



# Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride<sup>1</sup>

This standard is issued under the fixed designation C 761; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 1. Scope

1.1 These test methods cover procedures for subsampling and for chemical, mass spectrometric, spectrochemical, nuclear, and radiochemical analysis of uranium hexafluoride ( $UF_6$ ). All of these test methods are in routine use to determine conformance to  $UF_6$  specifications in the Department of Energy (DOE) gaseous diffusion plants or at other DOE installations.

1.2 The analytical procedures in this document appear in the following order:

	Sections
Subsampling of Uranium Hexafluoride	7 to 10
Gravimetric Determination of Uranium	11 to 19
Titrimetric Determination of Uranium	20 to 27
Preparation of High-Purity $U_3O_8$	28 to 34
Isotopic Analysis by Double-Standard Mass-Spectrometer Method	35 to 40
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Determination of Hydrocarbons, Chlorocarbons, and Partially Substituted Halohydrocarbons	47 to 53
Atomic Absorption Determination of Antimony	54 to 60
Spectrophotometric Determination of Bromine	61 to 68
Titrimetric Determination of Chlorine	69 to 75
Spectrophotometric Determination of Silicon and Phosphorus	76 to 82
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Spectrographic Determination of Metallic Impurities by Carrier Distillation	112 to 118
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Impurity Determination by Spark-Source Mass Spectrography	165 to 173
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Determination of Uranium-233 Abundance by Thermal Ionization Mass Spectrometry	178 to 184
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Determination of Fission Product Activity by Beta and Gamma Counting	192 to 198
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Atomic Absorption Determination of Chromium Soluble In Uranium Hexafluoride	220 to 226
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Metallic Impurities by ICP-AES	251 to 260
Molybdenum, Niobium, Tantalum, Titanium, and Tungsten by ICP-AES	261 to 270

1.3 Additional test methods have been developed and are included in Appendix X1.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* (For specific safeguard and safety consideration statements, see Section 6.)

## 2. Referenced Documents

2.1 The following documents of the issue in effect on date of material procurement form a part of this specification to the extent referenced herein:

### 2.2 ASTM Standards:

- C 696 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets<sup>2</sup>
- C 753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder<sup>2</sup>
- C 787 Specification for Uranium Hexafluoride for Enrichment<sup>2</sup>
- C 1219 Test Methods for Arsenic in Uranium Hexafluoride<sup>2</sup>
- C 1287 Test Method for Determination of Impurities in Uranium Dioxide by Inductively Coupled Plasma Mass Spectrometry<sup>2</sup>
- C 1295 Test Method for Gamma Energy Emission from Fission Products in Uranium Hexafluoride<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>3</sup>
- E 60 Practice for Photometric and Spectrophotometric

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and are the direct responsibility of Subcommittee C 26.05 on Methods of Test.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 12.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 11.01.

- Methods for Chemical Analysis of Metals<sup>4</sup>  
 E 115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis<sup>4</sup>  
 E 130 Practice for Designation of Shapes and Sizes of Graphite Electrodes<sup>4</sup>  
 2.3 U.S. Department of Energy Specifications:  
 Uranium Hexafluoride: Base Charges, Use Charges, Special Charges, Table of Enriching Services, Specifications, and Packaging<sup>5</sup>  
 Uranium Hexafluoride: Handling Procedures and Container Criteria<sup>5</sup>  
 2.4 American Chemical Society Specification:  
 Reagent Chemicals<sup>6</sup>

### 3. Significance and Use

3.1 Uranium hexafluoride is a basic material used to prepare nuclear reactor fuel. To be suitable for this purpose the material must meet criteria for uranium content, isotopic composition, metallic impurities, hydrocarbon and partially substituted halohydrocarbon content. These test methods are designed to determine whether the material meets the requirements described in Specification C 787.

3.1.1 The material is analyzed to determine whether it contains the uranium content specified.

3.1.2 The isotopic content of the material is measured to determine whether it contains the isotopic content specified.

3.1.3 The metallic impurity content is determined to ensure that the maximum concentration limit of specified impurity elements is not exceeded.

3.1.4 The hydrocarbon and partially substituted halohydrocarbon contents are measured to ensure that the maximum concentration limits are not exceeded.

### 4. Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all procedures. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>7</sup> Other grades may be used, provided that it is first established that the reagent to be used is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall mean reagent water conforming to Specification D 1193.

### 5. Rejection

5.1 Rejection or acceptance shall be by lot, a lot consisting of the contents of a shipping container.

### 6. Safety Considerations

6.1 Since UF<sub>6</sub> is radioactive, toxic, and highly reactive,

especially with reducing substances and moisture (see Uranium Hexafluoride: Handling Procedures and Container Criteria), appropriate facilities and practices for sampling and analysis must be provided.

6.2 *Committee C-26 Safeguards Statement:*

6.2.1 The material (uranium hexafluoride) to which these test methods apply, is subject to nuclear safeguards regulations governing its possession and use. The following analytical procedures in these test methods have been designated as technically acceptable for generating safeguards accountability measurement data: Gravimetric Determination of Uranium; Titrimetric Determination of Uranium; Isotopic Analysis by Double Standard Mass-Spectrometer Method; Isotopic Analysis by Single Standard Mass-Spectrometer Method.

6.2.2 When used in conjunction with appropriate certified Reference Materials (CRMs), these procedures can demonstrate traceability to the national measurement base. However, adherence to these procedures does not automatically guarantee regulatory acceptance of the resulting safeguards measurements. It remains the sole responsibility of the user of these test methods to assure that its application to safeguards has the approval of the proper regulatory authorities.

## SUBSAMPLING OF URANIUM HEXAFLUORIDE (1, 2)<sup>7</sup>

### 7. Scope

7.1 This test method is applicable to the subsampling (3) of UF<sub>6</sub> from bulk sample containers into smaller containers suitable for laboratory analyses. The procedure includes sample filtration that facilitates determination of both soluble and insoluble chromium compounds.

### 8. Summary of Test Method

8.1 The UF<sub>6</sub> in the bulk sample container is liquefied and homogenized by vigorous shaking. The container is inverted and connected to the top of a heated vacuum-manifold system, and the subsample container is attached to the appropriate port of the system. The system is evacuated, and the liquid UF<sub>6</sub> is allowed to flow by gravity into the subsample container.

### 9. Apparatus

- 9.1 *Hot Water Bath.*
- 9.2 *Heated Vacuum Manifold with Liquid Nitrogen Cold Trap* (Fig. 1).
- 9.3 *Isotopic Abundance Sample Tube* (Fig. 2).
- 9.4 *Fluorothene Sample Tube* (Fig. 3).
- 9.5 *Fluorothene Knockout Cylinder* (Fig. 4), closed with a Cajon<sup>8</sup> M-16 VCR-1 female nut and an M-16 VCR-4 male nut, or equivalent.
- 9.6 *Nickel Filter Disk*, porous, 2- $\mu$ m, free of chromium (Fig. 5). Mott Metallurgical Corp. or equivalent.<sup>9</sup>
- 9.7 *Gas Sample Cylinder*, 0.5 L.

<sup>4</sup> Annual Book of ASTM Standards, Vol 03.05.

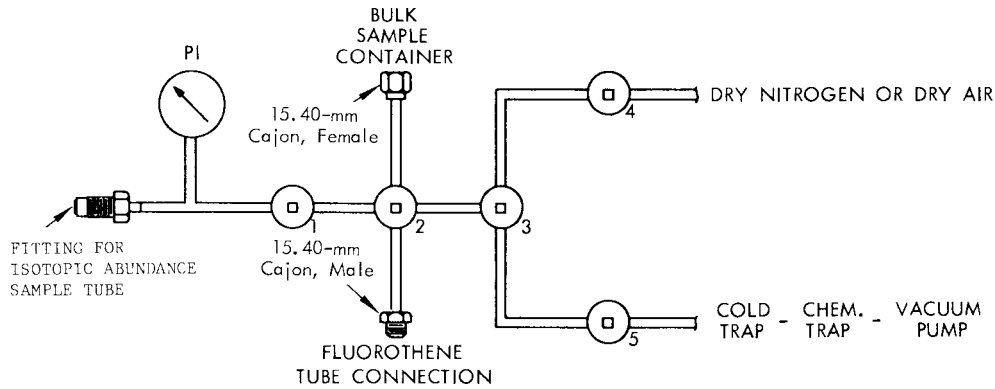
<sup>5</sup> United States Department of Energy, Oak Ridge, TN 37830.

<sup>6</sup> "Reagent Chemicals, American Chemical Society Specifications," Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, See "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

<sup>7</sup> The boldface numbers in parentheses refer to a list of references at the end of these test methods.

<sup>8</sup> Brand names mentioned in this procedure are intended to be typical, not limiting. Another brand of comparable characteristics could perform equally well.

<sup>9</sup> The filter disk should weigh approximately 1 g and be 16 mm in diameter by 0.6 m thick. It should be of nickel powder produced from carbonyl nickel and formed by the no pressure sintering method in graphite or ceramic molds.



- NOTE 1—All lines are 3/8-in. (9.5-mm) Monel tubing.  
 NOTE 2—All valves are Monel diaphragm-type valves.  
 NOTE 3—The valves and lines are wrapped with heating tape to maintain a system temperature of about 80°C.  
 NOTE 4—Valve 2 is a 3-way valve modified to make it a 4-way valve. When the valve is closed, the fluorothene tube is isolated from the system, but the lines from Valve 1 to Valve 3 and to the bulk container are open.

