ . Dilute 5 ml of calibration solution I to 500 ml to prepare calibration solution II containing 0.64  $\mu\text{g F/ml}$ .

Mercuric thiocyanate solution, saturated, in 95% ethanol. The concentration of mercuric thiocyanate is approximately 0.3 g in 100 ml.

#### PROCEDURE

##### Blank

At the beginning of each 8-hr shift, determine

the blank in duplicate starting with step 1 of the subsection Sample Analysis omitting the sample. The determined amount of fluoride must be less than 0.1  $\mu\text{g}$  in the first distillate fraction collected. The absorbance of the chloride blanks must correspond to less than 6  $\mu\text{g}$  of chloride. These blanks measured against water include the absorbance contributed by reagents which is equivalent to approximately 5  $\mu\text{g}$  of chloride. If the amounts of fluoride and chloride exceed these levels, change reagents and clean the apparatus until the blank levels are satisfactorily reduced before proceeding with samples.

As previously mentioned in the section DISCUSSION OF THE METHOD, chloride is a common contaminant encountered in laboratory operations. When seeking the cause of a high chloride blank, it often is expedient to check first the reagent solutions that are used for color development. To do this, add distilled water to a 10-ml volumetric flask and proceed with the color development as described in steps 16 through 18 of the subsection Sample Analysis.

An alternative to preparing two reagent blanks for both fluoride and chloride is to use as the blanks the third distillate fractions collected for each sample as described in Sample Analysis. These can be used if the measured fluoride and chloride levels are less than 0.1  $\mu\text{g}$  and 6  $\mu\text{g}$ , respectively. If the levels exceed these amounts, it is assumed that the fluoride, or chloride, or both, were still being distilled at the end of the third fraction collection. In this case, additional distillate fractions are collected until the fluoride and chloride levels decrease to less than 0.1  $\mu\text{g}$  and 6  $\mu\text{g}$ , respectively. This last fraction than can be used for blanks.

##### Calibration

To calibrate the fluoride-ion electrode, dilute 25-, 15-, 10-, 5-, 3-, and 1-ml aliquots of calibration solution II in separate flasks to 50 ml each to prepare solutions containing 0.32, 0.19, 0.13, 0.064, 0.038, and 0.013  $\mu\text{g F/ml}$ , respectively. Prepare and store all solutions in polyethylene containers. Determine

millivolt readings for each of the dilutions and of calibration solution II by transferring approximately 1 ml of each into the microsample dish and obtaining the reading according to steps 10 and 15 in Sample Analysis. Prepare a calibration curve by plotting the millivolt readings vs the  $\mu\text{g F/ml}$ .

To prepare a chloride calibration curve, pipet 0.2-, 0.5-, 1.0-, 2.5-, and 5.0-ml aliquots of the calibration solution (2 to 50  $\mu\text{g}$  of chloride) into separate 10-ml volumetric flasks. Follow the directions for color development and measurement in steps 16 and 17 in Sample Analysis. Include duplicate determinations for which no chloride is added to calculate the net absorbance. Prepare a calibration curve by plotting the net absorbance readings vs the micrograms of chloride.

The overall calibration of the method is accomplished with two sets of LASL-prepared calibration blends. One set consists of five blends in a uranium oxide matrix covering the nominal range of 2 to 50  $\mu\text{g F/g}$  and 2.5 to 50  $\mu\text{g Cl/g}$  to be used for samples of ceramic grade uranium dioxide and uranium dioxide insulator pellets. The other set consists of five blends in a mixed uranium-plutonium oxide material covering the same nominal ranges to be used for samples of ceramic grade plutonium dioxide and uranium-plutonium mixed oxide pellets.

For initial calibration, process each calibration blend in duplicate beginning at step 1 of Sample Analysis. Process the results for fluoride and chloride separately for each matrix materials using least-squares formulas to obtain the values of A and B in the equation

$$y = Ax + B$$

that best fits the data. In this equation, y is the amount of chloride or fluoride read from the respective calibration curve, x is the known amount of chloride or fluoride in the calibration blends, A is the slope (ratio of y/x or the recovery factor) which should approximate unity, and B is the intercept value which should approximate zero.

Each week, verify the calibration by processing duplicates of one of the calibration blends in the appropriate matrix material starting with step 1 under Sample Analysis. Maintain a quality control chart for the chloride and for the fluoride calibration data obtained each week in terms of A assuming that B is zero. If the average of the duplicate results disagrees at the .05 significance level with the average of previous results on the appropriate quality control chart, investigate the cause for the difference and rectify the cause before proceeding with further analyses.

Carefully store the spent calibration material samples from which chloride and fluoride have been separated during each calibration analysis. At the beginning of each 8-hr shift, verify the initial and weekly calibrations by adding 100  $\mu\text{l}$  of fluoride calibration solution I (64  $\mu\text{g F/ml}$ ) and 100  $\mu\text{l}$  of chloride stock solution (250  $\mu\text{g Cl/ml}$ ) to each of two 1-g portions of the spent calibration material residues contained in separate nickel boats. Add the solution aliquots as uniformly as possible to the 1-g portions of oxide powder. Allow the mixtures to stand until the small volume of moisture evaporates, and then analyze each sample starting with step 1 under Sample Analysis but omitting steps 3 and 4. Compare the average value obtained for A in the chloride and in the fluoride determinations to the values on the respective quality control charts. If the values disagree at the .05 significance level, investigate the cause and rectify the difficulty before proceeding with the analysis of samples.

#### Sample Analysis

1. Prepare the pyrohydrolysis apparatus for use as follows:
  - (a) turn on the tube furnace and allow it to heat to maximum temperature, (b) turn on the cooling water for the condenser attached to the reaction tube, (c) adjust the argon flow to 170 to 200 ml/min, (d) adjust the voltage to the heating coil of the steam gen-

erator to produce 8 ml of distillate in approximately 15 min with all components of the pyrohydrolysis apparatus at operating conditions, and (e) add 0.5 ml of water to each of three 15-ml polyethylene centrifuge tubes.

Refer to Figures 1 and 2 for details of the apparatus.

Use 15-ml polyethylene, conical, centrifuge tubes to collect the distillates for each blank or sample determination. These tubes are precalibrated for 8.5-ml volumes (see APPARATUS).

2. Disconnect the 29/42 cap from the pyrohydrolysis tube and place one of the 15-ml centrifuge tubes so that the open end of the exit tube is immersed in the water at a level just above the bottom of the centrifuge tube.
3. Grind uranium-plutonium mixed oxide and uranium dioxide insulator pellets for 2 to 5 min in a mixer-mill using a tungsten carbide container with tungsten carbide grinding balls.

Pellet samples must be ground to ensure complete pyrohydrolysis.

Omit this step for ceramic grade uranium dioxide and ceramic grade plutonium dioxide samples.
4. Transfer 1 g of powdered sample to a tared nickel boat, spread the sample uniformly over the middle half of the boat, and weigh the sample and boat.

Determine the weight of sample to  $\pm 10$  mg.
5. Transfer the boat and sample to a boat transfer unit, place the transfer unit and boat in the entrance end of the pyrohydrolysis tube, move the transfer unit and boat into the tube with a nichrome pusher rod, and immediately close the pyrohydrolysis tube with the 29/42 cap.

Place the boat on the transfer unit and quickly move the transfer unit to the hottest part of the pyrohydrolysis tube. Move the transfer unit into the tube and seal the tube rapidly to prevent any loss of fluoride or chloride.
6. Continue heating the sample with uniform steam and argon flow until 8.0 ml of distillate has been collected.

ted.

A fine taper on the tubing tip extending into the centrifuge tube minimizes the volume of distillate displaced by the tip to provide a more accurate measurement of the total 8.5-ml volume (see step 11).

7. Without removing the 29/42 cap from the pyrohydrolytic tube, remove the 15-ml centrifuge tube, replace it with another centrifuge tube containing 0.5 ml of water, and continue the pyrohydrolysis until 8.0 ml of distillate again has been collected.

These two 8-ml distillates are analyzed for chloride and fluoride starting at step 11. The second 8.0-ml distillate is collected to ensure complete recovery of chloride; both distillates are analyzed as the measure of total fluoride and chloride.
8. Remove the second centrifuge tube from the furnace exit tip, replace it with a third centrifuge tube containing 0.5 ml of water, and collect a third 8.0-ml of distillate.

This distillate may be used for blank determinations (see the subsection Blank).
9. Disconnect the 29/42 cap and pull the transfer unit with sample out of the furnace.

The sample should be set aside in case the amounts of fluoride and chloride collected in the third pyrohydrolysis fraction are significant (see steps 15 and 18).

Pull the transfer unit with sample from the hottest part of the pyrohydrolysis tube and allow it to cool slightly before completely removing it to prevent damage to the borosilicate glass furnace entrance.

If the sample is a calibration blend, carefully transfer the residue to a clean storage container for future daily calibrations (see subsection Calibration).
10. To begin the analysis of a new sample, place another 15-ml centrifuge tube containing 0.5 ml of water under the exit tube and continue the operations described in steps 4 through 9.

Pyrohydrolyze the next sample while the fluoride is being measured for the preceding sample.
11. Transfer the solutions from each centrifuge tube to separate 10-ml volumetric flasks with the aid

of 0.5-ml water rinse.

The flasks are precalibrated for 9-ml volumes (see section APPARATUS).

12. Add water to each volumetric flask to give volumes of 9 ml, stopper, and mix.

13. Transfer 1.00 ml of solution from each volumetric flask to separate microsample dishes for measurement of fluoride,

The 8 ml of solution remaining is used for the measurement of chloride starting at step 16.

14. Immerse the tips of the fluoride-ion-specific and calomel electrodes in the solution in the microsample cup and turn the Expandomatic pH meter to the expanded scale for each of the three fluoride measurements.

It is essential that contact be made between the tips of the two electrodes through the solution in the microsample cup.

15. For each measurement, record the millivolt reading from the pH meter when the reading becomes constant and read the corresponding fluoride concentrations from the fluoride calibration curve.

The electrodes respond slowly to traces of fluoride. A waiting period of 15 to 60 min is necessary, depending upon the particular electrode used and the fluoride concentration, to obtain the correct value.

If the millivolt reading indicates more than 0.6  $\mu\text{g}$  of fluoride in any 1-ml aliquot, take a second 1-ml aliquot and dilute to 10 ml with water in a 10-ml volumetric flask. Determine the fluoride in a 1-ml aliquot of this dilution according to steps 14 and 15.

If the amount of fluoride measured in the third distillate exceeds 0.1  $\mu\text{g}$ , replace the sample in the furnace and obtain additional distillates until this level is attained.

16. To the solutions remaining in each of the three volumetric flasks, add 1 ml of ferric ammonium sulfate solution, swirl the flask to mix the solution, add 1 ml of mercuric thiocyanate solution and distilled water, if necessary, to bring the volume to 10 ml, again mix, and allow each solution to stand for 10 min.

This order of addition of reagents and stated operations is important to obtain correct color de-

velopment (see section DISCUSSION OF THE METHOD).

17. Transfer a portion of the solution from each volumetric flask to separate clean, dry, 1-cm Corex cells and, without delay, determine the absorbance for each solution at 460 nm using distilled water as a reference liquid.

18. Compare the absorbance obtained with the values on the previously prepared chloride calibration curve.

If the apparent amount of chloride measured in the third distillate exceeds 6  $\mu\text{g}$ , replace the sample in the furnace and obtain additional distillates until this level is attained.

### Calculations

#### Fluoride

$$K = 9H, \quad (1)$$

$$K = 90H, \quad (2)$$

in which

K = total micrograms of fluoride in a distillate (blank or sample).

H = micrograms of fluoride in a 1-ml aliquot of a distillate read from the fluoride electrode calibration curve.

Equation (2) is used only if a second 1-ml aliquot was diluted to 10 ml for a fluoride measurement as described in step 15 of the subsection Sample Analysis.

$$F = (K_1 - K_b) + (K_2 - K_b) + \dots + (K_m - K_b),$$

in which

F = apparent micrograms of fluoride in sample,

$K_1$  = micrograms of fluoride in first distillate fraction,

$K_2$  = micrograms of fluoride in second distillate fraction,

$K_m$  = micrograms of fluoride in last distillate fraction containing greater than 1.0  $\mu\text{g}$  of fluoride (see step 15 of the subsection Sample Analysis and subsection Blank).

$K_b$  = micrograms of fluoride in reagent blank.

Note: If the last distillate fraction that was collected was used as the blank (see subsection Blank), the value

of  $K_b$  is the measured micrograms of fluoride in this last fraction.

$$R = \frac{F - B}{AW},$$

in which

R = micrograms of fluoride per gram of sample,

A, B = factors for fluoride calibration equation obtained using LASL-prepared blends (see subsection Calibration),

W = weight, grams, of sample.

S = micrograms of chloride per gram of sample,

A, B = factors for chloride calibration equation obtained using LASL-prepared blends (see subsection Calibration),

W = weight, grams, of sample.

### Chloride

$$Y = (Y_1 - Y_b) + (Y_2 - Y_b) + \dots + (Y_m - Y_b),$$

in which

Y = net absorbance,

$Y_1$  = absorbance of first distillate fraction,

$Y_2$  = absorbance of second distillate fraction,

$Y_m$  = absorbance of last distillate fraction in which the absorbance corresponds to 6  $\mu$ g or greater of chloride read from the calibration curve,

$Y_b$  = average absorbance of the duplicate reagent blanks.

Note: If the last distillate fraction that was collected was used as the blank (see subsection Blank), the value of  $Y_b$  is zero.

$$C = \frac{9L}{8}, \quad (3)$$

$$C = \frac{9L}{7}, \quad (4)$$

in which

C = total micrograms of chloride in sample,

L = micrograms of chloride corresponding to net absorbance Y read from the calibration curve.

Equation (4) is used only if a second 1-ml aliquot was diluted to 10 ml for a fluoride measurement as described in step 15 of the subsection Sample Analysis.

$$S = \frac{C - B}{AW},$$

in which

## DETERMINATION OF NITRIDE NITROGEN

### BY SPECTROPHOTOMETRY

#### SUMMARY

Nitrogen is measured spectrophotometrically at a wavelength of 410 nm following separation as ammonia by a Kjeldahl steam distillation and subsequent color development with Nessler's reagent. The quantity of nitrogen is calculated from the measured absorbance and the absorbance per microgram of nitrogen obtained for prepared solutions having known nitrogen contents. The relative standard deviation ranges from 20% for 3  $\mu\text{g}$  of nitrogen to 3% for 50 to 90  $\mu\text{g}$  of nitrogen.

#### APPLICABILITY

This method is applicable to the determination of nitride nitrogen in the concentration range between 3 and 500  $\mu\text{g/g}$  in unirradiated samples of sintered, uranium-plutonium mixed oxide pellets, ceramic grade plutonium dioxide, ceramic grade uranium dioxide, and sintered uranium dioxide insulator pellets. None of the impurities at the specification limits for these four materials interfere.

The recommended quantity of nitrogen for measurement is between 3 and 100  $\mu\text{g}$ . For samples containing 100 to 500  $\mu\text{g}$  of nitrogen, dilutions are made following the separation to reduce the quantity of nitrogen measured to less than 100  $\mu\text{g}$ . A single determination, exclusive of dissolution, requires 30 min, but 20 determinations can be made in an 8-hr shift.

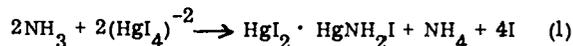
#### RELIABILITY

The relative standard deviation is 20% for a concentration of 3  $\mu\text{g/g}$ , 10% for a concentration of 10  $\mu\text{g/g}$ , and 3% for concentrations between 50 and 90  $\mu\text{g/g}$  in 1-g samples. For higher concentrations of nitrogen, an accurately measured aliquot of the distillate is taken that contains between 50 and 90  $\mu\text{g}$  of nitrogen so that the

relative standard deviation of the measurements is also 3%. The initial calibration of the method and weekly calibration verifications are done by analyzing LASL-prepared blends of mixed oxide and uranium oxide powders in which the nitrogen is present as uranium nitride. In addition, verification of the calibration is recommended each 8-hr shift by analyzing calibration solutions prepared from ammonium chloride because the Nessler's reagents are not stable for long periods.

#### DISCUSSION OF THE METHOD

A multitude of successful applications, since the method was first reported almost a century ago by Kjeldahl, [1] attest to the quantitative nature of the separation of nitride nitrogen by steam distillation as ammonia from strongly basic solution. The method requires the conversion of nitride nitrogen to ammonia in acid solution to avoid loss of nitrogen. This is conveniently accomplished by digesting the sample under reflux conditions in acids such as phosphoric or hydrochloric-perchloric. The conversion of nitride nitrogen to ammonium salts upon the acid dissolution of various metals, alloys, and compounds has been assumed to occur quantitatively. Although little fundamental work appears to have been directed toward any critical exploration of the correctness of this assumption, its general validity is supported by the reasonableness of thousands of analytical results on a great variety of samples. The completeness of the recovery of evolved ammonia during the distillation, however, is easily tested and is known to be complete. Winkler's technique [2] of trapping the ammonia in boric acid solution is used and is followed by the spectrophotometric measurement based on the color formed with Nessler's reagent. [3] This reagent contains  $(\text{HgI}_4)^{-2}$  and reacts with traces of ammonia to form an insoluble yellow-orange compound,  $\text{HgI}_2 \cdot \text{HgNH}_2\text{I}$ . [4]



[1] J. Kjeldahl, *Z. Anal. Chem.* **22**, 366 (1883).

[2] L. W. Winkler, *Z. Angew. Chem.* **26**, 321 (1913).

[3] J. Nessler, *Z. Anal. Chem.* **7**, 415 (1868).

[4] D. F. Boltz, *Colorimetric Determination of Non-metals*, Interscience, New York (1953), pp. 76, 84, 85.

This insoluble colored compound, in the presence of a stabilizer such as gum arabic, [5] forms a highly dispersed colloidal suspension. This suspension acts very nearly as a true solution and can be measured spectrophotometrically. Although successful adaptations of a titrimetric method have been made on the micro level, [6] colorimetry has been used almost exclusively for the measurement of microgram quantities of nitrogen. [4]

Contamination with organic nitrogen compounds or inorganic ammonium salts, or digestion of the samples in nitric acid, will cause high results. Aldehydes, acetone, and alcohols interfere with the development of the color with Nessler's reagent. [4] These interferences can be avoided with general laboratory cleanliness and due care in preparation and handling of reagents. There are few other substances which are volatile in the basic conditions used, thus making the method selective.

It is possible that other methods, including vacuum extraction of the Dumas method, [7] also may suffice for measuring the nitride nitrogen. Comparisons show that the difference between nitride nitrogen obtained by the Kjeldahl method and total nitrogen obtained by the Dumas method is negligible for the 12 different metals and alloys. A comparison of this type has not been made, however, for the oxide materials to which this method applies. The Kjeldahl method is preferred because it has the advantages of speed once the sample is dissolved, simplicity, freedom from interferences, and requires no special equipment.

Uranium dioxide and uranium-plutonium mixed oxides are dissolved slowly by refluxing the sample in concentrated phosphoric acid with a few drops of hydrofluoric acid. [8] Ceramic grade plutonium dioxide

generally is dissolved using the sealed-tube method as nitric acid digestion of the sample would cause high results. Fusion of plutonium dioxide with an acid flux probably would bring about solution, but some loss of ammonia would be anticipated. Basic fusion certainly would give low results.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Special care must be taken when handling concentrated acids. As a minimum precaution, rubber gloves should be worn. When preparing dilute sulfuric acid solutions, always add the acid carefully to the water and not the reverse. Hydrofluoric acid is especially dangerous to the skin and will cause slow-healing ulcerating sores. Consult your laboratory safety manual for further information.

### APPARATUS

Digestion apparatus, consisting of a condenser with a 24/40 inner joint sealed to the bottom, a 50-ml, round-bottom flask with a 24/40 outer joint, and an electric heating mantle to fit the flask.

Spectrophotometer, Beckman, Model DU, with matched 1-cm cells, or equivalent.

Steam distillation apparatus, see Figure 1.

Variable transformer, 5-A maximum load.

### REAGENTS

Ammonium chloride calibration solution. Dissolve 3.819 g of  $\text{NH}_4\text{Cl}$  in 1 l. of water. Dilute 10 ml to 1 l. with water to prepare a solution containing 10  $\mu\text{gN/ml}$ .

Boric acid, 5% aqueous solution.

Hydrochloric acid, 12M (37%).

[5] W. G. Frankenburg et al., *Anal. Chem.* **25**, 1784 (1953).

[6] D. A. Skoog and D. M. West, *Fundamentals of Analytical Chemistry*, Holt, Rinehart and Winston, New York (1963), p. 355.

[7] N. H. Furman, Ed., *Scott's Standard Methods of Chemical Analysis*, Vol 2, D. van Nostrand Co., Inc., New York (1939), p. 2488.

[8] N. L. Koski, T. K. Marshall, and G. R. Waterbury, USAEC Report LA-4307-MS (1969), p. 64.

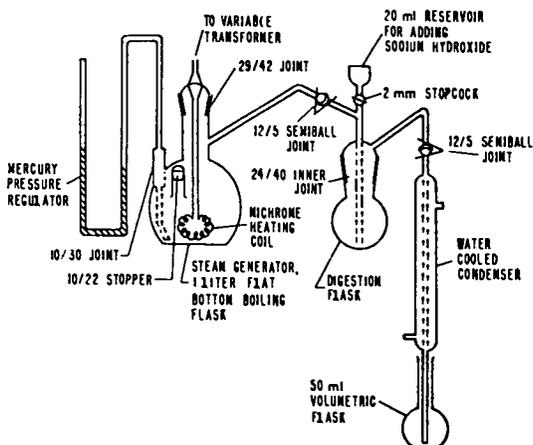


Figure 1. Steam distillation apparatus.

Hydrofluoric acid, 28M (48%).

Nessler's reagent. Dissolve 50 g of potassium iodide in 35 ml of water and add slowly, with stirring, a saturated solution of mercuric chloride until a slight precipitate of red mercuric iodide persists. Add 400 ml of clear 9M NaOH and dilute to 1 l. Allow to stand until clear and decant the clear liquid for use.

Nessler's stabilizer reagent. Dissolve 20 g of gum arabic in 400 ml of hot water and cool. Wash 20 g of Dowex 50-x 2, 200-400 mesh resin with 6M HCl followed by ammonia-free water, prepared by triple distillation or by deionization with mixed-bed, ion exchange resins, until the pH of the effluent increases to more than 4. Add the washed resin to the gum arabic solution, allow it to settle, and decant the solution to an amber bottle for storage. Be careful to avoid transfer of any precipitate.

Phosphoric acid, 14.7M (85%).

Sodium hydroxide, 12.5M (50%).

## PROCEDURE

### Blank

Determine the blank in duplicate by adding 5 ml of 14.7M  $H_3PO_4$  and 3 drops of 28M HF to each of two 50-ml, round-bottom flasks and digest the solution for 2 hr. Then proceed from step 3 in the subsection Sample Analysis through step 10 or 14, whichever is appropriate. Use this blank to correct the absorbances obtained for the calibration materials and samples.

### Calibration

For the initial calibration of each analysis apparatus, use a set of LASL-provided calibration blends. Use the set having a uranium-plutonium mixed oxide matrix for samples of mixed oxide pellets and ceramic grade plutonium dioxide and the set having a uranium oxide matrix for samples of ceramic grade uranium dioxide and uranium dioxide insulator pellets. Measure the nitrogen in duplicate samples of each of the five blends in the appropriate set starting with step 1 in the subsection Sample Analysis. Using a least-squares fit of the results data, calculate the linear calibration equation

$$y = Ax + B \quad (2)$$

in which  $y$  is the absorbance,  $x$  is the micrograms of nitrogen in the 50-ml distillate volume,  $A$  is the absorbance per microgram of nitrogen in the 50-ml distillate volume, and  $B$  is the intercept in terms of absorbance in the 50-ml distillate volume.  $B$  should be essentially zero. Maintain a quality control chart for the values of  $A$  and  $B$  calculated from each calibration.

Verify the calibration for each apparatus setup once each week during periods when samples are analyzed with one calibration blend in duplicate. Recalibrate when a difference at the .05 significance level is obtained for  $A$ .

At the beginning of each 8-hr shift, verify that reagents are ammonia-free and that the Nessler's reagent and Nessler's stabilizer reagent are stable by analyzing two 6-ml aliquots of the ammonium chloride calibration solution starting at step 1 in the subsection Sample Anal-

ysis. Maintain a separate quality control chart for these calibration data in terms of absorbance per microgram of nitrogen. When an average calibration result disagrees at the .05 significance level with the average of previous results, prepare all new reagents including the Nessler's reagent and Nessler's stabilizer reagent. Verify that the two new Nessler's reagents are satisfactory by obtaining a linear relationship between absorbance and micrograms of nitrogen when duplicate pipetted aliquots of 2, 6, 10, and 15 ml of the ammonium chloride calibration solution are carried through steps 9, 10, and 11 of the Sample Analysis. Then reanalyze two 6-ml aliquots of the ammonium chloride calibration solution starting at step 1 in the Sample Analysis subsection. Should the average result again disagree at the .05 significance level with the average of previous results, again prepare new reagents and repeat the above until agreement is obtained or until the results of two consecutive verifications agree. In the latter case, recalibrate the entire method with an appropriate set of LASL-provided blends.

It also is recommended that the above scheme be followed whenever one or both of the Nessler's reagents are changed.

#### Sample Analysis

1. Transfer an accurately weighed, 1-g portion of the sample into a digestion flask, then add 5 ml of 14.7M  $H_3PO_4$  and 3 drops of 28M HF.  
Dissolution of the sample by the sealed-tube method is often preferred, especially for plutonium dioxide materials. For samples dissolved by the sealed tube method, transfer an aliquot of the dissolver solution containing 1 g of sample to a 50-ml, round-bottom flask and proceed to step 3.
2. Clamp the flask on the digestion apparatus, place the condenser on the flask, reflux the sample until it dissolves, and then wash the condenser with 15 to 25 ml of distilled water.
3. Transfer the flask to the distillation apparatus, assemble the apparatus making sure all connections are tight, turn on the heater, but do not stopper the steam generator.

Refer to Figure 1 for a description of the parts of the apparatus. The stopper is not inserted in the steam generator until the distillation is started.

4. Place a 50-ml volumetric flask containing 2 ml of 5% boric acid and about 5 ml of ammonia-free water under the condenser with the condenser tip extending below the surface of the liquid, and place 15 ml of 12.5M NaOH in the reservoir above the digestion flask. (If the sample is known to contain less than 50  $\mu\text{g/g}$  of nitrogen, use as a receiver a 25-ml volumetric flask containing 2 ml of 5% boric acid and 3 to 5 ml of ammonia-free water.)  
The tip is kept below the surface of the boric acid to prevent the loss of ammonia.
5. When the water in the steam generator boils, allow the 12.5M NaOH to flow slowly into the sample solution. If the sodium hydroxide is forced up the side arm to the steam generator, momentarily place the stopper on the steam generator, but remove the stopper when the sodium hydroxide has been forced from the side arm.  
The reaction between the sodium hydroxide and acid is vigorous and the apparatus should be watched closely during this step.
6. Immediately following addition of the sodium hydroxide from the reservoir, close the reservoir stopcock, place the stopper in the steam generator, and steam distill until 25 to 30 ml of distillate has collected in the 50-ml receiver flask. (If a 25-ml flask is used, collect 10 to 15 ml of distillate).  
Stoppering the steam generator forces steam through the sample solution and starts the steam distillation.
7. Remove the stopper from the steam generator, quickly remove the clamps from the joints connecting the reservoir assembly to the condenser and to the steam generator, and wash the condenser with 2 to 3 ml of water as it is being removed from the receiver flask.
8. Dilute the distillate in the 50-ml receiver flask to volume with ammonia-free water, shake well, and pipet a 5-ml aliquot of the solution into a 25-ml vol-

umetric flask containing 15 to 20 ml of ammonia-free distilled water and 2 ml of 5% boric acid.

Retain a full 45 ml of distillate in the receiver flask; do not discard any excess solution taken up with the 5-ml pipet.

9. Pipet 1 ml of Nessler's stabilizer reagent and mix and then pipet 1 ml of Nessler's reagent into the flask.

The order of addition of reagents is important to obtain full color development and stability.

10. Dilute the solution to volume with ammonia-free distilled water, shake, and allow to stand for 10 min.

11. Measure the absorbance at 410 nm in a 1-cm cell using as a reference a solution containing 2 ml of 5% boric acid and 1.00 ml each of Nessler's stabilizer reagent and Nessler's reagent in a 25-ml volume.

Prepare the reference solution at the same time the two color-forming reagents are added to the samples.

12. Calculate the nitrogen content ( $\mu\text{g N/g}$  sample) from the absorbance ( $Y_1$ ) as shown under Calculations. If the calculated nitrogen content is between 200 and 500  $\mu\text{g/g}$ , use the value obtained for the 5-ml aliquot. For lower nitrogen concentrations, proceed to the appropriate step listed below:

<u>Nitrogen, <math>\mu\text{g/g}</math></u>	<u>Step</u>
10 to 100	13
100 to 200	15

13. To the remaining 45 ml of distillate in the 50-ml flask, add the reagents and perform the operations as directed in step 9.

14. Measure the absorbance at 410 nm in a 1-cm cell using a reference solution containing 2 ml of 5% boric acid and 1 ml each of Nessler's stabilizer reagent and Nessler's reagent in a 50-ml volume.

The absorbance is designated as  $Y_2$  for the 45-ml aliquot (step 14) and  $Y_3$  for the 20-ml aliquot (step 15) under Calculations.

15. Transfer a 20-ml aliquot of the distillate, step 8, to a 50-ml flask, add the reagents, dilute the solution to volume, and mix as directed in step 9. Repeat step 14 to measure the absorbance ( $Y_3$ ).

