Designation: C 761 – 96

Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride[1]

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 reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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:

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[2]

C 753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder[2]

C 787 Specification for Uranium Hexafluoride for Enrichment[2]

C 1219 Test Methods for Arsenic in Uranium Hexafluoride[2]

C 1287 Test Method for Determination of Impurities in Uranium Dioxide by Inductively Coupled Plasma Mass Spectrometry[2]

C 1295 Test Method for Gamma Energy Emission from Fission Products in Uranium Hexafluoride[2]

D 1193 Specification for Reagent Water[3]

E 60 Practice for Photometric and Spectrophotometric

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

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[2] *Annual Book of ASTM Standards*, Vol 12.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

Methods for Chemical Analysis of Metals[4]

E 115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis[4]

E 130 Practice for Designation of Shapes and Sizes of Graphite Electrodes[4]

2.3 *U.S. Department of Energy Specifications:*

Uranium Hexafluoride: Base Charges, Use Charges, Special Charges, Table of Enriching Services, Specifications, and Packaging[5]

Uranium Hexafluoride: Handling Procedures and Container Criteria[5]

2.4 *American Chemical Society Specification:*

Reagent Chemicals [6]

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.[7] 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_6 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)[7]

7. Scope

7.1 This test method is applicable to the subsampling **(3)** of UF_6 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_6 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_6 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[8] M-16 VCR-1 female nut and an M-16 VCR-4 male nut, or equivalent.

9.6 *Nickel Filter Disk*, porous, 2-µm, free of chromium (Fig. 5). Mott Metallurgical Corp. or equivalent.[9]

9.7 *Gas Sample Cylinder*, 0.5 L.

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[4] *Annual Book of ASTM Standards*, Vol 03.05.

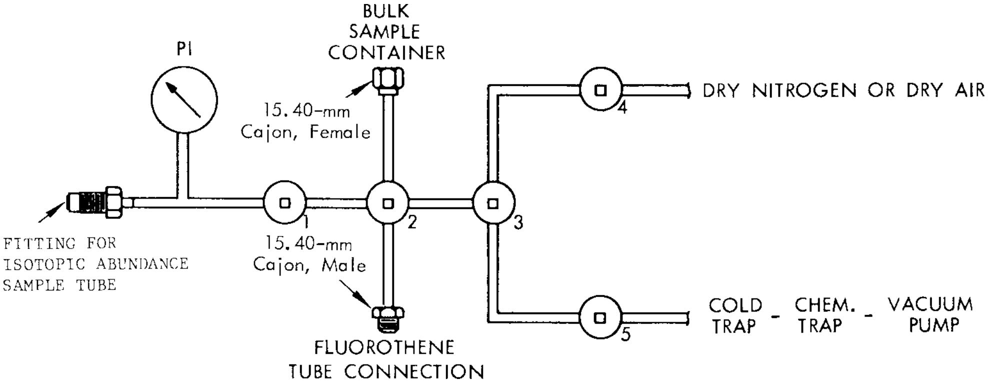
[5] United States Department of Energy, Oak Ridge, TN 37830.

[6] "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."

[7] The boldface numbers in parentheses refer to a list of references at the end of these test methods.

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

[9] 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 ⅜-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_6 from Small Containers

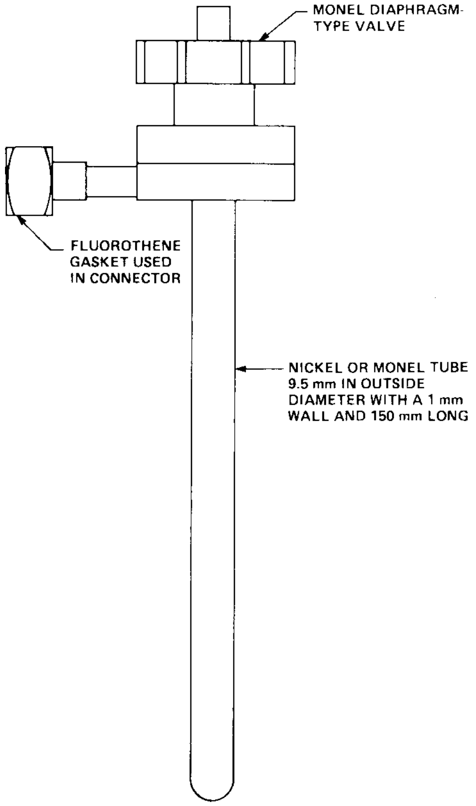


FIG. 2 Isotopic Abundance Sample Tube

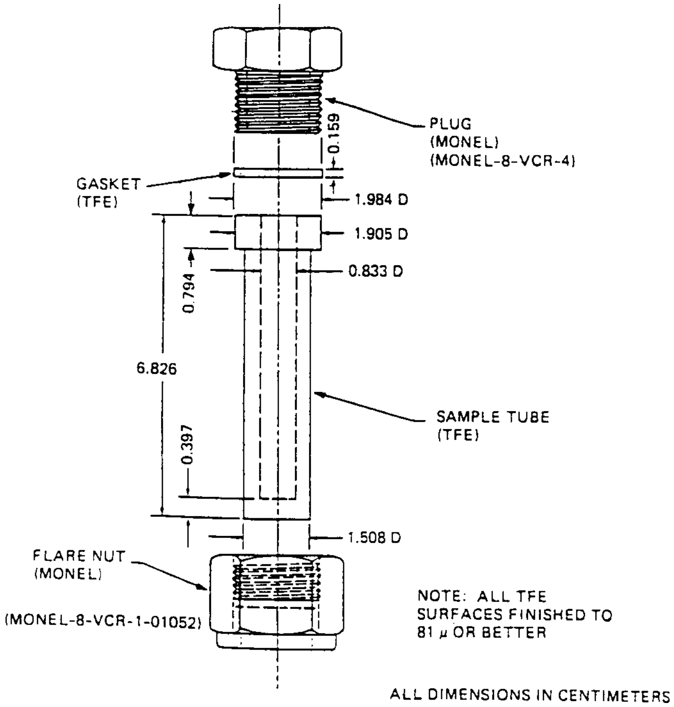


FIG. 3 Small TFCE Sample Tube

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_6 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 connection 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_6 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_6 to a fluorothene sample tube, as described below, and discard.