FIG. 1 System for Sampling Liquid UF<sub>6</sub> from Small Containers

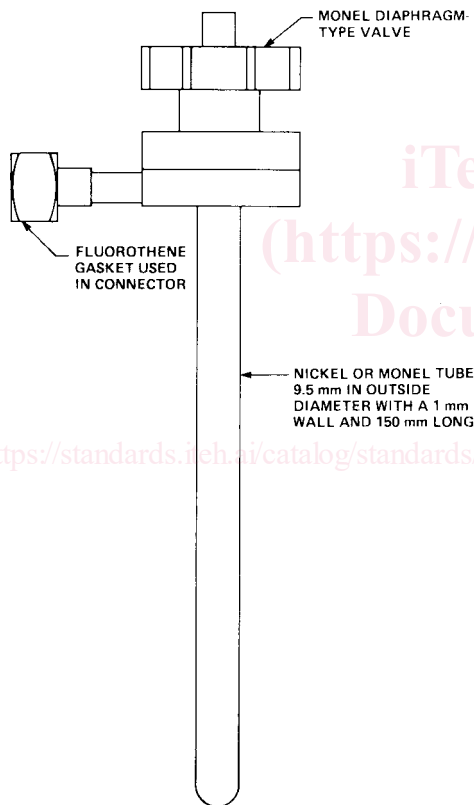


FIG. 2 Isotopic Abundance Sample Tube

10. Procedure

10.1 System Preparation:

10.1.1 Place the bulk sample container in a water bath at 90°C.

10.1.2 After the UF<sub>6</sub> has been liquefied, remove the container from the bath, shake to homogenize the sample, and connect it at the top of the vacuum-manifold system shown in Fig. 1.

10.1.3 If a subsample is required for uranium analysis, connect a tared fluorothene sample tube at the Cajon connec-

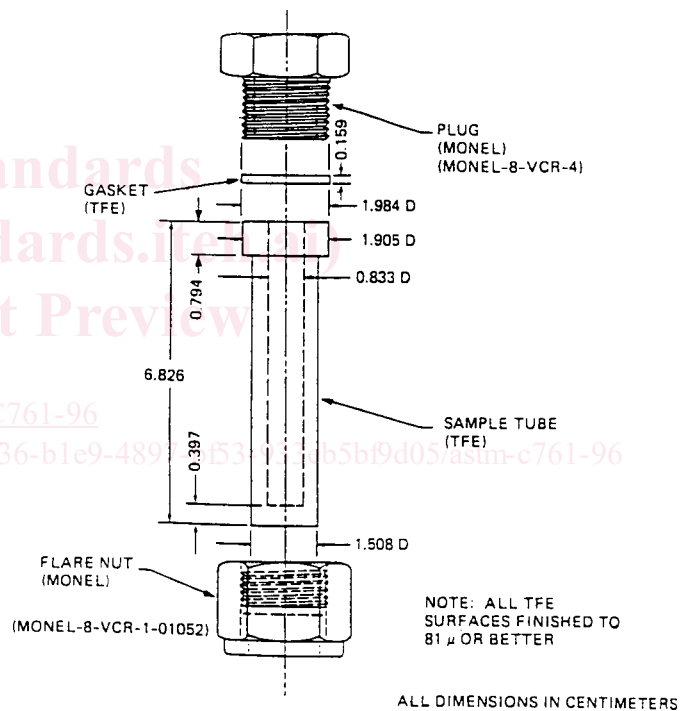


FIG. 3 Small TFE Sample Tube

tion at the bottom of the system. If this subsample is not required, attach a blind fitting at this point.

10.1.4 If a subsample is required for isotopic analysis, attach a tared isotopic abundance sample tube to the sample tube connection. If this subsample is not required, attach a cap at this point.

10.1.5 Close Valve 4, then evacuate the entire system, except for the UF<sub>6</sub> bulk sample container.

10.2 Sample Transfer to the Fluorothene Tube:

10.2.1 Close Valves 1, 2, and 3.

10.2.2 To remove solid impurities, which may be present in the bulk-container valve, open that valve and then close it quickly. Transfer this flush aliquot of liquid UF<sub>6</sub> to a fluorothene sample tube, as described below, and discard.

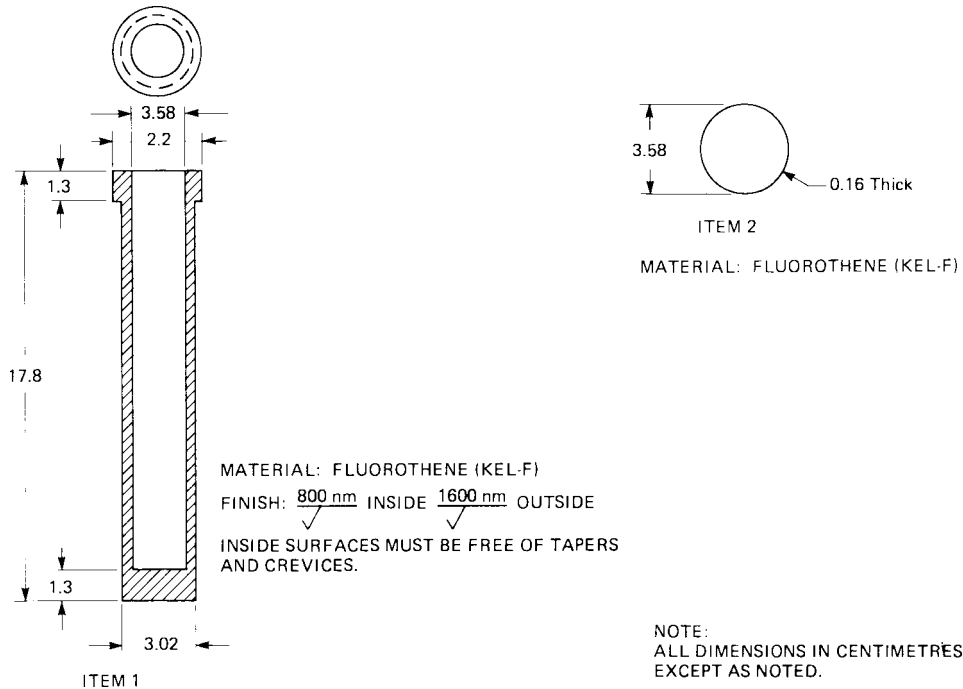


FIG. 4 Fluorothene Knockout Cylinder

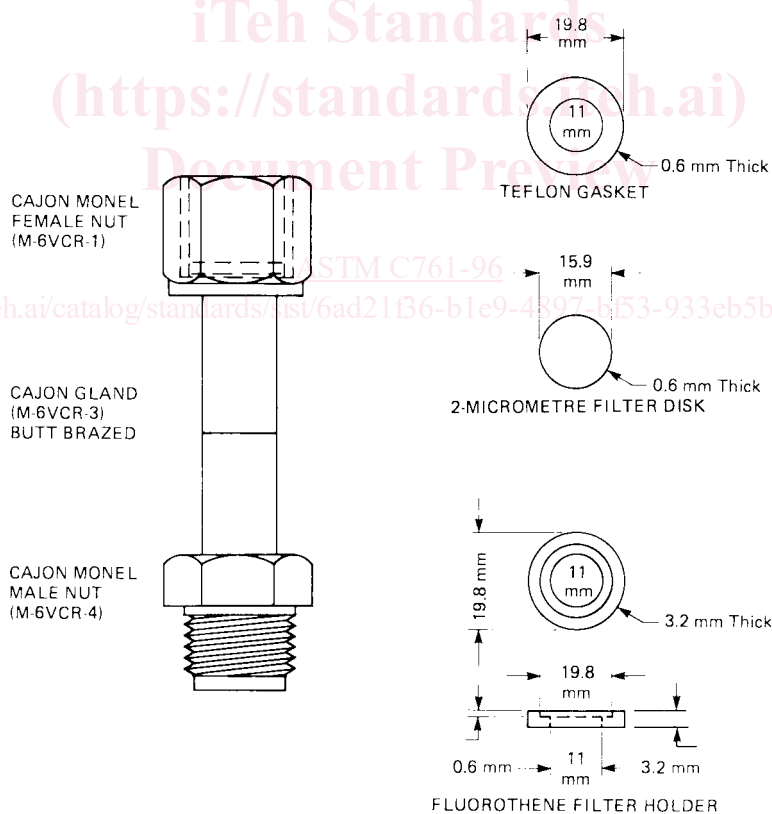


FIG. 5 Filter Disk Unit

10.2.3 Open the bulk-container valve; then open Valve 2 slowly, allowing liquid  $UF_6$  to flow into the fluorothene tube. When the tube is half full of liquid  $UF_6$ , close Valve 2.

10.2.4 Close the bulk-container valve.

10.2.5 Open Valve 3 to remove  $UF_6$  from the system. Open Valve 1 to ensure that the system is evacuated.

10.2.6 Close Valve 3.

10.2.7 Immerse the fluorothene tube in liquid nitrogen for 6 min.

10.2.8 Open Valve 2 to ensure that the sample does not exert a detectable vapor pressure.

10.2.9 Close Valve 5.

10.2.10 Open Valves 3 and 4, and admit dry nitrogen or dry air until a pressure slightly above 1 atm is reached.

10.2.11 Disconnect the fluorothene tube, seal with a fluorothene gasket and a Monel plug, and weigh the tube assembly.

10.2.12 Cap the manifold port and close Valves 2 and 4.

10.3 *Sample Transfer to an Isotopic Abundance Tube:*

10.3.1 Open Valves 1, 3, and 5, as well as the isotopic abundance tube valve, to evacuate the tube.

10.3.2 Close Valves 1, 2, and 3.

10.3.3 Immerse the lower half of the metal isotopic abundance tube, as shown in Fig. 2, in liquid nitrogen for 1 or 2 min. Immerse plastic tubing in ice water and observe desublimed  $UF_6$ .