#### Calculations

$$N = F_i(Y_i - B)/AW,$$

in which

$N$  = nitrogen in sample,  $\mu\text{g/g}$ ,

$Y_i$  = absorbance of sample solution at 410 nm,

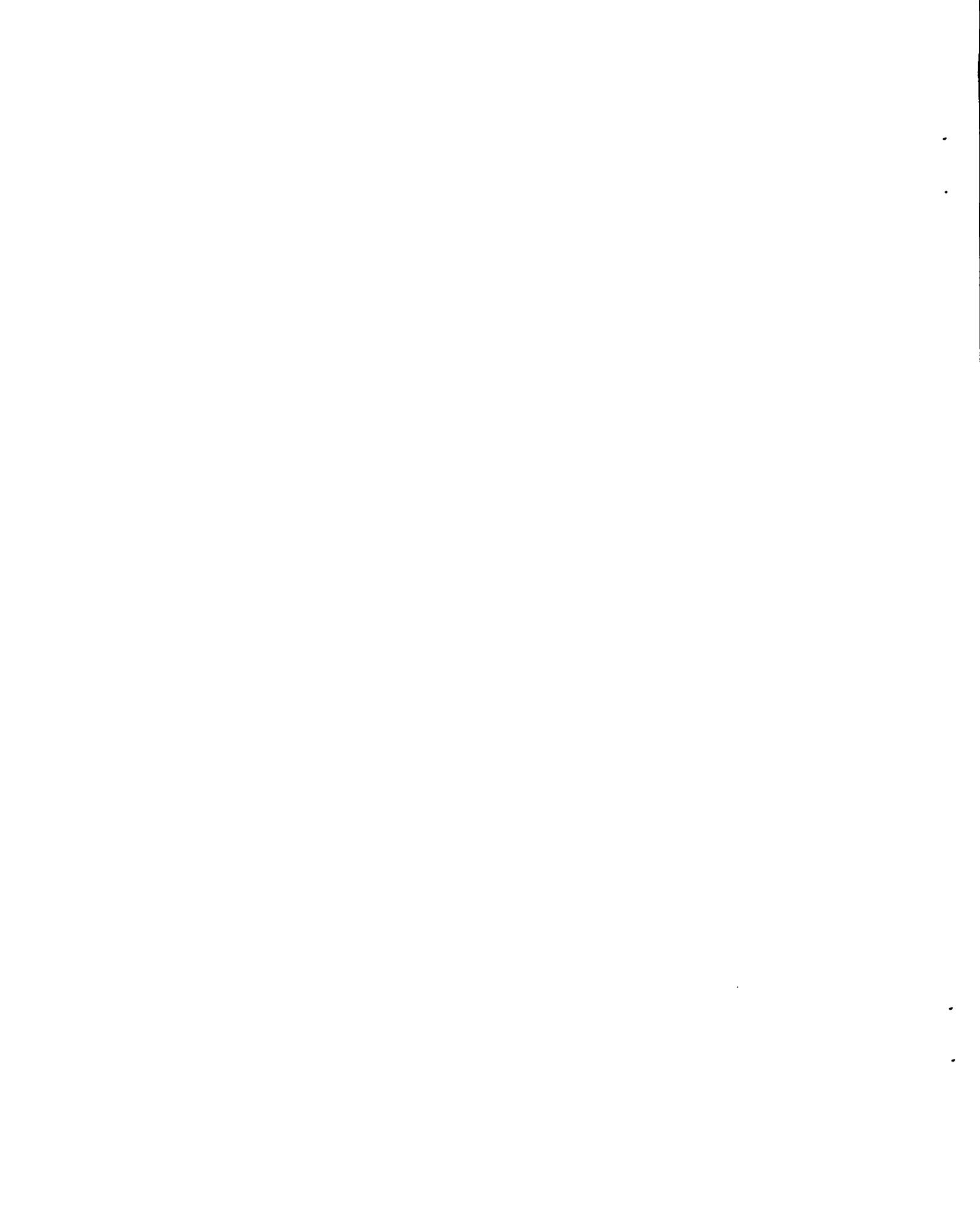
$A, B$  = constants determined from equation (2) in

Calibration subsection,

$W$  = weight of sample, g,

$F_i$  = dilution factor, with the following values:

<u>Absorbance Measured</u>	<u>Dilution Factor</u>
$Y_1$	$F_1 = (50/5)(25/50) = 5.00$
$Y_2$	$F_3 = (50/45) = 1.11$
$Y_3$	$F_4 = (50/20) = 2.50$



DETERMINATION OF PHOSPHORUS  
BY  
SPECTROPHOTOMETRY

SUMMARY

Phosphorus is measured spectrophotometrically as the blue reduced form of the heteropoly molybdo-phosphoric acid at a wavelength of 725 nm after separation from plutonium or uranium by extraction into n-butanol. The quantity of phosphorus is calculated from the measured absorbance and the absorbance per microgram of phosphorus obtained for calibration materials having known phosphorus contents. The relative standard deviation is 3% at phosphorus concentrations of 100  $\mu\text{g/g}$ , the average specification limit for the fuel materials in this program.

APPLICABILITY

This method is applicable to the determination of phosphorus at concentrations between 10 and 200  $\mu\text{g/g}$  in ceramic grade uranium oxide and plutonium oxide, uranium dioxide insulator pellets, and uranium-plutonium mixed oxide pellets. The calibration materials supplied by LASL are usable for this range. At the impurity specification limits for the materials in this program, only tantalum and tin interfere with this method. They do not interfere when present at one-tenth of their specification limits. The recommended quantity of phosphorus for measurement is between 0.5 and 10  $\mu\text{g}$ , and the specified sample size is optimum for this range. A single determination, exclusive of dissolution, requires about 0.5 hr, and six determinations can be done in about 1.5 hr.

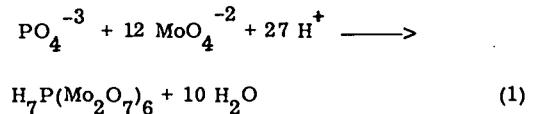
RELIABILITY

The standard deviation is about 1  $\mu\text{g/g}$  at a phosphorus concentration of 10  $\mu\text{g/g}$ , 1.6  $\mu\text{g/g}$  at a concentration of 40  $\mu\text{g/g}$ , and 3  $\mu\text{g/g}$  in the concentration range above 100  $\mu\text{g/g}$ . The recommended calibration materials are reagent grade monobasic potassium phosphate and

the blends supplied by LASL. When these materials are properly used there is no bias in the method.

DISCUSSION OF THE METHOD

A yellow heteropoly acid of phosphate and molybdate ions is formed in acid solution when a large excess of molybdate ion displaces equation (1) to the right. [1]



The acid is extracted into n-butanol which separates the phosphorus from most interfering ions, and from excess molybdate which would interfere in the reduction step. The yellow acid is then reduced to the blue form by washing the n-butanol with stannous chloride. The absorbance of the blue form, which has a molar absorptivity of 22,700, [2] is measured at 725 nm in the n-butanol solution.

Interfering elements include arsenic, cerium, germanium, gold, tantalum, and tin. Of these, tantalum and tin are the only two that have specification limits for the fuel materials in this program, but will not interfere if present at no more than one-tenth their specification limits. This is the expected situation. Silicon as silica can be a major interference as it also forms a blue heteropoly complex. It is eliminated by fuming the samples with a small amount of hydrofluoric acid. The remaining interfering elements are not ordinarily present in the fuel materials, with the possible exception of cerium, which may occur in recycled material and cause low results in the phosphorus measurement.

Uranium oxide, uranium-plutonium mixed oxide, and plutonium dioxide dissolve slowly in 15.6M  $\text{HNO}_3$  at its boiling point. Hydrofluoric acid at low concentrations in the nitric acid accelerates the dissolution, especially of samples containing plutonium dioxide or those contaminated with silica. The sealed-tube method [3] is

[1] C. Wadelin and M. G. Mellon, Anal. Chem. 25, 1668 (1953).

[2] C. H. Lueck and D. F. Boltz, Anal. Chem. 28, 1168 (1956).

[3] See p. 5.

recommended for high-fired plutonium dioxide. Either nitrate or chloride solutions are acceptable. Fuming the sample with sulfuric acid gives low, erratic results and is not recommended. Perchloric acid, however, may be safely used for fuming to eliminate volatile anions and impurities.

Phosphorus is a ubiquitous element; as a result, the equipment must be kept very clean to ensure good results. It is particularly important to wash rubber gloves to remove the phosphorus-containing talc powder.

In addition to speed, simplicity, and relative freedom from interferences, this method has the added advantages of requiring only small amounts of sample, about 50 mg for phosphorus concentrations between 10 and 200  $\mu\text{g/g}$ . The only equipment required is that usually found in a laboratory equipped to analyze plutonium materials spectrophotometrically.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Special care must be taken when handling concentrated acids. As a minimum precaution, rubber gloves should be worn. When preparing dilute sulfuric acid solutions, always add the acid carefully to the water and not the reverse. Hydrofluoric acid is especially dangerous to the skin and will cause slow-healing ulcerating sores. Consult your laboratory safety manual for further information.

### APPARATUS

Crucibles, platinum, 8-ml.

Spectrophotometer, Beckman, Model DU, or equivalent, with matched 1-cm cells.

### REAGENTS

Ammonium molybdate, 4% in 0.6M  $\text{H}_2\text{SO}_4$ . Prepare fresh daily to minimize contamination.

n-Butanol.

Ethanol, 100%.

Hydrochloric acid, 12M (37%).

Hydrofluoric acid, 28M (48%).

Nitric acid, 15.6M (70%).

Perchloric acid, 12M (70%), 1M. Use quartz-distilled acid and water, or equivalent purity.

Phosphorus reference solution, 1  $\mu\text{g P/ml}$ . Dissolve 274.6 mg of monobasic potassium phosphate in 500 ml of 1M  $\text{HClO}_4$ . Dilute a 4-ml aliquot to 500 ml with 1M  $\text{HClO}_4$ .

Stannous chloride, 1%. Dissolve 1 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 3 ml of 12M  $\text{HCl}$  and dilute to 100 ml with 0.6M  $\text{H}_2\text{SO}_4$ . Prepare fresh daily.

Sulfuric acid, 18M (96%), 0.6M. Use quartz-distilled acid and water, or equivalent purity.

## PROCEDURE

### Special Precaution

Cleanliness in this determination is extremely important to ensure good results. As a minimum effort, rinse all glassware with 18M  $\text{H}_2\text{SO}_4$  followed by large amounts of distilled water. Clean platinum dishes with fine sand and rinse with water. Be especially careful to remove powder from protective gloves by washing them with a non-phosphorus-containing soap and water.

### Blank

Determine the reagent blank in duplicate by starting at step 2 in the subsection Sample Analysis, omitting the sample, and going through step 15. If the measured absorbance is greater than 0.015, replace each reagent individually to determine the source of contamination.

### Calibration

Two sets of calibration blends are supplied by LASL. One set nominally contains 10, 20, 50, 100, and 200  $\mu\text{g/g}$  of phosphorus as uranium phosphide in uranium oxide. The other set contains like amounts of uranium phosphide in uranium-plutonium mixed oxide.

For the initial calibration of each analysis apparatus, process two accurately weighed 50-mg portions of each of the five calibration blends in the appropriate set as described under Sample Analysis. Use least-squares formulas to obtain the linear calibration equation

$$y = Ax + B \quad (2)$$

that best fits the calibration data. In this equation  $y$  is the absorbance,  $x$  is the micrograms of phosphorus,  $A$  is the slope, and  $B$  is the intercept on the  $y$ -axis;  $B$  should be approximately zero. Prepare a quality control chart for the values of  $A$  and  $B$  obtained for each analysis apparatus.

Once each week during periods when samples are analyzed, verify the calibration by processing duplicate 50-mg portions of one of the calibration blends. Dissolve each portion in a 8-ml platinum crucible and measure the phosphorus as described in Sample Analysis. Calculate the value of  $A' = y/x$ , and plot it on the quality control chart for  $A$ . If an individual value of  $A'$  disagrees at the .05 significance level with the value of  $A$  determined from the complete calibration set, investigate the cause for the difference and rectify the difficulty before proceeding with further analyses.

For initial tests of the method and prior to each calibration, use the 1  $\mu\text{g}$  P/ml reference solution prepared from monobasic potassium phosphate. It also is recommended that two 1.00- to 5.00-ml aliquots of this solution be processed each 8-hr shift starting with step 6 in Sample Analysis. These data may be incorporated into the quality control chart of phosphorus calibration data in terms of  $A''$ , the absorbance per microgram of phosphorus in the reference solution. If the daily value disagrees significantly at the .05 significance level with the average of previous results on the quality control chart, investigate the cause for the difference and rectify the difficulty before proceeding with further analyses.

#### Sample Analysis

1. Transfer an accurately weighed, 50-mg portion of uranium oxide, plutonium oxide, or uranium-plutonium mixed oxide sample into a 8-ml platinum crucible.

A 50-mg sample is appropriate for concentrations of 10 to 200  $\mu\text{g/g}$  of phosphorus.

The sealed-tube technique, p. 5, which gives faster dissolution rates, is recommended for plutonium-containing samples. If used, add 0.2 ml of 12M  $\text{HClO}_4$  to the dissolved sample and proceed to step 5.

2. Cover the sample with approximately 3 ml of 15.6M  $\text{HNO}_3$ , add a drop of 28M HF, and 0.2 ml of 12M  $\text{HClO}_4$ , and heat under infrared lamps to fumes of perchloric acid.  
This dissolves the sample.  
Perchloric acid is recommended rather than sulfuric acid. Fuming with sulfuric acid causes low and erratic results.
3. Add 1 ml of water and decant the dissolved portion into a 8-ml platinum crucible.
4. Repeat steps 2 and 3 until the sample completely dissolves.
5. Add 10 drops of 28M HF and fume the solution to near dryness.

Hydrofluoric acid volatilizes interfering silica.

6. Dissolve the residue in 1 ml of 0.6M  $\text{H}_2\text{SO}_4$  and quantitatively transfer the solution to a separatory funnel with 7 ml of 0.6M  $\text{H}_2\text{SO}_4$ .
7. Add 2 ml of 4% ammonium molybdate and mix the solution for 10 min.  
This allows time for the formation of the heteropoly acid of phosphate and molybdate ions.
8. Add 5 ml of  $n$ -butanol, mix for 2 min, allow the phases to separate, and discard the aqueous (lower) phase.  
The yellow heteropoly acid extracts into the  $n$ -butanol phase.
9. Add 5 ml of 0.6M  $\text{H}_2\text{SO}_4$ , mix the phases for 1 min, allow them to separate, and discard the aqueous (lower) phase.  
Excess ammonium molybdate in the  $n$ -butanol strips into the aqueous phase.

10. Repeat step 9.
11. Add 2 ml of 1% stannous chloride solution, mix the phases for 1 min, allow them to separate, and discard the aqueous (lower) phase.

The yellow heteropoly acid reduces to the intense blue form.

12. Transfer the organic phase to a 5-ml volumetric flask, rinse the sides of the extractor with ethanol, transfer the rinses to the volumetric flask, and dilute to volume with ethanol.

The butanol volume is approximately 4 ml at this time, because of its solubility in water. The ethanol, which is highly miscible with both n-butanol and water, ensures a quantitative transfer.

13. Measure the absorbance at 725 nm in 1-cm cells using ethanol as a reference solution.

#### CALCULATIONS

##### Sample Results

$$P = (S-B)/AW ,$$

in which P = phosphorus in sample,  $\mu\text{g/g}$  ,

S = absorbance of sample solution  
at 725 nm ,

A, B = constants determined from  
equation (2) in Calibration ,

W = weight of sample in grams.

## DETERMINATION OF SULFUR

### BY SPECTROPHOTOMETRY

#### SUMMARY

Sulfur is measured spectrophotometrically as Lauth's Violet following its separation by distillation as hydrogen sulfide. Higher oxidation states of sulfur are reduced to sulfide by a hypophosphorous-hydriodic acid mixture, the hydrogen sulfide is distilled into zinc acetate, and p-phenylenediamine and ferric chloride are added to form Lauth's Violet. The quantity of sulfur is calculated from the measured absorbance at 595 nm and the absorbance per microgram of sulfur obtained for calibration materials having known sulfur contents. The relative standard deviation ranges from 12 to 3% for the concentration range from 10 to 600  $\mu\text{g}$  of sulfur per gram of sample.

#### APPLICABILITY

The method is applicable to the determination of sulfur in the concentration range of 10 to 600  $\mu\text{g/g}$  for samples of ceramic grade uranium dioxide, ceramic grade plutonium dioxide, uranium-plutonium mixed oxide pellets, and uranium dioxide insulator pellets. The recommended absolute range of sulfur for measurement is 5 to 60  $\mu\text{g}$ . Two sample sizes are therefore specified; 0.5 g for the concentration range of 10 to 100  $\mu\text{g/g}$  and 0.1 g for concentrations greater than 100  $\mu\text{g/g}$ .

None of the specified impurity elements interfere with the method when present in amounts up to twice their specification limits for the above materials.

#### RELIABILITY

The standard deviation for 0.1-g samples ranges from 0.3  $\mu\text{g}$  sulfur at the 5- $\mu\text{g}$  level to 1.8  $\mu\text{g}$  at the 60- $\mu\text{g}$  level. For 0.5-g samples, the standard deviation ranges from 0.6  $\mu\text{g}$  sulfur at the 5- $\mu\text{g}$  level to 2.8  $\mu\text{g}$  at the 60- $\mu\text{g}$  level. The corresponding relative standard deviations in 0.1-g samples are 6 to 3% for the range of 50 to 600  $\mu\text{g/g}$  and in 0.5-g samples are 12 to 5% for

the range of 10 to 120  $\mu\text{g/g}$ .

Bias, especially between laboratories, is minimized by the use of calibration materials. The recommended calibration materials are potassium sulfate and the two sets of LASL-prepared calibration blends. One set has a uranium oxide matrix to be used for the analysis of ceramic grade uranium dioxide and uranium dioxide insulator pellets, the other set has a uranium-plutonium mixed oxide matrix to be used for the analysis of ceramic grade plutonium dioxide and uranium-plutonium mixed oxide pellets.

#### DISCUSSION OF THE METHOD

The major steps in the method are reduction of nitrate with formic acid, reduction of plutonium to the (III) oxidation state with hydroxylamine hydrochloride, reduction of sulfur to hydrogen sulfide with a hydriodic acid-hypophosphorous acid mixture, distillation of the hydrogen sulfide into a zinc acetate solution, formation of Lauth's Violet by adding p-phenylenediamine and iron (III) chloride, and spectrophotometric measurement at 595 nm.

A strongly colored heterocyclic compound is formed by the reaction of p-phenylenediamine with sulfide followed by oxidation with ferric chloride. The colored compound known as Lauth's Violet is a three-ring compound having S and N bridge atoms. The reaction comes to equilibrium in about 0.5 hr with some fading of color after approximately 1.5 hr. Beer's law is closely followed by the complex at equilibrium.

A mixture of hydriodic-hypophosphorous acid is an adequate reducing agent for higher oxidation states of sulfur. Prereduction of plutonium in plutonium-containing materials with hydroxylamine and of nitrate with formic acid reserves the reducing power of the acid mixture for reduction of the oxidized sulfur. The hydrogen sulfide produced by the reduction is distilled into neutral zinc acetate, the mixture is acidified, and p-phenylenediamine and ferric chloride are added. Addition of the reagents in this order and thorough mixing after each addition are necessary to attain complete color develop-

ment. [1]

Uranium oxide, uranium-plutonium mixed oxide, and plutonium dioxide dissolve slowly in 15.6M  $\text{HNO}_3$  at its boiling point. Hydrofluoric acid at low concentration in the nitric acid accelerates the dissolution, especially of the plutonium-containing oxides or samples contaminated with silica. Repeated intense fuming to dryness during dissolution should be avoided to prevent volatilization or mechanical carryover of sulfate. Heating to incipient dryness will not cause loss of sulfur. Do not introduce perchloric acid at any time during dissolution because perchlorate residues may react explosively with formic acid in subsequent operations. The sealed-tube dissolution technique, described on p. 5, is preferred for this method because it prevents possible loss of sulfur and because faster dissolution rates are achieved.

Nitrate or chloride solutions obtained by the dissolution techniques discussed above are the preferred forms of samples. Chloride solutions obtained by the sealed-tube technique can be used directly for analysis. Solutions containing nitrate and easily reduced cations that interfere with the reduction of higher oxidation states of sulfur to sulfide require additional treatments. Nitrate is destroyed in this method with formic acid. Plutonium(IV) and other interfering cations are reduced with hydroxylamine to eliminate the need for excessive amounts of the reducing acid mixture. Uranium is reduced slowly by the acid mixture without interfering with the reduction of higher oxidation states of sulfur. Because U(III) precipitates with phosphate in the reduced solution, calibration materials containing uranium are required to test for the occlusion of sulfide by the precipitate.

In addition to simplicity and freedom from interferences, this method had the added advantage of requiring small amounts of sample, about 0.1 g for sulfur concentrations between 100 and 600  $\mu\text{g/g}$ . The distilla-

tion apparatus is the only equipment required besides that normally found in a laboratory equipped to analyze plutonium materials spectrophotometrically. Materials for construction of the sulfur distillation apparatus should cost less than \$100. Two distillation apparatuses can be operated simultaneously by one analyst.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Special care must be taken when handling the concentrated acids used in this method. As a minimum precaution, rubber gloves should be worn. Face shields are mandatory when using the pressurized apparatus to prepare the sulfur-free reducing acid mixture. Hydrofluoric acid is especially dangerous to the skin and will cause slow-healing ulcerating sores. Consult your laboratory safety manual for further information.

### APPARATUS

Pressurized reducing acid boiler (see Figure 1).

Spectrophotometer, Beckman, Model DU, or equivalent, with matched 1-cm cells.

Sulfur distillation apparatus (see Figure 2).

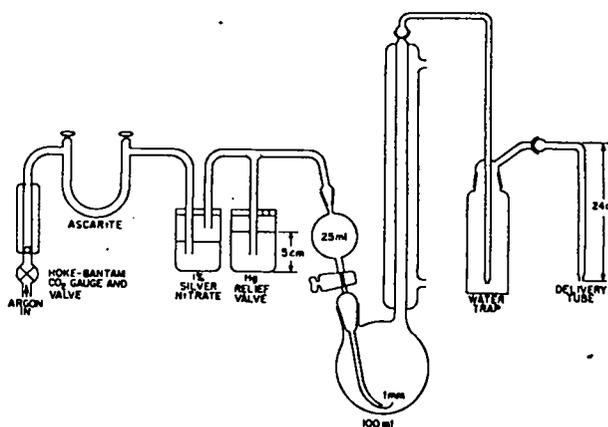


Figure 1. Pressurized reducing acid boiler.

[1] E. Booth and T. W. Evett, AERE Report AERE-AM-5 (1958).

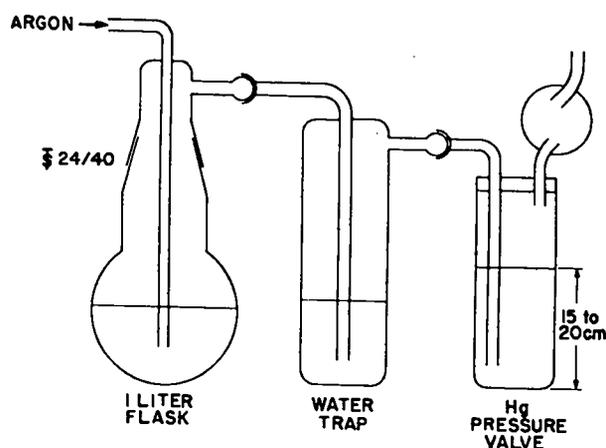


Figure 2. Sulfur distillation apparatus.

#### REAGENTS

Argon gas, cylinder

Ferric chloride, 2% in 6M HCl.

Formic acid, reagent grade, redistilled.

Hydriodic-hypophosphorous acid reducing mixture. Mix 400 ml of 7.6M (57%) HI with 200 ml of 31% hypophosphorous acid and boil the solution for 30 min in the pressurized apparatus. Test for sulfur content by analyzing a 15-ml aliquot as described in steps 10 through 18 of the subsection Sample Analysis, omitting step 12. Compare the results to a reagent blank containing zinc acetate, hydrochloric acid, p-phenylenediamine, and ferric chloride. Reboil in the pressurized apparatus if necessary to reduce the sulfur content to below 1 µg/15 ml.

Hydrochloric acid, 12M (37%), 6M, 3M, 0.6M. Check the 12M HCl for sulfur content by following steps 10 through 18, omitting step 12, of the Sample Analysis subsection. Use only a reagent in which the sulfur content is less than 1 µg/10 ml and prepare the diluted acids with this reagent and distilled water.

Hydrofluoric acid, 28M (48%).

Hydroxylamine hydrochloride, 20% aqueous solution.

Nitric acid, 15.6M (70%).

p-Phenylenediamine, 1%. Dissolve 1 g of p-phenylenediamine in 100 ml of 0.6M HCl.

Silver nitrate, 1% aqueous solution.

Sulfur calibration solution, 5 µg S/ml. Dissolve 2.7167 g of dry potassium sulfate in water and dilute to 1 l. Dilute 2.00 ml to 200 ml with water.

Zinc acetate, 4% aqueous solution. Dissolve 20 g of zinc acetate in 500 ml of water and filter.

#### PROCEDURE

##### Blank

Determine the blank in duplicate starting with step 3 under Sample Analysis. If the measured absorbance (step 18) is significantly greater than that measured in testing the hydriodio-hypophosphorous acid mixture (see REAGENTS) at the .05 significance level, replace each reagent individually to determine the source of contamination. Discard the contaminated reagent.

##### Calibration

Two sets of LASL-prepared calibration blends are provided. One set consists of five blends in a uranium oxide matrix covering the nominal range of 20 to 600 µg S/g to be used for samples of ceramic grade uranium dioxide and uranium dioxide insulator pellets. The other set consists of five blends in a uranium-plutonium mixed oxide matrix covering the same nominal range to be used for samples of ceramic grade plutonium dioxide and uranium-plutonium mixed oxide pellets. For the initial calibration of each analysis apparatus, process duplicates of each calibration blend in the appropriate set as described under Sample Analysis.

Process the results using least-squares formulas to obtain the values of A and B in the linear equation

$$y = Ax + B$$

that best fits the data. In this equation, y is the absorbance, x is the micrograms of sulfur, A is the slope, and B is the intercept with the y axis. B should be approximately zero. Prepare a quality control chart for the values of A and B obtained for each analysis apparatus.

Once each week during periods that samples are analyzed, verify the calibration by processing duplicates of an appropriate calibration blend. Calculate  $A' = y/x$  and plot it on the quality control chart for A. If an individual value of A' disagrees at the .05 significance level with the value of A from the complete calibration set, investigate the cause and rectify the difficulty before proceeding with the analysis of samples.

Use aliquots of the 5  $\mu\text{g S/ml}$  calibration solution during initial testing of the method and to check each analysis apparatus prior to a calibration with the LASL-prepared blends. It also is recommended that two aliquots, in the volume range of 1.00 to 10.0 ml, of the 5  $\mu\text{g S/ml}$  calibration solution be processed each 8-hr shift. The obtained results may be incorporated into the quality control chart in terms of  $A'' = y/x$ . If either daily result for A'' disagrees at the .05 significance level with the running average of A'', investigate the cause for and rectify the difficulty before proceeding with the analysis of samples.

#### Sample Analysis

1. Pulverize uranium-plutonium mixed oxide pellets and uranium dioxide insulator pellets.

The recommended apparatus is a mixer-mill with a tungsten carbide container and a tungsten carbide ball.

2. Transfer a sample, weighed to  $\pm 0.2$  mg, to a 20-ml beaker or a 30-ml platinum dish.

Use a 0.5-g sample when the expected level of sulfur is 100  $\mu\text{g/g}$  or less. Use a 0.1-g sample for expected levels above 100  $\mu\text{g/g}$ .

The sealed-tube technique, described on p. 5, is the preferred method of dissolution. If used, proceed to step 9.

A 30-ml platinum dish is recommended for ceramic grade plutonium dioxide samples which usually require long dissolution times.

3. Add 5 ml of 15.6M  $\text{HNO}_3$  and 3 to 4 drops of 28M HF and heat the solution below its boiling point.

Avoid spattering and consequent loss of sample. Watch glasses or platinum lids also are recommended.

4. If necessary, add additional amounts of 15.6M  $\text{HNO}_3$  and 28M HF and continue heating until the sample completely dissolves.

5. Evaporate the solution just to dryness.

Do not fume intensely to dryness because the sulfur may volatilize.

6. Dropwise add 0.5 ml of formic acid, heat the solution at moderate heat until the vigorous reaction subsides and gases are no longer evolved.

The reduction of nitric acid by formic acid is vigorous. To prevent loss of sample, cover the beaker or dish with a watch glass between each addition of formic acid.

7. Remove the watch glass, rinse it with water and collect the rinses in the beaker or dish, add 0.5 ml of formic acid, and slowly evaporate just to dryness.

Nitrate must be completely removed because it reacts explosively with the reducing acid, step 13.

Do not bake the residue because the sulfur may volatilize.

8. Dissolve the residue in a minimum volume of 3M HCl and dilute to a volume of approximately 5 ml with water.

9. Heat the solution to just below the boiling point and add 20% hydroxylamine hydrochloride until the reduction of plutonium to the blue (III) oxidation state is complete.

Omit this step for samples that do not contain plutonium. Usually 20 drops of hydroxylamine will completely reduce the plutonium.

10. Add 30 ml of water to the trap of the distillation apparatus (see Figure 2) and insert the trap tube.

Boil 15 ml of reducing acid in the distillation flask for at least 15 min at the beginning of each 8-hr shift to remove any sulfur residue.

11. Pipet 10.0 ml of 4% zinc acetate solution into a 50-ml, glass-stoppered, graduated cylinder, dilute to 35 ml with water, and position the cylinder so that the end of the delivery tube of the distillation apparatus is immersed in the solution.
12. Quantitatively transfer the sample solution (step 8 or 9) with minimum water rinses to the distillation flask

and insert the reducing acid delivery tube.

See Figure 2.

13. Add 15 ml of the reducing acid mixture and 10 ml of 12M HCl to the delivery bulb, insert the argon sweep gas tube, and start the flow of the reducing acid mixture to the distillation flask.

See Figure 2.

Adjust the flow rate of argon to 100 cm<sup>3</sup>/min.

14. Turn on the heating mantle and boil the solution for 35 min.
15. Disconnect the distillate delivery tube, rinse it with 2.00 ml of 3M HCl followed by ~ 2 ml of water, collecting these rinses in the zinc acetate solution.

Any zinc sulfide formed inside the tube is rinsed into the zinc acetate solution.

16. Pipet 1.00 ml of 1% p-phenylenediamine into the solution, mix rapidly by swirling the cylinder, pipet 1.00 ml of 2% ferric chloride, and again mix rapidly by swirling the cylinder.

Rapid mixing after each reagent addition prevents formation of a brown reduction product that interferes with the spectrophotometric measurement.