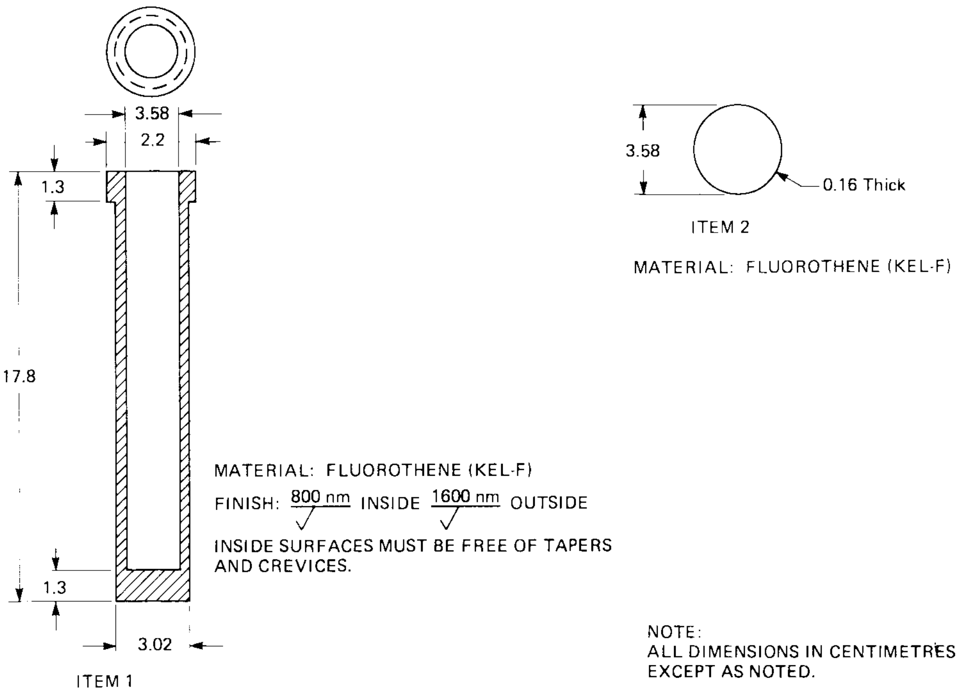


FIG. 4 Fluorothene Knockout Cylinder

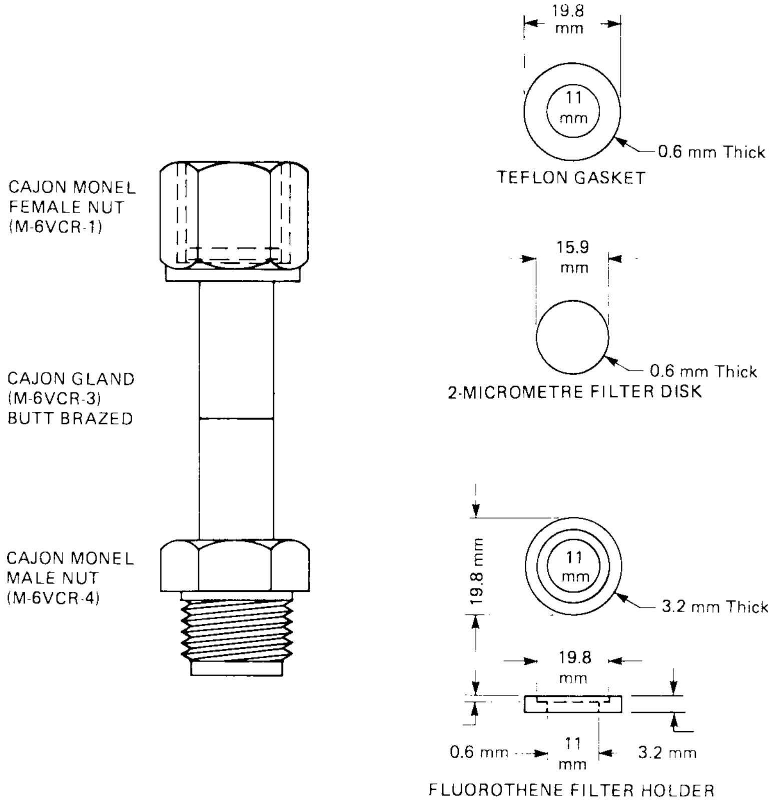


FIG. 5 Filter Disk Unit

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-µm 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 isoluble 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

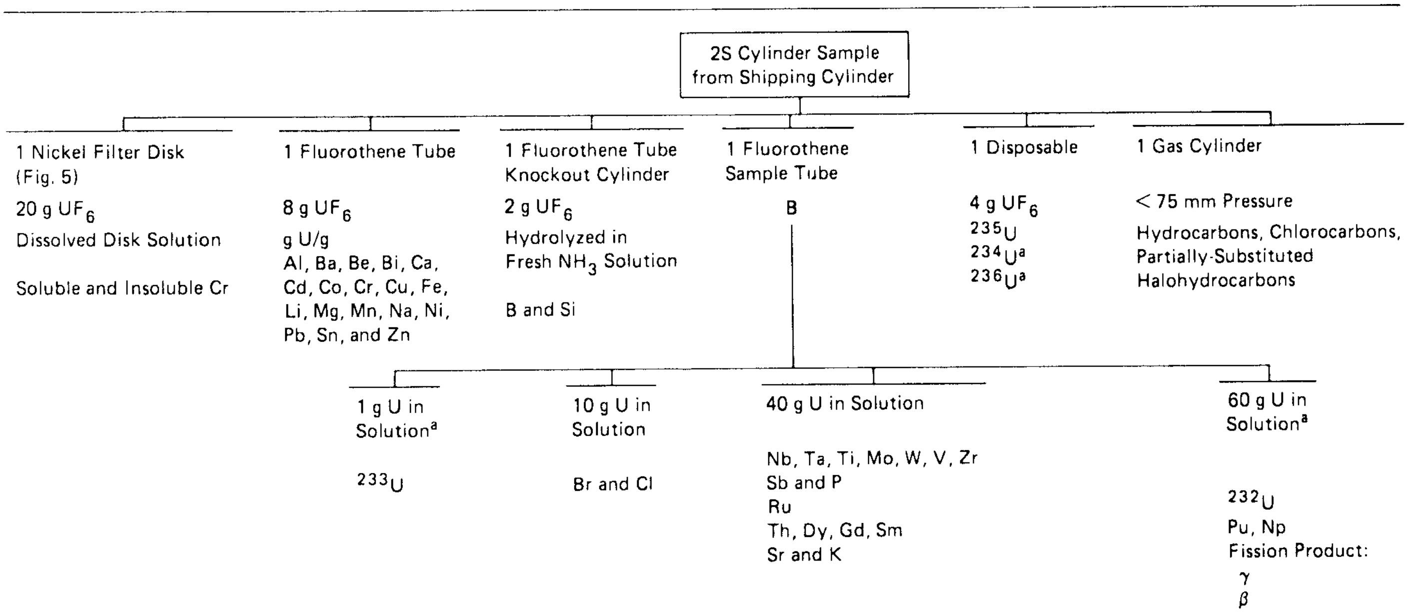
13.1 Nonvolatile impurities affect the accuracy of the method and must be measured by spectrographic analysis with corrections applied.

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_6 Specification Analyses



[a] Required only for reactor returns.

[B] 100 g UF_6 hydrolyzed in (1 + 4) HNO_3 and 100 g UF_6 hydrolyzed in ice water for ^{235}U, Br and Cl.

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_3).

15.3 *Nitric Acid* (4*M*)—Mix 500 mL of concentrated HNO_3 with 1500 mL of distilled water.

15.4 *Detergent*.

16. Sampling

16.1 A UF_6 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.

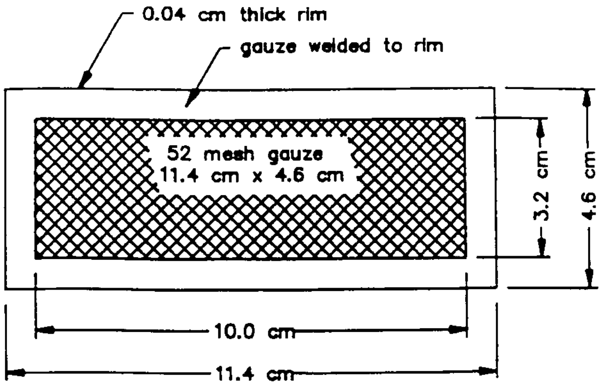
17.11 Remove the flare nut from the sample tube and immerse the tube and gasket in the chilled water in the tared platinum boat.

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

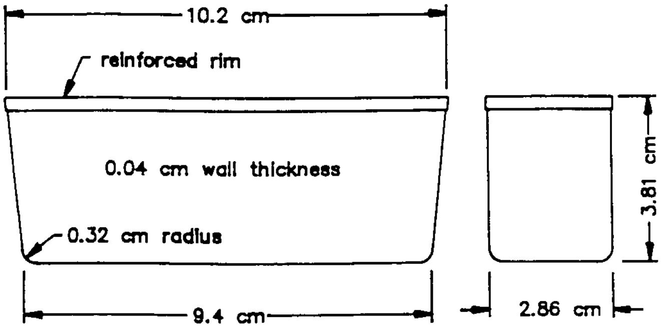
17.13 Remove the gasket with the forceps and rinse well with deionized water into the boat.

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_6 has been hydrolyzed (2 to 4 h).



Cover



Boat

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°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 4*M* HNO_3 at 75° to 80°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°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°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 4*M* 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:

$$\text{gU/g UF}_6 = (A - (AB))(\text{Gravimetric Factor})/W \tag{1}$$

where:

Gravimetric Factor = gU/g U_3O_8 which varies with isotopic composition. Theoretical stoichiomtry 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.

$$W = (1.00047)x - 0.0058 \tag{2}$$

where:

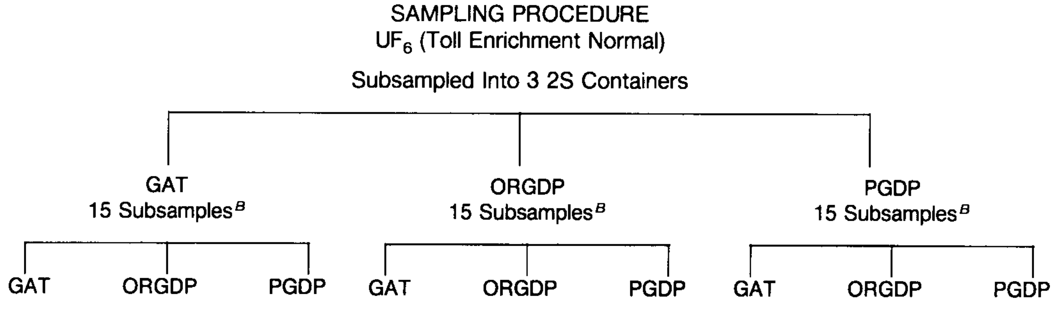
x = observed UF_6 sample weight, g.

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^A—Determination of Uranium in Uranium Hexafluoride



[A] 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).

[B] Five tubes analyzed at each laboratory.

TABLE 3 Results of Interlaboratory Study—U in UF_6

Analysis Site %U in UF_6		
GAT	ORGDP	PGDP
Subsampled at GAT:		
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
Subsampled at ORGDP:		
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
Subsampled at PGDP:		
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
Mean and Standard Deviation:		
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.[10] The results are shown in Table 4.