10.3.4 Remove the liquid nitrogen or ice water and allow frost to accumulate on the tube.

10.3.5 Open the bulk-container valve and then close.

10.3.6 Open Valve 1 slowly, and observe melting of the frost as the  $UF_6$  flows into the tube. As soon as the frost disappears, close the isotopic abundance tube valve.

10.3.7 Open Valve 3 to remove the  $UF_6$  from the manifold.

10.3.8 Close Valve 5 and open Valve 4 to admit dry nitrogen or dry air until a slight positive pressure is reached. Then close Valve 4.

10.4 *Sample Preparation for Boron and Silicon Analyses:*

10.4.1 Transfer approximately 5 g of liquid  $UF_6$  to a tared fluorothene sample tube, as in 10.2.3 through 10.2.12.

10.4.2 Prepare a fresh ammonia solution by bubbling ammonia gas through approximately 300 mL of distilled water in a clean 500-mL polyethylene bottle until the water is saturated.

10.4.3 Cool the fluorothene tube in liquid nitrogen, remove the metal fittings, and drop the tube into the ammonia water.

10.4.4 Immediately cap the bottle, and hydrolyze the contents of the fluorothene tube while shaking the bottle.

10.5 *Sample Preparation for Soluble and Insoluble Chromium in  $UF_6$ :*

10.5.1 Attach the porous nickel filter unit with a weighed 2- $\mu$ m filter, as shown in Fig. 5, to the bottom port of the vacuum manifold, and attach a tared fluorothene tube to the bottom of the filter unit.

10.5.2 Transfer 15 to 20 g of liquid  $UF_6$  through the filter to the fluorothene sample tube, as in 10.2.3 through 10.2.12.

10.5.3 Remove the porous nickel filter and dissolve it in 10 mL of 1.42 sp gr  $HNO_3$ .

10.5.4 Submit the dissolved filter solution for analysis of chromium insoluble in  $UF_6$  and the filtered  $UF_6$  in the fluorothene sample tube for chromium soluble in  $UF_6$ .

10.6 *Sample Transfer to Fluorothene Knockout Cylinder:*

10.6.1 Attach the fluorothene knockout cylinder, as shown in Fig. 4, to the bottom port of the manifold with a Cajon M-16 VCR-1 female nut, an M-16 VCR-4 male nut, and an M-16 VCR-3 gland.

10.6.2 Transfer approximately 200 g of liquid  $UF_6$  to a tared fluorothene knockout cylinder, as in 10.2.3 through 10.2.12, except that in 10.2.7, the knockout cylinder is immersed in liquid nitrogen for 15 min.

10.6.3 Allow the knockout cylinder to warm to ambient temperature and then weigh to the nearest gram.

10.6.4 Freeze the knockout cylinder in liquid nitrogen for

15 min, and remove the metal fittings and cover gasket. Transfer the sample to a tared, 2-L polypropylene beaker chilled in ice water, by inverting the knockout cylinder over the beaker and rapping the bottom of the knockout cylinder with a rubber mallet.

10.6.5 Immediately add chilled nitric acid ( $HNO_3$ ), 1 part in 4 parts distilled water, to form a solution of approximately 0.1 g U/g of solution.

10.6.6 Allow the solution to reach ambient temperature while stirring periodically with a polypropylene stirring rod until all of the solid has dissolved.

10.6.7 Weigh the solution and determine the uranium concentration per gram of solution.

10.6.8 Dispense aliquots of the solution for analysis according to Table 1.

10.7 *Sample Transfer for Mole Percent Hydrocarbons, Chlorocarbons, and Partially Substituted Halohydrocarbons:*

10.7.1 Using a tee connector, attach a 1-atm absolute vacuum gage and 0.5-L gas sample cylinder to the fitting for the spectrometer isotopic abundance tube (Fig. 1).

10.7.2 Open Valves 1, 3, and 5 and the gas sample cylinder valve, and evacuate the manifold and sample cylinder.

10.7.3 Close Valves 1 and 3.

10.7.4 Slowly open the bulk-sample container valve to admit liquid  $UF_6$  to the manifold and then close the bulk container valve.

10.7.5 Slowly open Valve 1 until a pressure of 75 mm is reached in the gas sample cylinder.

10.7.6 Close the gas sample cylinder valve and open Valves 1 and 3 to evacuate the manifold.

10.7.7 Close Valve 5, open Valve 4, and remove the bulk-sample container from the manifold.

10.7.8 Plug the bulk-sample container port on the manifold, close all valves, and remove the gas sample cylinder.

## GRAVIMETRIC DETERMINATION OF URANIUM

### 11. Scope

11.1 This test method is applicable to the direct gravimetric determination for uranium in uranium hexafluoride.

### 12. Summary of Test Method

12.1 A sample of uranium hexafluoride is weighed, cooled in liquid nitrogen, and hydrolyzed with water. The uranyl fluoride solution produced is evaporated to dryness and converted to uranouranic oxide by pyrohydrolysis. The uranium content is determined from the weight of the uranium oxide after correcting for stoichiometry based on isotopic content, ignition conditions, and nonvolatile impurities (4–7).

### 13. Interferences

13.1 Nonvolatile impurities affect the accuracy of the method and must be measured by spectrographic analysis with corrections applied.

### 14. Apparatus

14.1 *Polytrifluorochloroethylene (TFCE) Sample Tube, TFCE Gasket, Flare Nut, and Plug*, see Fig. 3.

14.2 *Platinum Boat and Cover*—The cover should be platinum gauze (52 mesh) and shaped to cover the boat (Fig. 6).



TABLE 1 Subsamples for UF<sub>6</sub> Specification Analyses

2S Cylinder Sample from Shipping Cylinder					
1 Nickel Filter Disk (Fig. 5)	1 Fluorothene Tube	1 Fluorothene Tube Knockout Cylinder	1 Fluorothene Sample Tube	1 Disposable	1 Gas Cylinder
20 g UF <sub>6</sub>	8 g UF <sub>6</sub>	2 g UF <sub>6</sub>	B	4 g UF <sub>6</sub>	< 75 mm Pressure
Dissolved Disk Solution	g U/g	Hydrolyzed in Fresh NH <sub>3</sub> Solution		<sup>235</sup> U <sup>234</sup> U <sup>a</sup> <sup>236</sup> U <sup>a</sup>	Hydrocarbons, Chlorocarbons, Partially-Substituted Halohydrocarbons
Soluble and Insoluble Cr	Al, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, Pb, Sn, and Zn	B and Si			
	1 g U in Solution <sup>a</sup>	10 g U in Solution	40 g U in Solution		60 g U in Solution <sup>a</sup>
	<sup>233</sup> U	Br and Cl	Nb, Ta, Ti, Mo, W, V, Zr Sb and P Ru Th, Dy, Gd, Sm Sr and K		<sup>232</sup> U Pu, Np Fission Product: γ β

<sup>a</sup> Required only for reactor returns.

B 100 g UF<sub>6</sub> hydrolyzed in (1 + 4) HNO<sub>3</sub> and 100 g UF<sub>6</sub> hydrolyzed in ice water for <sup>235</sup>U, Br and Cl.

iTeh Standards

(https://standards.itih.ai)

14.3 *Muffle Furnace*, must be capable of operating continuously at 875°C and maintain this temperature within ±25°C. The furnace shall be equipped with a steam supply that is passed through a tube furnace to preheat the steam to 875°C.

14.4 *Tube Furnace*, must be capable of operating continuously at 875°C and maintain this temperature within 25°C.

14.5 *Infrared Heat Lamps*, 250 watts.

14.6 *Analytical Balance*.

14.7 *Vacuum Oven*.

14.8 *Dewar Flask*, stainless steel.

14.9 *Spatula*, platinum.

14.10 *TFCE Rod*, 120 mm long and 1.6 mm in diameter.

14.11 *Forceps*, platinum tipped.

14.12 *Jig*, suitable for holding the TFCE sample tube so that it can be opened with a wrench.

14.13 *Box Wrench*, to fit sample tube plug.

14.14 *Beaker*, stainless steel, 125 mL capacity.

### 15. Reagents

15.1 *Liquid Nitrogen*.

15.2 *Nitric Acid* (sp gr 1.42)—concentrated nitric acid (HNO<sub>3</sub>).

15.3 *Nitric Acid (4M)*—Mix 500 mL of concentrated HNO<sub>3</sub> with 1500 mL of distilled water.

15.4 *Detergent*.

### 16. Sampling

16.1 A UF<sub>6</sub> sample is taken as described in 9.2.

### 17. Procedure

17.1 Inspect the TFCE sample tube for leaks.

NOTE 1—An indication of a leak is a yellow-green residue on the flare nut and cap or a yellow discoloration in the tube. Discard the sample if a leak is indicated.

17.2 Allow the sample tube to stand overnight in the laboratory.

17.3 Wipe the sample tube with a lint-free tissue to remove any moisture or foreign material that might be adhering.

17.4 Weigh the sample tube to the nearest 0.1 mg.

17.5 Heat the platinum boat and screen in the pyrohydrolysis furnace at 875°C for 20 min.

17.6 Cool the platinum boat and store in a desiccator for 40 min. Weigh the boat and screen to the nearest 0.1 mg.

17.7 Freeze the sample by immersing the sample tube in liquid nitrogen for 10 min.

17.8 Add enough chilled water to the tared platinum boat to immerse the sample tube (about 50 mL).

17.9 Place the sample tube in the jig and loosen the plug with the box wrench.

17.10 Remove the sample tube from the jig and unscrew the plug while holding the sample tube in an upright position.

17.11 Remove the flare nut from the sample tube and immerse the tube and gasket in the chilled water in the tared platinum boat.