17. Dilute to 50 ml with water, stopper the cylinder, mix the solution, and let stand exactly 1 hr.
18. Measure the absorbance within 10 min at a wavelength of 595 nm with water as the reference.

#### Calculations

$$S = \frac{y - B}{AW},$$

in which

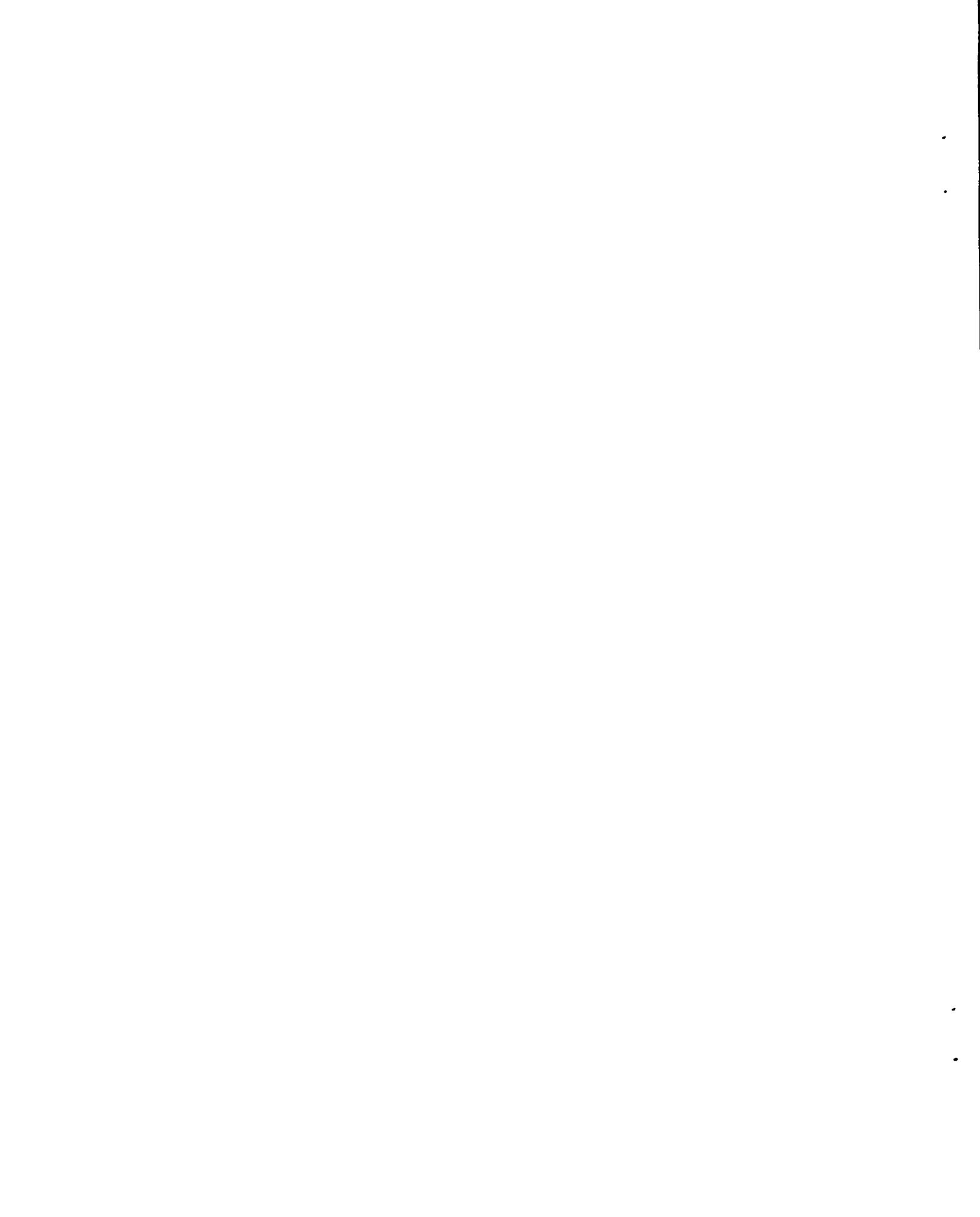
S = micrograms of sulfur per gram of sample,

y = sample absorbance corrected for the reagent blank absorbance,

A, B = constants from appropriate calibration equation

(see subsection Calibration),

W = weight of sample in grams.



DETERMINATION OF TUNGSTEN BY SPECTROPHOTOMETRY AFTER EXTRACTION INTO 3, 4-DIMERCAPTOTOLUENE

SUMMARY

Tungsten is reduced to W(V) by Ti(III) in hot 9M HCl and is extracted into a 1% solution of dithiol (3,4-dimercaptotoluene) in pentyl acetate. The concentration of tungsten is calculated from the absorbance of the tungsten-dithiol complex at 640 nm. Molybdenum interferes strongly and when present must be separated by a preliminary extraction into 0.5% dithiol-pentyl acetate before reduction of the tungsten. At the specification limit for tungsten of 100  $\mu\text{g/g}$  of sample, the relative standard deviation is 1%, and is 7% at a level of 2.5  $\mu\text{g/g}$ . Chemical calibration eliminates bias.

APPLICABILITY

This method is applicable to the determination of tungsten in uranium-plutonium mixed oxide pellets, uranium dioxide insulator pellets, ceramic grade uranium dioxide, and ceramic grade plutonium dioxide. Molybdenum, which may be present in the fuel materials, seriously interferes with the tungsten determination and must be separated by a preliminary extraction. [1] Metals which extract and also form colored complexes with dithiol include lead, palladium, platinum, and technetium. Interfering concentrations are 100  $\mu\text{g/g}$  of sample for platinum and technetium and 1000  $\mu\text{g/g}$  for lead and palladium. [1] The nominal concentrations of these four impurity elements in the four fuel materials are insignificant and special treatments are not required to separate them. The range of the method is from 5 to 150  $\mu\text{g/g}$  when 1 g of sample is taken for analysis. One sample may be analyzed in 3 hr and 12 samples in 8 hr.

RELIABILITY

Variations in tungsten content between individual mixed oxide and individual uranium dioxide pellets can be

[1] G. B. Nelson and G. R. Waterbury, USAEC Report TID-7629 (1962), p. 62.

significant because tungsten is introduced as an impurity from equipment in the pellet production process. For this reason, the only pertinent reliability data available are for within-pellet measurements. [2] The relative standard deviation for mixed oxide pellets containing 50 to 60  $\mu\text{g/g}$  of tungsten was 1.3%, and at the 5  $\mu\text{g/g}$  level was 15%.

The precision of the analytical procedure, applied to plutonium solutions containing known amounts of tungsten, was 7% relative standard deviation for 2.5  $\mu\text{g}$  of tungsten and 1% relative standard deviation for 60  $\mu\text{g}$  of tungsten in 1 g of mixed oxide. Bias in the method is eliminated by calibration with sets of LASL-provided blends and weekly verification of the calibration.

DISCUSSION OF THE METHOD

This method is based on the formation of a blue-green complex between W(V) and dithiol, after reduction of W(VI) with Ti(III) chloride. This complex is simultaneously formed and extracted into dithiol-pentyl acetate reagent from 8.4M HCl. Prior to complex formation and extraction, the sample is fumed with sulfuric acid to remove nitrate introduced during dissolution of the sample that would oxidize the dithiol if allowed to remain. Molybdenum, which also forms a green complex with dithiol, is removed by a preliminary extraction prior to the reduction of the tungsten. The absorbance of the tungsten-dithiol complex in the pentyl acetate is measured to determine the weight of tungsten.

The determination of trace amounts of tungsten can be accomplished with several colorimetric reagents. The thiocyanate, hydroquinone, and dithiol spectrophotometric methods are widely used. [3] The dithiol reagent provides the required sensitivity, selectivity, and simplicity. Greenberg's method [4] for the determination of tungsten

[2] J. E. Rein, R. K. Zeigler, and C. F. Metz, USAEC Report LA-4407 (1970).

[3] E. B. Sandell, Colorimetric Determination of Traces of Metals, 3rd ed., Interscience, New York, (1959), pp. 195, 640-664, 883-899.

[4] P. Greenberg, Anal. Chem. 29, 896 (1957).

and molybdenum in tantalum, titanium, and zirconium appeared to be highly reliable and was adopted for evaluation for application to uranium-plutonium samples.

To determine the effect of large amounts of plutonium on the color complex, known amounts of tungsten ranging from 11 to 120  $\mu\text{g}$  were added to 5M HCl solutions that contained 1 g of plutonium. The tungsten concentration then was determined by the procedure presented in this method. No bias in recovery was measurable and the relative standard deviations of 3% at the 11  $\mu\text{g}/\text{g}$  level and 1.4% at the 120  $\mu\text{g}/\text{g}$  level were no greater than those measured in the absence of plutonium. Similarly, uranium did not affect the results.

Metals that carry through the entire procedure and interfere are platinum and technetium which cause a bias of 5% or greater when present in amounts of 100  $\mu\text{g}/\text{g}$ . Lead and palladium interfere at levels of 100  $\mu\text{g}$ , and aluminum, arsenic, chromium, cobalt, copper, hafnium, iridium, mercury, niobium, rhenium, thallium, and vanadium interfere at the 4000  $\mu\text{g}/\text{g}$  level. These impurities are not normally encountered at these high levels in the fuel materials for which this method is intended.

Tungsten(V) reacts with dithiol in 8 to 11M HCl to form a blue-green complex which is soluble in organic solvents. The reactions involved when tungsten is extracted from warm, strong hydrochloric acid are obscure, as there is some evidence that disproportionation of the W(V) may occur. <sup>[3]</sup> Molybdenum(VI) also forms a green complex extractable by organic solvents. In materials containing both molybdenum and tungsten, their separation is achieved by extracting the molybdenum-dithiol complex from 6M HCl prior to the reduction of tungsten to W(V). <sup>[1]</sup> Under these conditions, the tungsten is not extracted. In Greenberg's procedure, titanium metal sponge is added to the hydrochloric acid solution to reduce the tungsten. The use of a Ti(III) solution in 12M HCl offers the advantage of adding in one step the reductant and acid required for the extraction. The formation of the color complex is complete in 20 min at 90°C. This agrees with Greenberg's findings, although the conditions are different. The molar absorptivity for the

tungsten-dithiol complex in pentyl acetate is 23,200 at 640 nm.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Special care must be taken when handling the concentrated acids used in this method. As a minimum precaution, rubber gloves should be worn. Hydrofluoric acid is especially dangerous to the skin and will cause slow-healing ulcerating sores. Consult your laboratory safety manual for further information.

### APPARATUS

Beakers, polyethylene, 25-ml.

Extraction vessel. Seal a Teflon stopcock to the bottom of a 25- x 150-mm test tube.

Heater-stirrer. Cole-Parmer Micro V Model 4805, or equivalent heater-stirrer, with an aluminum block drilled with holes for 200-ml tall-form beakers.

Platinum dish, 30-ml.

Spectrophotometer. Beckman Model DU, or equivalent, with matched 1.00-cm cells.

Stirrer, electric, with glass-propeller stirring rod.

### REAGENTS

Dithiol (3, 4-dimercaptotoluene). Eastern Chemical Corp. #042001, or equivalent. (Dithiol is supplied in sealed glass ampoules. It is a yellow crystalline material when pure. Ampoules containing any yellow liquid should be discarded).

Dithiol-pentyl acetate reagent. 1% dithiol in pentyl acetate. Break an ampoule containing 1 g of dithiol under 100 ml of pentyl acetate and stir until dissolved. Store at -5 to 0°C. Prepare a fresh batch each day it is to be used. Some ampoules of dithiol may contain decomposed reagent which will produce biased results. Therefore test each freshly made solution by placing duplicate 1-ml aliquots of the tungsten reference solution in two 200-ml tall form beakers, adding 17 ml of 6M HCl to each, and

starting at step 15 under Sample Analysis.

Hydrochloric acid, 12M (37%), 8.4M, 6M.

Hydrofluoric acid, 28M (48%), 5.6M, 0.56M.

Nitric acid. 15.6M (70%).

Pentyl acetate. Redistill the pentyl acetate if it turns yellow when dithiol is dissolved in it.

Potassium pyrosulfate (potassium bisulfate, fused powder).

Sodium tungstate dihydrate.

Sulfuric acid, 18M (96%), 1M.

Titanium (III) chloride solution. Place 450 ml of 12M HCl into a 500-ml volumetric flask. Pipet 10 ml of titanium tetrachloride ( $TiCl_4$ ) below the surface of the 12M HCl and mix. Add 12 g of stannous chloride dihydrate ( $SnCl_2 \cdot 2H_2O$ ) and mix until it dissolves. Dilute to volume with 12M HCl and mix. Do these operations in a well-ventilated hood. Prepare a fresh batch when the blue solution starts to turn brown.

Tungsten reference solution, 100  $\mu$ g/ml. Dissolve 100 mg of tungsten metal in a minimum quantity of 28M HF containing a few drops of 15.6M  $HNO_3$ . Transfer to a 100-ml polypropylene volumetric flask and dilute to the mark with 0.56M HF.

## PROCEDURE

### Blank

Beginning at step 2 in the Sample Analysis subsection, process duplicate blanks on each analysis setup at the beginning of any 8-hr working shift during which samples are analyzed.

### Calibration

Two sets of calibration blends are provided. One set consists of five levels of  $WO_3$  in a mixed oxide matrix for use with analysis setups for the tungsten determination in ceramic grade plutonium dioxide and in mixed oxide pellets. The second set consists of five levels of  $WO_3$  in a uranium oxide matrix for use with apparatus setups for the analysis of ceramic grade uranium dioxide and in-

solator uranium dioxide pellets.

The initial calibration of each apparatus setup is carried out in duplicate with these calibration materials starting at step 1 in the Sample Analysis subsection. Use least-squares formulas to obtain the linear calibration equation

$$y = Ax + B \quad (1)$$

that best fits the calibration data. In this equation y is the absorbance, x is the micrograms of tungsten, A is the slope, and B is the intercept on the y axis; B should be approximately 0. Prepare a quality control chart for the values of A and B obtained for each analysis apparatus.

Once each week during periods that samples are analyzed, verify the calibration by processing duplicates of an appropriate calibration blend. Calculate the value  $A' = y/x$  and plot it on the quality control chart for A. If an individual value of A' disagrees at the .05 significance level with the value of A determined from the complete calibration set, investigate the cause and correct the difficulty before proceeding with the analysis of samples. Unless some other cause is apparent, deterioration of the dithiol-pentyl acetate reagent is a likely reason.

### Sample Analysis

1. Place a weighed, whole, mixed oxide pellet or uranium dioxide pellet or a weighed 1-g quantity of ceramic grade uranium dioxide or plutonium dioxide in a mixture of 5 to 10 ml of 15.6M  $HNO_3$ , 0.5 to 1 ml of 28M HF, and 1 ml of 18M  $H_2SO_4$  in a 30-ml platinum dish and heat until the acids simmer.  

Do not boil the solution because loss by spattering will occur. An infrared lamp is recommended. If the solution looks clear, step 2 may be omitted.
2. When the volume has decreased to approximately 2 ml, repeat the addition of 5 to 10 ml of 15.6M  $HNO_3$  plus 0.1 to 0.2 ml of 28M HF and heat until the solution looks clear.  

The tungsten may not dissolve completely even though the solution looks clear. Steps 3 through 6 are intended to dissolve any tungsten-containing residue.
3. Decant the supernatant solution into a clean beaker.

4. Rinse the dish twice with 1 ml of water and transfer each rinse to the beaker.
5. Add 0.5 g of potassium pyrosulfate to the dish and fuse over a burner or in a furnace until  $\text{SO}_3$  fumes are no longer evolved.
 

Be sure the dish is dry before adding the potassium pyrosulfate. Tungsten converts to a soluble sulfate salt.
6. After the dish cools, add approximately 5 ml of water and heat for 5 min to dissolve the fused salt.
 

If dissolution is slow, 1 ml of 15.6M  $\text{HNO}_3$  may be added.
7. Transfer the solution from the beaker to the dish with the aid of at least three 1-ml rinses of water.
8. Evaporate the combined solutions to dryness and fume until  $\text{SO}_3$  fumes are no longer evolved.
 

Nitrate is removed which otherwise would destroy the dithiol.
9. Redissolve the residue in a minimum volume of 6M HCl and transfer the solution to an extraction vessel.
 

Do not use more than 8 ml of 6M HCl.
10. Rinse the dish twice with 2-ml portions of 6M HCl and add the rinses to the extraction vessel.
11. Adjust the volume in the extraction vessel to 12 ml with 6M HCl.
12. Add 5 ml of pentyl acetate plus 5 ml of 1% dithiol-pentyl acetate and stir for 3 min with an electric stirrer.
 

Molybdenum extracts into the pentyl acetate.
13. Separate the two liquid phases and drain the aqueous layer into a 200-ml tall-form beaker.
14. Wash the organic phase twice with 2.5-ml portions of 6M HCl and add the acid washes to the beaker.
 

The washed organic phase may be discarded into a collection bottle for plutonium-organic solvent waste.
15. Add 25 ml of Tl(III) chloride solution plus 5 ml of water to the beaker and mix.
 

The HCl concentration is now 8.4M. Tl(III) reduces W(VI) to W(V).
16. Place the beaker in the aluminum block of the heat-stirrer preheated to  $100^\circ\text{C}$  and heat for 5 min.
 

The solution must be hot to ensure complete formation of the tungsten-dithiol complex in the next step.
17. Add 10 ml of 1% dithiol-pentyl acetate and stir the mixture for 10 min while continuing to heat at  $90^\circ\text{C}$ .
 

Tungsten extracts into the dithiol-pentyl acetate.
18. Remove the beaker from the aluminum block and allow the mixture to cool to room temperature.
19. Transfer the mixture to an extraction vessel, rinse the beaker with three 1-ml portions of pentyl acetate, and add these rinses to the extraction vessel.
20. Allow the phases to separate, then drain the aqueous phase into a plutonium residue bottle.
 

Between 5 and 8 min may be required for good phase separation.
21. Wash the organic layer twice with 5-ml portions of 8.4M HCl, and add the washings to the residue bottle.
 

Be sure to allow time for good phase separation each time.
22. Drain the organic phase into a 25-ml graduated cylinder. Dilute to a volume of 15 ml with pentyl acetate and mix well.
23. Transfer a portion of the pentyl acetate to a matched 1-cm Corex absorption cell and measure the absorbance at 640 nm using pentyl acetate as the reference in a matched 1-cm cell.
 

Record the absorbance as y.

Calculations

$$R = \frac{y - B}{AW},$$

in which

R = micrograms of tungsten per gram of sample,

y = absorbance of sample corrected for the blank absorbance,

A, B = constants determined from equation (1) in Calibration subsection,

W = weight of sample in grams.

DETERMINATION OF METAL IMPURITIES BY EMISSION  
SPECTROSCOPY USING THE CARRIER-DISTILLATION  
TECHNIQUE

SUMMARY

Twenty-five metallic impurity elements are determined by the carrier-distillation technique using gallium oxide and silver chloride as the carriers. The concentration range covered is one-tenth or less to twice the specification limit for each impurity. The standard deviation is 20% or better when intensities are measured microphotometrically with internal standards and about 50% when intensities are estimated visually.

APPLICABILITY

This method<sup>[1]</sup> is applicable to ceramic grade uranium dioxide, ceramic grade plutonium dioxide, uranium dioxide insulator pellets, and uranium-plutonium mixed oxide pellets. The impurity elements determined and their concentration ranges are given in Table I.

Three or four analytical conditions are required to determine all 25 impurities in each type of sample as summarized in Table II.

The complete analysis of 12 samples, including a series of five calibration blends, may be done by one analyst working five 8-hr shifts.

RELIABILITY

The relative standard deviation is 20% or better when an internal standard is used and the line intensities are measured with a microphotometer. The estimated relative standard deviation for a visual comparison evaluation is 50%. The use of microphotometry without an internal standard gives intermediate precision.

Control of bias is maintained by processing a series of five calibration blends with each group of samples and comparing the intensities of the spectral lines of the

[1] J. V. Pena, W. M. Myers, C. J. Martell, H. M. Burnett, J. F. Murphy, C. B. Collier, O. R. Simi, and R. T. Phelps, USAEC Reports LA-4546-MS, (1970), pp. 26-28; LA-4595-MS (1971), p. 28.

TABLE I  
METALLIC IMPURITIES DETERMINED AND THEIR  
CONCENTRATION RANGES

<u>Impurity</u>	<u>Concentration Range, <math>\mu\text{g/g}</math></u>
Al, Fe, Na, Ni, V	25 to 1000
Si, Ta	40 to 800
Ca, Cr	25 to 500
Cu, K, Ti, Zn	20 to 400
Ag, Mg, Mn, Mo, Pb Sn, W	5 to 200
Cd	4 to 40
B, Be	2 to 40
Co	2 to 20
Li	1 to 20

samples to the corresponding lines of the calibration blends. The calibration blends and their use are described more fully below.

DISCUSSION OF THE METHOD

Spectrographic methods based on the carrier-distillation technique<sup>[2]</sup> are used routinely to determine trace levels of impurities in uranium and plutonium materials. In this technique, the impurity elements are separated from a refractory sample matrix by fractional distillation in a dc arc. The separation is obtained by adding to the sample a selected volatile material which serves as a carrier to sweep out the impurity elements, and which also may aid the separation by furnishing anions that form volatile compounds of the impurity elements. The latter role is illustrated by the greater detection sensitivity obtained with silver chloride or sodium fluoride carriers than with gallium oxide or indium oxide carriers. The carrier also stabilizes the arc. Under proper operating conditions, spectra of the impurity elements are obtained that are essentially free of interference by the complex spectra of uranium and plutonium.

The carrier must be highly pure, produce simple spectra, and be nonhygroscopic. Gallium oxide is a

[2] B. F. Scribner and H. R. Mullin, J. Res. Bur. Stand. 37, 979 (1946).

TABLE II  
SUMMARY OF THE ANALYTICAL CONDITIONS

<u>Material Analyzed</u>	<u>Elements Determined</u>	<u>Carrier</u>	<u>Internal Standard</u>	<u>Electrode Charge, mg</u>	<u>Arc Chamber Atmosphere</u>	<u>Current, A</u>	<u>Plate Emulsion</u>
Ceramic Grade Uranium Dioxide and Uranium Dioxide Insulator Pellets	Ag, Al, B, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Si, Sn, Zn	4% Ga <sub>2</sub> O <sub>3</sub> + 2.4% graphite	Co	100	Air	12	SA-3 SA-1
	K, Li, Na <sup>[a]</sup>	4% Ga <sub>2</sub> O <sub>3</sub> + 2.4% graphite		100	Air	12	I-N HIR-417
	Co, Mo, Ta, Ti, V, W	15% AgCl	Pd	130	O <sub>2</sub>	7	SA-3
Ceramic Grade Plutonium Dioxide	Ag, Al, B, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Si, Sn, Zn	4% Ga <sub>2</sub> O <sub>3</sub>	Co	100	O <sub>2</sub>	18	SA-1 SA-3
	K, Li, Na <sup>[a]</sup>	4% Ga <sub>2</sub> O <sub>3</sub>		100	O <sub>2</sub>	10	I-N
	Co, Mo, V, W	40% AgCl	Pd	50	O <sub>2</sub>	7	103-O
	Ta, Ti	15% AgCl	Hf	120	O <sub>2</sub>	6	SA-1
Uranium-Plutonium Mixed Oxide Pellets	Ag, Al, B, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Si, Sn, Zn	6.4% Ga <sub>2</sub> O <sub>3</sub>	Co	100	O <sub>2</sub>	18	SA-1
	K, Li, Na <sup>[a]</sup>	6.4% Ga <sub>2</sub> O <sub>3</sub>		100	O <sub>2</sub>	10	I-N
	Co, Mo, V, W	40% AgCl	Pd	50	O <sub>2</sub>	7	SA-3
	Ta, Ti	15% AgCl	Hf	120	O <sub>2</sub>	6	SA-3

[a] These three elements are determinable simultaneously with the elements listed above them with some spectrographs.

satisfactory carrier for many common elements including silver, but does not provide adequate detection sensitivity for Co, Mo, Ta, Ti, and W. These elements are determined using silver chloride as the carrier. The contamination of samples with silver is not a problem provided that good housekeeping is practiced.

The carrier-distillation technique permits the direct and simultaneous determination of many elements by a simple procedure that avoids the complex dissolution and separation procedures necessary to remove uranium and plutonium. It is, however, subject to variability that relates to the history of the sample and to

matrix differences between the calibration blends and the sample. These differences are minimized by using an internal standard element. This element added to the samples and the calibration blends in equal concentration reflects, by the magnitude of its intensity signal, matrix conditions that may affect the line intensity of an impurity element. The internal standard also serves to compensate for variations in the arcing conditions.

In the carrier distillation technique, the selection of the internal standard element depends on the impurity elements to be determined and on the matrix composition. The internal standards used for the various

analytical conditions are given in Table II.

The arcing of samples in air excites cyanogen molecules that emit complex band spectra which may interfere with lines arising from the impurities Al, Ca, Ti, and W. This interference is minimized in this method by arcing the sample in an oxygen atmosphere.

Selecting the analytical conditions to analyze the four materials listed in the APPLICABILITY subsection is based on consideration of sample preparation, reliability, and the effort required. Direct analysis of ceramic grade uranium dioxide is considered unreliable because this material may undergo partial oxidation to  $U_3O_8$  on exposure to air and also may contain moisture that is not readily removed by heating without oxidizing the sample. These uncertainties are minimized by igniting the sample to  $U_3O_8$  and using calibration blends having a  $U_3O_8$  matrix. The sintered uranium dioxide fuel pellets also are ignited to  $U_3O_8$  so they may be analyzed by the same calibration blends used for the ceramic grade uranium dioxide.

The ceramic grade plutonium dioxide is ignited at  $950 \pm 25^\circ C$  as prescribed<sup>[3]</sup> prior to analysis because as a low-temperature prepared material it may contain oxalate, nitrate, and moisture which could affect the excitation of the impurity elements. The calibration blends are prepared from pure plutonium dioxide which also has been heated at  $950 \pm 25^\circ C$ .

The uranium-plutonium mixed oxide pellets are prepared for analysis by grinding them in a niobium carbide mortar and passing the powder through a 200-mesh nylon screen. This simple procedure avoids the possibility of adding or removing impurities by ignition or chemical treatments that might be used to prepare the sample. The calibration blends are prepared in a matrix of similarly prepared mixed oxide powder.

The calibration blends and their use are very important to the obtaining of accurate results in the carrier distillation technique. These blends must simu-

late the sample, particularly with respect to matrix composition and bulk density. Hence, the mixed oxide samples are analyzed with calibration blends having a similar uranium to plutonium ratio. Bulk density depends on particle size and particle-size distribution. Although no attempt is made to measure these properties, the sample and calibration blends are subjected to similar grinding procedures and are packed similarly in the electrode cups. The internal standard, as discussed previously, can compensate for physical differences in the matrix. Also important is the processing of a set of five calibration blends simultaneously with samples to obtain spectra which serve to compensate for uncontrollable variables in the analysis.

Three series of LASL-prepared calibration blends are to be used by all laboratories to minimize between-laboratory differences. Each series consists of five blends with graded levels of the 25 impurities covering the nominal range of 1/10 to twice the specification limit for each impurity. The matrix materials of these blends are (a) uranium oxide ( $U_3O_8$ ) to be used for samples of ceramic grade uranium dioxide and uranium dioxide insulator pellets after their ignition to  $U_3O_8$ , (b) plutonium dioxide to be used for samples of ceramic grade plutonium dioxide, and (c) uranium-plutonium mixed oxide to be used for samples of uranium-plutonium mixed oxide pellets. As stated in the guideline directions to participating laboratories,<sup>[4]</sup> a complete series of five blends is to be processed simultaneously with samples such that every photographic plate or film contains a complete series that is used as the reference comparison for that plate or film. This like treatment of samples and calibration blends minimizes the variability effects of such factors as sample preparation, arc excitation conditions, and photographic film processing which otherwise are the major sources of bias in the method.

#### OPERATING INSTRUCTIONS

##### SAFETY PRECAUTIONS

Follow the regulations prescribed in the

[3] RDT Standard E13-1 "Fast Flux Test Facility Ceramic Grade Plutonium Dioxide" (October 1970).

[4] RDT Standard F2-6 "Qualification of Analytical Chemistry Laboratories for FFTF Fuel Analysis" (July 1970).

manufacturer's manual for use of the dc excitation source.

### APPARATUS

Atmosphere chamber, made from borosilicate glass and graphite (see Figure 1).

Comparator, projection-type having a magnification of at least 15X.

Crucibles, 10-ml, platinum, with covers.

Excitation source, 220 V dc, with a current range of 5 to 20 A.

Funnel, plastic, 5/8-in. diam to fit on the cupped end of a 1/4-in.-diam graphite electrode.

Microphotometer, capable of measuring line transmittances between 5 and 95% with a repeatability of at least  $\pm 1\%$  transmittance.

Mixer-mill, for mixing more than 3 g of materials as in preparing the carrier-internal standard mixtures.

Mortar and pestle, niobium carbide, 2-in.-diam bowl.

Mortars and pestles, boron carbide, titanium carbide, or agate, 2-in.-diam bowls.

Packing tool, stainless steel (see Figure 2).

Photographic processing equipment, providing a development temperature of  $20 \pm 0.5^\circ\text{C}$ .

Sample mixer, dental amalgamator type which uses a 1-in.-long x 1/2-in.-diam plastic vial.

Screen, nylon cloth, 200-mesh, Spex Industries, Inc., Metuchen, N. J., or equivalent.

Spectrograph, with not less than 90,000 resolving power and not more than  $5 \text{ \AA}/\text{mm}$  reciprocal linear dispersion for the spectral region 2200 to 8000  $\text{\AA}$ . In some of the procedures, a reciprocal linear dispersion of about  $2.5 \text{ \AA}/\text{mm}$  is needed.

Spoon, micro, platinum.

Venting tools, stainless steel and titanium (see Figure 3).

Vials, plastic, 1-in. x 1/2-in. diam, and 2-in. x 7/8-in. diam.

Weighing dish, platinum.