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_3O_8 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_3O_8 produced by the hydrolysis of the UF_6 and ignition of the resulting UO_2F_2 is dissolved in H_3PO_4-HF to give a solution containing about ⅓uranium(IV) and ⅔ 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_3O_8, of the U_3O_8 sample so that the uranium in the original UF_6 sample can be calculated.

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

Control UF_6 Date^A	Method	Number of Measurements	%Uranium		Bias Estimate^B
			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	

[A] Control UF_6 used in 9/78 was a different batch of material from that used in 1982 and 1983.

[B] Potentiometric titration results are used as the reference values for the bias estimates.

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[10] Standard reference material, now available as NIST SRM 136e.

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_3O_8 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_3 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_2SO_4 to 750 mL of water, add 280 g of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) 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 $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in 400 mL of water; add 500 mL of HNO_3 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* ($VOSO_4 \cdot 2H_2O$), 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_3PO_4, 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_3PO_4 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_3O_8) 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_2SO_4, 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_3-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_3O_8 sample taken and then calculate the gravimetric factor to determine the weight of uranium in the weight of UF_6 sample taken.

26. Calculations

26.1 Calculate the volume of $K_2Cr_2O_7$ solution used in the titration according to the following example:

Volume, mL	Potential, *V*	*dV*	d^2V
6.00	0.470	21	+ 143
6.10	0.491	164	−132
6.20	0.655	32	
6.30	0.687		

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

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

$$\text{U, g} = (D + vC)/F \tag{4}$$

where:

D = weight of solid $K_2Cr_2O_7$ added, g,

v = volume of $K_2Cr_2O_7$ titrant solution used, mL,

C = concentration of $K_2Cr_2O_7$ titrant solution, g/mL, and

F = $\dfrac{\text{molecular weight of } K_2Cr_20_7/6}{\text{atomic weight of uranium}/2}$

= 0.41198 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:

$$\text{Gravimetric factor} = U/U_3O_8 \tag{5}$$

where:

U = 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 replaceable stainless steel screens.[11]

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

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[11] Similar to Spex Industries Stock No. 3540.

allow the pressure of the system to become greater than ⅓atm, 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 UF_6 is normally sufficient to prepare 200 g of U_3O_8.)

33.1.5 Dry the knockout cylinder and weigh to determine the amount of UF_6 transferred. If additional 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 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 UF_6 falls to the bottom of the container. Immediately add the chilled, distilled water to the container to hydrolyze the UF_6 to UO_2F_2.

33.1.8 When the 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 UO_2F_2 solution is thoroughly mixed.

33.2 *Conversion of UO_2F_2 to U_3O_8*:

33.2.1 Transfer the UO_2F_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 UO_2F_2 to U_3O_8 at 850°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 U_3O_8 to $UO_2(NO_3)_2$ with Nitric Acid*:

33.3.1 Weigh 200-g portions of the oxide into separate beakers (Note 3). Dissolve the U_3O_8 in a minimum amount of 2 *N* HNO_3; use heat to accelerate dissolution.

33.3.2 Filter the $UO_2(NO_3)_2$ 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}U enrichment and on the nuclear safety requirement to limit the amount of material procesed at any one time to 350 g of ^{235}U.

33.4 *Uranium Peroxide Precipitation*:

33.4.1 Transfer portions of the $UO_2(NO_3)_2$ 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 U × 1.3 = 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 $UO_4 \cdot 2H_2O$.)

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 $UO_4 \cdot 2H_2O$ from $UO_2(NO_3)_2$ and H_2O_2 results in an increase in acidity.) Remove the stirrer and allow the $UO_4 \cdot 2H_2O$ 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 % H_2O_2 in 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 % H_2O_2 in 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 U_3O_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 $UO_4 \cdot 2H_2O$ to U_3O_8 at 900°C for 4 h. Weigh to determine the amount of U_3O_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 U_3O_8 at 900°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 U_3O_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_6 samples. The test method as described is specific for the direct determination of the ^{235}U concentration of UF_6 samples having a ^{235}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_6 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 ^{235}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 ^{235}U to the total of the other isotopes of uranium. These measurements together with the known composition of the standards permit calculation of the ^{235}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 nonlinearity 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_6/h will result in a total ion current for UF_5^+ ions of approximately 10^{-9} 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_6 into the ion source, and a variable leak to control the flow of UF_6 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 ^{235}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 ^{235}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^{-15} 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 ^{235}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 ^{235}U still passes through the slit, but the measurement is now a function of the ratio of the other isotopes to the ^{235}U isotope.

37.1.5 The resolving power of the instrument should be such that the $^{235}UF_5^+$-$^{238}UF_5^+$ valley height should be less than 3.0 % of the $^{235}UF_5^+$ peak height after the peak height has been normalized. The normalization conists of dividing the observed peak height by the sample ^{235}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 ^{235}U ion beam.

37.1.6 If the concentrations of the minor isotopes, ^{234}U and ^{236}U, are to be measured, the $^{234}UF_5^+$-$^{235}UF_5^+$ valley should be less than 50 % of the $^{234}UF_5^+$ 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_6 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 ^{235}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_6 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 ±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}U, determine the weight percents ^{238}U, ^{234}U, and ^{236}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}U to the other isotopes, ^{234}U to the other isotopes, or ^{236}U to the other isotopes. Obtain the ^{235}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:

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

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

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

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

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

39.4.3 Then correct the sample R_D values as follows:

$$R_{DT} = F_1 R_D - F_2. \tag{14}$$

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 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 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}U isotopic composi tions 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 UF_5^+ ions of the isotopes are focused through a mass-resolving collector slit. For ^{235}U concentrations below about 70 mol %, measurements are made which are proportional to the ratio of ^{235}U to the total of the other isotopes. These measurements, with the known composition of the standard, permit calculation of the ^{235}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}U concentrations greater than about 70 mol %, measurements are made which are proportional to the ratio of ^{238}U to the total of the other isotopes. The ^{234}U and ^{236}U isotopes are determined independently, and the ^{235}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 $^{235}UF_5^+$ ion peak and the $^{238}UF_5^+$ ion peak should be less than 3.5 % of the height of the smaller peak (see

45.1). When minor isotopes, ^{234}U and ^{236}U, are measured, the interpeak valleys between the ^{235}U and minor isotope peaks must be less than 60 % of the minor isotope peaks; and the collector resolving slit must be narrowed to reduce beam transmission to 75 % for these measurements.

43.1.1.4 The sample inlet system has two sample holders to which UF_6 containers can be attached. A single adjustable leak for admitting the sample into the spectrometer ion source is preferred. The manifold should be nickel or Monel and have minimum volume.

43.1.1.5 The pumping system of the spectrometer analyzer tube must maintain a pressure less than 5×10^{-8} torr with sample flowing into the ion source.

43.1.1.6 The memory of the spectrometer must be consistent with the accuracy and precision required, since a high-memory level is usually more variable than a low one. Memory values of 2 to 3 % are typical, but up to 10 % memory can be tolerated. The memory characteristics of a spectrometer must be established from periodic measurement of the effect, and usually apply until the ion source is replaced, repairs are made on the sample inlet system, or the instrument is refocused so the rate of flow of UF_6 is altered significantly.

44. Procedure

44.1 *Calibration of Isotopic Standards*:

44.1.1 One standard is required for the analysis of a sample at any specific concentration of ^{235}U. Two standards are required to determine memory corrections. Memory can be measured more precisely with a large difference between two standards, but the adverse effect of introducing wide concentration ranges into the mass spectrometer must be considered. Ideally, the values obtained from the high- and low-memory standards should symmetrically bracket those of the sample to be corrected. Standards about 10 % apart (having a ratio or ratios of 1:1) are suitable for most applications.

44.1.2 A reasonable limit for the difference between the unknown sample and the standard to which it is compared is 5 %. A series of memory standards spaced at 10 % intervals and used also for sample comparisons thus enables this 5 % limit.

44.1.3 Prepare a working standard and standardize against an oxide blend of National Institute of Standards and Technology (NIST) standards which is within 0.2 % of the value of the working standard.

44.1.4 If a working standard is used as one of a pair of standards for evaluation of memory, verify the ratio of the two standards in the pair by another oxide dilution as follows:

44.1.4.1 Convert a few grams of the higher standard to U_3O_8 and blend gravimetrically with a quantity of a third standard greatly depleted in ^{235}U so that the mixture will have the isotopic composition of the lower standard (**20**) of the memory pair.

44.1.4.2 Convert the U_3O_8 blend to UF_6.

44.1.4.3 Compare the blend to the lower standard, and calculate the ratio: $[^{235}U/(1 - {}^{235}U)$ (for the higher standard)$]/[^{235}U/(1 - {}^{235}U)$ (for the lower standard)$]$.

44.1.4.4 Substitute ^{238}U or ^{234}U for ^{235}U in the preceding ratio if those isotopes are being compared.

44.2 *Analysis*:

44.2.1 Attach tubes containing the appropriate standard, *S*, and the sample, *X*, to the spectrometer inlet system, and prepare the materials for introduction into the ion source, as follows:

44.2.1.1 Open all valves beween the sample and standard containers and the pumping system, except the valves on the sample and standard containers.