17.12 Let the gasket remain in the chilled water about 30 min.

17.13 Remove the gasket with the forceps and rinse well with deionized water into the boat.

17.14 Place the plug-nut assembly and gasket into a stainless steel beaker for drying.

17.15 Allow the tube to remain in the water until the UF<sub>6</sub> has been hydrolyzed (2 to 4 h).

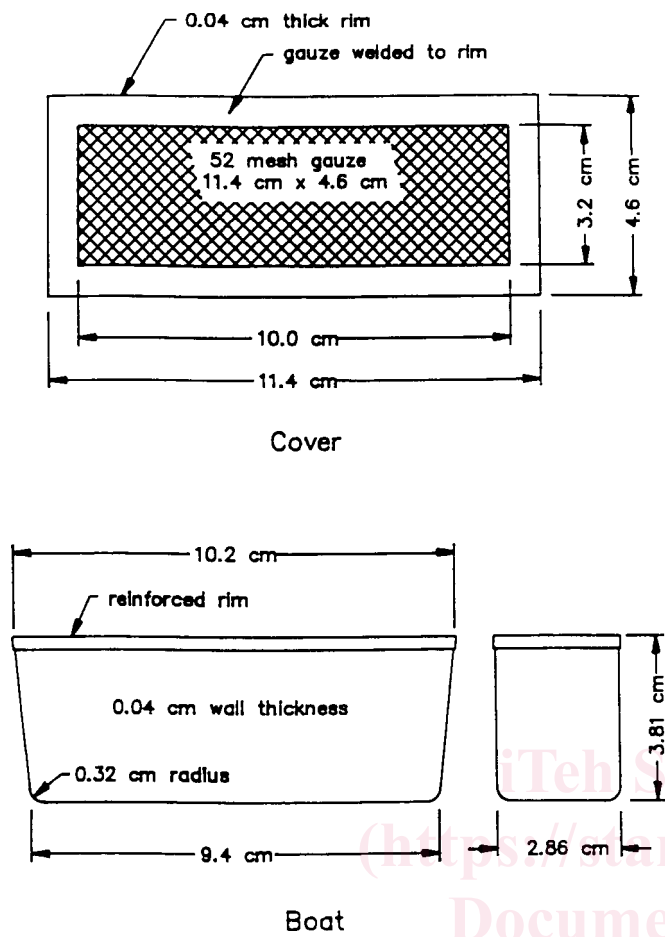


FIG. 6 Platinum Boat and Cover

17.16 Remove the tube from the sample solution by inserting the TFCE rod or platinum spatula into the tube and lifting directly above the boat.

17.17 Rinse the sample tube with deionized water into the boat using extreme care to prevent splashing.

17.18 Cover the sample boat containing the  $UO_2F_2$  solution with the matching cover shown in Fig. 6. Place under the infrared head lamps and evaporate to dryness for 16 h.

17.19 Shake the excess water from the sample tube and place in the stainless beaker containing the plug-nut assembly and gasket.

17.20 Dry the sample tube parts in the vacuum oven at  $80^\circ C$  and 29 in Hg for 2 h.

17.21 Allow the unassembled parts to sit in the room overnight.

17.22 Assemble the empty sample tube and weigh to the nearest 0.1 mg.

17.23 Disassemble the sample tube and soak the tube and gasket in 4M  $HNO_3$  at  $75^\circ$  to  $80^\circ C$  for 1 h.

17.24 Rinse with deionized water and place in the stainless steel beaker.

17.25 Clean the metal parts with detergent and rinse with deionized water and acetone.

17.26 Place the metal parts to the stainless steel beaker and dry all parts in the vacuum oven at  $80^\circ C$  and 29 in Hg overnight.

17.27 Reassemble the sample tube for the next sample.  
17.28 Set the temperatures of the furnace and tube furnace at  $875^\circ C$ .

17.29 Establish a steam flow to the furnace equal to 1 L of water per hour.

17.30 Place the boat into the furnace with the platinum cover on the boat and pyrohydrolyze the sample for 1 h.

17.31 Remove the boat from the furnace, cool, and place in a desiccator while still warm.

17.32 Desiccate the sample for 1 h and weigh quickly to the nearest 0.1 mg.

17.33 Transfer a portion of the  $U_3O_8$  residue to a vial and submit for spectrographic analysis to determine the weight of nonvolatile impurities.

17.34 Place the platinum boat in hot 4M  $HNO_3$  for 3 to 4 h and rinse with deionized water acetone.

18. Calculation

18.1 Calculate the weight fraction of uranium in the sample as follows:

$$gU/g UF_6 = (A - (AB))(\text{Gravimetric Factor})/W \quad (1)$$

where:

- Gravimetric Factor =  $gU/g U_3O_8$  which varies with isotopic composition. Theoretical stoichiometry for  $U_3O_8$  cannot be assumed and the actual  $gU/g U_3O_8$  must be established by potentiometric titration (4-7). (Tri-diffusion plant committee with DOE approval has established 0.8479 g U/g  $U_3O_8$  by titration as the factor for natural uranium,
- A = grams of  $U_3O_8$  from the pyrohydrolysis of  $UO_2F_2$ ,
- B = grams of impurity metal oxides per gram of  $U_3O_8$ ,
- W = corrected sample weight in grams.

The correction is for the combined effects of cover gas trapped over the  $UF_6$  in the sample tube and the air buoyancy correction (8). The following equation has been determined for the sample tube in Fig. 3 and the subsampling conditions described in 10.2. The correction equation is applicable for sample weights in the range of 7 to 13 g.

$$W = (1.00047)x - 0.0058 \quad (2)$$

where:

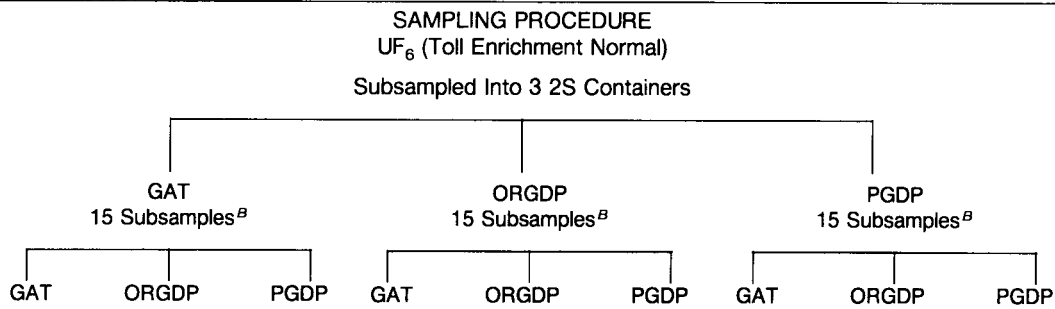
- x = observed  $UF_6$  sample weight, g.

19. Precision and Bias

19.1 Precision—The precision within a laboratory and between laboratories was established by analyzing 15 samples at each laboratory. The sampling scheme is shown in Table 2. Within a laboratory, based on 15 measurements made on separate days the relative standard deviation is 0.021 %. The results from all the laboratories are shown in Table 3.

19.2 Bias—To establish an estimate of bias for the gravimetric method, a series of comparative analyses of  $UF_6$  control batches were made using the gravimetric and potentiometric

TABLE 2 Interlaboratory Study<sup>A</sup>—Determination of Uranium in Uranium Hexafluoride



<sup>A</sup> Date of study—October 1983; Participating laboratories—Goodyear Atomic Corporation, Portsmouth, Ohio (GAT); Martin Marietta Energy Systems, Inc., Oak Ridge, Tennessee (ORGDP); Martin Marietta Energy Systems, Inc., Paducah, Kentucky (PGDP).  
<sup>B</sup> Five tubes analyzed at each laboratory.

TABLE 3 Results of Interlaboratory Study—U in UF<sub>6</sub>

Analysis Site %U in UF <sub>6</sub>			
GAT	ORGDP	PGDP	
<i>Subsampled at GAT:</i>			
67.600	67.619	67.589	
67.601	67.574	67.575	
67.583	67.607	67.612	
67.611	67.600	67.612	
67.618	67.606	Sample Lost	
<i>Subsampled at ORGDP:</i>			
67.614	67.580	67.611	
67.611	67.621	67.598	
67.587	67.600	67.501	
67.599	67.606	67.610	
67.617	67.596	67.624	
<i>Subsampled at PGDP:</i>			
67.616	67.588	67.591	
67.586	67.602	67.620	
67.573	67.612	67.612	
67.614	67.606	67.612	
67.607		67.586	
<i>Mean and Standard Deviation:</i>			
67.602 ± 0.014	67.601 ± 0.013	67.603 ± 0.014	

titration methods. The potentiometric titration was used as the reference method because the uranium was measured directly using NIST potassium dichromate.<sup>10</sup> The results are shown in Table 4.

<sup>10</sup> Standard reference material, now available as NIST SRM 136e.

## TITRIMETRIC DETERMINATION OF URANIUM

### 20. Scope

20.1 This test method (9) provides a highly precise and accurate determination of uranium. It is an adaptation of a basic method for determining uranium described in Ref. 10. It should only be used for the analysis of U<sub>3</sub>O<sub>8</sub> which is dissolved with the formation of near-theoretical amounts of uranium(IV).