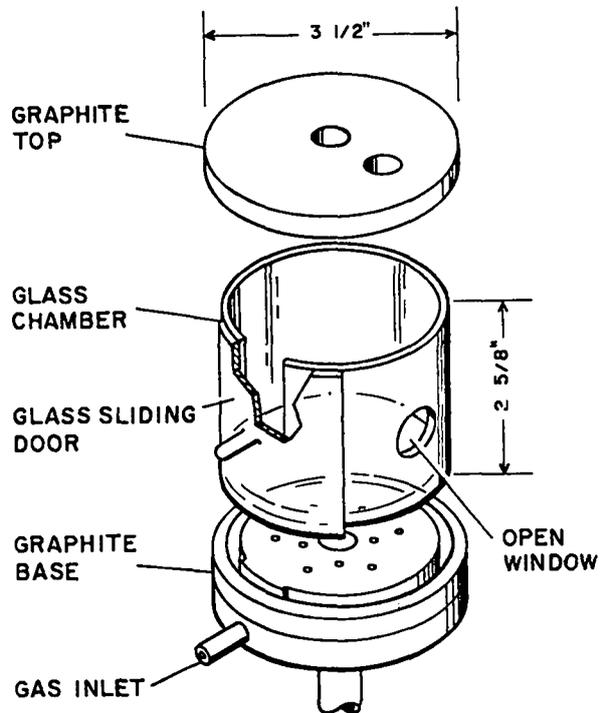


Figure 1. Atmosphere chamber.

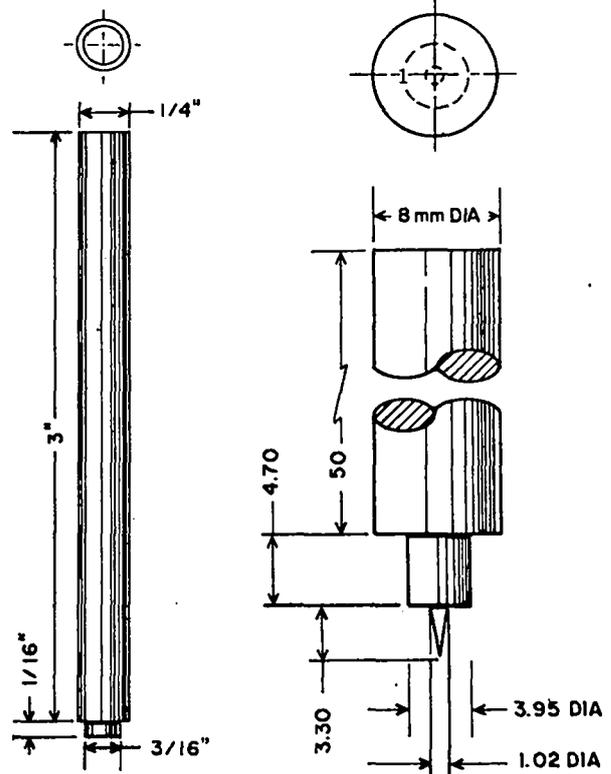


Figure 2. Packing tool.

Figure 3. Venting tool.

REAGENTS AND MATERIALS

Calibration blends. These blends contain the 25 impurity elements in a matrix of either  $U_3O_8$ ,  $PuO_2$ , or uranium-plutonium mixed oxide. They have been prepared at LASL by blending weighed, finely ground mixtures of the impurity-element compounds, chiefly as oxides, with the matrices as fine powders. A set of five blends is supplied for each matrix material in which the impurity element concentrations range from one-tenth of the specification limit to twice the value. Additional blends to include other concentrations of the impurity elements are prepared from the supplied blends and the appropriate matrix material.

Carrier-internal standard mixtures (see Table III).

Cobalt oxide ( $Co_3O_4$ ), 99.95% purity.

Electrodes, graphite, AGKSP grade or equivalent.

Upper: 1-1/2 in. x 1/8-in. diam, one end pointed (ASTM Designation: E130-66, type C-1).

Lower: 1-1/2 in. x 1/4-in. diam with undercut cup 1/16-in. deep x 3/16-in. diam. (ASTM Designation: E130-66, type S-4).

Anode cup 1/4-in. diam (ASTM Designation: E130-66, type S-2 used on type S-1 pedestal), or 1-3/16 in. x 1/4-in. diam with cup 8-mm deep x 4-mm diam.

Gallium oxide ( $Ga_2O_3$ ), 99.99% purity.

Graphite powder, 200-mesh, high-purity, National Carbon Co. No. SP-2 or equivalent.

Hafnium dioxide, with less than 1% of zirconium and 0.2% total specification elements.

Matrix materials, 99.98% pure with respect to the 25 specification impurity elements, supplied by LASL.

Uranium oxide ( $U_3O_8$ )

Plutonium dioxide

Uranium dioxide-plutonium dioxide powder.

Palladium chloride, 99.9% purity.

Photographic plates or films. Eastman Kodak Co. types SA-1, SA-3, 103-O, I-N, and HIR-417.

Silver chloride, 99.99% purity.

TABLE III  
CARRIER-INTERNAL STANDARD MIXTURES

Designation	Sample	Contents	Preparation
"A"	uranium dioxide	$Ga_2O_3$ -graphite- $Co_3O_4$	Grind together 52.8 mg of $Co_3O_4$ , 3.73 g SP-2 graphite, and 6.22 g of $Ga_2O_3$ in a niobium carbide or titanium carbide mortar.
"B"	plutonium dioxide and uranium-plutonium mixed oxide	$Ga_2O_3$ - $Co_3O_4$	Grind together 86.4 mg $Co_3O_4$ and 5.92 g $Ga_2O_3$ in a niobium carbide or titanium carbide mortar.
"C"	uranium dioxide	$AgCl$ - $PdCl_2$ - $U_3O_8$	Grind together 33.7 mg of $PdCl_2$ and 8.00 g of pure $U_3O_8$ in a boron carbide or agate mortar. To 6.64 g of this mixture in a plastic vial, add 5.86 g of $AgCl$ and mix using a mixer mill.
"D"	plutonium dioxide	$AgCl$ - $PdCl_2$ - $PuO_2$	Grind together 25.1 mg of $PdCl_2$ and 6.00 g of pure $PuO_2$ in a boron carbide or agate mortar. To 5.00 g of this mixture in a plastic vial, add 10.7 g of $AgCl$ and mix using a mixer mill.
"E"	uranium-plutonium mixed oxide	$AgCl$ - $PdCl_2$ - $(U, Pu)O_2$	Same as "D" except use pure $(U, Pu)O_2$ in place of the $PuO_2$ .

TABLE III

## CARRIER-INTERNAL STANDARD MIXTURES (Cont.)

<u>Designation</u>	<u>Sample</u>	<u>Contents</u>	<u>Preparation</u>
"F"	plutonium dioxide	AgCl-HfO <sub>2</sub> -PuO <sub>2</sub>	Grind together 47.4 mg of HfO <sub>2</sub> and 8.00 g of pure PuO <sub>2</sub> in a boron carbide mortar. To 6.00 g of the mixture, add 5.33 g of AgCl and mix in a plastic vial using the mixer mill.
"G"	uranium-plutonium mixed oxide	AgCl-HfO <sub>2</sub> -(U,Pu)O <sub>2</sub>	Same as "F" using pure (U,Pu)O <sub>2</sub> in place of the PuO <sub>2</sub> .

## PROCEDURE

Blank

Blanks are not required for this method.

Calibration

Process a set of five appropriate calibration blends through the procedures listed under Sample Analysis, omitting the Preparation of Samples for Spectrographic Analysis steps. Single exposures of a set of five blends are made on every photographic plate. In setting up a procedure, the calibration blends are processed and evaluated at least four times to furnish data for constructing the analytical calibration curves and estimating the repeatability of the operations.

Sample AnalysisPreparation of Samples for Spectrographic Analysis

Samples are ignited under controlled furnace conditions in an air atmosphere. Test the ignition procedure for contamination by using pure U<sub>3</sub>O<sub>8</sub> or PuO<sub>2</sub> as the sample. The grinding is done in a niobium carbide mortar or other mortars that do not contaminate the sample with specification elements. The grinding should yield a fine powder that readily passes through a 200-mesh

nylon screen or does not feel gritty in the mortar.

1. Prepare the samples for analysis as follows.

Uranium Dioxide. Ignite an insulator pellet or 1 g of ceramic grade powder in a covered platinum crucible at 800°C for 1 hr. Grind to a fine powder.

Plutonium Dioxide. Ignite 1 g of the ceramic grade powder in a covered platinum crucible at 950° ± 25°C for 30 min. Grind to a fine powder.

The ignition may be omitted if previously done as specified in RDT Standard E13-1.

Uranium-plutonium mixed oxide pellets. Grind a pellet until all of it is screened through a 200-mesh nylon cloth.

2. Transfer the sample to a properly labeled vial. Use as directed in Parts A through D below.

Part A. Determination of Ag, Al, B, Be, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Si, Sn, and Zn in Uranium Dioxide, Plutonium Dioxide, and Uranium-Plutonium Mixed Oxide.

Electrode Charge

1. U<sub>3</sub>O<sub>8</sub> (ignited uranium dioxide). Weigh 18.0 mg of Ga<sub>2</sub>O<sub>3</sub> carrier-graphite-internal standard mixture "A" in the weighing dish and add 258 mg of the ignited sample.

The graphite is included to aid mixing the sample in the plastic vial and to enhance the Al, Ca, and Si spectra.

Plutonium dioxide. Weigh 10.0 mg of Ga<sub>2</sub>O<sub>3</sub> carrier-internal standard mixture "B" in the weighing dish and add 240 mg of the sample.

The graphite is omitted because it would enhance the plutonium spectrum.

Uranium-plutonium mixed oxide. Weigh 16.0 mg of Ga<sub>2</sub>O<sub>3</sub> carrier-internal standard mixture "B" in the weighing dish and add 234 mg of the sample.

2. Transfer the weighed mixture to a plastic vial and cap it.

The vial size is 1-in. x 1/2-in. diam.

3. Shake the vial for 30 sec using the sample mixer.

4. Weigh a 100-mg portion of the mixture, using the weighing dish.

Weigh an additional 100-mg portion for the determination of K, Li, and Na if their spectra are not recorded simultaneously with the ultraviolet spectra.

5. Save the remainder of the mixture in case further analysis is needed.
6. Transfer the 100-mg portion to the cup of a graphite electrode, using the plastic funnel.  
The electrode is ASTM type S-2.
7. Gently tap the lower end of the loaded electrode to level the charge.

Excessive tapping may compress the charge so that step 8 is not properly done.

8. Pack and vent the charge using the titanium venting tool.

This tool should pack the charge to a constant volume while forming the vent hole.

#### Electrode System

1. Place the atmosphere chamber in position in the arc stand.

For the analysis of  $U_3O_8$  (ignited uranium dioxide), the atmosphere chamber and the use of oxygen may be omitted.

2. Flow oxygen through the chamber at the rate of 5 l./min.
3. Place an electrode in the upper clamp of the arc stand.

The electrode is ASTM type C-1. It is held by friction in a graphite sleeve.

4. Mount the loaded electrode in the lower clamp of the stand.

This electrode is connected to the positive terminal of the power source.

5. Position and align the electrodes with a gap of 4 mm.

This is done by observing the electrode images on the graduated screen of the auxiliary optical system.

#### Excitation Conditions

Produce the spectra under the following conditions:

1. Adjust the current from the arc power source to 12 A for the analysis of  $U_3O_8$  and to 18 A for plutonium dioxide or uranium-plutonium mixed oxide on short-circuit using empty electrodes.

2. Arc the empty electrodes for 3 min to preheat the electrode clamps and the chamber.

After the preheating, the chamber temperature does not vary significantly from arcing-to-arcing.

3. Arc the sample and maintain the 4-mm gap by adjusting the clamps.

#### Exposure Conditions

1. Adjust the spectrograph to record spectra in the wavelength ranges of 2200 to 4500 Å and 5500 to 8500 Å.

2. Select either type SA-1 or SA-3 photographic emulsion for the lower wavelength range, and either type I-N or HIR-417 for the upper range.

3. Set the slit width to 15  $\mu$ .

4. Use the following exposure times: 90 sec for  $U_3O_8$ , 60 sec for plutonium dioxide, and 55 sec for uranium-plutonium mixed oxide.

5. Use a filter or a rotating sector in front of the spectrograph slit to control the exposure level.

A two-step filter is useful for controlling the exposure range.

6. Use Corning C.S. No. 3-72 glass filters to absorb the second order ultraviolet which interferes with the K, Li, and Na lines recorded in the upper wavelength region.

#### Part B. Determination of Co, Mo, Ta, Ti, V, and W in Uranium Dioxide.

##### Electrode Charge

1. Weigh 96.0 mg of the silver chloride-internal

standard mixture "C" in the weighing dish.

2. Add 204 mg of the sample to the weighing dish.
3. Transfer the weighed mixture to a plastic vial and cap it.

The vial size is 1-in. x 1/2-in. diam.

4. Shake the vial for 30 sec using the sample mixer.
5. Weigh a 130-mg portion of the mixture, using the weighing dish.

Save the remainder of the mixture in case further analysis is needed.

6. Transfer the weighed portion to the cup of a graphite electrode, using the plastic funnel.

The electrode is ASTM type S-2.

7. Gently tap the lower end of the loaded electrode to level the charge.

Excessive tapping may compress the charge so that step 8 is not properly done.

8. Pack and vent the charge using the stainless steel venting tool.

#### Electrode System

Use the system of Part A Procedure.

#### Excitation Conditions

Follow the steps in Part A Procedure using a current of 7 A.

#### Exposure Conditions

1. Adjust the spectrograph to record spectra in wavelength range of 2200 to 4500 Å.
2. Use the SA-3 photographic emulsion.
3. Set the slit width to 15  $\mu$ .
4. Use an exposure time of 60 sec.  
A preexposure arcing time of 10 sec precedes the exposure.
5. Use a filter or rotating sector in front of the slit to control the exposure level.

A two-step filter is useful for controlling the exposure range.

### Part C. Determination of Co, Mo, V, and W in Plutonium Dioxide and Uranium-Plutonium Mixed Oxide.

#### Electrode Charge

1. Weigh 78.0 mg of the silver chloride-internal standard mixture in the weighing dish.

Use mixture "D" for plutonium dioxide samples and mixture "E" for uranium-plutonium mixed oxide samples.

2. Add 53.0 mg of the sample to the weighing dish.
3. Transfer the weighed mixture to a plastic vial and cap it.

The vial size is 1-in. x 1/2-in. diam.

4. Shake the vial for 30 sec using the sample mixer.
5. Weigh a 50-mg portion, using the weighing dish.

Save the remainder of the mixture in case further analysis is needed.

6. Transfer the weighed portion to the cup of a graphite electrode, using the plastic funnel.

The electrode is ASTM type S-4.

7. Pack the charge with the packing tool.

This size charge does not require venting.

#### Electrode System

Use the system of Part A Procedure.

#### Excitation Conditions

Follow the steps in Part A Procedure using a current of 7 A.

#### Exposure Conditions

1. Adjust the spectrograph to record spectra in the wavelength range of 2200 to 4500 Å.
2. Use either type 103-O or SA-3 photographic emulsion.
3. Set the slit width to 15  $\mu$ .
4. Use an exposure time of 30 sec.

5. Use a filter or rotating sector in front of the slit to control the exposure level.

A two-step filter is useful for controlling the exposure range.

#### Part D. Determination of Ta and Ti in Plutonium Dioxide and Uranium-Plutonium Mixed Oxide.

##### Electrode Charge

1. Weigh 96.0 mg of the silver chloride-internal standard mixture in the weighing dish.

Use mixture "F" for plutonium dioxide samples and mixture "G" for mixed oxide samples.

2. Add 204 mg of the sample to the weighing dish.

3. Transfer the weighed mixture to a plastic vial and cap it.

The vial size is 1-in. x 1/2-in. diam.

4. Shake the vial for 30 sec using the sample mixer.

5. Weigh a 120-mg portion of the mixture, using the weighing dish.

Save the remainder of the mixture in case further analysis is needed.

6. Transfer the weighed portion to the cup of a graphite electrode, using the plastic funnel.

The electrode is ASTM type S-2.

7. Gently tap the lower end of the loaded electrode to level the charge.

Excessive tapping may compress the charge so that step 8 is not properly done.

8. Pack and vent the charge using the stainless steel venting tool.

##### Electrode System

Use the system of Part A Procedure.

##### Excitation Conditions

Produce the spectra according to the following conditions.

1. Adjust the current from the arc power source to 6 A on short-circuit using empty electrodes.

2. Arc the empty electrodes for 3 min to preheat the electrode clamps and the chamber.

3. Arc the sample and maintain the 4-mm gap by adjusting the clamps.

##### Exposure Conditions

1. Adjust the spectrograph to record spectra in the wavelength range of 2200 to 4500 Å.
2. Use the following photographic emulsions: SA-1 for plutonium dioxide and SA-3 for uranium-plutonium mixed oxide samples.
3. Set the slit width to 15 μ.
4. Use an exposure time of 60 sec.

For uranium-plutonium mixed oxide samples, use a preexposure arcing time of 30 sec.

5. Use a filter or rotating sector in front of the slit to control the exposure level.

A two-step filter is useful for controlling the exposure range.

##### Photographic Processing for Parts A, B, C, and D.

1. Develop the plate for 5 min in Kodak D-19 at 20°C.
2. Place in acetic acid shortstop bath for 15 sec.
3. Fix in a rapid fix for 5 min.
4. Wash in running water for 10 min.
5. Sponge and dry.

##### Microphotometry

1. Measure the percent transmittance, or optical density, of the analytical and internal standard lines listed in Tables IV, V, or VI in the spectrograms of the calibration blends and the samples.
2. Measure, also, the percent transmittance of the background associated with the lines.

##### Calibration

Emulsion. Calibrate the photographic emulsions

by the Two-Step Preliminary Curve Method. [5]

Analytical Curves

1. Convert the percent transmittances of the lines measured for the calibration blends to intensities, using the emulsion calibration data.
2. Correct the line intensities for the background intensities.  
The correction may be omitted if it has been shown to have negligible effect on the concentration result.
3. Calculate the intensity ratios of the line pairs listed in Table IV, V, or VI.
4. Plot intensity ratio vs concentration ( $\mu\text{g/g}$ ) on log-log paper to obtain the analytical curve for each element.
5. Plot corrected line intensity vs concentration ( $\mu\text{g/g}$ ) on log-log paper to obtain the analytical curve for each element determined without use of an internal standard.

Calculations

Microphotometry with an Internal Standard

1. Convert the transmittances measured for the line pairs of the sample to intensities, using the emulsion calibration data.
2. Correct the line intensities for background intensities.
3. Calculate the intensity ratios of the line pairs.
4. Convert the intensity ratios to concentration ( $\mu\text{g/g}$ ) by reference to the appropriate analytical curve.

Microphotometry without an Internal Standard

1. Convert the transmittances measured for the analytical lines of the sample to intensities, using the emulsion calibration data.

TABLE IV  
ANALYTICAL LINES FOR ANALYSIS OF  $\text{UO}_2$

Element	Concn Range, $\mu\text{g/g}$	Element Line, $\text{\AA}$	Internal Standard, $\text{\AA}$
Ag	5 to 100	3280.68	
	5 to 200	3382.89	
Al	25 to 500	3082.16	Co 3044.00
	100 to 1000	2575.10	Co 2521.36
B	1 to 40	2497.73	Co 2521.36
Be	1 to 40	2348.61	
Ca	15 to 500	4226.73	
Cd	2 to 40	2288.02	
Co	2 to 20	3506.32	
Cr	15 to 500	2835.63	Co 3044.00
Cu	10 to 400	3273.96	Co 3044.00
Fe	25 to 1000	2522.85	Co 2521.36
K	10 to 400	7698.98	
Li	1 to 20	6707.84	
	5 to 50	2852.13	
Mg	5 to 100	2802.70	
	20 to 200	2782.97	
Mn	5 to 200	2576.10	Co 2521.36
Mo	5 to 200	3170.35	
Na	25 to 250	5895.92	
	250 to 1000	8183.27	
Ni	25 to 1000	3002.49	Co 3044.00
Pb	5 to 200	2833.06	
Si	20 to 800	2514.32	Co 2521.36
	20 to 800	2519.21	Co 2521.36
Sn	5 to 200	3175.05	
Ta	20 to 800	2647.47	Pd 2476.42
	20 to 800	2653.27	Pd 2476.42
	20 to 800	2714.67	Pd 2476.42
Ti	10 to 400	3199.92	Pd 3302.13
	20 to 400	3329.46	Pd 3302.13
V	25 to 1000	3056.33	
	25 to 1000	3118.38	
W	5 to 200	2946.98	Pd 3302.13
Zn	10 to 400	3302.59	
	40 to 400	3282.33	

[5] "Recommended Practices for Photographic Photometry in Spectrochemical Analysis," ASTM Methods for Emission Spectrochemical Analysis, American Society for Testing Materials (1968).

TABLE V  
ANALYTICAL LINES FOR ANALYSIS OF PuO<sub>2</sub>

Element	Concn Range, $\mu\text{g/g}$	Element Line, $\text{\AA}$	Internal Standard, $\text{\AA}$
Ag	5 to 200	3280.68	
Al	25 to 500	3961.53	Co 2535.96
	25 to 1000	3092.71	Co 2535.96
B	1 to 20	2497.73	
	4 to 40	2496.78	
Be	1 to 40	3130.42	
	1 to 40	3131.07	
Ca	10 to 400	3933.67	
	10 to 400	3968.47	
Cd	10 to 40	3261.06	
	10 to 40	3466.20	
	4 to 40	2288.02	
Co	2 to 20	3405.12	Pd 3027.91
	2 to 20	3453.50	Pd 3027.91
Cr	10 to 400	3021.56	Co 2535.96
Cu	10 to 400	3247.54	
	10 to 400	3273.96	
Fe	25 to 500	2483.27	Co 2535.96
	50 to 1000	2490.64	Co 2535.96
K	10 to 400	7664.91	
	20 to 400	7698.98	
Li	0.5 to 20	6707.84	
Mg	5 to 100	2852.13	
	5 to 200	2802.70	
Mn	5 to 20	2576.10	Co 2535.96
	5 to 50	2593.73	Co 2535.96
Mo	5 to 200	3193.97	Pd 3027.91
Na	25 to 250	5889.95	
	100 to 1000	8183.27	
Ni	25 to 1000	3003.63	Co 2535.96
	25 to 500	3002.49	Co 2535.96
Pb	5 to 100	4057.83	
	10 to 200	2801.99	
Si	20 to 400	2516.11	Co 2535.96
	40 to 800	2514.32	Co 2535.96
Sn	5 to 200	2839.99	
	20 to 200	3262.34	

TABLE V  
ANALYTICAL LINES FOR ANALYSIS OF PuO<sub>2</sub> (Cont.)

Element	Concn Range, $\mu\text{g/g}$	Element Line, $\text{\AA}$	Internal Standard, $\text{\AA}$
Ta	40 to 800	2647.47	Hf 2638.71
	40 to 800	2714.67	Hf 2638.71
Ti	10 to 400	3234.52	Hf 2638.71
	10 to 400	3349.41	Hf 2638.71
V	25 to 750	3183.41	Pd 3027.91
	25 to 1000	3185.40	Pd 3027.91
	100 to 1000	3118.38	Pd 3027.91
W	20 to 200	2724.35	Pd 3027.91
	20 to 200	2944.40	Pd 3027.91
	20 to 200	2946.98	Pd 3027.91
Zn	10 to 400	3345.02	

2. Correct the line intensities for background intensities.
3. Convert the corrected line intensities to concentration ( $\mu\text{g/g}$ ) by reference to the appropriate analytical curve.

The steps above, beginning with step 1 under Calibration, can be readily done by a procedure programmed for computer calculation. [6]

#### Visual Comparison

Place the plate or film containing the spectrograms of the sample and the calibration blends in the comparator. Align the plate with a master plate which identifies the analytical lines (Table IV, V, or VI).

Visually compare the blackening of the lines produced by the sample with the blackening shown by the corresponding lines of the calibration blends. Report the concentration value obtained from the comparison.

[6] J. R. Phillips, J. F. Murphy, and C. J. Martell, "Computer-Calculations in Spectrochemical Analysis," CONF-691037-1 (October 10, 1969).

TABLE VI

ANALYTICAL LINES FOR ANALYSIS OF URANIUM-  
PLUTONIUM MIXED OXIDE

Element	Concn Range, $\mu\text{g/g}$	Element Internal	
		Line, $\text{\AA}$	Standard, $\text{\AA}$
Ag	5 to 200	3280.68	
	5 to 200	3382.89	
Al	25 to 500	3082.16	Co 2535.96
	100 to 1000	2575.10	Co 2535.96
B	1 to 40	2497.73	Co 2535.96
Be	1 to 40	3131.07	Co 2535.96
Ca	25 to 500	3968.47	
	25 to 500	4226.73	
Cd	4 to 40	3261.06	
	10 to 40	3466.20	
	4 to 40	2288.02	
Co	2 to 20	3405.12	Pd 3027.91
Cr	25 to 500	2843.25	Co 2535.96
Cu	10 to 100	3273.96	
	100 to 400	2824.37	
Fe	25 to 1000	2483.27	Co 2535.96
K	10 to 400	7698.98	
Li	0.5 to 20	6707.84	
Mg	5 to 50	2795.53	Co 2535.96
	10 to 200	2782.97	
Mn	5 to 200	2576.10	Co 2535.96
Mo	5 to 100	3158.16	Pd 3027.91
	10 to 200	3208.83	Pd 3027.91
Na	25 to 250	5895.92	
	100 to 1000	8183.27	
Ni	25 to 1000	3002.49	Co 2535.96
	50 to 1000	3003.63	Co 2535.96
Pb	5 to 200	2833.06	
Si	20 to 800	2519.21	Co 2535.96
Sn	5 to 200	3175.05	
	5 to 200	3262.34	
Ta	40 to 800	2647.47	Hf 2638.71
	40 to 800	2653.27	Hf 2638.71
Ti	10 to 400	3349.41	Hf 2940.77
	40 to 400	3236.57	Hf 2940.77
V	50 to 1000	3118.38	Pd 3027.91
	25 to 500	3183.41	Pd 3027.91

TABLE VI

ANALYTICAL LINES FOR ANALYSIS OF URANIUM-  
PLUTONIUM MIXED OXIDE (Cont.)

Element	Concn Range, $\mu\text{g/g}$	Element Internal	
		Line, $\text{\AA}$	Standard, $\text{\AA}$
W	10 to 200	2946.98	Pd 3027.91
Zn	20 to 400	3345.02	
	100 to 400	3282.33	

DETERMINATION OF DYSPROSIUM, EUROPIUM,  
GADOLINIUM, AND SAMARIUM BY EMISSION  
SPECTROSCOPY FOLLOWING AN AMINE EXTRACTION  
SEPARATION

SUMMARY

Dysprosium, europium, gadolinium, and samarium are determined by the copper spark emission spectrographic technique after separation of the uranium and plutonium by extraction into tri-n-octylamine in xylene. The relative standard deviation is 15% or better for the concentration range of 10 to 200  $\mu\text{g}$  of each rare earth per gram of sample.

APPLICABILITY

This method<sup>[1]</sup> is applicable to the determination of dysprosium, europium, gadolinium, and samarium in ceramic grade uranium dioxide, ceramic grade plutonium dioxide, uranium-plutonium oxide fuel pellets, and uranium dioxide insulator pellets. The concentration range covered is 10 to 200  $\mu\text{g/g}$  for each rare earth to meet the requirements of adequate detection sensitivity and coverage of the specification value of 100  $\mu\text{g/g}$  for the sum of these four rare-earth impurities. Americium and other impurity elements do not interfere at their stated specification limits.

The analysis of 12 samples and five calibration blends may be done by one analyst working three 8-hr shifts.

RELIABILITY

The precision was evaluated by analyzing samples of uranium dioxide, plutonium dioxide, and uranium-plutonium mixed oxide to which known quantities of the four rare earth elements and other specification metal impurities had been added. The relative standard deviation was 15% or better over the concentration range of 10 to 200  $\mu\text{g/g}$  for each rare earth. The method is calibrated using the series of LASL-prepared blends to minimize bias between laboratories.

[1] H. M. Burnett and O. R. Simi, USAEC Reports LA-4546-MS (1970), p. 23-24; LA-4595-MS (1970), p. 27.

DISCUSSION OF THE METHOD

Spectrographic methods for the determination of trace levels of rare earths usually include an initial separation of uranium and plutonium when they are present as major components of the sample. Separation techniques frequently used include ion exchange,<sup>[2]</sup> fluoride precipitation,<sup>[3,4]</sup> and solvent extraction.<sup>[5,6]</sup> Ko<sup>[5]</sup> reported that two contacts with tri-n-octylamine (TNOA) in xylene extract more than 99.9% of plutonium from 6M  $\text{HNO}_3$ . Later he proposed a method<sup>[7]</sup> in which both the uranium and plutonium are separated by two contacts with TNOA-xylene from 6M  $\text{HCl}$  - 1.5M  $\text{HNO}_3$  - 0.005M  $\text{HF}$  and the unextracted rare earths in the aqueous phase are determined by the copper spark technique. This latter method, proposed for FFTF fuel materials, consisted of (1) the dissolution of the sample in a nitric acid-hydrofluoric acid mixture, (2) addition of 6.7M  $\text{HCl}$ , yttrium internal standard, and boric acid to complex fluoride, (3) a double extraction of the uranium and plutonium into 20% TNOA-80% xylene, (4) evaporation of the aqueous phase and redissolution in 1M  $\text{HCl}$ , and (5) copper spark excitation in an air atmosphere.

Ko's method was evaluated<sup>[1]</sup> in detail for the analysis of the four FFTF fuel materials including the effect of americium and all the metallic impurity elements at their stated specification limits. Several modifications were found to be necessary to permit reliable rare-earth determinations in FFTF fuel materials containing impurities at their specification limits. A third contact with 20% TNOA-xylene was added to increase the

- [2] J. K. Brody, J. P. Faris, and R. F. Buchanan, *Anal. Chem.* **30**, 1909 (1958).  
[3] M. E. Smith, USAEC Report LA-1995 (1956).  
[4] G. W. Boyes, Jr., J. B. Ramsay, and R. T. Phelps, *Talanta* **6**, 209 (1960).  
[5] R. Ko, paper presented at American Chemical Society Northwest Regional Meeting, Salt Lake City, Utah, June 12-13, 1969.  
[6] M. G. Atwell, C. E. Pepper, and G. L. Stukenbrocker, USAEC Report TID-7658, Pt. 1 (1958).  
[7] R. Ko, Method 20.9, USAEC Report WHAN-IR-5 (August 1970).

extraction of uranium and plutonium to prevent their spectral interference. Steps were added to remove residual boron and organic matter which decreased the spectral intensity of the rare earths. The boron was volatilized as methyl borate, and the organic matter was destroyed by igniting the evaporated aqueous phase from the third extraction at 400°C. The 25 general metal impurities (total specification limit of about 5400 µg/g of sample, see INTRODUCTION to this report) generally do not extract. Their presence on the electrodes seriously suppressed the rare-earth spectra and also adversely affected the precision. The substitution of argon for air as the spark excitation atmosphere increased the intensity of the rare-earth spectra and improved the precision. Americium at the specification limit of about 2400 µg/g of plutonium did not significantly affect either the rare-earth spectral intensity or the precision.