44.2.1.2 Open the valve on the sample container and then close quickly to vent gases to the pumping system.

44.2.1.3 After the pumping system has evacuated the vented gases, repeat 44.2.1.2.

44.2.1.4 Repeat 44.2.1.2 and 44.2.1.3 for the standard.

44.2.2 Use the following alternative method of sample purification if the amount of sample or standard is limited:

44.2.2.1 Operate the appropriate valves to remove air entrapped in the connectors and to determine that there are no leaks into the inlet system.

44.2.2.2 Freeze the UF_6 by immersing the sample container in a slurry of dry ice and alcohol.

44.2.2.3 Open the valve on the container to permit evacuation of volatile impurities from the container, and then close the container valve.

44.2.2.4 Remove the coolant from around the container, allowing the UF_6 to return to room temperature.

44.2.3 Prepare the instrument for analysis as follows:

44.2.3.1 Operate the appropriate valves to admit the standard into the ion source.

44.2.3.2 Adjust the mass spectrometer high voltage or magnet current to focus the $^{235}UF_5^+$ ion beam (for samples containing about 70 mol % ^{235}U or less) through the collector slit to the low-current collector, while the other UF_5^+ ions are collected on the high-current collector. This *peaking up* is complete when the current to the low-current collector is maximized.

44.2.3.3 Zero the amplifiers as frequently as indicated by their drift rate. Some must be zeroed prior to each determination; others may require zeroing only once per day.

44.2.3.4 Adjust the variable leak until the flow of UF_6 into the ion source produces a current of approximately 10^{-9} A to the high-current collector. If the analyzer pressure is not within 2×10^{-8} torr of that observed when the sample is admitted in 44.2.4, further purify the UF_6 having the higher pressure.

44.2.3.5 Terminate the flow of the standard, and evacuate the ion source.

44.2.4 The shortest sequence for the analytical determination is *X, S, X,* where *X* and *S* represent introductions of the sample and standard, respectively. Follow each introduction by evacuation of the ion source before the next introduction. Timing of the introductions and evacuations depends on the instruments being used but is usually about 2 min for sample introduction followed by 30-s evacuation. The number of introductions per analytical sequence depends on the precision required. To minimize errors caused by drift in the spectrometer, always begin and end the sequence with the same material in the spectrometer source. A five-introduction sequence (*X, S, X, S, X*) is most commonly used. An extra preliminary or equilibration introduction, during which no data are recorded, precedes the determination to make the sample-standard interaction more uniform and to improve the validity of the memory correction. During each introduction of UF_6 into the ion source, conduct the following functions either manually or automatically:

44.2.4.1 Regulate the ion intensity to within 2 % of the desired level by adjusting the variable leak.

44.2.4.2 Adjust the magnet current or high voltage to obtain a maximum low-current collector signal and maintain at this value for the entire sample introduction period; or repeatedly sweep across this maximum to obtain a series of scans of the peak maxima during the period.

44.2.4.3 With the instrument peaked up, or while scanning the peak, obtain a reading with the electrometers for the two collectors connected in a null-type circuit. This reading is proportional to the ratio of the number of ions striking the low-current collector to the number of ions striking the high-current collector.

44.2.5 Average all the readings for the standard; likewise, those for the sample, to obtain two values, R_x and R_s, for each analytical sequence.

44.2.6 Repeat the sequence as many times as needed to obtain the desired analytical precision.

44.2.7 For samples in which the ^{235}U content is greater than about 70 mol %, measure the ^{238}U, ^{234}U, and ^{236}U isotopes as follows:

44.2.7.1 For ^{238}U, focus the ^{238}U ion beam through the collector resolving slit, and follow the same procedure as for ^{235}U, as described in 43.2.3.2; the readings are proportional to the ratio of ^{238}U to all the other isotopes.

44.2.7.2 For ^{234}U and ^{236}U isotopes, when suitable standards are available, follow the same procedure while focusing on the ^{234}U or ^{236}U ion beam.

44.2.7.3 When a suitable standard is not available for the ^{236}U isotope, compare the ^{236}U to the ^{234}U or ^{238}U isotopes in the sample, alternately focusing the two isotopes being compared. Average three ^{234}U readings and two ^{236}U readings and designate as R_4 and R_6.

44.2.8 To correct for memory, intersperse analytical sequences with sample sequences, using two standards which bracket the sample isotopic composition, and which differ in isotopic composition by about 10 %. Designate the results of the memory sequences R_A and R_B for memory standards *A* and *B*, respectively. Usually less than 5 % of the total number of determinations need to be made on memory standards. For maximum precision and accuracy, schedule memory measurements more frequently, and plot on a time scale. Interpolate the memory factor from this plot at the time a sample is analyzed (**21**).

45. Calculation

45.1 *Percent Valley*—From readings taken to determine whether the instrument is resolving adequately, make the following calculation:

$$\text{Percent valley} = [\text{valley } (^{235}\text{U},\ ^{238}\text{U})/\text{peak } ^{235}\text{U}] \times 100 \tag{15}$$

45.2 If the sample contains less than 1 % ^{235}U, multiply the observed valley by the percent ^{235}U before applying the 3.5 % valley limitation stated under Section 43 of this procedure.

45.3 *Ion Beam Transmission (Dropout)*—Calculate this factor daily using the following equation and high-current amplifier-output-meter readings obtained by sweeping with the magnet controls:

$$\text{Dropout} = (4I - I_4 - I_5 - I_6 - I_8)/I \tag{16}$$

where:

I = maximum with all peaks on the high-current collector,
I_4 = minimum with ^{234}U through the collector slit,
I_5 = minimum with ^{235}U through the collector slit,
I_6 = minimum with ^{236}U through the collector slit, and
I_8 = minimum with ^{238}U through the collector slit.

45.4 Calculate the memory factor as follows:

$$M = (R - 1)/(R_O - 1) \tag{17}$$

where:

M = memory factor,
R = ratio of mol ratios for isotope of interest, calculated from known mol ratios of the two memory standards, and
R_O = the observed ratio of mol ratios, in this case R_A/R_B, from the results obtained in 44.2.8.

45.5 Use the memory factor calculated from the ^{238}U or ^{235}U comparisons as an approximate correction for the ^{234}U and ^{236}U observations.

45.6 Calculate the observed ratio of the mol ratios, R_O, for the isotopes of interest from the following equations:

45.6.1 For isotopes for which adequate standards are available,

$$R_o = R_x/R_s \tag{18}$$

where:

R_x = ratio of isotope of interest to all other isotopes in the sample, as measured in 44.2.4, 44.2.7.1, or 44.2.7.2, and
R_s = ratio of isotope of interest to all other isotopes in the standard, as measured in 44.2.4 or 44.2.7.

45.6.2 For isotopes for which suitable standards are not available (usually ^{236}U).

$$R_o = R_6/R_4 \tag{19}$$

where:

R_6 = measured ratio of the isotope ^{236}U to all other isotopes in the sample as measured in 44.2.7, and
R_4 = measured ratio of the isotope ^{234}U to all other isotopes in the sample as measured in 44.2.7.

45.7 The observed ratios, R_O, are corrected for memory as follows:

$$R_c = MR_o - (M - 1) \tag{20}$$

where:

R_c = corrected ratio of ratios.

45.8 For samples having a ^{235}U content of about 70 mol % or less:

45.8.1 Calculate the weight percent ^{235}U (U_5) in the sample from:

$$U_s = 100\, R_c Z/(100 + R_c Z) \tag{21}$$

where:

R_c = corrected ratio of mol ratios obtained from ^{235}U peak comparisons, and

Z = $100z/(100 - z)$, where z is weight percent ^{235}U in the standard.

45.8.2 If suitable standards are available, calculate the weight percent ^{234}U (U_4) and the weight percent ^{236}U (U_6) in the same manner as for ^{235}U in Eq 21, using the data obtained in 44.2.7.

45.8.3 If a suitable standard is not available for the ^{236}U isotope, calculate the weight percent ^{236}U as follows:

$$U_6 = 100.86\, R_O E/(100 + R_O E) \tag{22}$$

where:

E = $100e/(100 - e)$, e being weight percent ^{234}U in the standard, and

R_O = ratio of mol ratios for the isotope ^{236}U as calculated in 45.6.2 from data obtained in 44.2.7.

45.8.4 Calculate the weight percent ^{238}U (U_8) as follows:

$$U_8 = 100 - U_4 - U_5 - U_6 \tag{23}$$

45.9 For samples having a ^{235}U content of more than about 70 mol %:

45.9.1 Calculate the weight percent ^{238}U as follows:

$$U_8 = 100\, R_C Q/(100 + R_C Q) \tag{24}$$

where:

R_C = corrected ratio of mol ratios obtained from measurements made on ^{238}U peak comparisons, and

Q = $100q/(100 - q)$, q being weight percent ^{238}U in the standard.