### 21. Summary of Test Method

21.1 A sample of the U<sub>3</sub>O<sub>8</sub> produced by the hydrolysis of the UF<sub>6</sub> and ignition of the resulting UO<sub>2</sub>F<sub>2</sub> is dissolved in H<sub>3</sub>PO<sub>4</sub>-HF to give a solution containing about 1/3 uranium(IV) and 2/3 uranium(VI) instead of all uranium(VI). The uranium(VI) is then reduced by the addition of ferrous sulfate in phosphoric acid. The reduction of all the uranium to uranium(IV) is ensured by the addition of more ferrous sulfate. Excess ferrous ion is destroyed by the addition of nitric acid with molybdate catalyst at an optimum temperature. The solution is diluted and vanadium(IV) is added as solid vanadyl sulfate and the uranium(IV) is titrated potentiometrically with potassium dichromate. The quantity of uranium found is then used to determine the actual gravimetric factor, U/U<sub>3</sub>O<sub>8</sub>, of the U<sub>3</sub>O<sub>8</sub> sample so that the uranium in the original UF<sub>6</sub> sample can be calculated.

TABLE 4 Determination of Uranium in Uranium Hexafluoride—Comparison of Gravimetric and Potentiometric Titration Methods

Control UF <sub>6</sub> Date <sup>A</sup>	Method	Number of Measurements	%Uranium		Bias Estimate <sup>B</sup>
			Mean	SD	
9/78	Gravimetric	24	67.610	0.009	-0.001
	Potentiometric Titration	9	67.611	0.015	
5/82–8/82	Gravimetric	30	67.596	0.010	-0.009
	Potentiometric Titration	8	67.605	0.011	
7/83–9/83	Gravimetric	25	67.610	0.006	+ 0.005
	Potentiometric Titration	8	67.605	0.010	

<sup>A</sup>Control UF<sub>6</sub> used in 9/78 was a different batch of material from that used in 1982 and 1983.

<sup>B</sup>Potentiometric titration results are used as the reference values for the bias estimates.



**22. Interferences**

22.1 Milligram quantities of silver, mercury, vanadium, manganese, or platinum metals can interfere. Halides including large amounts of uncomplexed fluoride can interfere. The impurities normally found in U<sub>3</sub>O<sub>8</sub> do not interfere.

**23. Apparatus**

23.1 *pH Meter*, equipped with calomel and platinum electrodes. Construct the platinum electrode by making a short coil of stout wire and clean daily by immersing in hot HNO<sub>3</sub> and flaming to a red heat.

23.2 *Magnetic Stirrer* with 33-mm-long TFE-fluorocarbon-coated stirring bar.

23.3 *Buret*, 10-mL.

**24. Reagents**

24.1 *Ferrous Sulfate Solution* (1 M)—Add 100 mL of H<sub>2</sub>SO<sub>4</sub> to 750 mL of water, add 280 g of ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O) and stir the mixture until the salt dissolves. Dilute the solution to 1 L with water and mix well.

24.2 *Hydrofluoric Acid* (48 %).

24.3 *Nitric Acid-Sulfamic Acid-Ammonium Molybdate Reagent*—Dissolve 4.0 g of ammonium molybdate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O] in 400 mL of water; add 500 mL of HNO<sub>3</sub> and 100 mL of the 1.5 M sulfamic acid. Mix the solution well.

24.4 *Orthophosphoric Acid* (85 %).

24.5 *Potassium Dichromate*, solid, primary-standard grade.

24.6 *Potassium Dichromate Solution* (0.60000 g/L)—Prepare from primary-standard grade material weighed to 0.02 mg, and correct the weight for purity and buoyancy.

24.7 *Sulfamic Acid* (1.5 M)—Dissolve 150 g of sulfamic acid in 1 L of cold water.

24.8 *Sulfuric Acid* (1 M and 8 M).

24.9 *Vanadyl Sulfate* (VOSO<sub>4</sub>·2H<sub>2</sub>O), solid.

**25. Procedure**

25.1 Prepare sample as described in 17.1 to 17.20.

25.1.1 Weigh a 2-g sample to 0.02 mg into a 500-mL tall-form beaker. Apply a buoyancy correction if necessary.

25.1.2 Add a mixture of 50 mL of H<sub>3</sub>PO<sub>4</sub>, 1 mL of 48 % HF, and 1 mL of the potassium dichromate solution. Heat the solution on a hot plate to near boiling, but do not allow it to boil. Swirl the beaker and heat until the sample is completely dissolved as observed with a white background placed under the beaker.

25.1.3 Cool the solution and wash down the beaker sides with about 50 mL of water. Dissolve any salt that has precipitated by swirling. Place the uncovered beaker on a steam bath overnight to allow time for reconstituting the H<sub>3</sub>PO<sub>4</sub> solution.

25.1.4 Add a sufficient quantity of 1 M ferrous sulfate solution calculated to reduce the uranium(VI) portion of the sample (millilitres of ferrous solution = 4.7 × weight of U<sub>3</sub>O<sub>8</sub>) measuring the solution to 0.1 mL. Swirl the solution and digest for 1 h on the steam bath. Cool the solution to room temperature, about 25°C.

25.1.5 From this point on follow each step without delay except as indicated. Add 5 mL of 8 M H<sub>2</sub>SO<sub>4</sub>, 5 mL of the 1.5

M sulfamic acid and 2 mL of the 1 M ferrous sulfate solution in the order given. Swirl the solution to wash the beaker sides.

25.1.6 Place a thermometer in the solution, adjust the temperature to 35°C, and wash down the beaker sides with 10 mL of the HNO<sub>3</sub>-sulfamic acid-ammonium molybdate reagent. Swirl the solution for exactly 2.5 min and allow it to stand for an additional 0.5 min. Remove the thermometer, washing it with 100 mL of water. Add a previously weighed quantity (corrected for buoyancy and purity) of solid potassium dichromate about 7.5 mg less than that required to oxidize the uranium(IV).

25.1.7 Add 100 to 125 mg of solid vanadyl sulfate.

25.1.8 Insert the electrodes and titrate with the standard dichromate solution in a 10-mL buret to a potential of about 480 mV. Complete the titration through the end point by adding 0.10-mL increments of titrant, reading the potential a few seconds after each addition.

25.1.9 Calculate the volume of dichromate solution that was needed to reach the inflection point in the conventional way from the second derivative of the potentials. Add the weight of dichromate in this volume of solution to the weight of solid used previously.

25.1.10 Calculate the grams of uranium in the U<sub>3</sub>O<sub>8</sub> sample taken and then calculate the gravimetric factor to determine the weight of uranium in the weight of UF<sub>6</sub> sample taken.

**26. Calculations**

26.1 Calculate the volume of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution used in the titration according to the following example:

Volume, mL	Potential, V	dV	d <sup>2</sup> V
6.00	0.470	21	+ 143
6.10	0.491	164	-132
6.20	0.655	32	
6.30	0.687		

$$\text{Volume of titrant} = V = 6.10 + 0.10 [143/(143 + 132)] = 6.15200 \quad (3)$$

26.2 Calculate the grams of uranium in the sample as follows:

$$U, g = (D + vC)/F \quad (4)$$

where:

- D = weight of solid K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> added, g,
- v = volume of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> titrant solution used, mL,
- C = concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> titrant solution, g/mL, and
- F =  $\frac{\text{molecular weight of K}_2\text{Cr}_2\text{O}_7/6}{\text{atomic weight of uranium}/2}$

$$= 0.41198 \text{ for normal uranium.}$$

This calculation is based on normal uranium. If the uranium in the sample is of an isotopic composition different from natural, a correction must be made as given in 11.1 of Methods C 696.

26.3 Determine the gravimetric factor for the ignition conditions used and for the isotopic composition of the uranium in the sample, as follows:

$$\text{Gravimetric factor} = U/U_3O_8 \quad (5)$$

where:

$$U = \text{weight of uranium found in sample, g, and}$$

$U_3O_8$  = weight of  $U_3O_8$  sample taken, g.

26.4 With this gravimetric factor, continue with the calculation of the g U/g  $UF_6$  as given in the Gravimetric Procedure.

## 27. Reliability

27.1 From the data of 10 sets of analyses (each set consisting of at least five measurements), the pooled relative standard deviation of a single determination was calculated to be 0.0044 %.

27.2 The accuracy was assessed by gravimetric analysis of uranium metal by ignition to  $U_3O_8$  which was then analyzed by the titrimetric method. Seven analyses by this method gave a value which indicated no bias relative to the gravimetric value. Analysis of the National Institute of Standards and Technology (NIST) SRM 950a by the titrimetric procedure gave a value of 99.926 % instead of the certified value of 99.94 %  $U_3O_8$  after ignition at 900°C for 1 h.

## PREPARATION OF HIGH-PURITY $U_3O_8$

### 28. Scope

28.1 The procedure describes the preparation of chemically ultrapure urano-uranic oxide ( $U_3O_8$ ) in batches of 200 g. For larger quantities of oxide, several batches can be composited by blending, grinding, sieving, and reblending. The procedure, as presented, utilizes uranium hexafluoride ( $UF_6$ ) as the starting material. Other uranium compounds, however, such as the oxides or the nitrate salt, can be used by starting at the appropriate step in the procedure.

### 29. Summary of Test Method

29.1 Uranium hexafluoride is purified by vapor-phase transfer from a larger cylinder to a clean knockout cylinder, Fig. 4, by using an appropriate vacuum manifold. The  $UF_6$  is hydrolyzed in ice-cold distilled water and the resultant uranyl fluoride ( $UO_2F_2$ ) solution is evaporated to dryness. The solid, dry  $UO_2F_2$  is converted to  $U_3O_8$  by pyrohydrolysis. The  $U_3O_8$  is dissolved in 2 N  $HNO_3$  and filtered. The uranyl nitrate [ $UO_2(NO_3)_2$ ] solution is adjusted to pH 1 with freshly prepared ammonium hydroxide ( $NH_4OH$ ). Uranium peroxide ( $UO_4 \cdot xH_2O$ ) is precipitated from the solution by the slow addition of hydrogen peroxide ( $H_2O_2$ ) solution adjusted to pH 1 with  $HNO_3$ . After settling, the precipitate is washed by decantation, filtered, washed, and ignited to  $U_3O_8$ .