The use of yttrium as an internal standard is essential to compensate for the variable effects on the rare-earth spectral intensities caused by sample-to-sample and sample-to-calibration blend differences in the impurity elements and their concentrations.

At the completion of the dissolution of the sample or calibration blend, small amounts of insoluble residue may remain. These residues have been found to contain Be, Cr, Si, Sn, Ta, Ti, and W. The quantities of rare earths in these residues has been found to be insignificant.

#### OPERATING INSTRUCTIONS

##### SAFETY PRECAUTIONS

Follow the regulations prescribed in the manufacturer's manual for use of the high-voltage spark source.

##### APPARATUS

Atmosphere chamber, made from borosilicate glass, phenolic board, and metal. See Figure 1.

Crucibles, 10-ml, machined from 1-in. diam Teflon rod 1-3/16-in. high x 1-1/16-in. deep inside, 1/8-in. wall, with covers.

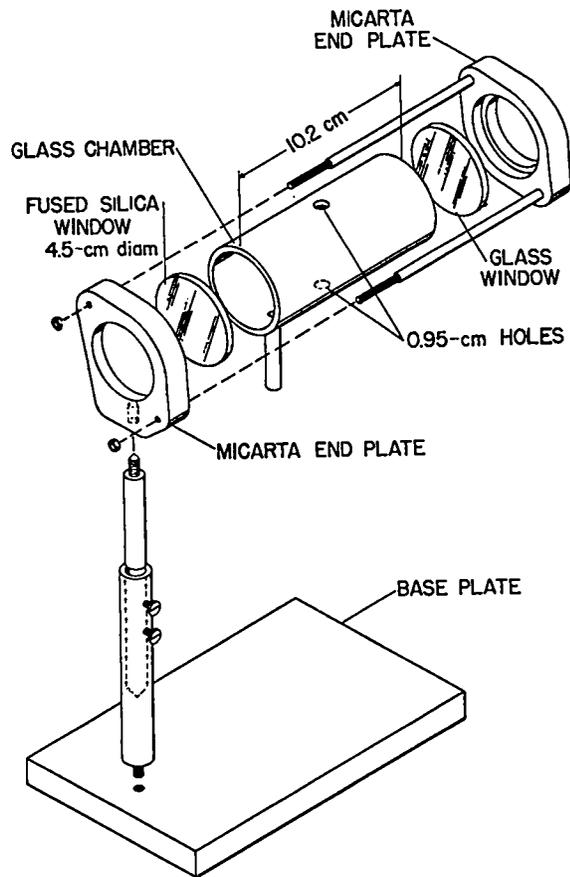


Figure 1. Atmosphere chamber.

Electrode-drying apparatus. See Figure 2.

Electrode block, copper, 4-in. diam, 12 holes.

Electrode holder, wood, 24 holes.

Hot plate, electric, 4-in. diam.

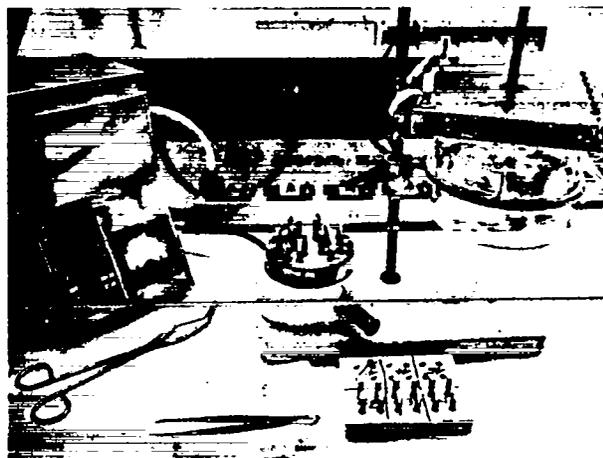


Figure 2. Evaporating apparatus and electrode-drying apparatus.

Evaporating apparatus. See Figures 2 and 3.

Chamber, borosilicate glass, connected to water aspirator.

Heater, stainless steel reflector and Nichrome elements.

Controller, Brown Elektronik, to regulate power to heater.

Equivalent arrangements to control temperature and to exhaust acid fumes may be used.

Excitation source, spark, 5-kW, Jarrel-Ash Vari-source, or equivalent.

Magnetic stirrer, 5-in. diam. See Figure 3.

Protective holder, Lucite.

Stirring bar, Teflon-covered, 3/4- or 1-in.

Microphotometer, capable of measuring line transmittances between 5 and 95% with a repeatability of at least  $\pm 1\%$  absolute.

Photographic processor, capable of providing a development temperature of  $20^{\circ} \pm 0.5^{\circ}\text{C}$ .

Pipets, plastic-disposable, graduated, 1-ml.

Recovery bottles, 1-l., vacuum-tested. See Figure 3.

Spectrograph, with not less than 90,000 resolving power and not more than  $5\text{\AA}/\text{mm}$  reciprocal linear dispersion for the spectral region 2200 to  $5000\text{\AA}$ .

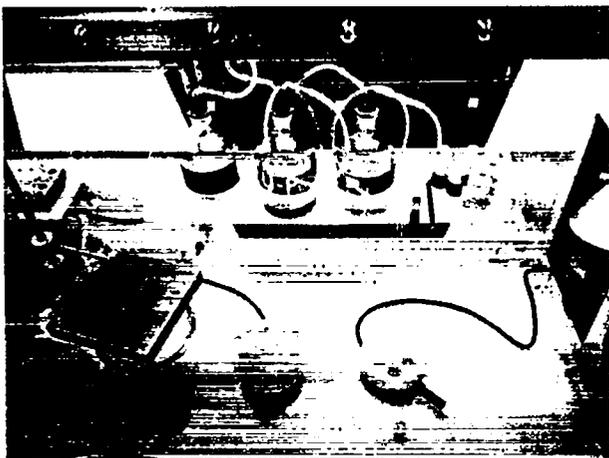


Figure 3. Miscellaneous equipment.

## REAGENTS AND MATERIALS

Boric acid, crystals.

Calibration blends. LASL-prepared blends containing known concentrations of 29 metallic impurity elements in matrices of uranium oxide, plutonium oxide, and uranium-plutonium mixed oxide. For each matrix, a set of five blends is available in which nominal concentrations of the four rare earths are 10, 20, 50, 100, and  $200\ \mu\text{g/g}$ , respectively, and the concentrations of the other 25 metallic impurities range from one-tenth, or less, to twice the specification limit.

Electrodes, electrolytic copper rod, 1.5-in. long  $\times$  1/4-in. diam. Prepare a smooth top surface by stroking the end of the electrode with 600-grit abrasive paper. Immerse about 1/4-in. of this end of the electrode in  $8\text{M}$   $\text{HNO}_3$  for 15 to 30 sec. Rinse thoroughly with distilled water and blot dry with cleaning tissue or cheesecloth. By using a wood block holding 24 electrodes, this is a simple batch operation.

Hydrochloric acid,  $6.7\text{M}$ ,  $1\text{M}$ .

Methyl alcohol, 100%.

Mixed acid,  $15.6\text{M}$   $\text{HNO}_3$  -  $0.05\text{M}$   $\text{HF}$ , for sample dissolution.

Nitric acid,  $15.6\text{M}$  (70%),  $8\text{M}$ .

Perchloric acid,  $12\text{M}$  (70%).

Photographic plate, Eastman Kodak Co. type SA-3.

Tri-n-octylamine in xylene, 20 vol %. Dilute 200 ml of tri-n-octylamine to 1000 ml with xylene. The tri-n-octylamine may be obtained from Chemical Procurement Laboratories, Inc., College Point, N. Y.

Xylene

Yttrium oxide ( $\text{Y}_2\text{O}_3$ ), 99.9% purity, ignite to  $900^{\circ}\text{C}$  just before use to remove carbon dioxide and water.

Yttrium stock solutions. Prepare each of the following solutions and store in polyethylene bottles.

1 mg/ml Dissolve 0.1270 g  $\text{Y}_2\text{O}_3$  in 100 ml of  $6.7\text{M}$   $\text{HCl}$ .

0.1 mg/ml Dilute 10.0 ml of the above solution to 100 ml with 6.7M HCl.

Yttrium internal standard solution, 0.008 mg/ml. Dilute 8.00 ml of the 0.1 mg/ml solution to 100 ml with 6.7M HCl and store in a polyethylene bottle.

#### PROCEDURE

##### Blank

Determine a single blank with each series of samples starting at step 1, omitting the sample, in the Sample Analysis subsection. The measured concentrations of each of the four rare earths in the blank shall be not greater than the equivalent of 12.5  $\mu\text{g/g}$  of sample. If any concentration is greater, investigate the cause, and rectify the difficulty before analyzing further samples. A likely source of difficulty is contamination of reagents.

##### Calibration

One spectrum of each of five blends in a calibration set with the same matrix as the samples and processed through the entire Sample Analysis subsection is placed on each spectrographic plate. These calibration spectra are used as the comparison basis to calculate results for the sample spectra on this same plate. In the procedure, a 1-ml volume of solution is the end product of the chemical separation (step 17 in the Sample Analysis subsection) of which 50  $\mu\text{l}$  is placed on a pair of electrodes for the spectrographic analysis. By storing the final solutions obtained for the calibration blends under conditions that prevent concentration changes by evaporation or contamination, one processing gives 10 to 20 measurements.

The linear fit of the calibration curve for each rare earth for each plate should be such that the average deviation from the linear fit does not exceed  $\pm 15\%$  relative. If this criterion is not satisfied and the total rare earth concentration for a sample exceeds 50  $\mu\text{g/g}$ , such samples should be reanalyzed.

To gain experience with the method, it is recommended that each analyst process three sets of calibration blends through the entire procedure. The calibra-

tion curves should meet the criterion stated above before the analyst is given responsibility for samples.

#### Sample Analysis

##### Dissolution and Preparation for Extraction

1. To a Teflon crucible, add 200 mg of the sample and 1 ml of 15.6M  $\text{HNO}_3$  - 0.05M HF; cover and heat until dissolution is apparently complete.

Weigh the sample to  $\pm 1$  mg.

2. Add 0.5 ml of 12M  $\text{HClO}_4$  and fume just to dryness.

Do not bake the residue because it will not readily dissolve in the next step.

This fuming removes most of the fluoride and aids the dissolution of many impurity elements.

3. Add 2 ml of 6.7M HCl and heat to dissolve the residue.

Disregard any small residue. See DISCUSSION OF THE METHOD.

4. Transfer the solution to a 30-ml beaker using four 2-ml rinses of 6.7M HCl.

Inscribe an identifying number on each beaker that will remain after ignition at 400°C.

5. Add 500  $\mu\text{l}$  of yttrium internal standard solution.

The amount of yttrium is 4  $\mu\text{g}$ .

6. Add 5 mg of boric acid.

Boric acid complexes the remaining traces of fluoride.

7. Add a magnetic stirring bar.

##### Extraction of Uranium and Plutonium

1. Add 10 ml of 20% TNOA-xylene to the beaker from step 7 in the previous subsection.

All operations given in this subsection for a sample are done in the same beaker. This minimizes transfer losses.

2. Stir vigorously for 3 min.

3. Allow 10 min for phase separation.

4. Remove the organic (upper) phase by suction with a micropipet connected to a recovery bottle.

See Figure 3.

Uranium and plutonium extract into the organic phase.

5. Repeat steps 1 through 4.

6. Add 2 ml of xylene, stir for 30 sec, and allow 5 min for phase separation.
7. Repeat step 4.
8. Withdraw the magnetic stirring bar from the beaker and rinse it with a small amount of water.
9. Evaporate the aqueous solution in the beaker to dryness in an evaporating chamber.

See Figures 2 and 3.

10. Add 2 ml of 6.7M HCl and a magnetic stirring bar.
11. Repeat steps 1 through 4.
12. Repeat steps 6 through 9.
13. Add 5 ml of methyl alcohol and evaporate to dryness in an evaporating chamber.

Boron volatilizes as methyl borate.

14. Add 1 ml of 15.6M HNO<sub>3</sub> and evaporate to dryness in an evaporating chamber.
  15. Heat in a muffle furnace for 30 min at 400°C.
- Organic matter is destroyed.
16. Add approximately 0.9 ml of 1M HCl, cover with a watch glass, and reflux on a hot plate for 10 min.
- Rare earth oxides formed in the ignition are dissolved.
17. Transfer the solution to a 1-ml volumetric flask with the aid of a few drops of 1M HCl rinses and make to volume with 1M HCl.

#### Electrode System

1. Transfer 50 μl of the solution obtained from step 17 of the last subsection in nearly equal portions to a pair of copper electrodes placed in a copper drying block and heat until the solution evaporates to dryness.

The electrode preparation is given in the section REAGENTS AND MATERIALS. Maintain the copper drying block at a temperature to evaporate the solution without spattering.

2. Place the loaded electrodes in a wood block and transfer them to the excitation glove box.

Mark the wood block to identify each electrode pair.

3. Place the atmosphere chamber in position in the spark stand.

See Figure 1.

4. Flow argon through the chamber at a rate of 4 l./min.
5. Place the electrodes in the electrode clamps of the spark stand and align the electrodes with an analytical gap of 2 mm.

Optical alignment is accomplished by observing the electrode images on a graduated scale of an auxiliary optical system.

#### Excitation and Exposure Conditions

1. Produce and record the spectra as follows:

##### Spark Parameters

Powerstat	44 V
Spark power setting	5
Capacitance	0.0025 μF.
	155 μH
Resistance (secondary)	Residual
RF current	4.8 A
Discharges per half cycle	11
Auxiliary air gap	3.5 mm

The parameter values may vary slightly from the values recommended here. The conditions, however, must be constant for all calibration blends and samples.

##### Exposure Conditions

Spectral region	3200 to 4400 Å
Emulsion	SA-3 plate
Slit width	15 μ
Exposure time	30 sec.
Rotating sector	50% T/20% T.

The two-step filter is useful for controlling the exposure range.

2. Make a single exposure of each sample and of each calibration blend.

##### Photographic Processing

1. Develop the plate or film for 5 min in Kodak D-19 developer at 20°C.
2. Place in an acetic acid shortstop batch for 15 sec.
3. Fix in a rapid fix for 5 min.
4. Wash in running water for 10 min.

5. Sponge and dry.

#### Microphotometry

1. Measure the percent transmittance, or optical density, of the analytical and internal standard line pairs, listed below, in the spectrograms of the calibration blends and the samples.

<u>Rare Earth</u>	<u>Analytical Line, Å</u>	<u>Yttrium Line, Å</u>
Sm	3634.29	3832.88
Eu	3724.94	3832.88
Gd	3768.39	3832.88
Dy	4000.48	3832.88

2. Also measure the background associated with all lines.

#### Calibration

1. Calibrate the emulsions by the Two-Step Preliminary Curve Method. [ 8]
2. Prepare a calibration curve for each element
  - a. Convert the percent transmittances of the lines and background measured for the calibration materials to intensities, using the emulsion calibration data.
  - b. Correct each line intensity for the background intensity.
  - c. Calculate the intensity ratios of the line pairs listed in the previous table.
  - d. Plot intensity ratio vs concentration ( $\mu\text{g/g}$ ) on log-log paper to obtain the calibration curve.

#### Calculation of Sample Results

1. Convert the percent transmittances of the lines and background for the sample to intensities.
2. Correct each line intensity for the background intensity.
3. Calculate the intensity ratios of the line pairs.
4. Convert the intensity ratios to concentration ( $\mu\text{g/g}$ ) using the appropriate calibration curve.

[ 8 ] "Recommended Practices for Photographic Photometry in Spectrochemical Analysis," ASTM Methods for Emission Spectrochemical Analysis, American Society for Testing Materials (1964), pp. 67-90.

## DETERMINATION OF URANIUM IN PLUTONIUM DIOXIDE BY SPECTROPHOTOMETRY

This method is issued on a tentative basis. Studies are in progress to improve it, especially that part related to the separation of the uranium from the plutonium. In its present form, the separation requires a two-cycle anion exchange treatment in which each exchange step uses large volume columns. The desired improvement is a faster separation, preferably with a single, small-volume column. When completed, the new method will be forwarded to each holder of this report.

### SUMMARY

Uranium is measured spectrophotometrically as the U(VI)-Arsenazo I colored complex following its separation from plutonium by anion exchange. The relative standard deviation is about 7% at uranium concentrations less than 500  $\mu\text{g/g}$  and improves to 1% at 3000  $\mu\text{g/g}$ .

### APPLICABILITY

This method is applicable to the determination of uranium at concentrations between 300 and 3000  $\mu\text{g/g}$  in ceramic grade plutonium dioxide. The method also is applicable to measurement of uranium at concentrations as low as 3  $\mu\text{g/g}$  provided suitable calibration materials are available. The set of calibration blends supplied by LASL is usable for the 300 to 3000  $\mu\text{g/g}$  concentration range. At the specification limits for impurities in ceramic grade plutonium dioxide, there are no interferences in the determination of uranium by this method. The recommended quantity of uranium for measurement is between 10 and 200  $\mu\text{g}$ . For the concentration range of 300 to 3000  $\mu\text{g/g}$ , a sample size of 70 mg is near ideal. Fourteen determinations, exclusive of dissolution, require about 16 hr. of elapsed time and an operator time of about 11 hr.

### RELIABILITY

The standard deviation is 30  $\mu\text{g/g}$  at a uranium concentration range between 500 and 3000  $\mu\text{g/g}$ , and 20  $\mu\text{g/g}$  at a concentration of 300  $\mu\text{g/g}$ . The recommended calibration materials are NBS  $\text{U}_3\text{O}_8$  (SRM 950) and a LASL-supplied calibration blend with a plutonium dioxide matrix.

## DISCUSSION OF THE METHOD

The major steps after dissolution of the sample are separation of the uranium from the plutonium by absorbing the uranium on anion exchange resin, addition of cyanide and EDTA to the uranium-containing effluent to mask nonseparated impurities, buffering of the solution to pH 7.9, addition of Arsenazo I, and spectrophotometric measurement. A highly colored chelate complex is formed in a ratio of 1 to 1 between uranyl ion and Arsenazo I. The reaction is complete at a pH of 8 to 9 and Beer's law is followed closely. [1] At a wavelength of 600 nm, the molar absorptivity is 23,000. [2]

Many metals besides uranium form highly colored complexes with Arsenazo I. Some of these metals, when present at low concentration, can be effectively masked by EDTA or sodium cyanide without adversely affecting the uranium-Arsenazo I color development. Interference from other actinide elements, however, cannot be controlled by masking reagents, and a quantitative separation of the uranium from other actinides is necessary. The separation factor for plutonium, the sample matrix element, must be exceedingly large because the molar absorptivity of the Pu(IV)-Arsenazo I complex is 21,000. [3]

Ion exchange resin and liquid-liquid extraction systems generally are favored for separating uranium and plutonium. In this method, U(VI) is absorbed on an anion exchange resin column from 12M HCl after reduction of plutonium to the nonabsorbed (III) oxidation state. Kraus and Nelson [4] report a distribution coefficient of 1000 for U(VI) between Dowex-1 resin and 12M HCl, while under the same conditions, the distribution coefficient for

[1] H. P. Holcomb and J. H. Yoe, *Anal. Chem.* **32**, 612 (1960).

[2] A. D. Hues and A. L. Henicksman, USAEC Report LA-3226 (1965).

[3] C. F. Metz and G. R. Waterbury, *Treatise on Analytical Chemistry*, Part II, Vol. 9, Kolthoff, Elving, and Sandell, Eds., Interscience, New York, N.Y. (1962), p. 309.

[4] K. A. Kraus and F. Nelson, *Proc. Intern. Conf. Peaceful Uses At. Energy*, Geneva, 1955, 7, 113 (1956).

Pu(III) is less than 1. [ 5] Effective separation is thus attained by reducing plutonium with a mixture of hydroxylamine hydrochloride and stannous chloride. The uranium is eluted from the column with 0.1M HCl, evaporated to dryness, and the separation is repeated to remove any nonreduced plutonium which had adsorbed on the first column. The recommended resin particle size is 100-200 mesh: larger resin particles permit the solution to flow too rapidly for complete uranium absorption. The resin is held conveniently in 10-cm columns with coarse glass frits.

Interferences in this method are few because of the effectiveness of the separation, and the use of complexing agents during the color development. At the impurity specification limits for ceramic grade plutonium dioxide, [ 6] the impurity most likely to interfere is iron; however, the specification limit of 250 µg/g for iron is less than one-half of the level where there is a significant interference. The specification limits of other impurities are well within the tolerance of the method.

Plutonium dioxide dissolves slowly in hot 15.6M HNO<sub>3</sub> with hydrofluoric acid present in low concentrations. The hydrofluoric acid acts catalytically for dissolution of plutonium dioxide and aids the dissolution of silica impurity. After dissolution, the sample is fumed with sulfuric acid to remove nitrate, which hinders the reduction of plutonium to the (III) oxidation state. The sealed-tube method of dissolution, described on p. 7, gives faster dissolution without the need for sulfuric acid fuming.

The sensitivity of the method permits the determination of as little as 10 µg of uranium with a standard deviation of 1 µg. Therefore a 70-mg sample may be used for a uranium concentration range of 300 to 3000 µg/g, which brackets the 2000 µg/g specification limit. If the 70-mg sample should contain more than 200 µg of uranium, a small aliquot of the final colored solution may be taken into another flask and diluted. More buffer

and Arsenazo reagent are added, the new solution is diluted to volume, and the absorbance is measured spectrophotometrically as in step 23. Being able to measure an aliquot of the colored solution in this manner is a real advantage and eliminates the need to repeat the analysis of a sample with an unusually high uranium content.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Special care must be taken when handling concentrated acids. As a minimum precaution, rubber gloves should be worn. When preparing dilute sulfuric acid solutions, always add the acid carefully to the water and not the reverse. Hydrofluoric acid is especially dangerous to the skin and will cause slow-healing ulcerating sores. Consult your laboratory safety manual for further information.

### APPARATUS

Columns, ion exchange, 1- x 10-cm. Seal a 1-cm diam x 10-cm-long filter tube with a coarse glass frit to the bottom of a 40-ml centrifuge cone and cut off the tube diagonally just below the frit. Fill the column to a height of 10 cm with Dowex 1-x 2 anion exchange resin, chloride form, 100-200 mesh. Wash the resin column with 50 ml of 12M HCl.

Dishes, platinum, 30-ml.

Spectrophotometer, Beckman, Model DU or equivalent, with matched 1-cm cells.

### REAGENTS

Ammonium hydroxide, 1M.

Arsenazo I, 0.05% aqueous solution. Purify the reagent [ 3-(2-arsenophenylazo)-4, 5-dihydroxy-2, 7-naphthalenedisulfonic acid, disodium salt] in the following manner. Add a saturated aqueous solution of the Arsenazo I to an equal volume of 12M HCl, filter the orange precipitate, wash with acetonitrile, and dry for 1 hr at 100°C.

Hydrochloric acid, 12M(37%), 0.1M.

Hydrofluoric acid, 28M(48%).

Hydroxylamine hydrochloride, 10% aqueous solution.

[ 5] R. D. Gardner and W. H. Ashley, USAEC Report LA-3551 (1966).

[ 6] RDT Standard E13-1, "Fast Flux Test Facility Ceramic Grade Plutonium Dioxide" (October 1970).

Nitric acid, 15.6M(70%).

Phenolphthalein solution, 0.025% in 1:1 water-ethanol solution.

Sodium cyanide, 5% aqueous solution.

Sulfuric acid, 6M.

Stannous chloride, 7% in 12M HCl. Prepare fresh daily.

Triethanolamine buffer-EDTA complexing solution. Dissolve 74.5 g of triethanolamine and 72 mg of the disodium salt of EDTA in a mixture of 750 ml of water and 14.0 ml of 15.6 M HNO<sub>3</sub>, and dilute to 1 l. Allow the solution to stand overnight before using.

Uranium calibration solution, 30 µg U/ml. Dissolve 35.40 mg of NBS U<sub>3</sub>O<sub>8</sub> (SRM 950) in 1 ml of 6M HNO<sub>3</sub> and dilute to 1 l. with 2M H<sub>2</sub>SO<sub>4</sub>.

Uranium calibration solution in plutonium dioxide matrix. Dissolve 700 mg of the LASL-prepared calibration blend that has a nominal uranium content of 300 µg/g, according to steps 1 through 5 in the subsection Sample Analysis. Dissolve the residue obtained in step 5 in 6M HCl and dilute to 100 ml with 6M HCl.

#### PROCEDURE

##### Blank

Determine the reagent blank in duplicate by starting at step 1 of the subsection Sample Analysis without a sample. If the measured absorbance is greater than zero at the .05 significance level, replace each reagent individually to determine the source of contamination.

##### Calibration

For the initial calibration of each analysis apparatus, pipet eight 10-ml aliquots of the uranium calibration solution in plutonium dioxide matrix into separate 30-ml platinum dishes and add 2 ml of 6M H<sub>2</sub>SO<sub>4</sub> to each. Add 2 ml of the uranium calibration solution to each of two dishes, 4 ml to each of two more dishes, and 6 ml to each of a third pair of dishes. This gives a set of duplicate calibration solutions with nominal uranium contents of 21, 81, 141, and 201 µg per dish. Analyze

each solution as described under subsection Sample Analysis, steps 5 through 23. Process the results using least-squares formulas to obtain the linear equation

$$y = Ax + B$$

that best fits the data. In this equation, y is the absorbance, x is the micrograms of uranium, A is the slope, and B is the intercept on the y axis. B should be approximately zero. Prepare a quality control chart for the values of A and B obtained for each analysis apparatus. Once each week during periods that samples are analyzed, verify the calibration by processing duplicate 10-ml aliquots of the uranium calibration solution in plutonium dioxide matrix plus 3-ml aliquots of the 30 µg U/ml uranium solution. (The nominal contents of each duplicate are 111 µg of uranium and 70 mg of plutonium dioxide). Pipet the aliquots into 30-ml platinum dishes and proceed through steps 5 through 23 in the Sample Analysis subsection. Calculate  $A' = y/x$  and plot it on the quality control chart for A. If an individual calibration value of A' disagrees at the .05 significance level with the value of A from the complete calibration set, investigate the cause for the difference and rectify the difficulty before proceeding with the analysis of samples.

##### Sample Analysis

1. Transfer an accurately weighed 70- mg sample into a 30-ml platinum dish.

This weight is recommended to cover the uranium concentration range of 300 to 3000 µg/g.

The sealed-tube technique, described on p. 5, will give faster dissolution rates and is recommended. If used, proceed to step 7.

2. Add 5 ml of 15.6M HNO<sub>3</sub>, 3 or 4 drops of 28M HF, and 0.5 ml of 6M H<sub>2</sub>SO<sub>4</sub>, then heat under an infrared lamp to fumes of sulfuric acid.

This dissolves the sample and volatilizes nitrate (see section DISCUSSION OF THE METHOD).

3. Add 2 ml of water to the residue, mix, and decant the supernatant solution into a 50-ml beaker.
4. Repeat steps 2 and 3 until the sample is completely dissolved.
5. Evaporate to dryness the combined solutions in the

50-ml beaker.

6. Dissolve the residue in 2 ml of 12M HCl.
7. Add 3 ml of 10% hydroxylamine hydrochloride solution, and warm the solution under an infrared lamp.  
Plutonium reduces to the (III) oxidation state, which is blue. If the solution is not blue, add more hydroxylamine hydrochloride solution and again warm the sample.
8. After the solution cools to room temperature, add 2 drops of stannous chloride solution.  
The stannous chloride helps prevent air oxidation of the Pu(III).
9. Prepare an ion exchange column for use by washing it with 20 ml of 12M HCl.
10. Add 10 ml of 12M HCl to the reduced solution, mix, and quantitatively transfer it to the ion exchange column with five 1-ml rinses of 12M HCl.  
The HCl concentration in the sample solution should be at least 9M.
11. Wash the column with five 5-ml portions of 12M HCl.  
Plutonium(III) elutes from the column.
12. Elute the uranium into a 50-ml beaker with six 5-ml portions of 0. 1M HCl.
13. Evaporate the eluted uranium solution to dryness.
14. Dissolve the residue in 2 ml of 12M HCl, add 10 drops of 10% hydroxylamine hydrochloride solution, and heat for 5 min.
15. After the solution cools to room temperature, add 2 drops of stannous chloride solution and 10 ml of 12M HCl, and mix.
16. Prepare a second ion exchange resin for use by washing it with 20 ml of 12M HCl.
17. Transfer the solution to the resin column with five 1-ml rinses of 12M HCl and repeat steps 11 through 13.
18. Dissolve the residue in 3 drops of 12M HCl and wash the sides of the beaker with water.
19. Add 4 drops of 5% sodium cyanide solution and 2 drops of phenolphthalein.

The cyanide complexes certain foreign ions which may have carried through the separation with the uranium.

20. Adjust the pH with 1M  $\text{NH}_4\text{OH}$  to the slightly pink color of the indicator.
21. Pipet 5 ml of triethanolamine buffer-EDTA complexing solution and 3 ml of 0.05% Arsenazo I solution into the sample solution.  
The buffer stabilizes the pH at 7.9 and the EDTA masks certain foreign ions which may have carried through the separation with the uranium.
22. Transfer the solution to a 25-ml volumetric flask and dilute to volume with water.
23. Allow the solution to stand for 1 hr, then measure the absorbance at 600 nm in a 1-cm cell against a reference prepared from the reagents starting at step 19.  
The 1-hr wait ensures maximum color development.

#### Calculations

$$R = \frac{Y - B}{AW},$$

in which

R = micrograms of uranium per gram of sample,

Y = absorbance of sample,

A, B = constants in the linear calibration equation,

W = weight, grams, of sample.

DETERMINATION OF TOTAL GAS IN MIXED OXIDE  
FUEL PELLETS AND URANIUM DIOXIDE INSULATOR

PELLETS  
(Method A)

SUMMARY

Uranium dioxide insulator and uranium-plutonium mixed oxide fuel pellets are heated inductively at 1600°C in a vacuum extraction apparatus to liberate volatiles. Water vapor is adsorbed from the released gases on anhydrous magnesium perchlorate; the remaining gases are collected with a Toepler pump; and the pressure, volume, and temperature of the collected gases are measured for the calculation of the volume at standard conditions.