45.9.2 If suitable standards are available for the ^{234}U and ^{236}U isotopes, calculate U_4 and U_6 in the same manner as U_8 in Eq 24, using the data obtained in 44.2.7.

45.9.3 If a suitable standard is not available for the ^{236}U isotope, calculate U_6 using (Eq 22) for samples having less than about 70 mol % ^{235}U.

45.9.4 Calculate the weight percent ^{235}U as follows:

$$U_5 = 100 - U_4 - U_6 - U_8 \tag{25}$$

46. Reliability

46.1 Adequate estimates of the reproducibility on one instrument can best be obtained by making repeated determinations on the same samples over a period of several days during which the spectrometer has run a typical range of samples, and has been refocused, or has had components changed or repaired. Measurements of the same samples on several different spectrometers provide the most valid estimate of the precision of the test method.

46.2 Precision is influenced strongly by the range of concentrations assigned to a given spectrometer. With instruments assigned samples between 1 and 5 weight % ^{235}U, a 95 % confidence limit, for a single determination, of ±0.2 % relative was obtained on 100 samples analyzed over a period of one year at two laboratories. With instruments assigned samples in a very narrow range (93 to 93.5 weight % ^{235}U), a 95 % confidence limit, for a single determination, of ± 0.04 % relative was obtained on the analysis of more than 200 control samples analyzed with two instruments over a period of one year. A95 % confidence limit of ±0.02 % relative or less has been obtained by narrowing the range of isotopic concentrations and adjusting the instrument to meet more rigorous performance specifications than those listed.

DETERMINATION OF HYDROCARBONS, CHLOROCARBONS, AND PARTIALLY SUBSTITUTED HALOHYDROCARBONS

47. Scope

47.1 This test method is applicable for detecting hydrocarbons, chlorocarbons, and partially substituted halohydrocarbons in UF_6. Although the test method is only semiquantitative, it is adequate for certifying that the subject impurities do not exceed 0.01 mol % of the UF_6.

48. Summary of Test Method

48.1 UF_6 is admitted to a mass spectrometer through a gas sample leak, and magnetic scanning is employed to record a spectrum of peaks. A representative group of recorded peaks is compared to the same peaks in a pure UF_6 standard scan to determine whether appreciable ion fragments from subject impurities are present.

49. Interferences

49.1 If detectable impurities are present, a complete mass scan of the range from 12 to 400 is performed. All impurities are then identified from their cracking patterns, and calculations are performed using ionization efficiency factors for the compounds present. Since cracking patterns vary with ionization potential and ionization efficiencies vary with focus conditions, this measurement can only be performed by one proficient in analytical mass spectrometery.

50. Apparatus

50.1 A mass spectrometer with resolution adequate to distinguish between adjacent peaks at m/e = 400 is required. For example, a 152-mm radius, 60-deg, Nier-type spectrometer modified for spectrum recording **(22)** is suitable. The sample inlet system should be of nickel or Monel, equipped with an adjustable viscous-flow or molecular leak for delivering the sample to the ion source.

50.2 The ion source must be fabricated from nonmagnetic material such as Nichrome V, and must be designed so it can be disassembled for cleaning. The magnetic field of the analyzer magnet must be continuously variable from about 200 to 6500 gauss. A single ion collector electrode is suitable, and a vibrating-reed electrometer and 304-mm strip chart recorder are optimum for amplifying and recording ion signals.

50.3 It is quite possible that quadrupole or time-of-flight instruments could be adapted to this measurement.

51. Procedure

51.1 *UF_6 Standard Measurements*:

51.1.1 Select a standard material that has been given repetitive flash purifications to rid it of all volatile impurities. Isotopic UF_6 standards usually fall in this category.

51.1.2 With the electrometer sensitivity set at 1⁄100 of the most sensitive usable operating range, adjust the gas flow to the ion source to record a mass (Note 5) 333 peak (UF_5^+) approximately 80 % of full scale (80 divisions).

NOTE 5—The term "mass" in this procedure alludes to *m/e*, the mass-to-charge ratio.

51.1.3 Measure the ratio of mass 333 (UF_5^+) to 147.5 (UF_3^{++}). Mass 333 is measured on a sensitivity range one-hundredth that of mass 147.5. Depending on focus conditions, a ratio of the order of 10^2 is obtained. Measure this ratio only once per day and use for calculating results of all samples analyzed that day.

51.1.4 With the electrometer sensitivity set at 1⁄100 of the most sensitive usable operating range, increase the gas flow to provide an output signal of approximately 80 divisions at the 147.5 mass position. This gives a detectability limit of the order of 2 ppm per chart division: 50 to 100 due to ratio between UF_5^+ and UF_3^{++}, 100 due to sensitivity shunts, and approximately 80 on the recorder chart.

51.1.5 Record a scan of mass range from 12 to 150 using the most sensitive usable operating shunt, and use this scan as a background for all samples analyzed that day.

51.2 *UF_6 Sample Measurement*:

51.2.1 Introduce the sample to the spectrometer source such that an output intensity of approximately 80 chart divisions is obtained at the 147.5 mass number (UF_3^{++}), using 1⁄100 the most sensitive usable operating range.

51.2.2 Record a scan of mass range from 12 to 150 using the most sensitive usable operating range.

51.2.3 Repeat 51.2.1 and 51.2.2 for each sample to be analyzed that day.

52. Calculation

52.1 Due to mass spectrometer cracking patterns, low-mass ion fragments are produced from all compounds, even the high-mass ones.

52.2 It is practical to look for a representative group of such ion fragments at specific masses. Thus, initially monitor the following masses for purposes of this procedure:

Mass Number	Positively Charged Ion Fragment
15	CH_3
26	C_2H_2
27	C_2H_3
31	CF
43	C_3H_7
47	CCl^{35}
49	CCl^{37}
69	CF_3

52.3 Read sample intensities for the representative ion fragments from the recorder chart.

52.4 Subtract the background intensities observed on the pure standard from respective sample intensities.

52.5 Examine the net intensity at each of the eight mass numbers. (It will be recalled that one recorder chart division of net intensity is equivalent to about 2 ppm on a UF_6 basis; however, ionization efficiencies of compounds differ, and a specific ion fragment may result from many different compounds. Thus, the net intensity at a specific mass number is only qualitative and not a quantitative measurement of impurity.)

52.5.1 If the net ion intensity does not exceed 2 ppm at any of the mass positions, report the sample as containing less than 0.01 mol % of the subject impurities.

52.5.2 Where detectable impurities are apparent, perform a complete mass scan of the range from 12 to 400, identify impurities, and perform calculations using ionization efficiency factors for the compounds present.

53. Reliability

53.1 This simplified procedure was designed specifically to certify that a UF_6 sample contains less than 0.01 mol % hydrocarbons, chlorocarbons, and partially substituted halohydrocarbons. Thus, the procedure is qualitative rather than quantitative in cases where the impurity level is below 100 ppm.

53.2 The detectability limit for any ion fragment is about 2 ppm. The detectability limit for the parent compound could be greater or less than 2 ppm depending on ionization efficiency and cracking pattern. If one of the subject compounds were present to 10 ppm or more, it would be evident from monitoring the eight masses. Thus, a quoted result of less than 0.01 mol % is conservative.

53.3 The results are considered quantitative when the impurity being determined is present to a level greater than 100 ppm. In such instances the impurity is identified and measured. The 95 % symmetrical confidence interval for such a measurement is ±50 % of the quoted impurity.

ATOMIC ABSORPTION DETERMINATION OF ANTIMONY

54. Scope

54.1 This test method provides for the microanalysis of antimony in UF_6 by atomic absorption spectroscopy. Antimony (along with several other elements) is extracted as a chloride complex with amyl acetate from uranium in 8 *N* hydrochloric acid (HCl).

55. Summary of Test Method

55.1 Atomic absorption offers an excellent approach to the analysis of antimony in uranium at the 1-µg/g uranium level. Combining atomic absorption spectroscopy with solvent extraction of the antimony has four advantages: (*1*) solvent extraction reduces the volume of the antimony matrix, (*2*) the interference of uranium in the antimony spectrum is eliminated, (*3*) radioactivity contamination problems arising from aspirating uranium solutions are eliminated, and (*4*) use of an organic medium in the atomic absorption of antimony enhances its sensitivity by nearly a factor of three.

55.2 The extraction system presented (that is, amyl acetate extraction of chloride complexes from 8 *N* HCl) can also be applied to the determination of several other elements by atomic absorption. Walker, et al **(23)** used this procedure for analyzing antimony, iron, and molybdenum in either nickel or uranium samples.

56. Interferences

56.1 The extracted matrix contains no spectral interferences.

57. Apparatus

57.1 *Atomic Absorption Spectrometer* equipped with a Boling burner or equivalent.

58. Reagents

58.1 *n-Amyl Acetate (purified grade)*.