### 30. Apparatus

30.1 *Electric Muffle Furnace*, 1000°C capability, equipped with automatic temperature controller and an inlet for a steam supply, to provide pyrohydrolysis conditions.

30.2 *Nickel Cylinder*, 76 mm in diameter by 204 mm long, 3-mm wall thickness, equipped with two Monel or nickel-plated diaphragm-type valves.

30.3 *Fluorothene Cylinder*, as shown in Fig. 4.

30.4 *Critically Safe Container* (Note 2), polyethylene, 127 mm in diameter and 1224 mm tall, with a polyethylene screw-type cap.

30.5 *Platinum Dishes*, 200 to 300-mL capacity.

30.6 *Büchner funnel*, 127 mm in diameter.

30.7 *Sieve*, constructed of acrylic plastic, with easily re-

placeable stainless steel screens.<sup>11</sup>

30.8 *Mortar and Pestle*, boron carbide.

NOTE 2—While this procedure describes the preparation of oxide in batches of 200 g, some of the starting apparatus can easily handle larger quantities, which may be convenient for some laboratories.

### 31. Reagents

31.1 Use only reagent grade chemicals and distilled water.

### 32. Cleaning of Equipment

32.1 Wash the knockout cylinders with a 10 weight % sodium carbonate-5 volume % hydrogen peroxide solution, rinse thoroughly with tap water followed by distilled water, and dry at 110°C. Assemble the dry cylinder and treat with 1 atm of approximately 10 % fluorine in nitrogen at 110°C for 16 h. After cooling, evacuate the cylinder to remove the fluorine and close the valves while the cylinder is under vacuum. The cylinder is ready at this point to receive  $UF_6$ .

32.2 Wash the *critically safe* polyethylene containers with 8 N  $HNO_3$ , rinse thoroughly with warm tap water, and rinse with distilled water.

32.3 Clean polyethylene beakers, bottles, and vinyl tubing in the same manner as the polyethylene *critically safe* containers.

32.4 Wash the Büchner funnel with 8 N  $HNO_3$ , rinse with hot tap water and with distilled water.

32.5 Place the platinum dishes in 8 N  $HNO_3$  and heat to boiling. Decant the acid and replace with fresh 8 N  $HNO_3$  at least three times. Remove the platinum dishes and rinse with distilled water.

32.6 Clean the body, cap, and pan of the sieve with 4 N  $HNO_3$ , rinse in warm tap water, followed by distilled water, drain, and dry at room temperature. Vapor degrease the stainless steel screen, clean with 4 N  $HNO_3$ , rinse with warm tap water followed by distilled water, and dry at 110°C.

32.7 Wipe the boron carbide mortar and pestle clean with tissue, clean with 2 % (V/V) hydrochloric acid (HCl) in ethyl alcohol, rinse with distilled water, and dry at 110°C. Place a 10-g portion of the oxide to be ground in the mortar and grind with the pestle for 10 min. Repeat this cleaning and grinding procedure using a second 10-g portion of oxide. Discard both portions of oxide. Again, clean the mortar and pestle with 2 % HCl in ethyl alcohol, rinse with distilled water, and dry at 110°C.

### 33. Procedure

33.1 *Vapor Transfer and Hydrolysis of  $UF_6$* :

33.1.1 Attach the nickel cylinder, containing the  $UF_6$  which has been transferred from a larger supply, and also a clean and tared knockout cylinder to an appropriate vacuum manifold.

33.1.2 Place a constant-temperature (50°C) water bath around the sample cylinder and an ice-and-water bath around the receiving knockout cylinder.

33.1.3 After the cylinders have reached the temperatures of their baths, evacuate the connecting lines and receiving cylinder. Transfer the  $UF_6$  vapor to the knockout cylinder but do not

<sup>11</sup> Similar to Spex Industries Stock No. 3540.

allow the pressure of the system to become greater than  $\frac{1}{3}$ atm, absolute. Control the pressure in the system by adjusting the valve of the sample cylinder.

33.1.4 When it is estimated that sufficient uranium has been transferred to the knockout cylinder, close the valves and remove the knockout cylinder from the manifold. (250 g of  $\text{UF}_6$  is normally sufficient to prepare 200 g of  $\text{U}_3\text{O}_8$ .)

33.1.5 Dry the knockout cylinder and weigh to determine the amount of  $\text{UF}_6$  transferred. If additional  $\text{UF}_6$  is needed, repeat 33.1.1 through 33.1.5.

33.1.6 Cool 1 to 2 L of distilled water to near-freezing for hydrolysis of 250 g of  $\text{UF}_6$ .

33.1.7 Cool the nickel knockout cylinder in liquid nitrogen for 30 min. Remove the cap, invert the cylinder over the *critically safe* container, and rap the bottom of the cylinder sharply with a hammer or mallet until the solid  $\text{UF}_6$  falls to the bottom of the container. Immediately add the chilled, distilled water to the container to hydrolyze the  $\text{UF}_6$  to  $\text{UO}_2\text{F}_2$ .

33.1.8 When the  $\text{UF}_6$  has hydrolyzed and the solution has reached room temperature, fasten the cap securely, on the *critically safe* container, invert and roll the container until the  $\text{UO}_2\text{F}_2$  solution is thoroughly mixed.

### 33.2 Conversion of $\text{UO}_2\text{F}_2$ to $\text{U}_3\text{O}_8$ :

33.2.1 Transfer the  $\text{UO}_2\text{F}_2$  solution to platinum dishes by siphoning directly into dishes or into an intermediate polyethylene beaker and then pouring into the dishes. The siphon can be started by filling the tube with distilled water.

33.2.2 Evaporate the solution in the platinum dishes to dryness under infrared heat lamps.

33.2.3 Ignite the dried  $\text{UO}_2\text{F}_2$  to  $\text{U}_3\text{O}_8$  at  $850^\circ\text{C}$  for 3 h in a pyrohydrolysis furnace (pyrohydrolysis prevents volatilization of uranium and removes fluorides which interfere with subsequent precipitation of the uranium).

### 33.3 Conversion of $\text{U}_3\text{O}_8$ to $\text{UO}_2(\text{NO}_3)_2$ with Nitric Acid:

33.3.1 Weigh 200-g portions of the oxide into separate beakers (Note 3). Dissolve the  $\text{U}_3\text{O}_8$  in a minimum amount of 2 N  $\text{HNO}_3$ ; use heat to accelerate dissolution.

33.3.2 Filter the  $\text{UO}_2(\text{NO}_3)_2$  solution, using a fine-textured, low-ash, acid-washed filter paper. Collect the filtered solution in a 127-mm polyethylene *critically safe* container.

33.3.3 When all of the material has been collected in the container, homogenize the solution by air agitation.

NOTE 3—The number of beakers permissible will depend on the  $^{235}\text{U}$  enrichment and on the nuclear safety requirement to limit the amount of material processed at any one time to 350 g of  $^{235}\text{U}$ .

### 33.4 Uranium Peroxide Precipitation:

33.4.1 Transfer portions of the  $\text{UO}_2(\text{NO}_3)_2$  solution, containing about 150 to 175 g of uranium, to separate 4000-mL beakers. The volume of solution in each beaker should not exceed 2000 mL.

33.4.2 Adjust the pH of the solutions to 1.0 on a pH meter, using freshly prepared ammonium hydroxide made by bubbling ammonia gas through distilled water. (Ammonium hydroxide prepared in this manner contains a minimum amount of silica.) Remove the electrodes from the solution when a pH of 1.0 is reached.

33.4.3 Calculate the amount of peroxide required to precipitate the uranium, using the following equation: g

$\text{U} \times 1.3 = \text{mL of 30 \% reagent hydrogen peroxide.}$

33.4.4 Dilute the calculated amount of reagent peroxide with four times its volume of nitric acid solution at a pH of 1.0. Readjust the acidity to a pH of 1. (The purpose of this dilution is to avoid a localized precipitation of the  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ .)

33.4.5 Add the diluted hydrogen peroxide slowly to the uranium solution while mixing with a motor-driven glass stirring rod.

33.4.6 After 30 min stirring, adjust the pH of the solution again to 1.0, using ammonium hydroxide prepared as in 33.4.2. (The formation of  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$  from  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{H}_2\text{O}_2$  results in an increase in acidity.) Remove the stirrer and allow the  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$  to settle at least 16 h. Keep the solution covered during this time.

33.4.7 Decant the supernatant solution. Wash the precipitate with two 1000-mL portions of 1 %  $\text{H}_2\text{O}_2$  in  $\text{HNO}_3$  at a pH of 1.0, allowing the precipitate to settle between washes and decanting the supernatant solution. Vacuum-filter the precipitate, using a 127-mm Büchner funnel and fine-textured, low-ash, acid-washed filter paper.

33.4.8 When the uranium precipitate from a single beaker is on the filter paper, wash three times by covering the filter cake with a solution of 1 %  $\text{H}_2\text{O}_2$  in  $\text{HNO}_3$  at a pH of 1.0. Do not continue suction after the cake becomes dry, since this practice may introduce airborne impurities, unless the funnel is covered with a filter paper held tightly with rubber bands.