APPLICABILITY

This method<sup>[1]</sup> is applicable to the measurement of volatiles other than water in uranium-plutonium mixed oxide fuel and uranium dioxide insulator pellets in which the specification limit for both materials is 0.09 STP cm<sup>3</sup> of total gas per gram of pellet.<sup>[2,3]</sup> This vacuum outgassing method uses a smaller calibrated volume than does the alternative method, given on p. 133, and hence provides greater sensitivity in the pressure measurement. Total gas is not a specification for either ceramic grade uranium dioxide or ceramic grade plutonium dioxide.

Interferences in the method are not expected with the exception of water in the sample which partially reacts with the tungsten crucible to produce hydrogen (see "Determination of Water by Thermal Evolution and Measurement with a Moisture Monitor," p. 139). The gases normally released from the two types of pellets obey the ideal gas laws sufficiently to permit simple ratio

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[1] D. E. Vance, M. E. Smith, and G. R. Waterbury, Los Alamos Scientific Laboratory, private communication (September 1970).

[2] RDT Standard E13-6 "Fast Flux Test Facility-Driver Fuel Pin Fuel Pellet" (October 1970).

[3] RDT Standard E13-7 "Fast Flux Test Facility-Driver Fuel Pin Insulator Pellet" (October 1970).

conversion of pressure and temperature to standard conditions.

The lower limit of the method using the described equipment and a ~1-g (one pellet) sample is 0.01 STP cm<sup>3</sup> per gram of sample and can be extended by using more than one pellet as the sample. The time required for five analyses is about 8 hr with one analyst.

RELIABILITY

The reliability of this method is not known because pellets having standardized volatile contents are not available. The pooled standard deviation obtained by seven laboratories for the analysis of one lot of mixed oxide pellets by the two methods described here and on p. 133 was 0.012 STP cm<sup>3</sup>/g.<sup>[4]</sup> This precision estimate included the between-pellet variability and the analytical measurement error. The mean gas content in the analyzed pellets was 0.050 STP cm<sup>3</sup>/g, so that the relative standard deviation was 24%.

DISCUSSION OF THE METHOD

A weighed pellet sample is transferred into the outgassing section of the apparatus in a position for subsequent dropping into a tungsten crucible. The system is evacuated and the tungsten crucible without the sample is outgassed at 1600°C until the "blank crucible" gas release during a 35-min collection period decreases to less than 0.01 cm<sup>3</sup> at STP conditions. After the crucible cools, the sample is dropped into it and heated at 1600°C for 35 min. The released gas passes through a magnesium perchlorate trap to remove water and thence into a calibrated volume where the temperature and pressure are measured. The gas content of the sample is calculated at STP conditions assuming that the released gas is ideal.

The gas measuring section of the apparatus, located outside the glove box containing the furnace, in-

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[4] J. E. Rein, R. K. Zeigler, and C. F. Metz, USAEC Report LA-4407 (1970).

cludes a Toepler pump and sample tube which can be used for collection of an aliquot of the gas for mass spectrometric or other type of analysis for gas composition.

One known source of error is the reaction of released water with the tungsten crucible to form hydrogen. However, tungsten crucibles are used because ceramics give a higher and more variable "blank" gas release that is not acceptable for the nominal low gas contents of mixed oxide pellets. Other metals or alloys of comparable cost to tungsten do not react with water appreciably less than does tungsten. The magnitude of this error, although unknown, probably is insignificant because of rapid removal of water vapor from the vicinity of the crucible.

Close attention to proper construction and maintenance of the apparatus is essential to obtain reliable results. Seals and valves must be high-vacuum tested and the entire system must be leak-tested when assembled. The vacuum pumps used must be maintained at a high level of efficiency. Because the nominal gas contents of the analyzed pellets are low, of the order of  $0.05 \text{ STP cm}^3/\text{g}$ , the requirement of attaining a stable crucible blank no greater than  $0.01 \text{ cm}^3$  for 35 min before analyzing the sample is essential for attaining reliable analyses.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

The gas measuring section of the apparatus should be located in a hood and the glass portions operating at high vacuum should be handled carefully to prevent breakage. Do not attempt to repair fragile components without bringing the system to ambient pressure.

Do not touch the furnace induction leads which can cause burns and electrical shocks.

### APPARATUS

Vacuum outgassing and gas measuring apparatus, see Figures 1, 2, and 3. The outgassing section (Figures 1 and 2) consists of a water-cooled, fused-silica

furnace tube heated with induction coils, and a pellet-loading arm with an externally operated magnet feed. A glass wool plug is placed in the line just after the furnace tube adapter to prevent transfer of small uranium-plutonium oxide particles outside the glove box.

The gas measuring section (Figure 3) consists of a mercury diffusion pump capable of transferring the gas against a forepressure equivalent to 5 Torr, a magnesium perchlorate trap to remove water, another mercury diffusion pump also capable of transferring against a forepressure equivalent to 5 Torr, a Toepler pump fitted with a removable calibrated-volume sample tube, and a McLeod gauge, a mercury diffusion pump, and a mechanical forepump.

The Toepler pump cycle is controlled by electrically timed solenoid valves in the vacuum and pressure lines. This method of control eliminates the possibility of reactions caused by electrical sparks in a system con-

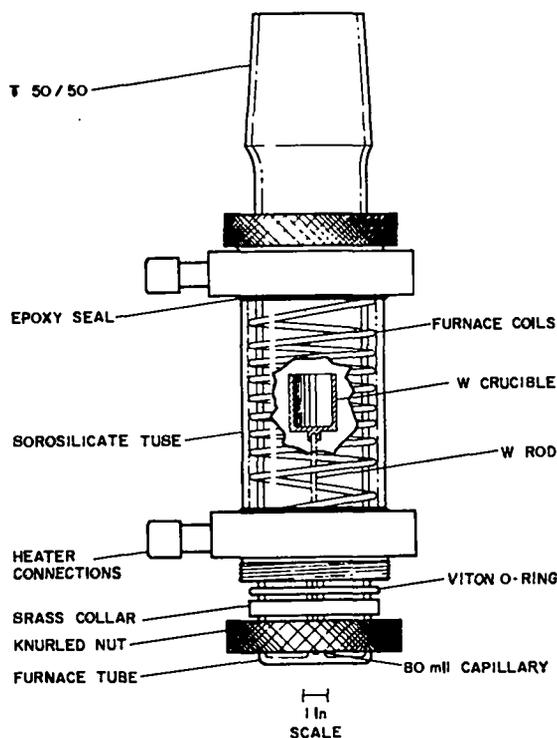


Figure 1. Induction furnace.

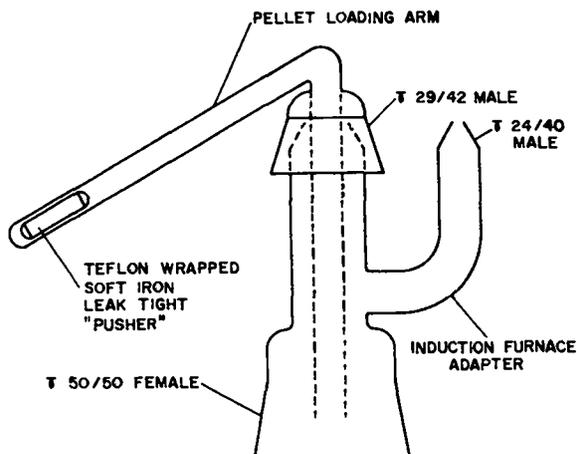


Figure 2. Furnace tube adapter and sample loader.

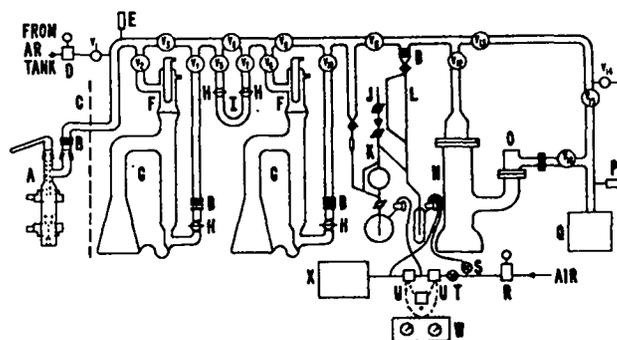


Figure 3. Outgassing and gas measuring apparatus; A, induction furnace; B, monel bellows; C, glove box wall; D, low-pressure regulator; E, thermocouple gauge; F, water-cooled condenser; G, mercury diffusion pumps; H, semi-ball joint; I, magnesium perchlorate (anhydrous) trap; J, calibrated sample volume; K, Toepler pump; L, McLeod gauge; M, mercury reservoir; N, mercury diffusion pump; O, water-cooled condenser; P, thermocouple gauge; Q, mechanical forepump; R, low-pressure regulator; S, needle valve; T, needle valve; U, solenoid valves; V, electric counter; W, electric timers; X, mechanical vacuum pumps.

trolled by mercury contacts. When the apparatus is not in use, keep the mechanical pump operating to maintain vacuum in the system.

#### REAGENTS

Silicone grease, high vacuum.

Magnesium perchlorate, anhydrous.

#### PROCEDURE

##### Blank

Determine a crucible blank for the entire system in operation before each and every sample. The procedure for the crucible blank is included in the Sample Analysis subsection.

##### Calibration

Two techniques can be used to calibrate the vacuum outgassing apparatus. One is to measure the

volume of the removable sample tube on the Toepler pump. The second and more accurate technique is to introduce known volumes of gas into the system through valve  $V_1$  in Figure 3 and measure these in the gas measuring section in the same manner as samples are measured. The calibration gas for this method can be hydrogen, usually a major component of the samples. A series of known volumes covering the range of the samples, in this case from 0.01 to  $\sim 0.2$  STP  $\text{cm}^3$ , is recommended for this method. This second technique takes into account slight losses in vacuum pumps.

##### Sample Analysis

Note: Accept results for samples only within the linear range of the calibration. Above the linear range, repeat

the analysis with a smaller sample.

1. Start the 3 diffusion pumps.

Refer to Figure 3 for all steps.

2. Close valves  $V_2$  and  $V_3$ .
3. Open valve  $V_1$  and flush the furnace tube with argon while the sample is being placed in the sample loader.
4. Transfer a weighed pellet into the arm of the sample loader.
5. Replace the sample loader on the furnace tube adapter, using silicon grease to make a seal.
6. Close valves  $V_1$ ,  $V_4$ ,  $V_5$ ,  $V_7$ ,  $V_8$ ,  $V_{10}$ ,  $V_{12}$ , and  $V_{16}$ .
7. Slowly open valve  $V_3$  to evacuate the system with mechanical pump Q.

Rapid opening of valve  $V_3$  will cause violent agitation of the mercury in the Toepler pump and possible breakage of the pump.

8. When the pressure indicated on thermocouple gauge, P, decreases to 0.5 Torr, open valves  $V_2$ ,  $V_4$ ,  $V_5$ ,  $V_7$ ,  $V_8$ ,  $V_{10}$ ,  $V_{12}$ , and  $V_{16}$ , and close valves  $V_3$ ,  $V_6$ ,  $V_9$ ,  $V_{13}$ , and  $V_{15}$ .
9. When the pressure decreases to less than 0.01 Torr, start the induction generator and slowly heat the crucible over approximately 4 hr to 1600°C.

A slow outgassing rate is required to prevent excessive coating of the furnace tube walls with tungsten oxides formed by the reaction between tungsten and water vapor. An excessive deposit will cause overheating of the O-ring seals and leakage of cooling water.

10. Heat the crucible at 1600°C for 0.5 hr, then close valve  $V_{11}$ , and adjust the pressure in the mercury reservoir M, using needle valve S, until mercury half-fills the side arm leading to the Toepler pump.
11. Turn on the Toepler pump timer, W, and collect the gas evolved from the crucible in the sample tube, J, for 70 cycles of the Toepler pump as registered on the counter, V.

The time required for collection is dependent on the construction of the Toepler pump. The use

of large-bore stopcocks and tubing will permit a cycle rate of 1 cycle/25 to 30 sec.

12. At the completion of the collection period, close the stopcock between the Toepler pump mercury reservoir and the expansion volume with the mercury at the top of its cycle.
13. Open valve  $V_{11}$  and raise the mercury in the side arm, by opening needle valve S, until the level reaches a predetermined calibration mark on the sample tube.
14. Measure the difference in heights of the columns of mercury in the sample tube and in the adjacent McLeod gauge, L.  
This difference is the total pressure of the collected gas.
15. Record the temperature of the sample tube and the pressure of the gas, and calculate the volume of the gas at STP conditions.
16. Evacuate the sample tube by turning the two-way stopcock on the mercury reservoir, M, to vacuum and lowering the level of mercury in the side-arm.
17. When a stable crucible blank of less than 0.01 cm<sup>3</sup> is attained, turn off the induction generator and allow the crucible to cool.
18. Transfer the sample pellet to the crucible by pushing it along the arm of the sample loader with an iron piece guided from outside with a magnet.
19. Close valve  $V_{11}$  and start the induction generator to heat the crucible and pellet to 1600°C.
20. Collect the evolved gases in the same manner as in the blank determination.
21. Turn off the induction generator and record the pressure and temperature of the sample tube.
22. If a gas sample is desired for a gas composition analysis, remove the sample tube and transfer it to the desired analytical apparatus.

The sample tube is fitted to the Toepler pump using a ground glass taper joint.

## CALCULATIONS

Case where the sample tube has been calibrated with a series of known volumes of gas.

Use least-squares formulas to calculate the best linear equation relating the introduced known volumes of gas in STP  $\text{cm}^3$  to the measured pressures in the sample tube in torr corrected to  $273^\circ\text{K}$ .

$$P_M = a + b (\text{STP cm}_I^3),$$

in which

$P_M$  = measured pressure in Torr corrected to  $273^\circ\text{K}$ ,

$$= \frac{273 P_O}{T_O + 273},$$

$a$  = intercept of least-squares equation,

$b$  = slope of least-squares equation.

$\text{STP cm}_I^3$  = known volumes introduced corrected to 760 Torr and  $273^\circ\text{K}$ ,

$$= \frac{P_O}{760} \cdot \frac{273 V_O}{273 + T_O},$$

where  $P_O$  = observed pressure,

$V_O$  = observed volume,

$T_O$  = observed temperature.

The sample result is:

$$\text{STP cm}_S^3/\text{g} = \frac{P_S - P_B}{bW},$$

in which

$\text{STP cm}_S^3/\text{g}$  =  $\text{cm}^3$  of total gas per gram of sample at 760 Torr and  $273^\circ\text{K}$  ( $0^\circ\text{C}$ ),

$P_S$  = measured pressure for sample in Torr corrected to  $273^\circ\text{K}$ ,

$P_B$  = pressure for blank in Torr corrected to  $273^\circ\text{K}$ ,

$a$  = intercept of least-squares equation,

$b$  = slope of least-squares equation,

$W$  = weight of sample, g.

Case where the volume of the sample tube has been measured.

Calculate the total gas content of the pellet by:

$$\text{STP cm}_S^3/\text{g} = \frac{\frac{273 P_S V}{760 T_S} - \frac{273 P_B V}{760 T_B}}{W},$$

in which

$\text{STP cm}_S^3/\text{g}$  =  $\text{cm}^3$  of total gas per gram of sample at 760 Torr and  $273^\circ\text{K}$  ( $0^\circ\text{C}$ ),

$P_S$  = recorded pressure, Torr, for sample,

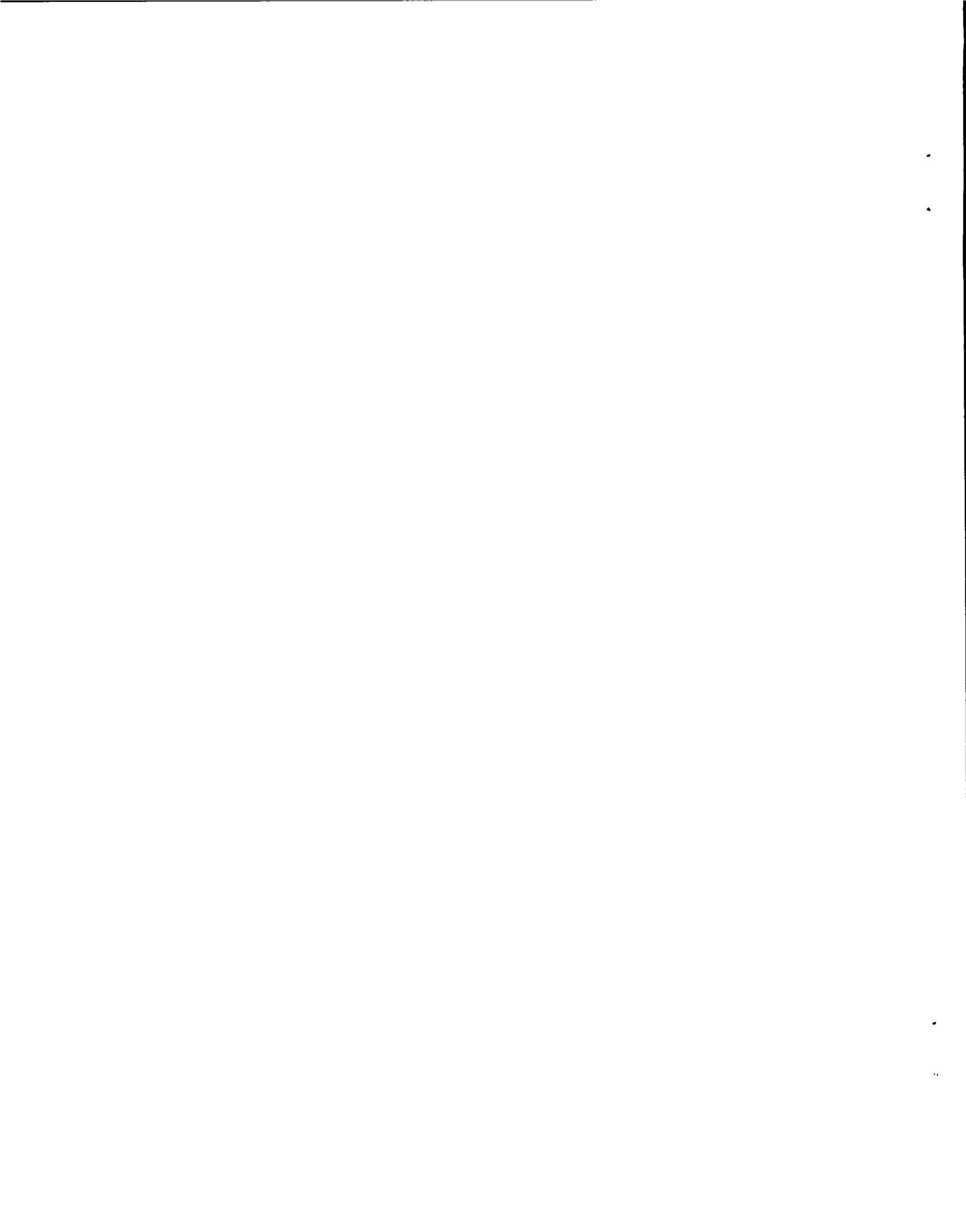
$V$  = measured volume,  $\text{cm}^3$ , of sample tube,

$T_S$  = recorded temperature of sample tube, for sample gas,  $^\circ\text{K}$  ( $^\circ\text{C} + 273$ ),

$P_B$  = pressure, Torr, for blank,

$T_B$  = recorded temperature of sample tube for blank,  $^\circ\text{K}$ ,

$W$  = weight of pellet, g.



DETERMINATION OF TOTAL GAS IN MIXED OXIDE  
FUEL PELLETS AND URANIUM DIOXIDE INSULATOR

PELLETS  
(Method B)

SUMMARY

Uranium dioxide insulator and uranium-plutonium mixed oxide fuel pellets are heated inductively at 1600°C in a vacuum furnace, the released gas passes through a magnesium perchlorate trap to adsorb water, the pressure and temperature of the remaining gas are measured in a calibrated volume, and the volume is corrected to STP conditions.

APPLICABILITY

This method<sup>[1]</sup> is applicable to the measurement of volatiles other than water in insulator and uranium-plutonium mixed oxide fuel pellets in which the specification limit for both materials is 0.09 STP cm<sup>3</sup> of total gas per gram of pellet.<sup>[2,3]</sup> An alternative vacuum outgassing method, using a different gas measurement system consisting of a smaller calibrated volume and a Toepler pump, is given on p. 127 for this same purpose. Total gas is not a specification for either ceramic grade uranium dioxide or ceramic grade plutonium dioxide; this method can be used, however, for such materials and the equipment will accept powdered samples.

Interferences in the method are not expected, with the exception of water in the sample that partially reacts with the tungsten crucible to produce hydrogen (see "Determination of Water by Thermal Evolution and Measurement with a Moisture Monitor, p. 139). The gases normally released from the two types of pellets obey the ideal gas laws sufficiently to permit simple

ratio conversion of pressure and temperature to standard conditions.

The lower limit of the method using the described equipment and an ~ 1-g (one pellet) sample is 0.03 STP cm<sup>3</sup> per gram of sample and can be extended by using more than one pellet as the sample. The upper limit is dependent on the type of vacuum measurement gauges. The time required for a group of six analyses is about 8 hr with one analyst.

RELIABILITY

The reliability of this method is not known because pellets having standardized volatile contents are not available. The pooled standard deviation obtained by seven laboratories for the analysis of one lot of mixed oxide pellets by the two methods described here and on p. 129 was 0.012 STP cm<sup>3</sup>/g.<sup>[4]</sup> This precision estimate included both the between-pellet variability and the analytical measurement error. The mean value for the total gas in the analyzed pellets was 0.050 STP cm<sup>3</sup>/g, so that the relative standard deviation was 24%. The analytical measurement error is 7% relative standard deviation<sup>[1]</sup> indicating that the major source of variability is the between-pellet differences.

DISCUSSION OF THE METHOD

A weighed pellet sample is placed in the apparatus in a position for subsequent drop into a tungsten crucible. The system is evacuated to 0.001 Torr and the tungsten crucible without the sample is outgassed at 1600°C until the "blank crucible" gas release rate decreases to less than 0.001 Torr/min. The sample is dropped into the crucible after it cools, and reheated at 1600°C until the gas release rate becomes equal to that of the crucible blank. The released gas passes through a magnesium perchlorate trap to remove water and thence into a calibrated volume where the temperature and pressure are measured. The gas content of the sample is calculated at STP conditions assuming that the released gas is ideal.

[1] M. C. Burt, Method 20.6, USAEC Report WHAN-IR-5 (August 1970).

[2] RDT Standard E13-6 "Fast Flux Test Facility Driver Fuel Pin Fuel Pellet" (October 1970).

[3] RDT Standard E13-7 "Fast Flux Test Facility Driver Fuel Pin Insulator Pellet" (October 1970).

[4] J. E. Rein, R. K. Zeigler, and C. F. Metz, USAEC Report LA-4407 (1970).

The furnace section of the apparatus usually is located in a glove box and, if desired, may include provisions for powder samples. The gas measuring section of the apparatus, located outside the glove box, can include a Toepler pump and bulb for collection of an aliquot of the gas for mass spectrometric or other technique for the analysis of gas composition.

One known source of error is the reaction of released water with the tungsten crucible to form hydrogen. Tungsten crucibles are used, however, because ceramics give a higher and more variable "blank" gas release that is not acceptable for the nominal low gas contents of the materials to which the method applies. Other metals, or alloys of comparable cost to tungsten, do not react with water appreciably less than does tungsten. The magnitude of this error, although unknown, probably is insignificant because of rapid removal of water vapor from the vicinity of the crucible.

Close attention to proper construction and maintenance of the apparatus is essential to obtain reliable results. Seals and stopcocks must be high-vacuum tested and the entire system must be leak-tested when assembled. The vacuum pumps used must be maintained at a high level of efficiency. Because the nominal gas contents of the pellets are expected to be low, of the order of 0.05 STP  $\text{cm}^3/\text{g}$ , it is very important that the crucible blank release rate must be no greater than 0.001 Torr/min before proceeding with the analysis of the sample.

#### OPERATING INSTRUCTIONS

##### SAFETY PRECAUTIONS

The gas measuring section of the apparatus should be located in a hood and the glass portions operating at high vacuum should be handled carefully to prevent breakage. Do not attempt to repair components such as frozen stopcocks without bringing the system to ambient pressure.

Do not touch the furnace induction leads which can cause burns and electrical shocks.

#### APPARATUS

The apparatus described in this method is illus-

trated in Figures 1, 2, and 3. The outgassing section (Figures 1 and 2) consists of a water-cooled, fused-silica furnace tube heated with induction coils, a pellet loading arm with an externally operated magnet feed, a magnet driven device for raising and lowering the crucible into the furnace, and a high-speed mercury diffusion pump for transferring the gas to the gas measuring section located outside the glove box. A quartz wool plug is placed in the line just after the mercury diffusion pump to prevent transfer of small uranium-plutonium oxide particles outside the glove box. The furnace section also includes the means for loading a powder sample.

The gas measuring section (Figure 3) consists of a roughing mechanical pump, a magnesium perchlorate trap to remove water, a mercury diffusion pump with capability of transferring the gas against a 5-Torr forepressure, and the gas measuring components. These components include three (McLeod, thermocouple, and ionization) vacuum gauges, an expansion volume, a Toepler pump and removable sample bulb for gas composition analysis, a cold trap, and a polyphenylether diffusion pump exhausting to a mechanical pump.

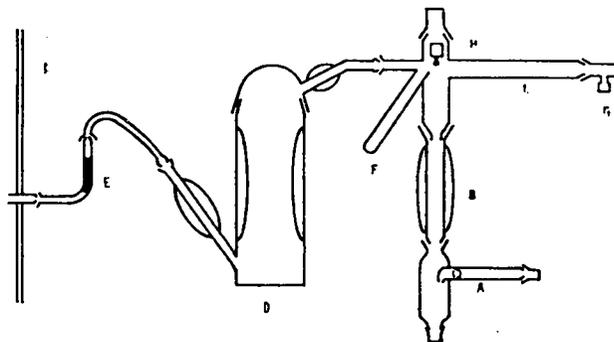


Figure 1. Outgassing section: A, powder loading device; B, furnace tube; C, pellet loading arm; D, mercury diffusion pump; E, quartz wool plug; F, magnet arm; G, thermocouple gauge; H, hook and pulley; I, glove box wall.

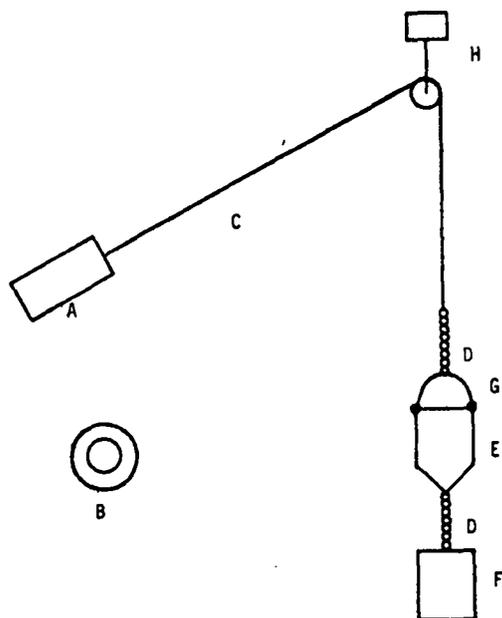


Figure 2. Crucible raising and lowering device: A, magnet (located in arm "F," Figure 1); B, ring magnet (around "A" - outside glass arm); C, gold chain; D, tantalum chain; E, tungsten crucible; F, nickel cylinder; G, tantalum ball; H, hook and pulley (see "H," Figure 1).

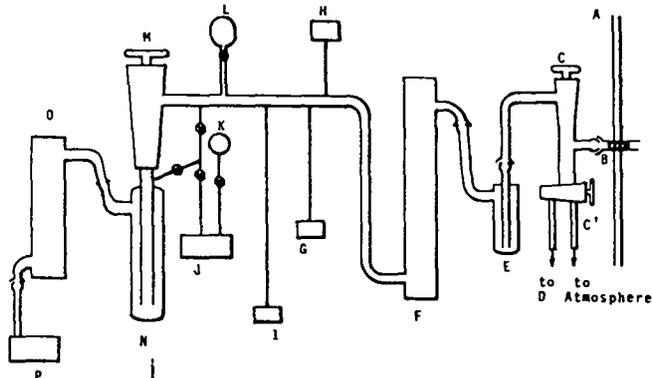


Figure 3. Gas measuring section: A, glove box wall; B, quartz wool plug; C, stopcocks (C and C'); D, mechanical pump; E, magnesium perchlorate trap; F, mercury diffusion pump; G, McLeod gauge; H, thermocouple gauge; I, ionization gauge; J, Toepler pump; K, sampling bulb; L, calibrated expansion bulb; M, stopcock; N, cold trap; O, oil diffusion pump; P, mechanical pump.

## REAGENTS

Liquid nitrogen

Magnesium perchlorate, anhydrous

## PROCEDURE

### Blank

Determine the crucible blank for the entire system in operation before each and every sample. The procedure for the crucible blank is included in the Sample Analysis subsection.

### Calibration

Two techniques can be used to calibrate vacuum outgassing apparatus. One is to measure the volume of each component, in this case from the mercury diffusion pump designated F up to the stopcock designated M in Figure 3, then add these to obtain the total volume. The second and more accurate technique is to introduce known volumes of gas into the system such as at point C' in Figure 3 and measure these in the gas measuring section in the same manner as samples are measured. The calibration gas for this method can be hydrogen, usually a major component of the samples. A series of known volumes covering the range of the samples, in this case from 0.01 to  $\sim 0.2$  STP  $\text{cm}^3$ , is recommended for this method. This second technique takes into account all perturbations in the system including hard-to-measure volumes, slight losses in vacuum pumps, and nonlinear vacuum gauge responses. It is further recommended that the calibration be verified at no less than monthly intervals.

### Sample Analysis

NOTE: Operate the mechanical vacuum pump continuously to keep the system evacuated, extending through periods when it is not in use. Accept results for samples only within the linear range of the calibration. Above the linear range, repeat the analysis with a smaller sample.

1. Start the diffusion pumps F and O.

Refer to Figure 3 for steps 1 through 4.