58.2 *Antimony Trioxide* (Sb_2O_3)—Dissolve the pure reagent in concentrated HCl (sp gr 1.19) to prepare standard solutions containing 1, 10, and 50 µg Sb/mL, respectively.

58.3 *Potassium Nitrite* (KNO_2)—20 g/100 cm^3 in water.

58.4 *Sodium Sulfite* (Na_2SO_3)—10 g/100 cm^3 in water.

59. Procedure

59.1 *Calibration*:

59.1.1 Prepare five 5-g uranium standards spiked with 0, 1, 10, 20, and 50 µg of antimony.

59.1.2 Analyze the standards by the described procedure.

59.1.3 Prepare a calibration curve as required from the atomic absorption data.

59.2 *Analysis*:

59.2.1 Measure a sample aliquot of hydrolyzed UF_6(UO_2F_2 solution) containing approximately 5 g of uranium and transfer it to a platinum dish.

59.2.2 Add 10 mL of concentrated H_2SO_4(sp gr 1.84), and fume the solution to dryness.

59.2.3 Dissolve the residue with 10 mL of 8 *N* HCl, and transfer the solution to a 125-mL separatory funnel, using 8 *N* HCl to rinse the dish. The total volume should be about 15 mL.

59.2.4 Add 1 mL of 10 g/100 mL Na_2SO_3 solution to the separatory funnel, and mix the solution thoroughly.

59.2.5 Add 6 mL of concentrated HCl to the separatory funnel.

59.2.6 Add 2 mL of 20 g/100 mL KNO_2 solution to the funnel, and mix the solution thoroughly.

59.2.7 Add 10 mL of *n*-amyl acetate carefully to the funnel with a pipet and shake the funnel for 5 min.

59.2.8 Allow the phases to separate for 10 min, and discard the raffinate.

59.2.9 Analyze the amyl acetate solution for antimony at a wavelength of 2176 Å. Adjust the instrument settings for optimum response at this wavelength.

59.2.10 Measure the absorptions of sample and standard extracts.

59.2.11 Determine the antimony content of the sample aliquot from the calibration curve; then calculate the antimony content of the UF_6 from the amount of uranium in the aliquot, using the equation: ppm antimony (uranium basis) = micrograms antimony/grams uranium in aliquot.

60. Reliability

60.1 The sensitivity of the test method depends on the size of the sample taken; with a sample containing 5 g of uranium, 0.25 µg antimony/g uranium can be detected.

60.2 The precision at the 95 % confidence interval is about ±4 % for 1 µg antimony/g uranium.

SPECTROPHOTOMETRIC DETERMINATION OF BROMINE

61. Scope

61.1 This test method is suitable for the determination of microgram amounts of bromine when it exists as bromides or bromates in UO_2F_2 solution. Its sensitivity may be extended by suitably increasing the sample size.

62. Summary of Test Method

62.1 Bromine is determined spectrophotometrically by the bromination of fluorescein to form eosin after the oxidation of bromide **(24)**. The bromides and bromates in hydrolyzed UF_6 are recovered by the reduction of bromates with sodium nitrite, followed by oxidation of bromides with permanganate. The oxidation is apparently the limiting step in all procedures involving bromide. To avoid loss of bromine during the oxidation, the bromine produced is extracted by carbon tetrachloride concurrently with its production in the nitrous acid solution of permanganate. Prior chilling of the sample and reagent solutions is necessary. Fluorescein is added to the bromine-carbon tetrachloride solution, and the absorbance of the resulting eosin is measured at 510 nm.

63. Interferences

63.1 The nitrous acid is helpful in that iodide, although generally absent, may be oxidized by the nitrous acid and extracted before the addition of the permanganate. The iodine may then be determined by existing test methods. If iodine need not be determined, it does not interfere in the basic procedure since iodide is oxidized rapidly to iodate by acidic permanganate. Chloride up to 1000 µg/g does not interfere.

64. Apparatus

64.1 *Spectrophotometer* with 1-cm cells as described in Practice E 60.

64.2 *Centrifuge*, clinical.

65. Reagents

65.1 *Bromide, Stock Solution*—Dissolve 0.3723 g of potassium bromide (KBr) in water, dilute to 250 mL in a volumetric flask, and mix well.

65.2 *Bromide, Standard Solution*—Dilute a 10.00-mL aliquot of the stock bromide solution to 1 L in a volumetric flask. One millilitre of this solution contains 10 µg of bromine.

65.3 *Carbon Tetrachloride* (CCl_4), boiling range 0.4°C or less.

65.4 *Fluorescein Stock Solution*—Dissolve 0.100 g of disodium fluorescein in water and dilute to 1 L.

65.5 *Fluorescein, Buffered Solution*—Dissolve 35 g of sodium dihydrogen phosphate (NaH_2PO_4) in 500 mL of water. Using a pH meter, adjust the pH to 6.0 with saturated disodium phosphate (Na_2HPO_4) solution. Then add 40 mL of stock fluorescein solution, dilute the mixture of 1 L, and store in a brown bottle.

65.6 *Potassium Permanganate Solution*—Dissolve 0.500 g of $KMnO_4$ in water and dilute to 100 mL. Store in a brown bottle, and prepare a fresh sodium every 2 to 3 weeks.

65.7 *Sodium Nitrite Solution*—Dissolve 0.500 g of $NaNO_2$ in water and dilute to 250 mL.

66. Procedure

66.1 *Calibration*—Transfer the quantities 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 mL of standard bromide solution, representing 0, 1.0, 2.0, 3.0, 4.0, 5.0, and 10 µg of bromine, to a series of 100-mL beakers. Transfer an aliquot of a hydrolyzed sample of bromine-free UF_6[12] containing about 5 g of uranium, to each beaker. Process each standard, one at a time, through the procedure as outlined below. Subtract the absorbance of the blank (0.0 mL of bromine added) from the absorbance of each of the standards, and plot the resulting absorbances versus micrograms of bromine on coordinate paper.

66.2 *Analysis*:

66.2.1 By means of a suitable subsampling system, transfer approximately 7 g of liquid UF_6 to a tared fluorothene tube. Cool the sample in liquid nitrogen, disconnect from the sampling system, and seal.

66.2.2 Weigh the filled tube to obtain the sample weight.

66.2.3 Immerse the tube in liquid nitrogen for 15 min, remove the flare connection, and place the tube into 50 mL of cold water in a platinum dish.

66.2.4 After hydrolysis of the UF_6, remove the fluorothene tube from the dish and rinse with distilled water. Add the rinse water to the contents of the dish.

66.2.5 Cool the sample and reagents to 15°C in an ice bath.

66.2.6 Transfer the cooled UO_2F_2 solution to a 60-mL separatory funnel; add 1 mL of $NaNO_2$ solution, and swirl the mixture to mix; add 10 mL of CCl_4 and 1 mL of $KMnO_4$ solution, and shake the funnel for 5 to 10 s.

66.2.7 Transfer the organic layer to a second 60-mL separatory funnel. Immediately, add another 10 mL of CCl_4 to the first funnel and shake it for 10 s (Note 6).

66.2.8 Transfer the organic layer to the second funnel, and discard the aqueous layer. Add 10 mL of water to the organic solution, and shake the mixture for 5 s.

66.2.9 Transfer the organic layer to a third funnel, and discard the water layer.

66.2.10 Add 5 mL of buffered fluorescein solution to the organic solution, and shake the mixture for 1.5 min. Discard the organic layer; then transfer the aqueous layer to a centrifuge tube and centrifuge until a clear solution is obtained.

66.2.11 Determine the absorbance of the sample solution at 510 nm. Use a buffered fluorescein solution (Note 7), which has been extracted for 1.5 min with 10 mL of CCl_4 as a reference solution.

66.2.12 Determine a reagent blank by carrying 30 mL of water through the procedure.

66.2.13 Determine the micrograms of bromine represented by the absorbance of the solution corrected for the absorbance of the blank from the calibration curve (Note 8).

NOTE 6—The pink color of permanganate should persist throughout the extraction which should be completed as rapidly as possible. Samples should be run one at a time and not several concurrently.

NOTE 7—The wavelength of maximum absorbance varies from 505 to 515 nm, depending upon the concentration. With 5 µg it is 505, with 10 µg it is 510, and with the maximum 15 µg it is 515. From 0 to 10 µg the standard curve is nearly linear for wavelengths 505 and 515 nm. However, at 505 and 510 nm, the molar absorbance starts to decrease rapidly when the concentration is over 11 to 15 µg of bromine.

NOTE 8—Chloride, up to a concentration of 1000 ppm (uranium basis), does not interfere.

67. Calculation

67.1 Calculate the concentration of bromine as follows: Bromine (uranium basis), ppm = micrograms bromine/grams uranium in aliquot.