### 33.5 Conversion to $\text{U}_3\text{O}_8$ , Sieving, and Final Ignition:

33.5.1 Dry the filter cake in the funnel under an infrared lamp until the precipitate can be easily separated from the paper and transferred to a weighed platinum dish. (To minimize the presence of carbon in the uranium oxide, do not ignite the filter paper.)

33.5.2 Ignite the  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$  to  $\text{U}_3\text{O}_8$  at  $900^\circ\text{C}$  for 4 h. Weigh to determine the amount of  $\text{U}_3\text{O}_8$ .

33.5.3 Sieve the oxide in small lots, using the acrylic plastic sieve with stainless steel screen. (In the absence of any other sieve-size requirement, general needs for handling and blending are met by passage through a 60-mesh screen.) The oxide which passes through the sieve is placed into a blending jar (less than 127 mm in diameter).

33.5.4 Grind the oxide that does not pass the screen with a boron carbide mortar and pestle until it passes the screen.

33.5.5 Reignite the  $\text{U}_3\text{O}_8$  at  $900^\circ\text{C}$  for 16 h.

33.6 *Blending and Sampling*—Blend the oxide to assure homogeneous composition and representatively sample the batch for spectrochemical and chemical analysis, to assure high purity.

## 34. Purity

34.1 The chemical purity of  $\text{U}_3\text{O}_8$  properly prepared by the prescribed procedure will be 99.995 weight % or better. The combined impurities, detected by spectrographic analysis for 61 metallic elements and chemical analysis for carbon, sulfur, and phosphorus, in several final oxide supplies prepared in kilogram quantities, ranged from 10 to 40 ppm (uranium basis).



## ISOTOPIC ANALYSIS BY DOUBLE-STANDARD MASS-SPECTROMETER METHOD

### 35. Scope

35.1 This test method is applicable to the determination of the isotopic composition of UF<sub>6</sub> samples. The test method as described is specific for the direct determination of the <sup>235</sup>U concentration of UF<sub>6</sub> samples having a <sup>235</sup>U content of 60 mol % or less. However, the test method is equally appropriate for the direct determination of any of the isotopes of uranium of any enrichment when suitable UF<sub>6</sub> isotopic standards are available. This test method is designed to minimize all known sources of analytical bias.

### 36. Summary of Test Method

36.1 The unknown sample and two standards whose <sup>235</sup>U contents bracket that of the unknown are introduced in sequence into the mass spectrometer, and measurements are made which are a function of the mol ratio of <sup>235</sup>U to the total of the other isotopes of uranium. These measurements together with the known composition of the standards permit calculation of the <sup>235</sup>U composition of the sample by linear interpolation (**11 to 16**).

36.2 The symmetrical, 6-entry sequence of sample-standard introductions is designed to minimize biases resulting from instrument drift, sample interaction or memory, and the non-linearity of the relationship between the measured resistance ratios and the true sample mol ratios. Corrections generally are not required for instrument memory.

### 37. Apparatus

37.1 *Mass Spectrometer* with the following features and capabilities (**12, 14, 17**):

37.1.1 The instrument must have an electron bombardment ion source having an efficiency such that a sample flow rate of about 0.03 std ml of UF<sub>6</sub>/h will result in a total ion current for UF<sub>5</sub><sup>+</sup> ions of approximately 10<sup>-9</sup> A.

37.1.2 The sample inlet system must have a minimum of three points for attachment of samples, the necessary valves to evacuate the sample lines and admit the UF<sub>6</sub> into the ion source, and a variable leak to control the flow of UF<sub>6</sub> into the ion source.

37.1.3 A dual ion collector (**18**) must be used. The first detector, called the high-current collector, contains a central slit, preferably adjustable, to permit passage of 95 to 100 % of the ions of the <sup>235</sup>U isotope (mass 330). This detector intercepts ions of the other isotopes of uranium within a mass range of about 1.5 % of mass 330. The <sup>235</sup>U ions passing through the slit are intercepted by a second detector, called the low-current collector.

37.1.4 The measuring system must provide a precise null-balance measurement of the ratio of the ion signals from the low-current and high-current detectors. Such a system usually consists of two electrometer amplifiers, a constant-impedance ratio decade, a ratio recorder or two amplifiers, and a digital ratiometer. The sensitivity of the system should be such that a change of 1 × 10<sup>-15</sup> A ion current can be detected. An attenuation range of at least a factor of 100 should be provided

for the low-current amplifier. If <sup>235</sup>U concentrations greater than 60 mol % are to be determined directly, a switch must be provided to reverse the amplifier leads to the ratio decade panel, and a similar attenuation range must be provided for the high-current amplifier. For those measurements the <sup>235</sup>U still passes through the slit, but the measurement is now a function of the ratio of the other isotopes to the <sup>235</sup>U isotope.

37.1.5 The resolving power of the instrument should be such that the <sup>235</sup>UF<sub>5</sub><sup>+</sup>-<sup>238</sup>UF<sub>5</sub><sup>+</sup> valley height should be less than 3.0 % of the <sup>235</sup>UF<sub>5</sub><sup>+</sup> peak height after the peak height has been normalized. The normalization consists of dividing the observed peak height by the sample <sup>235</sup>U concentration, expressed as a percentage. This resolution requirement should be met with the collector slit width adjusted to pass at least 95 % of the <sup>235</sup>U ion beam.

37.1.6 If the concentrations of the minor isotopes, <sup>234</sup>U and <sup>236</sup>U, are to be measured, the <sup>234</sup>UF<sub>5</sub><sup>+</sup>-<sup>235</sup>UF<sub>5</sub><sup>+</sup> valley should be less than 50 % of the <sup>234</sup>UF<sub>5</sub><sup>+</sup> peak height. To meet this requirement it will be necessary to narrow the collector slit width and reduce the ion beam transmission to 70 to 80 %.

### 38. Procedure

#### 38.1 *Sample Preparation:*

38.1.1 A bias will be introduced into the analysis if impurities are present in the vapor phase of the sample or either standard. Prepare the UF<sub>6</sub> sample containers for the analysis as follows:

38.1.1.1 Attach the sample and standard containers to the sample inlet system. The low standard, *A*, should have a <sup>235</sup>U concentration lower than that of the sample, *X*, and the high standard, *B*, should have a concentration higher than the sample. The ratio of mol ratios of the standard pair should be about 1.3.

38.1.1.2 Open the appropriate valves to evacuate the sample lines of the inlet system.

38.1.1.3 After the system has been evacuated, open the valve on the sample container and then close quickly to vent the gas phase of the sample to the pumping system.

38.1.1.4 After the pumping system has had sufficient time to evacuate the vented gases, repeat 38.1.1.3.

38.1.1.5 Repeat 38.1.1.3 and 38.1.1.4 separately for the *A* and *B* standard containers.

38.1.1.6 Admit the *B* standard through the variable leak into the ion source for about 15 s, observe the ion source pressure, and remove the sample from the source.

38.1.1.7 Repeat 38.1.1.6 for the sample and for the *A* standard.

38.1.1.8 If the source pressure readings are the same, the samples are ready for the analysis (see 38.2).

38.1.1.9 If a high pressure is observed for one of the samples, immerse the sample container in a mixture of trichloroethylene and dry ice; open the container valve; and pump off the volatile impurities.

38.1.1.10 Close the container valve, allow the sample to reach ambient temperature, and repeat 38.1.1.6. If the source pressure reading is the same as the other samples, the samples are ready for the analysis (see 38.2).

38.1.1.11 If the pressure is still high, liquefy the UF<sub>6</sub> by heating the sample container to 70°C; then open the valve on

the container and close quickly to vent the gas phase to the pumping system.

38.1.1.12 After the pumping system has had sufficient time to evacuate the vented gases, repeat 38.1.1.6. If necessary, repeat 38.1.1.9 or 38.1.1.11, or both, until no increase in pressure is observed.

### 38.2 Instrument Preparation:

38.2.1 Prepare the instrument for the analysis as follows:

38.2.1.1 Operate the appropriate valves to admit the low standard, A, through the variable leak into the ion source.

38.2.1.2 Adjust the mass spectrometer high voltage or magnet current, or both, to focus the  $UF_5^+$  ions on the upper detector plate.

38.2.1.3 Make a fine adjustment of the high-voltage or magnet current to focus the  $^{235}U$  ion beam (for samples containing 60 mol %  $^{235}U$  or less) of the  $UF_5^+$  ion group through the slit to the lower detector plate, while the other ions of the  $UF_5^+$  ion group are focused on the upper collector plate. This step, known as *peaking up*, is completed when the signal for the low-current collector plate is maximized.

38.2.1.4 Adjust the variable leak so that the flow of  $UF_6$  into the ion source produces the desired signal for the ions striking the upper collector plate. This ion current should be equivalent to approximately  $10^{-9}$  A.

38.2.1.5 Operate the valves to remove the flow of the A standard from the ion-source region, and evacuate the region for a period of 1 min or more.

### 38.3 Mass Spectrometer Measurements:

38.3.1 The sequence for the analytical determination during which the actual measurements are made is as follows: A, X, B, B, X, A, where A, X, and B represent a constant, precisely timed introduction of Standard A, Sample X, and Standard B, respectively. Each introduction is followed by a somewhat shorter, but precisely timed, period during which there is no flow of sample or standard material into the ion source. During each introduction of  $UF_6$  into the ion source, perform the following operations:

38.3.1.1 Regulate the intensity of the ions striking the upper collector plate to the desired level, and within as close a tolerance range as can be attained, by adjusting the variable leak to control the sample flow.