2. Fill cold trap N with liquid nitrogen.
3. Close stopcock C.
4. Vent the apparatus inside the glove box through stopcock C'.
5. Transfer a weighed pellet into arm C.  
Refer to Figure 1.
6. Seal the end caps with black wax and allow to cool.
7. Evacuate the system through stopcock C' with mechanical pump D.  
Refer to Figure 3.
8. Start diffusion pump D when the pressure decreases to 0.5 Torr.  
Refer to Figure 1.
9. Close stopcock C' and open stopcock C to connect the outgassing and gas measuring sections.
10. When the pressure decreases to less than 0.001 Torr, start the induction generator to heat the crucible at 1600°C.
11. After 5 min, close stopcock M, observe the crucible outgassing rate, and open stopcock M.
12. Repeat step 11 until the crucible outgassing rate decreases to less than 0.001 Torr/min, at which time the blank measurement is started.
13. Close stopcock M to start the measurement of the blank.
14. Record the pressure every 5 min until the outgassing rate becomes constant.
15. Turn off the induction generator, record the pressure and temperature of the gas measuring system, and open stopcock M.
16. Allow the crucible to cool, then raise it to the funnel mouth at the top of the furnace.
17. Transfer the sample pellet to the crucible by pushing it along arm C with an iron rod guided from outside with a magnet.
18. Lower the crucible and pellet into the heating position.

19. Close stopcock M and start the induction generator to heat the crucible and pellet at 1600°C.
20. Record the pressures every 5 min until the outgassing rate equals that of the blank.  
This normally requires a total of 30 min.
21. Turn off the induction generator and record the pressure and temperature of the gas measuring system.
22. If a gas sample is desired for a gas composition analysis, open the stopcock to Toepler pump J and collect gas in bulb K.  
Refer to Figure 3.
23. Open stopcock M.  
This evacuates the system.
24. After the crucible cools, drop the spent sample to the bottom of A with the aid of nickel cylinder F and external magnet manipulation.

### CALCULATIONS

Case where the system has been calibrated with a series of known volumes of gas.

Use least-squares formulas to calculate the linear equation relating the introduced known volumes of gas in STP  $\text{cm}^3$  and the measured pressures in the system in Torr corrected to 273°K.

$$P_M = a + b (\text{STP cm}_I^3),$$

in which

$$P_M = \text{pressure in Torr corrected to } 273^\circ\text{K},$$

$$= \frac{273 P_O}{273 + T_O},$$

a = intercept of least-squares equation,

b = slope of least-squares equation,

$$\text{STP cm}_I^3 = \text{known volumes introduced, corrected to } 760 \text{ Torr and } 273^\circ\text{K},$$

$$= \frac{P_O}{760} \cdot \frac{273 V_O}{273 + T_O},$$

where  $P_O$  = observed pressure ,  
 $T_O$  = observed temperature ,  
 $V_O$  = observed volume .

$T_B$  = recorded temperature of gas measuring  
system for blank,  $^{\circ}\text{K}$  ,  
 $W$  = weight of pellet, g .

The sample result is:

$$\text{STP cm}^3/\text{g} = \frac{P_S - P_B}{bW} ,$$

in which:

$\text{STP cm}^3/\text{g} = \text{cm}^3$  of total gas per gram of  
sample at 760 Torr and  $273^{\circ}\text{K}$  ( $0^{\circ}\text{C}$ ),

$P_S$  = measured pressure for sample  
in Torr corrected to  $273^{\circ}\text{K}$ ,

$P_B$  = pressure for blank in Torr  
corrected to  $273^{\circ}\text{K}$  and calculated  
for a collection time equal to that  
of the sample ,

$a$  = intercept of least-squares equa-  
tion ,

$b$  = slope of least-squares equation,

$W$  = weight of sample, g.

Case where the volume of the system has been calculated

Calculate the total gas content of the pellet by:

$$\text{STP cm}^3/\text{g} = \frac{\frac{273 P_S V}{760 T_S} - \frac{273 P_B V}{760 T_B}}{W} ,$$

in which:

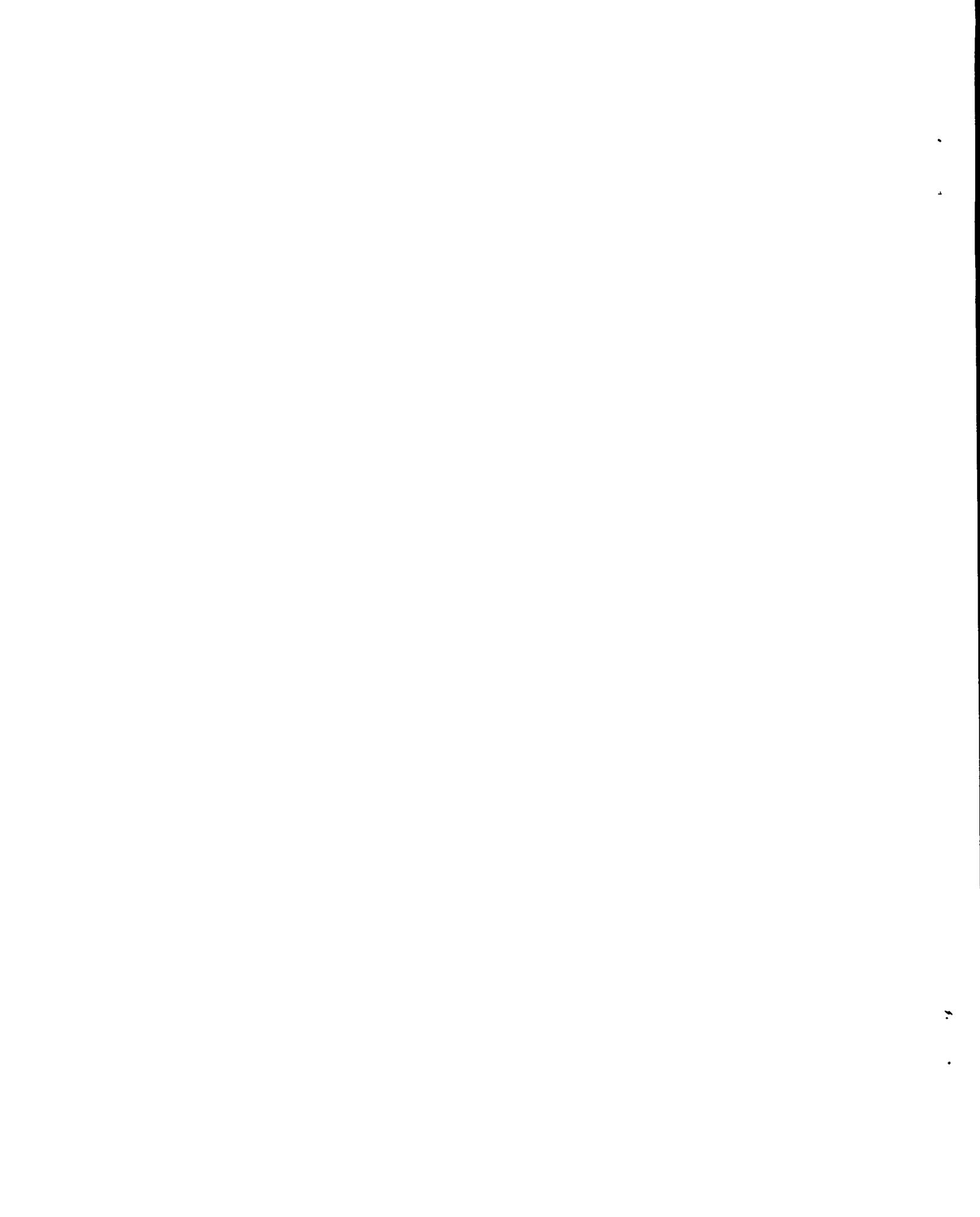
$\text{STP cm}^3/\text{g} = \text{cm}^3$  of total gas per gram of sample  
at 760 Torr and  $273^{\circ}\text{K}$  ( $0^{\circ}\text{C}$ ),

$P_S$  = recorded pressure, Torr, for  
sample,

$V$  = calculated volume,  $\text{cm}^3$ , of system,

$T_S$  = recorded temperature of gas mea-  
suring system for sample,  $^{\circ}\text{K}$ , ( $^{\circ}\text{C}$   
+ 273) ,

$P_B$  = pressure, Torr, for blank calculated  
for a collection time equal to that of  
the sample ,



DETERMINATION OF WATER BY THERMAL  
EVOLUTION AND MEASUREMENT WITH A  
MOISTURE MONITOR

SUMMARY

Whole uranium-plutonium mixed oxide pellets, uranium dioxide insulator pellets, and ceramic grade uranium dioxide powder are heated at 400°C and the evolved water is measured with a moisture analyzer. Preliminary heating at 110°C removes water adsorbed during normal room temperature storage conditions. The relative standard deviation is 4% at a water level of 8.5 µg per sample.

APPLICABILITY

This method<sup>[1]</sup> is applicable to the determination of water in uranium-plutonium mixed oxide fuel pellets, uranium dioxide insulator pellets, and ceramic grade uranium dioxide. The stated specification limits are 30 µg/g for a lot of pellets and 50 µg/g for individual pellets for uranium-plutonium mixed oxide fuel<sup>[2]</sup> and for uranium dioxide insulator pellets.<sup>[3]</sup> The specification limit is 0.5 wt % for ceramic grade uranium dioxide.<sup>[4]</sup> A specification for water is not given for ceramic grade plutonium dioxide; rather, it is determined as one of the components in the specification analysis for total volatiles (see "Determination of Total Volatiles in Ceramic Grade Plutonium Dioxide and Sample Preparation of Plutonium Dioxide for Impurity Analysis," p. 145).

The calibrated range of the method is 0 to 100 µg of water, designed for the specification analysis of single pellets of uranium-plutonium mixed oxide and uranium

dioxide, whose weight is approximately 1 g. For ceramic grade uranium dioxide with higher levels of water, a smaller sample of 10 to 20 mg is used.

The estimated time for a series of six samples and two calibration verifications is an 8-hr shift with one analyst and one apparatus setup.

RELIABILITY

Because no standardized samples of uranium-plutonium oxide are available that contain known amounts of water the reliability of this method, or of any method for the determination of water in such materials, cannot be obtained. The relative standard deviation, obtained from calibration data (see Calibration subsection), was 19% at 1 µg of water and 4% at 8.5 µg of water. The difficulty of delivering microliter quantities of calibration material may account for a significant part of this uncertainty. The accuracy of the method is difficult to evaluate because completeness of water release as a function of temperature and time is not well characterized. As discussed in the next section a temperature of 400°C seems to give the most accurate results.

DISCUSSION OF THE METHOD

Because uranium and plutonium oxide materials are hygroscopic, sample storage conditions such as relative humidity, length of storage, and temperature of storage may introduce significant errors. This was demonstrated by an experiment in which three mixed oxide fuel pellets were heated at 600°C and then stored in different environments and analyzed for adsorbed water.<sup>[5]</sup> The results, summarized in Table I, clearly show that adsorption of atmospheric moisture is significant and is directly proportional to the moisture content of the atmosphere in which the pellets are stored.

The second variable of prime importance to the method of analysis is the temperature selected for volatilizing the water. Experimental data obtained at LASL<sup>[5]</sup>

[1] D. E. Vance, M. E. Smith, and G. R. Waterbury, Los Alamos Scientific Laboratory, private communication (September 1970).

[2] RDT Standard E13-6 "Fast Flux Test Facility Driver Fuel Pin Fuel Pellet" (October 1970).

[3] RDT Standard E13-7 "Fast Flux Test Facility Driver Fuel Pin Insulator Pellet" (October 1970).

[4] RDT Standard E13-2 "Fast Flux Test Facility Ceramic Grade Uranium Dioxide" (October 1970).

[5] D. E. Vance, M. E. Smith, and G. R. Waterbury, USAEC Report LA-4546-MS (1970), pp. 25-6.

Table I

EFFECT OF STORAGE CONDITIONS ON ADSORPTION  
OF ATMOSPHERIC MOISTURE BY URANIUM-  
PLUTONIUM MIXED OXIDE PELLETS PREVIOUSLY  
HEATED TO 600°C

<u>Storage Conditions</u>	<u>µg of Water per g of Pellet Released at 400°C</u>
1. Sealed in a desiccator containing magnesium perchlorate for 28 hr.	< 0.1
2. Sealed in a desiccator containing magnesium perchlorate for 24 hr and then placed in a dry box with an air atmosphere at 40% relative humidity for 24 hr.	0.7
3. Sealed over water in a container for 24 hr.	3.4

with uranium-plutonium mixed oxide pellets previously stored in a glove box with an air atmosphere of about 50% relative humidity show an immediate release of water when pellets are placed in a furnace at 200°C. As the temperature increases there is no further change until 280 to 300°C, when a second release occurs that is complete at about 400°C. No further release is obtained between 400°C and 950°C. This indicates that two states of water, one weakly bound and the other more tightly bound, are present in the pellets.

The weakly bound state undoubtedly also contains water adsorbed on the surface of the pellets from the air. In the absence of well-defined storage conditions for pellets, the amount adsorbed will vary in a manner dependent on the storage history of the pellets and thus introduce a variable bias in the determination of the bound water. From the viewpoint of a practical and meaningful analysis, it has been found that the pellets should be heated at 110°C for 2 hr to remove this surface-adsorbed water, stored in a desiccator until analyzed, and heated at 400°C for

the analysis. These conditions are prescribed for this method. In addition to giving an accurate measure of bound water, these conditions will eliminate the effects of variable conditions of preanalysis storage, whether at the shipper's facility, in transit, or at the fuel fabricator. Most important, all laboratories will be on a common basis for the analysis, and differences between fuel fabricator and receiver will be minimized.

The initial heating at 110°C is not prescribed for ceramic grade uranium dioxide for two reasons. It is a powder with a large surface area to volume ratio and the specification limit of 0.5 wt % water is much greater than are the specification limits for the two types of pellets.

The method includes other features designed to produce reliable results. The apparatus is calibrated by injecting a series of known quantities of hydrogen which converts to water by passage through a tube furnace containing copper oxide at 500°C. A crucible is not used to contain the sample, but instead the sample is dropped directly onto a bed of silica always maintained at 400°C in the furnace. This eliminates the need for obtaining a blank value. Tungsten crucibles may react with released water from the sample at 400°C to produce hydrogen; platinum crucibles do not react. Ceramic crucibles, exposed to the atmosphere, adsorb water and require a preheating period for each analysis. The argon sweep gas, before contact with the sample, is passed through a Molecular Sieve 5A column to remove traces of water and then through a tube containing uranium metal turnings at 650°C to remove traces of oxygen. Oxygen is removed because it may react with hydrogen either present in the sample or released from such apparatus components as the silica tube in the furnace to produce traces of water.

#### OPERATING INSTRUCTIONS

##### SAFETY PRECAUTIONS

In addition to the general precautions presented in the INTRODUCTION of this report, the glove box installation must be designed for furnace operation including protection of personnel and the burning of gloves.

## APPARATUS

Combustion train, see Figures 1, 2, and 3.

Desiccator containing magnesium perchlorate or equivalent desiccant.

Moisture analyzer, CEC Model 26-303, or equivalent, with strip chart potentiometric recorder output.

Oven, 110°C operation, for initial drying of pellet samples.

Planimeter. An electronic integrator, such as Infotronics Model CRS-100T, may be used instead.

## REAGENTS

Argon sweep gas. Nitrogen gas may be substituted.

Cupric oxide, wire-form.

Hydrogen, high-purity.

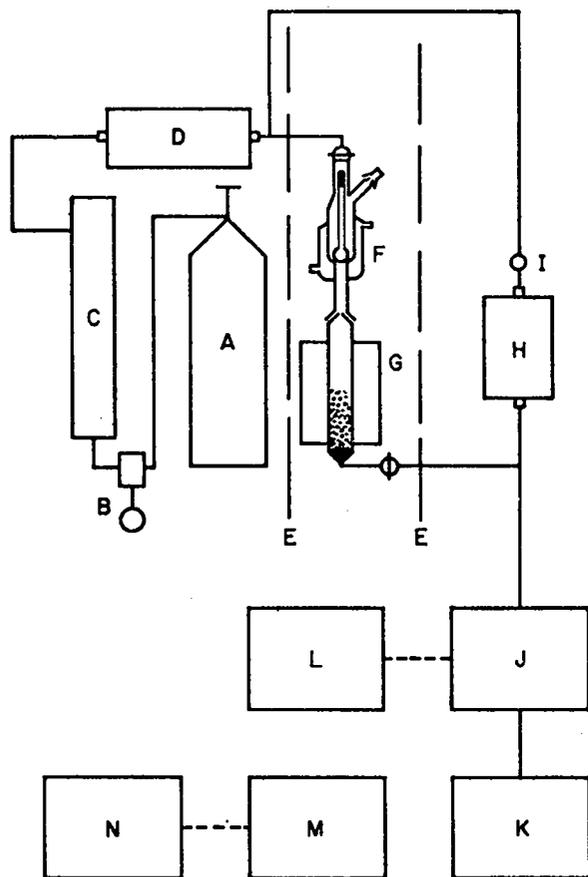


Figure 1. Layout of system components.

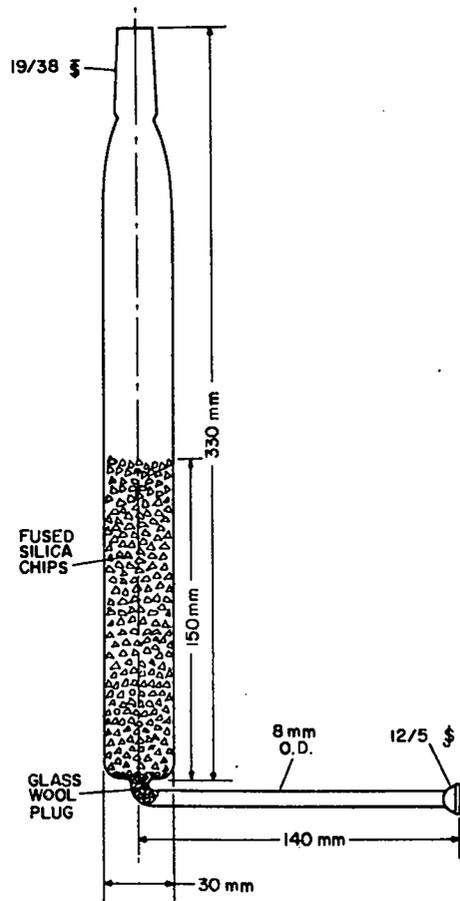


Figure 2. Fused silica furnace tube for heating samples.

Magnesium perchlorate, anhydrous.

Tin foil for containment of ceramic grade uranium dioxide powder samples. Small tin capsules, available from the Leco Company, are conveniently used for this purpose.

Uranium turnings, natural or depleted.

## PROCEDURE

### Blank

A blank measurement is not required provided that the combustion furnace is maintained at the operating temperature of 400°C, that argon is swept through the system continuously or at least 12 hr prior to the analysis of samples, and that the Molecular Sieve 5A column

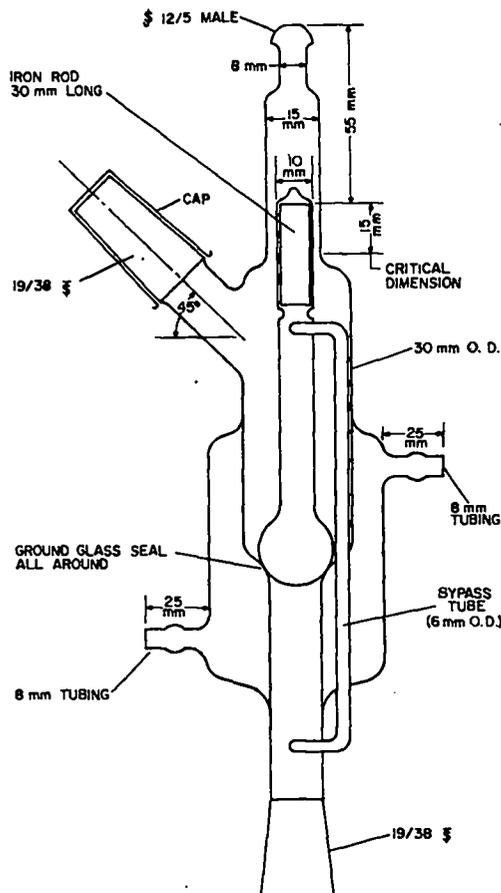


Figure 3. Sample dropper.

and the furnace containing the uranium metal turnings are kept in prime condition. Verify at least weekly that the system is giving an insignificant blank value by passing the argon sweep gas through the system for 30 min and recording the water release.

Ceramic grade uranium dioxide samples are packaged in tin foil or capsules before transfer to the furnace. Keep the foil or capsules in a desiccator until just before use. Determine a blank on each batch of foil or capsules after desiccator storage for at least 24 hr. Periodic measurement of this blank is not necessary if the blank is small compared to sample values and if the atmospheric conditions do not change after the foil or capsules are removed from the desiccator.

### Calibration

Process three each of at least six different volumes of hydrogen gas between 1  $\mu\text{l}$  and 100  $\mu\text{l}$  by injecting them into the septum with chromatographic micro-pipets and flowing them through the cupric oxide furnace at 500°C (see Figure 1).

Calculate the equivalent micrograms of water injected by:

$$\begin{aligned} \mu\text{g H}_2\text{O} &= \frac{(18)(273)(P)(\mu\text{lH}_2)}{(760)(22.4)(T)}, \\ &= \frac{0.289(P)(\mu\text{lH}_2)}{T}, \end{aligned}$$

in which

P = atmospheric pressure, Torr,

$\mu\text{l H}_2$  = microliters of hydrogen injected,

T = ambient temperature, °K(°C + 273).

Compute a least-squares, linear calibration equation:

$$A = B + m(\mu\text{g H}_2\text{O}),$$

in which

A = integrated area from recorder output,

B = intercept value,

m = slope value,

$\mu\text{g H}_2\text{O}$  = equivalent micrograms of water injected.

Verify this equation each shift during periods when samples are analyzed by processing two hydrogen gas injections, such as 10 and 50  $\mu\text{l}$ . Maintain a quality control chart for these verification results. If the results from both injections do not agree with the least-squares linear equation within the .05 significance level, investigate the cause for the difference, rectify the difficulty before analyzing samples, and prepare a new calibration if necessary.

### Sample Analysis

NOTE: Before analyzing samples, start the cooling water flow to the sample dropper and sweep argon through the system at a flow rate of 100  $\text{cm}^3/\text{min}$  with the

furnace operating at 400°C until the base line stabilizes. The output of the integrator, if used, must be essentially zero before analyzing samples (see subsection Blank). If not, rectify the difficulty.

1. Heat a weighed uranium-plutonium mixed oxide or uranium dioxide insulator pellet at 110°C for 1 hr and immediately transfer the pellet to the water analysis apparatus or to a desiccator containing anhydrous magnesium perchlorate.

This step removes surface adsorbed moisture (see DISCUSSION OF THE METHOD). The pellet is weighed before heating because water may be reabsorbed if the pellet were exposed to an ambient atmosphere when cool. The loss in weight of the surface moisture does not significantly affect the calculation of the final results.

2. Transfer a surface-dried pellet from the desiccator or a weighed 10- to 20-mg sample of ceramic grade uranium dioxide wrapped in a piece of tin foil or placed in a tin capsule to the sample dropper.

Refer to Figure 3.

Store the tin foil or capsules in a desiccator. The atmosphere in which the sample is weighed and placed in the tin foil or capsule must be maintained at a consistent relative humidity and temperature to maintain a consistent adsorption of atmospheric moisture (see Blank subsection).

3. Position the cap over the sample dropper, flush the cap with argon set at a flow rate of 100 cm<sup>3</sup>/min for at least 30 sec, then cap the dropper.
4. Start the moisture monitor and potentiometric recorder and observe the baseline trace.
5. When the baseline trace has stabilized, drop the sample into the furnace set at 400°C.

The time required for baseline stabilization usually is about 3 min.

6. Continue the analysis until the potentiometric recorder trace returns to the previously recorded baseline for at least 1 min.

The usual time of heating for pellet samples is 30 to 45 min.

#### Calculations

Measure the integrated area on the potentiometric

recorder scan with a planimeter or with an electronic integrator for each sample.

Calculate the micrograms of water per gram of pellet sample by:

$$\mu\text{g H}_2\text{O/g} = \frac{A_S - B}{mW},$$

in which

$A_S$  = integrated area from recorder output,

$B$  = intercept value from the least-squares linear calibration equation,

$m$  = slope value from the least-squares linear calibration equation,

$W$  = weight of sample, g.

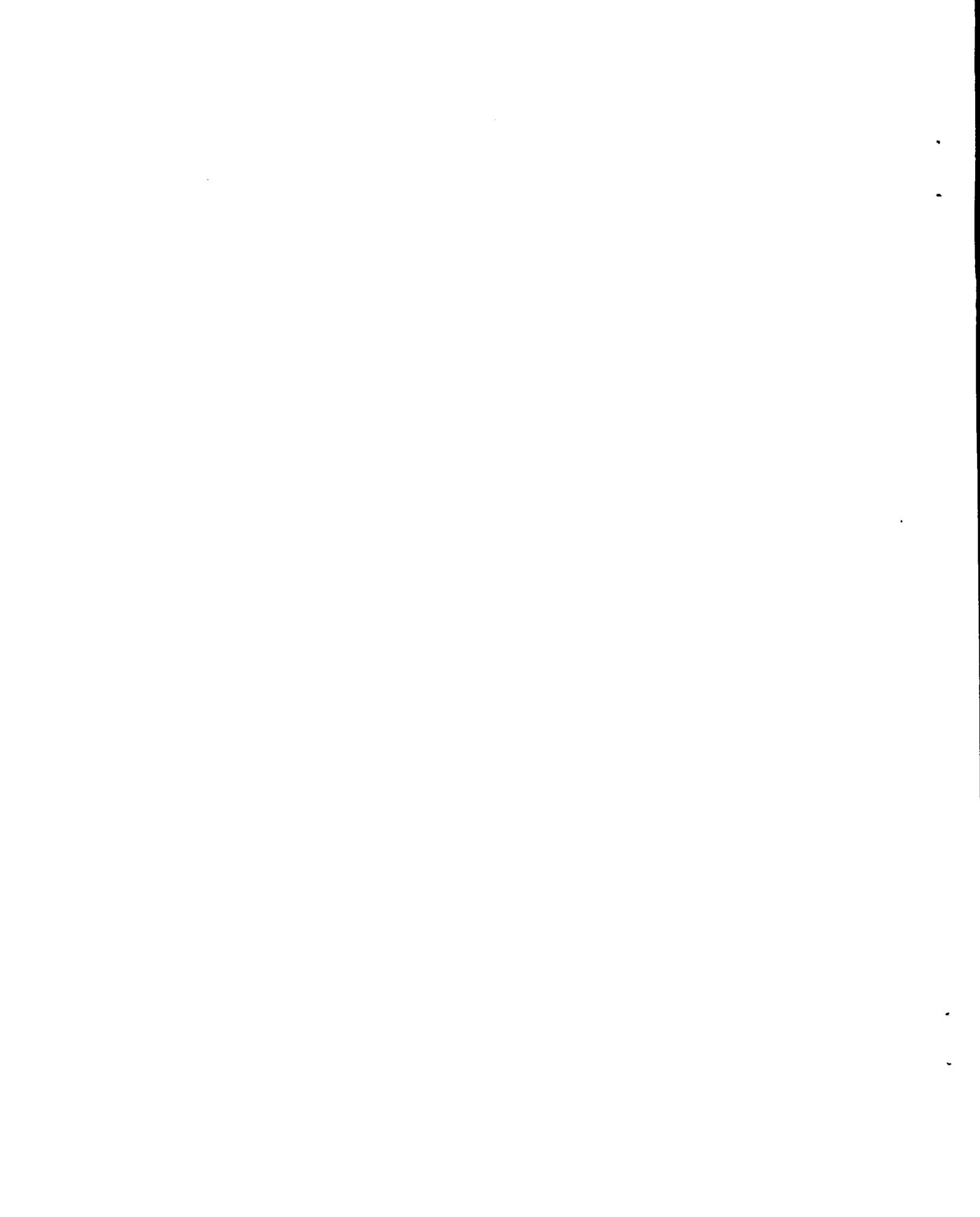
Calculate the micrograms of water per gram of ceramic grade uranium dioxide sample by:

$$\mu\text{g H}_2\text{O/g} = \frac{A_S - B - b}{mW},$$

in which

all terms are the same as above, and

$b$  =  $\mu\text{g}$  of water for tin foil or capsule blank.



DETERMINATION OF TOTAL VOLATILES IN  
CERAMIC GRADE PLUTONIUM DIOXIDE AND  
SAMPLE PREPARATION OF PLUTONIUM  
DIOXIDE FOR IMPURITY ANALYSIS

SUMMARY

Total volatile material in ceramic grade plutonium dioxide is determined simply by measuring the weight loss of a sample when heated at  $950 \pm 25^{\circ}\text{C}$ . With a 1-g sample, the relative standard deviation ranges from 1.2 to 6% over the range of 2.5 to 0.5% total volatiles.

APPLICABILITY

This method is applicable to ceramic grade plutonium dioxide as described in RDT Standard E13-1.<sup>[1]</sup> The specification limit for total volatiles in this material is 2.5 wt %. The lower limit of the method is controlled only by the sensitivity of the balance used for the weight measurements. A 1-g sample is recommended for material containing between 0.5 and 2.5% total volatiles. Interferences are not considered because the specification states that only a weight loss is to be measured under defined conditions. The actual man-power time to analyze a group of four or more samples is about 15 min per sample.

RELIABILITY

For 1-g samples and the use of a balance with a standard deviation of 0.2 mg, the precision is between 1.2 and 6% relative standard deviation for a total volatile material content of 2.5 to 0.5 wt %.

DISCUSSION OF THE METHOD

The ceramic grade plutonium dioxide presently used for LMFBR/FFTF fuel is produced by heating precipitated plutonium oxalate or plutonium nitrate at the relatively low temperature of  $550^{\circ}\text{C}$ . Such material may contain relatively large amounts of water and carbonaceous matter, and after cooling may also adsorb atmospheric water and gases. The purpose of the analysis is

to provide a common basis for assay results both by the producer and by the consumer. The method also provides for the requirement, stated in RDT Standard E13-1, that ceramic grade plutonium dioxide must be ignited at  $950 \pm 25^{\circ}\text{C}$  prior to analysis of the material for impurity contents.

The method is straightforward and simple, involving the ignition of a weighed sample to constant weight at the specified temperature. Because the results are important, especially as they apply to the plutonium assay value, careful laboratory operations are required to maintain a reasonable level of reliability.