68. Reliability

68.1 A precision of ±0.7 ppm at the 95 % confidence level has been obtained at the 1-ppm bromine level.

TITRIMETRIC DETERMINATION OF CHLORINE

69. Scope

69.1 This test method is applicable to the determination of total chlorine in UF_6. As described, the test method is applicable over a range from 10 to 100 ppm chlorine; however, higher concentrations can be measured by appropriate sample dilution.

70. Summary of Test Method

70.1 The test method consists of treating a hydrolyzed sample of UF_6 with ferrous sulfate in sulfuric acid solution to reduce chlorates, and then with potassium permanganate to liberate free chlorine. The chlorine gas is carried by a nitrogen stream into a potassium iodide solution, and the liberated iodine is titrated with sodium thiosulfate. Bromine, if present, is determined separately, and a correction is applied to the chlorine result.

70.2 It is recommended that the potassium iodide-sodium acetate solution be made up fresh once each week. Any color change signals the need for a new solution. As the solution ages, the blank result increases; therefore, the same potassium iodide solution is used for both sample and blank.

70.3 If the sample solution is allowed to boil too vigorously when chlorine gas is being released, liquid droplets may be carried by the nitrogen stream into the potassium iodide solution, resulting in sample bias.

71. Apparatus

71.1 *Distillation Apparatus*, shown in Fig. 7.

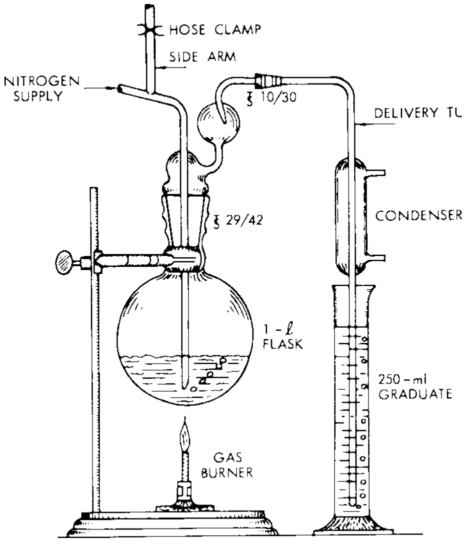

FIG. 7 Apparatus for Distillation of Chlorine

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[12] Available through the Oak Ridge Operations Office of the U.S. Department of Energy.

72. Reagents

72.1 *Boric Acid* (H_3BO_3), reagent grade, crystal or powder.

72.2 *Ferrous Sulfate Solution*—5 g $FeSO_4{\cdot}7H_2O$ dissolved in 500 mL of 3.6 *M* sulfuric acid.

72.3 *Potassium Iodide* (KI), reagent grade.

72.4 *Potassium Iodide-Sodium Acetate Solution*—Dissolve 100 g of KI and 100 g of $NaC_2H_3O_2{\cdot}3H_2O$ in distilled water and dilute to 2 L.

72.5 *Potassium Permanganate Solution* (1 %)—Prepare a 1 % solution of $KMnO_4$ in water.

72.6 *Sodium Acetate* ($NaC_2H_3O_2$), reagent grade.

72.7 *Sodium Thiosulfate Solution* (0.025 *N*)—Prepare a 0.025 *N* solution of $Na_2S_2O_3$ in water.

72.8 *Starch Indicator Solution*, pH 7.

72.9 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

73. Procedure

73.1 *Sample Preparation*:

73.1.1 Hydrolyze the sample of UF_6 with distilled water. Approximately 250 g of UF_6 from a nickel knockout container (Note 2) may be hydrolyzed to provide a sample for various chemical measurements, or about 20 g from two fluorothene sample tubes may be hydrolyzed to provide the chlorine sample. The procedure for hydrolyzing the contents of the fluorothene tubes is described here.

73.1.1.1 Immerse the tubes in liquid nitrogen and cool for 10 min.

73.1.1.2 Remove the top flare plugs and collars, and place the tubes into a platinum dish or a fluorothene beaker containing 100 mL of chilled distilled water.

73.1.1.3 After hydrolysis of the UF_6, remove the fluorothene tubes and rinse with distilled water. Add the rinse solution to the UO_2F_2 solution.

73.2 *Analysis*:

73.2.1 Fill the graduated cylinder in Fig. 6 to the 150-mL level with KI-$NaC_2H_3O_2$ solution. Then connect the delivery tube so its tip is near the bottom of the solution in the receiving graduate.

73.2.2 Dispense 20 g of H_3BO_3 into the 1-L round-bottom flask.

73.2.3 Transfer the sample solution containing UO_2F_2 from approximately 20 g of UF_6 in 100 mL of solution to the flask.

73.2.4 Add 10 mL of concentrated H_2SO_4(sp gr 1.84) to the flask, and swirl the contents for mixing.

73.2.5 Add 10 mL of the $FeSO_4$ solution, rinse the mouth of the flask, and connect the flask immediately to the apparatus as in Fig. 7.

73.2.6 Initiate nitrogen flow through the solution at a rate of 2 to 3 bubbles per second, and start the water flow through the condenser.

73.2.7 Heat the contents of the flask until boiling and allow to boil for 30 s.

73.2.8 Remove the heat, add 10 mL of 1 % $KMnO_4$ solution through the sidearm, and close the sidearm by clamping the rubber tube that is attached to the end of the sidearm.

73.2.9 Reapply heat, and allow the contents of the flask to simmer for 5 min.

73.2.10 Remove the heat, but continue the nitrogen purge for an additional 5 min.

73.2.11 Rinse the delivery tube into the receiving graduate, and transfer the contents of the graduate to a 300-mL Erlenmeyer flask. Add 1 mL of starch solution, and titrate the iodine with 0.025 *N* $Na_2S_2O_3$ solution to the starch end point. (The iodine may be measured spectrophotometrically rather than titrimetrically.)

73.2.12 Perform a blank analysis by carrying 100 mL of distilled water through procedural steps, 73.2.1 through 73.2.11, and subtracting from the sample titration.

74. Calculation

74.1 Calculate the concentration of chlorine in parts per million chlorine on a uranium basis as follows: Cl, ppm = $(V_1 - V_2)\ (N)\ (0.03545 \times 10^4)/S$.

where:

V_1 = millilitres of thiosulfate for sample,
V_2 = millilitres of thiosulfate for blank,
N = normality of $Na_2S_2O_3$ solution, and
0.03545 = grams of chlorine per milliequivalents, and
S = grams of uranium.

75. Reliability

75.1 The precision at the 95 % confidence level is ±10 % at the 100-ppm level.

SPECTROPHOTOMETRIC DETERMINATION OF SILICON AND PHOSPHORUS

76. Scope

76.1 This test method provides similar procedures for the spectrophotometric analysis **(24, 25, 26, 27)** of phosphorus or silicon in UF_6. With these procedures about 0.5 µg silicon or phosphorus per gram of uranium can be detected.

77. Summary of Test Method

77.1 The test methods are based on the development of the color known as molybdenum blue obtained by the reduction of silico- or phosphomolybdate ions.

77.2 Reduction of the silico- or phosphomolybdate ions with a combination 1-amino-2-naphthol-4-sulfonic acid, sodium sulfite, sodium pyrosulfite solution produces the same molybdenum blue complex that is measured spectrophotometrically, directly in the uranium solution at 710 nm. One gram of uranium absorbs slightly at this wavelength, but its absorbance is easily corrected by the use of an additional aliquot to which no reducing agent is added as the blank.

78. Interferences

78.1 Phosphate interference in the silicon determination is eliminated by the addition of oxalic acid to decompose any phospho-molybdate formed. Silicon in small amounts does not interfere in the phosphorus analysis since silicomolybdate does not form at the acid concentration at which the phosphomolybdic acid is formed.

78.2 Fluoride, which would be a serious interference in the silicon analysis, is complexed with boric acid. A high concentration of silicon which could interfere in the phosphorus analysis is prevented by handling hydrolyzed UF_6 samples in platinum or plastic. Other potential interferences rarely present in significant amounts are arsenic and tungsten.

79. Apparatus

79.1 *Polyethylene Bottles*, 100 and 500-mL.

79.2 *Polyethylene Beakers*, 100-mL.

79.3 *Polyethylene Pipets;* 1, 2, 5, and 10-mL.

79.4 *Spectrophotometer*, equipped with 1 and 5-cm cells as described in Practice E 60.

80. Reagents

80.1 *Ammonium Hydroxide Silicon-Free*—Distill 500 mL of saturated NH_4OH through plastic tubing into 300 mL of distilled water.

80.2 *Ammonium Molybdate Solution* (10 %)—Dissolve 100 g of reagent grade $(NH_4)_6Mo_7O_{24}$ in water, and dilute the solution to 1 L with distilled water.

NOTE 9—Not all commercially available $(NH_4)_6Mo_7O_{24}$ is suitable. Material supplied by J. T. Baker Chemical Co. or Baker and Adamson Products, however, has been found to be satisfactory consistently.

80.3 *Boric Acid Solution* (5 %)—Dissolve 25 g of reagent grade H_3BO_3 in water, and dilute the solution to 500 mL.