38.3.1.2 Adjust the high-voltage or magnet-current fine control to maximize the low-current detector signal; maintain the adjustment at this maximum value for the remainder of the timed introduction period, or sweep repeatedly across this maximum reading to obtain a series of scans of the peak maxima during the remainder of this period.

38.3.1.3 With the instrument peaked up, or while scanning the peak, obtain a reading while the electrometers for the two detecting plates are connected in a null-type measuring circuit. This reading is a function of the ratio of the number of ions striking the lower detector plate to the total number of ions striking the upper plate. Use only the data taken during the last half of the timed introduction period.

38.3.1.4 For each analytical sequence of A, X, B, B, X, A, obtain six ratio values, two for each standard and two for the sample. Average the two values obtained for each standard and the sample to obtain three ratio values designated  $R_A$ ,  $R_X$ , and

$R_B$  for each A, X, B, B, X, A sequence.

38.3.1.5 For samples in which the  $^{235}U$  content is greater than 60 mol %, reverse the amplifier leads to the ratio decade to obtain a null-balance measurement. The measurements are then a function of the ratio of the number of ions other than  $^{235}U$  to the number of  $^{235}U$  ions. As an alternative procedure, make the focus in 38.2.1.3 on the  $^{238}U$  ion beam instead of the  $^{235}U$  ion beam. This procedure will result in the determination of the weight percent  $^{238}U$ . To determine the  $^{235}U$  content, determine the minor isotopes independently, and subtract the sum of the weight percent  $^{238}U$  and the weight percent of the minor isotopes from 100 to obtain the weight percent  $^{235}U$ .

38.3.1.6 The small residual bias associated with this test method is no larger than  $\pm 0.02$ , and even this may be corrected by making end-point determinations. The end-point controls are additional measurements with one of the standards, A or B, substituted for the unknown in the analytical sequence. Thus, for an end-point measurement, follow one of the sequences A, A, B, B, A, A, or A, B, B, B, B, A, and use the results to make corrections for residual bias in the measurements on the unknown.

## 39. Calculation

39.1 For uranium having a concentration of 50 mol %  $^{235}U$  or less, calculate the weight percent  $^{235}U$  as follows:

39.1.1 Calculate the ratio of differences,  $R_D$ , as follows:

$$R_D = (R_X - R_A)/(R_B - R_A) \quad (6)$$

where:

$R_X$  = average reading for sample entries,

$R_A$  = average reading for low-standard entries, and

$R_B$  = average reading for high-standard entries.

39.1.2 Calculate the sample weight ratio,  $H_X$ , using the linear interpolation, as follows:

$$H_X = R_D (H_B - H_A) + H_A \quad (7)$$

where:

$H_X$  = weight ratio of  $^{235}U$  to other isotopes in the sample,

$H_A$  = weight ratio of  $^{235}U$  to other isotopes in the low standard,

$H_B$  = weight ratio of  $^{235}U$  to other isotopes in the high standard, and

$R_D$  = value from Eq 6

39.1.3 Calculate the weight percent  $^{235}U$  ( $U_5$ ) in the sample as follows:

$$U_5 = 100 H_X / (100 + H_X) \quad (8)$$

39.2 For samples having a  $^{235}U$  concentration greater than 60 mol %, reverse the amplifier leads to the ratio decade, and obtain reciprocal readings which are a function of the ratio of the mols of other isotopes to the mols of  $^{235}U$ . Calculate the weight percent  $^{235}U$  as follows:

39.2.1 Calculate the ratio of differences,  $R_D$ , using Eq 1.

39.2.2 Calculate the reciprocal of the weight ratio,  $H_X$ , from the relationship:

$$1/H_X = R_D [(1/H_B) - (1/H_A)] + 1/H_A \quad (9)$$

39.2.3 Calculate the weight percent  $^{235}U$  in the sample, using Eq 8.

39.3 As an alternative method of analyzing samples having



concentrations greater than 60 mol %  $^{235}\text{U}$ , determine the weight percents  $^{238}\text{U}$ ,  $^{234}\text{U}$ , and  $^{236}\text{U}$ . In each case pass the isotope of interest through the collector slit, and obtain measurements for the sample and the two bracketing standards. Use these measurements together with the known composition of the standards to calculate the sample composition by linear interpolation (Eq 7). The standard values used in the calculations are the weight ratios of  $^{238}\text{U}$  to the other isotopes,  $^{234}\text{U}$  to the other isotopes, or  $^{236}\text{U}$  to the other isotopes. Obtain the  $^{235}\text{U}$  composition by difference.

39.4 To correct for the small residual bias, intersperse analytical sequences in which each standard is treated as the sample with the sample-analysis sequences. The number of standard sequences should be about 10 % of the number of sample sequences. Run one half of the standard sequences as A, A, B, B, A, A and the other half as A, B, B, B, B, A. Designate the ratio values from these sequences  $R_A$ ,  $R_{AX}$ , and  $R_B$ ; and  $R_A$ ,  $R_{BX}$ , and  $R_B$ . Correct the sample  $R_D$  values in the following manner:

39.4.1 Calculate the end-point biases,  $R_{DA}$  and  $R_{DB}$ , from Eq 10 and Eq 11:

$$R_{DA} = (R_{XA} - R_A)/(R_B - R_A) \quad (10)$$

$$R_{DB} = (R_{XB} - R_A)/(R_B - R_A) \quad (11)$$

39.4.2 Calculate two correction factors,  $F_1$  and  $F_2$ , from Eq 12 and Eq 13:

$$F_1 = 1/(R_{DB} - R_{DA}) \quad (12)$$

$$F_2 = R_{DA}(R_{DB} - R_{DA}) \quad (13)$$

39.4.3 Then correct the sample  $R_D$  values as follows:

$$R_{DT} = F_1 R_D - F_2 \quad (14)$$

## 40. Reliability

40.1 The following tabulation shows the percent limit of error, at the 95 % confidence level, for a single determination which has been obtained using the method described.

Difference Between Standards, %	Limit of Error, %	
	Routine	Special
5	0.04	...
15	0.06	0.01
30	0.08	0.01
45	0.10	...

40.2 These values are based on thousands of determinations on a variety of  $\text{UF}_6$  samples during a 10-year period. Single-focusing, 152-mm radius, 60-deg deflection mass spectrometers were used.

40.3 Routine precision is obtained without end-point corrections and without special emphasis on instrument stability or limitations on isotopic concentrations analyzed on a given instrument. Greater selectivity with respect to instrument stability, resolving power, and other operating characteristics, as well as limitation of the isotopic range of samples exposed to the instrument and end-point corrections, are required to achieve the special precision quoted.

## ISOTOPIC ANALYSIS BY SINGLE-STANDARD MASS-SPECTROMETER METHOD

### 41. Scope

41.1 This method is applicable to the determination of the

isotopic relation between two  $\text{UF}_6$  samples. If the abundance of a specific isotope of one sample (the standard) is known, its abundance in the other can be determined. The method is flexible in that the number of times a given material is admitted to the ion source may be adjusted to the minimum required for a specified precision level.

41.2 The method may be used for the entire range of  $^{235}\text{U}$  isotopic compositions for which standards are available, and it is adaptable to the determination of any uranium isotope.

41.3 The sensitivity with which differences between two materials can be detected depends on the measuring system used, but ratio-measuring devices can generally read ratio-of-mol-ratio differences as small as 0.0001.

### 42. Summary of Test Method

42.1 The unknown sample and a standard whose isotopic composition is close to that of the sample are introduced in sequence into the mass spectrometer, and  $\text{UF}_5^+$  ions of the isotopes are focused through a mass-resolving collector slit. For  $^{235}\text{U}$  concentrations below about 70 mol %, measurements are made which are proportional to the ratio of  $^{235}\text{U}$  to the total of the other isotopes. These measurements, with the known composition of the standard, permit calculation of the  $^{235}\text{U}$  composition of the sample.

NOTE 4—The exact concentration depends on the relation of the input resistances for the low- and high-current preamplifiers.

42.2 For  $^{235}\text{U}$  concentrations greater than about 70 mol %, measurements are made which are proportional to the ratio of  $^{238}\text{U}$  to the total of the other isotopes. The  $^{234}\text{U}$  and  $^{236}\text{U}$  isotopes are determined independently, and the  $^{235}\text{U}$  is calculated by difference. Memory corrections are applied, based on the periodic measurement of the ratio of two standards.

### 43. Apparatus

#### 43.1 Mass Spectrometer:

43.1.1 A single-focusing spectrometer with a 127-mm minimum deflection radius is satisfactory when equipped and focused as follows:

43.1.1.1 Use a dual collector, so that ions from one isotope are passed through a resolving slit and focused on a low-current collector, and ions from all other isotopes are focused on a high-current collector. A resolving slit of adjustable width facilitates measurement of all isotopes.

43.1.1.2 The measuring circuit provides a precise null-balance measurement of the ratio of the two ion currents. By the use of a voltage divider or decade resistors, ratio recorders (19), or ratiometers (18), the portion of the signal on the high-current collector that equals the signal on the low-current collector can be determined. A high-current ion beam of  $10^{-10}$  to  $10^{-9}$  A is necessary, with a signal-to-noise ratio greater than 3000 in the low-current amplifier system.

43.1.1.3 Focus the instrument for resolution consistent with precision and accuracy requirements. Specify slit widths, or the percentage of the designated ions which will pass through the collector slit. Normally, adjust the collector slit to transmit at least 95 % of an ion beam (see 45.1). Under this condition, the valley between the  $^{235}\text{UF}_5^+$  ion peak and the  $^{238}\text{UF}_5^+$  ion peak should be less than 3.5 % of the height of the smaller peak (see