OPERATING INSTRUCTIONS

SAFETY PRECAUTIONS

In addition to meeting the requirements for radiological control, the glove box design and operations must be such to minimize fire and personnel hazards from the furnaces.

APPARATUS

Analytical balance, minimum weighing precision of 0.2 mg standard deviation over range of 5 to 50 g.

Crucibles, 5-ml, platinum, zirconia, quartz, or ceramic, capable of use at  $\sim 1000^{\circ}\text{C}$ .

Desiccator, filled with a maintained supply of fresh desiccant such as silica gel.

Furnace, large enough for at least six crucibles, capable of sustained operation at  $950^{\circ}\text{C}$  with regulation to  $\pm 10^{\circ}\text{C}$ .

REAGENTS

No reagents are required.

PROCEDURE

Blank

A blank measurement is not required.

Calibration

Inasmuch as the analytical measurement is only a weight change, no calibration materials will be provided for this method. The analytical balance weights shall be calibrated in place in the glove box with at

[1] RDT Standard E13-1 "Fast Flux Test Facility-Ceramic Grade Plutonium Dioxide" (October 1970).

least class S weights prior to production startup and at monthly intervals during production periods.

The furnace temperature readout system shall be verified at the 950°C level at monthly intervals during production periods.

#### Sample Analysis

Note: In many of the steps, heating to constant weight is required. Constant weight is defined as a maximum difference of 0.2 mg between two successive weighings.

The operations shall be repeated until constant weight is attained.

1. Transfer about 1 g of the sample to a crucible that has been tared to constant weight at 950 ± 25°C.

Various crucibles are satisfactory; see section APPARATUS. Larger amounts of material may be used to give improved precision. Also, larger amounts may be desirable when preparing material for other analytical measurements; see section DISCUSSION OF THE METHOD.

2. Weigh the crucible and contents to ± 0.2 mg.

3. Place the crucible in a cold furnace.

Loss by spattering may occur when a moisture-laden sample is placed in a hot furnace.

4. Raise the temperature to 110°C, hold at this temperature for 30 min, then raise the temperature to 950 ± 25°C for 1 hr.

Too rapid heating may cause spattering loss caused by rapid expansion of adsorbed water.

5. Remove the crucible from the furnace, let cool to about 200°C, and place in a desiccator for final cooling to room temperature.

Atmospheric moisture and gas may be reabsorbed should the sample be allowed to cool to ambient temperature in the glove box atmosphere.

6. Weigh the crucible and its contents.

7. Repeat steps 4, 5, and 6 until constant weight is attained.

On repeated heating cycles, the sample may be placed directly in the furnace at 950 ± 25°C for 20-min periods.

8. Reserve the ignited sample in a desiccator for other specification analyses.

See section DISCUSSION OF THE METHOD.

#### Calculations

$$V = \frac{100(I - C)}{S - C},$$

in which

V = total volatiles in sample, wt % ,

I = constant weight of ignited sample and crucible, g ,

C = constant weight (tare) of crucible, g ,

S = weight of sample and crucible, g .

Note: Where the weighings are made to constant weight, use the average weight for calculations.

## DISCUSSION OF THE OXYGEN TO METAL (O/M) RATIO DETERMINATION

The ratio of oxygen to uranium plus plutonium (O/M ratio) in sintered mixed oxide fuels affects certain physical and chemical properties of these fuels that are very important to nuclear reactor core performance. For example, the melting point of  $(U_{0.8}Pu_{0.2})O_{1.972}$  is approximately  $100^{\circ}C$  higher than the melting point of a mixed oxide with the same U/Pu ratio but a stoichiometric O/M ratio of 2.00.<sup>[1]</sup> The thermal conductivity of a sintered uranium-plutonium mixed oxide with an O/M ratio of 1.95 or 2.05 is about one-half the thermal conductivity for the stoichiometric ratio of 2.00.<sup>[2]</sup> The O/M ratio also influences the number of phases present in the mixed oxide. A second phase has been reported<sup>[3]</sup> which is thought to depend both on the U/Pu ratio and the extent and direction of departure from the stoichiometric composition.

Other properties affected by the O/M ratio are chemical reactivity toward the cladding and ceramic strength. The former is of particular importance because it involves the amount of oxygen available for reaction with cladding material, particularly in the early stages of core life. It also influences the formation of oxides of certain fission-product elements.

Because of the influence on important physical and chemical properties indicated above, which, in turn, have important bearings on core behavior, it is essential that an accurate and precise method be developed for measurement of the O/M ratio. The problem is complicated by the lack of well-characterized materials necessary for the calibration of methods. Further complications may arise from the fact that  $UO_2$  does not exist as a hypo-stoichiometric oxide and  $PuO_2$  does not exist as a hyper-

stoichiometric oxide. In this latter case, excess oxygen corresponding to a formula  $PuO_{2+x}$  is considered to be caused by adsorbed oxygen.

One of the first methods for this measurement<sup>[4]</sup> involves oxidation of the mixed oxide sample (in pellet form) in air at  $750^{\circ}C$  long enough to produce an oxygen-rich oxide, after which the resultant product is reduced to a constant-weight oxide at  $700^{\circ}C$  in a flowing dry atmosphere of 95% He - 6%  $H_2$ . The sample is cooled to room temperature in this same flowing dry atmosphere, then weighed. The O/M ratio is calculated from the change in weight between the original sample and the cooled product on the basis that the product is stoichiometric  $MO_{2.00}$ . This assumption was not proved at the time of the original announcement of the method. Subsequent work<sup>[5]</sup> with starting materials of highly purified plutonium and uranium metals showed clearly that oxides obtained under the conditions of reduction stated above are oxygen-rich and that a temperature of  $1000^{\circ}C$  was required to produce stoichiometric oxides. These results, however, cannot be unequivocally extrapolated to mixed oxides with their single phase or solid compound composition.

A similar gravimetric method, described by Chikalla and McNeilly,<sup>[6]</sup> is based on thermodynamic considerations. This technique involves measuring the weight change that occurs when an oxide sample is heated at  $800^{\circ}C$  for 6 hr in an atmosphere in which the oxygen potential is maintained at approximately -100 kcal/mol. It was postulated that an atmosphere having an oxygen potential of approximately -100 kcal/mol produces an O/M ratio of 2.00 regardless of whether the

[1] W. L. Lyon and W. E. Bailey, *Trans. Amer. Nucl. Soc.* **8**, 376 (1965).

[2] J. C. Van Craeynest and J. C. Weilbacher, *J. Nucl. Mater.* **26**, 132 (1968).

[3] T. L. Markin and R. S. Street, *J. Inorg. Nucl. Chem.* **29**, 2265 (1967).

[4] W. L. Lyon, General Electric Company Report, GEAP-4271 (1963).

[5] J. W. Dahlby, T. K. Marshall, G. C. Swanson, and G. R. Waterbury, USAEC Report LA-4284-MS (1969), pp. 17-18.

[6] T. D. Chikalla and C. E. McNeilly, "Determination of Oxygen/Metal Ratios for Uranium, Plutonium, and (U, Pu) Mixed Oxides," National Ceramic Society Meeting, Washington, D. C., May 3-8, 1969.

starting oxide is hyper- or hypostoichiometric and is applicable to materials containing from 0 to 100% PuO<sub>2</sub> in UO<sub>2</sub>. The thermodynamic considerations upon which this technique is based involve the range of the partial molar free energy of oxygen in the vicinity of the stoichiometric composition. Based on galvanic cell measurements, [7] this value of  $\Delta\bar{G}(\text{O}_2)$  at an O/M ratio = 2.00 varies from about -75 to -115 kcal/mol O<sub>2</sub> at 800°C and is essentially independent of the composition of the mixed oxide up to 30% PuO<sub>2</sub>. From these considerations, it would appear that a one-step heat treatment in an atmosphere having an oxygen potential in this range should produce a stoichiometric oxide regardless of whether the sample was initially hypo- or hyperstoichiometric. In the procedure, the sample of sintered mixed oxide is heated at 800°C for 6 hr in a flowing gas of 92% Ar-8% H<sub>2</sub> containing water at a partial pressure of 4 Torr obtained by circulating this gas over water at 0°C. The sample is cooled to room temperature in the same flowing gas, then weighed. Again the O/M ratio is calculated from the change in weight.

Although reproducible results were obtained, the supposition that the final product was indeed the stoichiometric oxide was never proven by chemical analysis. Subsequent work [8] at LASL in which U<sub>3</sub>O<sub>8</sub> and oxygen-rich PuO<sub>2.017</sub> prepared from high-purity uranium and plutonium metals were subjected to the above conditions showed that the oxides produced were not stoichiometric MO<sub>2</sub>, but had compositions UO<sub>2.019</sub> and PuO<sub>2.016</sub>. When the starting materials subjected to the treatment were high-purity uranium and plutonium metals, oxides of UO<sub>2.008</sub> and PuO<sub>2.000</sub> were obtained when the exposure time was increased from 6 to 32 hr. Upon increasing the temperature to 1250°C and by using a water-free atmosphere of 92% Ar-8% H<sub>2</sub>, UO<sub>2.00</sub> was formed after 20 hr of treatment.

[7] T. L. Markin and E. J. McIver in "Plutonium 1965," Chapman and Hall, London (1967), pp. 845-857.

[8] J. W. Dahlby, G. R. Waterbury, and C. F. Metz, "The Determination of Oxygen to Metal Atom Ratios in Sintered Oxides," 13th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tennessee, Sept 30-Oct 2, 1969.

Recent unpublished work by Chikalla and co-workers [9] has indicated that the conditions of their earlier method [6] should be modified so that the sample at the end of the 6-hr heating is cooled in dry 92% Ar-8% H<sub>2</sub> gas in order to obtain nearly stoichiometric oxides. Starting with high-purity plutonium and uranium metal samples, the resulting products were PuO<sub>2.002 ± 0.0057</sub> and UO<sub>1.996 ± 0.002</sub>.

Another oxidation-gas-reduction method [10], widely used at Harwell for determining O/U ratios in UO<sub>2+x</sub> uses CO at 850°C to reduce the hyperstoichiometric oxide to UO<sub>2.00</sub>. The amount of CO<sub>2</sub> produced is considered a measure of the "excess" oxygen in the original sample. A similar method [11] has been used to determine the O/Pu ratios in hypostoichiometric PuO<sub>2</sub> by producing an oxygen-rich product with a measured amount of oxygen. If the oxide is a powder, the conversion may be followed by reaction with CO at 850°C and subsequent measurement of the CO<sub>2</sub> produced. This latter method has been applied to determining O/M ratios in oxygen-rich mixed oxides by Markin and co-workers [12] who related the method to the thermodynamically based high-temperature galvanic cell data for O/U ratios. From these data,  $\Delta\bar{G}(\text{O}_2)$  for UO<sub>2.00</sub> has been found to vary between -103 and -108 kcal/mol at 850°C. Since this range is essentially the value of  $\Delta\bar{G}(\text{O}_2)$  for CO<sub>2</sub>/CO ratios of 1/10, it was reasoned that such a mixture of CO<sub>2</sub> and CO should reduce a hyperstoichiometric UO<sub>2</sub> to stoichiometric UO<sub>2</sub>. Values of  $\Delta\bar{G}(\text{O}_2)$  very close to the expected values were reported to be obtained by this reduction procedure. This report also states that data obtained in unpublished work for PuO<sub>2</sub> and mixed oxides

[9] T. D. Chikalla to C. F. Metz, private communication (December 1969).

[10] L. E. J. Roberts and E. A. Harper, UKAEA Report AERE-C/R 885 (1952).

[11] T. L. Markin, E. R. Gardner, and R. J. Bones, UKAEA, unpublished work.

[12] T. L. Markin, A. J. Walter, and R. J. Bones, UKAEA Report-AERE-R-4608 (1964).

agreed very closely when these oxygen-rich materials were reduced with a 1/10 mixture of  $\text{CO}_2/\text{CO}$  at  $850^\circ\text{C}$ . The final composition reached should not be critically dependent on the composition of the gas used since  $\Delta\bar{G}(\text{O}_2)$  varies widely with only a slight change in composition in this region as indicated in Figure 1.<sup>[11]</sup> For the mixed oxides in particular, an enormous change in  $\Delta\bar{G}(\text{O}_2)$  occurs between compositions of  $\text{MO}_{1.99}$  and  $\text{MO}_{2.01}$ . The obvious inference is that the stoichiometric composition occurs at the steepest part of the curve, i. e.,  $\Delta\bar{G}(\text{O}_2) = -100 \text{ kcal/mol}$ .

A nondestructive method has been reported by Markin and Bones<sup>[13]</sup> which involves a high-temperature galvanic cell of the type  $\text{Ni}, \text{NiO}/\text{ZrO}_2, \text{CaO}/\text{UO}_{2+x}$ . The cell operated reversibly so long as the oxygen potential of the uranium oxide was higher than that of the  $\text{Ni}, \text{NiO}$  standard. A plot of emf isotherms at  $877^\circ\text{C}$  and  $977^\circ\text{C}$  versus O/U ratio as determined by  $\text{CO}$  reduction of uranium oxide at  $850^\circ\text{C}$  with a 1/10  $\text{CO}_2/\text{CO}$  mixture forms the basis of the analysis. The composition of an unknown oxide may be determined by measuring the emf of a pellet of the oxide versus the  $\text{Ni}/\text{NiO}$  standard. Values of the emf at  $877^\circ\text{C}$  and  $977^\circ\text{C}$  may then be read from the above plot. Errors in estimating the oxygen content by this method are estimated to be  $\pm 0.005$  O/U units. This method has not been applied to the determination of O/M ratios of mixed oxides.

Another method<sup>[14]</sup> has been reported which seems to have promise for the measurement of O/M ratios, especially for high-purity fuels. Involved is the direct measurement of the three elements in question, U, Pu, and O. Using an inert gas-fusion method for the oxygen and a controlled-potential coulometric method for the uranium and plutonium, the precision of the method was found to be  $\pm 0.005$  for the O/M ratio. In this technique, the accuracy and precision of the final result

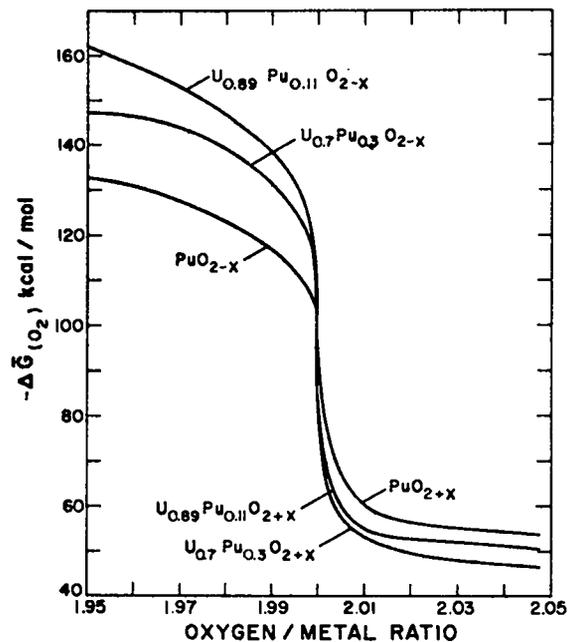


Figure 1. Effect of O/M ratio on  $\Delta\bar{G}(\text{O}_2)$  (see Ref. 12).

are the statistical combination of the measurement reliability for each element. The method appears useful in verifying thermogravimetric methods for high-purity oxide fuels.

A thermogravimetric technique has been described by D. H. Schmitt<sup>[15]</sup> which uses samples weighing between 5 and 25 mg. The method has the distinct advantage of permitting one analysis per sample in about 2 hr as compared to 8 hr or more required for larger samples. Another advantage of a small sample size is that it permits replicate analyses of a single sample, such as a pellet, thereby permitting more reliable statistical information on the precision of the method because differences between pellets do not become involved. For this to be true, however, the assumption must be made that the O/M ratio is constant throughout the pellet.

In Schmitt's method, one or more pieces from a crushed (not ground) mixed oxide pellet are weighed,

[13] T. L. Markin and R. J. Bones, UKAEA Report AERE-R-4042 (1962).

[14] C. S. MacDougall, M. E. Smith, and G. R. Waterbury, *Anal. Chem.* **41**, 372 (1969).

[15] D. H. Schmitt, Babcock and Wilcox Report-4088-1 (1969).

oxidized in air at 850°C, and then reduced at 850°C in an atmosphere of 6% H<sub>2</sub>-94% N<sub>2</sub>. The assumption is made in this method, as in the other thermogravimetric methods, that the final product is (U, Pu)O<sub>2.00</sub>. Because no adequate standards are available to calibrate this or any method, an unbiased method must be assumed. The weighing is done by an electrobalance and weight changes are followed by a suitable recorder. The thermogram as plotted by the recorder is a complete record of the weight changes as well as the initial and final weights. The relative standard deviation was reported to be 0.176%.

During the development of the method, it was found that high-purity stoichiometric U<sub>3</sub>O<sub>8</sub> (NBS SRM 950a) could not be used as a standard because its reduction behavior was quite different from that of sintered mixed oxide, and required a higher temperature of 1050°C to obtain U<sub>2.00</sub>. Subsequent experiments with PuO<sub>2</sub> indicated that some reduction of PuO<sub>2</sub> occurred at this higher temperature to form a slightly hypostoichiometric oxide.

Aside from the correlation between emf measurements of high-temperature cells and the O/U ratios as determined by CO reduction of uranium oxide at 850°C with a 1/10 gas mixture of CO<sub>2</sub>/CO<sup>[13]</sup>, there has been little cross-verification of results by various methods. One exception to this situation is known. In 1969, a program<sup>[16]</sup> of analysis of LMFBR/FFTF fuel included the determination of O/M by seven laboratories using a batch of sintered pellets prepared at 1600°C in a hydrogen atmosphere which should have produced a fairly uniform and hypostoichiometric (U<sub>0.66</sub>Pu<sub>0.22</sub>)O<sub>2-x</sub> material. At the time the program was initiated, the method of Lyon<sup>[1]</sup> was available to all participating laboratories and it, therefore, was recommended. The essential conditions were oxidation of the sample pellet in a flowing air stream for 30 min at 750°C followed by a reduction with a flowing stream of 94% He-6% H<sub>2</sub> for 9 hr at 700°C. Generally, the participating laboratories did not adhere to these conditions, preferring other conditions of temperatures

and times which they considered would yield stoichiometric oxides. The conditions used by the various laboratories for the thermogravimetric conversions are summarized in Table I.

The laboratories were asked to analyze three pellets, two whole pellets and a crushed pellet. Laboratories M, W, and Q did not do this but analyzed three whole pellets instead. The data are summarized in Table II.

A statistical analysis of variance showed a significant difference between laboratories. This difference includes both the between-laboratory component and the between-pellet component. The data were bimodal in that laboratories Q and G formed one group with no

TABLE I.  
Conditions Used for the Thermogravimetric Analysis  
of the O/M Ratio of Sintered Mixed Oxide

Laboratory	Method	Oxidation	Reduction
D	Lyon unmodified	750°C, 0.5 hr	700°C, 9 hr
	Lyon modified	900°C, 1 hr	900°C, 3 hr
G	Lyon modified	750°C, 1 hr	1000°C, 9 hr
L	Lyon modified	900°C, 0.5 hr	900°C, 8.5 hr
M	Lyon modified	950°C, 2.5 hr <sup>(a)</sup>	950°C, 5 hr <sup>(b)</sup>
W	Chikalla	800°C, 8 hr (one step)	
Q	Lyon modified	850°C <sup>(c)</sup>	850°C <sup>(b)(c)</sup>
N	Lyon unmodified	750°C, 0.5 hr	700°C, 9 hr

(a) Used pure oxygen rather than air.

(b) Used 94% N<sub>2</sub>-6% H<sub>2</sub> rather than 94% He-6% H<sub>2</sub>.

(c) Heated until constant weight was obtained.

TABLE II.  
Reported Results, Averages, and Standard Deviations  
for the O/M Ratio

Laboratory	Reported Values			Average	Standard Deviation
D (Lyon unmodified)	1.972	1.967	1.994 <sup>(a)</sup>	1.975	0.012
	(Lyon modified)	1.965	1.963		
G	1.980	1.985	1.992 <sup>(a)</sup>	1.985	0.005
L	1.965	1.967	1.963 <sup>(a)</sup>	1.965	0.002
M	1.972	1.971	1.987	1.975	0.005
		1.978	1.980		
W	1.974	1.971	1.970	1.972	0.002
Q	1.967 <sup>(b)</sup>	1.986 <sup>(b)</sup>	1.992 <sup>(b)</sup>	1.985	0.003
N	1.972	1.973	1.964 <sup>(a)</sup>	1.970	0.005
Pooled Data				1.975	0.005

(a) Crushed whole pellet analyzed.

(b) Small pieces of pellet analyzed.

[16] J. E. Rein, R. K. Zeigler, and C. F. Metz, USAEC Report LA-4407 (1970).

statistical difference between them and laboratories M, D, W, N, and L formed another such group. There was a significant statistical difference between the two groups.

An attempt to correlate the results of those laboratories using Lyon's method with the stated conditions of temperature and time was not successful. Although not statistically significant, the O/M results using crushed pellets or small pieces of pellet as the sample tend to be higher than the results obtained with whole pellets. Higher results reflect a more complete reduction of the oxidized sample, which can be attributed to the larger surface area of smaller sample pieces. Gas-solid reactions are characteristically slow and require large contact areas to attain completion in reasonable times. For this reason, the use of crushed samples is recommended.

The above study also provided a comparison of the method that used a small sample size<sup>[15]</sup> (laboratory Q) with the method using a large sample size and oxidation-reduction conditions that had produced stoichiometric  $UO_{2.00}$  and  $PuO_{2.00}$  starting with high-purity uranium and plutonium metals (laboratory G). Since the results obtained by these two laboratories were not statistically different, it suggests that neither method is biased significantly. On the other hand, it may be argued that the methods used by the other five laboratories are not biased since the results obtained by them agree. This argument, however, should be tempered by the fact that the reduction temperatures used for large samples by the five laboratories were lower than the temperature used by laboratory G, and the reduction times also were generally less. It is expected that the product obtained at a lower reduction temperature and shorter time will be oxygen-rich which results in a calculated O/M ratio value that is biased low.

Based on the considerations discussed above and the fact that laboratories in the United States have the equipment and personnel experienced with the thermogravimetric methods using large samples, such a method is given here for the determination of the O/M ratio in uranium and plutonium oxide samples. It is a modifica-

tion of Lyon's method using higher temperatures both for the oxidation and reduction phases. It has the status of an interim method until a method can be developed that is proved to give unbiased results. It is important to the LMFBR/FFTF program that all laboratories use the same method to minimize between-laboratory differences.

The method of Schmitt,<sup>[15]</sup> with its advantage of speed and use of small samples, merits careful consideration for future use by other laboratories. Before adoption by a laboratory, experimental data should be obtained which show that results obtained by the method agree with results obtained by the method given here.



# DETERMINATION OF THE OXYGEN TO METAL RATIO BY THERMOGRAVIMETRY

## SUMMARY

The dried sample is heated in air at 1000°C for 1 hr to produce an oxygen-rich oxide and is then heated at this temperature in a flow of dry 94% He-6% H<sub>2</sub> for 6 hr to reduce it to the dioxide. The dioxide is allowed to cool while the same gas mixture is circulated over it, weighed again, and the result is calculated from the measured weight change. The standard deviation is about 0.001 O/M ratio units.

## APPLICABILITY

The method is applicable to all four oxide materials. Impurities in the materials can cause a bias because the relative weight change produced in them during the ignition is different from the relative weight change produced in the uranium and plutonium. For the relatively pure material nominally produced, this effect is expected to be negligible.

## RELIABILITY

The standard deviation of the method is about 0.001 in the O/M ratio with high-purity samples and a sample size of 2 g. The bias of the method has not been determinable because well-characterized uranium-plutonium mixed oxide with known O/M values have not been available. Based on the studies presented in the preceding discussion, the bias, however, is believed to be small. More important, the use of this method by all laboratories will minimize between-laboratory differences.

## DISCUSSION OF THE METHOD

The method is based on the reduction of an oxygen-rich oxide sample to constant weight, assumed to be the stoichiometric oxide, by a flowing gas mixture of 94% He-6% H<sub>2</sub> at 1000°C. As in many gas-solid reac-

tions, the reaction rate is slow, requiring the use of small particle samples and a relatively long reaction time. Pellet samples should be crushed in a diamond mortar with a hammer to particles whose individual weight is not greater than 75 mg. Grinding to a powder is not recommended because exposure of a large surface area may result in adsorption of the containment atmosphere.

This is considered an interim method for the reasons presented in the discussion preceding this method. Reading of this section is strongly recommended to gain a fuller understanding of the many problems associated with the determination of the O/M ratio.

## OPERATING INSTRUCTIONS

### SAFETY PRECAUTIONS

Special precautions applying to this method are proper design of the furnace and proper operational procedures to prevent electrical shocks and thermal burns to personnel.

### APPARATUS

Boats, fused silica, 120-mm length, 19-mm width, and 12-mm depth.

Drying tower, glass, containing anhydrous magnesium perchlorate, for predrying of gases flowing to furnace tube.

Flo-Gage, Bantam, 5 to 100 cm<sup>3</sup>/min of carbon dioxide, recalibrated for 5 to 100 cm<sup>3</sup>/min of hydrogen, Hoke No. 62224, or equivalent.

Flo-Gage, Bantam, 100 to 700 cm<sup>3</sup>/min of oxygen, recalibrated for 100 to 2000 cm<sup>3</sup>/min of helium, Hoke No. 62223, or equivalent.

Furnace, tube-type, 12-in. long and 1.25-in. diam, 750 W, Hevi-Duty, or equivalent.

Gas mixing apparatus, consisting of the above Flo-Gages, two needle valves (Hoke No. 4171 M2B, or equivalent) and the necessary copper tubing and connectors. The flow

rates of hydrogen and helium from cylinders are regulated with the needle valves to approximately  $1400 \text{ cm}^3/\text{min}$  of helium and  $90 \text{ cm}^3/\text{min}$  of hydrogen as measured by the respective flow meters.

Induction heating unit, 2.5-kW, with accessory equipment.

Pyrometer, 0 to  $1000^\circ\text{C}$  range with Chromel-Alumel thermocouple.

Timer, interval, 0 to 12 hr.

Tube, furnace fused-silica, 500-mm length and 28-mm o.d., with 29/26 joint end cap.

Variac, 110-120 V, 10 A.

Water bubbler, consisting of U-tube containing water and submerged in ice in a 1-l. Dewar flask.

#### REAGENTS AND MATERIALS

Argon, high-purity.

Helium, high-purity.

Hydrogen, high-purity.

Plutonium metal, high-purity with total impurity concentration less than  $200 \mu\text{g/g}$ .

Plutonium oxide. Prepare by oxidizing an accurately weighed portion of the high-purity metal slowly in air at  $150$  to  $200^\circ\text{C}$  until the weight is constant, and then heating at  $800^\circ\text{C}$  for 16 hr. Calculate the O/Pu ratio from the weight change.

Uranium metal, high-purity with total impurity concentration less than  $200 \mu\text{g/g}$ .

Uranium oxide. Prepare by oxidizing an accurately weighed portion of the high-purity metal in air by heating slowly to  $900^\circ\text{C}$  for about 24 hr, then maintaining this temperature for 16 hr. Calculate the O/U ratio from the weight change.

#### PROCEDURE

##### Blank

A blank is not required in this method.

#### Calibration

No calibration materials are available. Test the apparatus at least weekly by ensuring that a 3/1 blend of  $\text{U}_3\text{O}_8$  and  $\text{PuO}_2$  prepared from the high-purity metals converts to an oxide having a weight equal to that of stoichiometric dioxide by the operations described in steps 2 through 10 of the subsection Sample Analysis.

#### Sample Analysis

1. Crush two or three pellets in a diamond mortar immediately prior to the analysis.

One or two blows with a hammer usually are sufficient. Avoid excessive crushing that produces fine particles.

2. Heat a sample boat to  $1000^\circ\text{C}$  in air for about 1 hr, cool to room temperature in a stream of dry argon, and weigh to  $\pm 0.1 \text{ mg}$ .

3. Transfer about 2 g of the crushed sample to the sample boat.

Do not use any pieces larger than 75 mg. After experience is gained, visual selection of the pieces is adequate.

4. Place the boat with sample into the furnace tube and heat for 1 hr at  $100^\circ\text{C}$  in a stream of dry argon at a flow rate of about  $500 \text{ cm}^3/\text{min}$ .

Surface adsorbed moisture is removed.

5. Let the sample cool to room temperature while remaining in the dry argon flow, then weigh to  $\pm 0.1 \text{ mg}$ .

The difference between this weight and the tare weight of the boat (step 2) is the initial sample weight.

6. Replace the sample in the furnace tube and, with the end cap removed, increase the temperature to  $1000^\circ\text{C}$ .

This requires about 1 hr.

Air diffuses to the sample to produce the oxygen-rich oxide.

7. Place the end cap on the furnace tube and flow the dry 94% He-6%  $\text{H}_2$  gas mixture through the furnace tube at a flow rate of  $1500 \text{ cm}^3/\text{min}$  for 6 hr.

Maintain the temperature at  $1000^\circ\text{C}$  during the 6-hr period.

The sample reduces to the assumed stoichiometric oxide.

- Turn off the furnace and let the sample cool to room temperature while remaining in the dry 94% He-6% H<sub>2</sub> gas mixture flow.

Proceed immediately to the next step after the sample reaches room temperature. Prolonged exposure of the sample to air may result in a weight change.

- Weigh the boat with sample to  $\pm 0.1$  mg.
- Repeat steps 6 through 9.

The allowable difference in the two obtained weights is  $\pm 0.2$  mg. If this difference is exceeded, repeat steps 6 through 9 until agreement is attained.

#### Calculations

$$R = 2.000 - \frac{M(W_f - W_i)}{16(W_f - W_b)} ,$$

in which

R = O/M ratio,

M = mean molecular weight of the uranium-plutonium mixed oxide sample calculated on the basis of the nominal U/Pu ratio and an assumed O/M ratio of 2.000,

W<sub>f</sub> = final weight, g, of boat with sample after reduction (step 9 in subsection Sample Analysis),

W<sub>i</sub> = weight, g, of boat with sample after initial drying at 100°C in dry argon (step 5 in subsection Sample Analysis),

W<sub>b</sub> = tare weight, g, of boat after heating to 1000°C for 1 hr (step 2 in subsection Sample Analysis).