80.4 *Oxalic Acid Solution* (5 %)—Dissolve 25 g of reagent grade $H_2C_2O_4$ in water, and dilute the solution to 500 mL. (This solution is not required for determination of phosphorus.)

80.5 *Phosphorus Standard Solution* (25 µg P/mL)—Dissolve 4.6422 g of ammonium dihydrogen phosphate $[(NH_4)H_2PO_4]$ in distilled water and dilute the solution to 1 L with distilled water. Transfer 20 mL of this solution to a 1-L volumetric flask and dilute to 1 volume with distilled water to obtain a solution containing 2.0 µg P/mL.

80.6 *Reducing Mix*—Dissolve 0.1 g of 1-amino-2-naphthol-4-sulfonic acid, 1.0 g of sodium sulfite (Na_2SO_3), and 10.0 g of sodium pyrosulfite ($Na_2S_2O_5$) in water; then dilute the solution to 100 mL.

80.7 *Silicon Standard Solution* (2.5 µg Si/mL)—Dissolve 10.7 mg of precipitated silica (SiO_2) and 0.5 g of sodium hydroxide (NaOH) in a platinum dish. Transfer the solution to a 2-L plastic bottle, and dilute to volume.

NOTE 10—Silicon in solution as sodium silicate is not stable when stored in polyethylene bottles. New standard solutions should be prepared monthly.

80.8 *Sulfuric Acid—Boric Acid Solution* (10 % H_2SO_4—4 % H_3BO_3)—Dissolve 20 g of reagent grade H_3BO_3 in water. Add 50 mL of concentrated H_2SO_4(sp gr 1.84), and dilute the solution to 500 mL.

80.9 *Uranium Oxide* (U_3O_8, UO_2, or UO_3), phosphorus- and silicon-free.

NOTE 11—All standard solutions should be made and stored in plastic containers to prevent silicon contamination from glassware.

81. Procedure

81.1 *Sample Preparation*:

81.1.1 Hydrolyze a weighed portion of 6 to 10 g of UF_6 in a platinum boat in 80 mL of distilled water as described in 17.7 through 17.17.

81.1.2 Transfer the solution to a 100-mL plastic bottle and dilute to 100 mL.

81.1.3 Transfer an aliquot equivalent to 1 g of UF_6 to a 100-mL TFE-fluorocarbon beaker, and add 1 mL of 6 *N* H_2SO_4. (Phosphorus aliquots should contain 1 to 50 µg of phosphorus.)

81.1.4 Add 20 mL of 5 % H_3BO_3, and heat the solution for 20 min to complex the fluoride.

81.1.5 For phosphorus analysis only, transfer the solution to a 100-mL borosilicate beaker and evaporate to 20 mL (see 81.3).

81.2 *Determination of Silicon*:

81.2.1 *Preparation of Calibration Curve*:

81.2.1.1 Pipet standard aliquots containing 0, 2.5, 5.0, 7.5, 10.0, and 12.5 µg of silicon into plastic beakers.

81.2.1.2 Add silicon-free uranium, 0.1 g as uranyl nitrate solution, to each beaker. Prepare the uranyl nitrate solution by dissolving silicon-free uranium oxide in nitric acid in a TFE-fluorocarbon beaker.

81.2.1.3 Add from 1.0 to 1.5 mL of 18 *N* H_2SO_4 to each beaker and dilute to 25 mL. Then proceed with the analysis starting with 81.2.2.4. Plot the absorbances corrected for the blank against the known quantities of silicon taken to obtain a calibration curve. In a typical case, 10 µg of silicon gave a corrected absorbance of about 0.285 in a 5-cm cell. Up to about 150 µg can be handled using a 1-cm absorbance cell and an appropriate calibration curve.

81.2.2 *Analysis*:

81.2.2.1 A blank containing all the reagents in the amounts used in the sample aliquot must be analyzed with the samples. Normally 10 mL of 1 *N* NaOH solution gives an absorbance of 0.030 to 0.050 in this procedure. Most other reagents were found to be nearly silicon-free.

81.2.2.2 Dilute the aliquot of the sample in a 100-mL plastic beaker to 25 mL with water.

81.2.2.3 Add from 1 to 1.5 mL of 18 *N* H_2SO_4.

81.2.2.4 Place the TFE-fluorocarbon beaker containing the sample in a water bath or an oven and heat to 90 to 95°C.

81.2.2.5 Remove the beaker from the water bath or the oven, and add 5 mL of 10 % $(NH_4)_6Mo_7O_{24}$ solution immediately.

81.2.2.6 Adjust the acidity to a pH of 1.2 to 1.3 while the solution is still warm by adding silicon-free NH_4OH or HCl.

81.2.2.7 Allow the sample to stand 10 min to permit the formation of the silico-molybdate complex.

81.2.2.8 Add 10 ml of 5 % $H_2C_2O_4$ solution to the beaker and swirl. Allow the solution to stand for 2 min to decompose any phosphomolybdate.

81.2.2.9 Add 2 mL of reducing mix to the beaker and swirl.

81.2.2.10 Add sufficient 6 *N* HCl immediately to the sample to obtain a 1 *N* acid solution.

81.2.2.11 After all the precipitate is dissolved, transfer the solution to a 50 or 100-mL volumetric flask and dilute to volume with 1 *N* HCl.

81.2.2.12 Determine the absorbance of the solutions in a 5-cm cell at 710 nm.

NOTE 12—The uranyl ion shows a slight absorbance at 710 nm, and samples must be corrected for this absorbance. This is best determined by taking an additional aliquot from the sample solution and treating it as indicated in the procedure up to the point the pH is adjusted with NH_4OH. Any precipitate is dissolved with a minimum of H_2SO_4 and the solution diluted to 50 mL. The absorbance of this solution is used as an additional blank correction.

81.2.2.13 Determine the quantity of silicon in the aliquot from a previously prepared calibration curve.

81.3 *Determination of Phosphorus*:

81.3.1 *Preparation of Calibration Curve*—Using a TFE-fluorocarbon beaker, dissolve sufficient uranium oxide (phosphorus-free) containing 20 g of uranium in HNO_3. Dilute it to 200 mL in a plastic bottle. To separate 10-mL aliquots, add 0, 5, 10, 25, and 50 µg of phosphorus. Analyze by the procedure described below. Plot the absorbances corrected for the blanks against the known quantities of phosphorus to obtain a calibration curve.

81.3.2 *Analysis*:

81.3.2.1 Neutralize the sample aliquot containing 1 to 50 µg of phosphorus in a volume of 20 mL or less in a 100-mL borosilicate beaker with NH_4OH until a precipitate begins to form.

81.3.2.2 Add sufficient 6 *N* HCl to make the sample 1 *N* in acid.

81.3.2.3 Transfer the sample to a 100-mL volumetric flask and dilute to about 50 mL with 1 *N* HCl.

81.3.2.4 Add 5 mL of $(NH_4)_6Mo_7O_{24}$ solution.

81.3.2.5 Heat the sample to 90 to 95°C in a water bath.

81.3.2.6 Allow the sample to cool to room temperature in a water bath; add 2 mL of reducing mix to the solution and swirl.

81.3.2.7 Dilute the solution in the 100-mL volumetric flask to volume with 1 *N* HCl.

81.3.2.8 After 1 h, measure the absorbance of the solution in a 5-cm cell at 710 nm against a reagent blank.

NOTE 13—Since the uranyl ion absorbs slightly at this wavelength, a correction must be made for the quantity of uranium present. This can be done by measuring the absorbance of an additional untreated aliquot of the original sample made to a 50-mL volume or by applying a previously determined standard correction when the amounts of uranium in the aliquot are known (typically, each gram of uranium in a 50-mL volume gives an absorbance reading of 0.038 at 710 mm).

81.3.2.9 Determine the quantity of phosphorus present in the aliquot from a previously prepared calibration curve. Then calculate the phosphorus content of the original material on the basis desired.

82. Reliability

82.1 At the 10-µg level of either element, the precision at the 95 % confidence level is ±10 %.

SPECTROGRAPHIC DETERMINATION OF BORON AND SILICON

83. Scope

83.1 This test method provides for the determination of boron and silicon in UF_6 in the concentration ranges from 0.5 to 100µ g/g for boron and 2 to 100 µg/g for silicon.

84. Summary of Test Method

84.1 A sample of UF_6 is transferred as a liquid into a fluorothene tube, frozen with liquid nitrogen, and hydrolyzed in freshly prepared ammonia water in a closed polyethylene bottle. The solution is evaporated to dryness in a platinum dish, and the residue is analyzed spectrographically for boron and silicon.

85. Limitations

85.1 Precautions must be taken to prevent loss of the highly volatile fluorides of boron and silicon, especially from warm acid fluoride solutions. In the hydrolysis step, boron and silicon are converted to the fluoborate and fluosilicate ions, respectively. Temperatures in excess of 100°C must be avoided during the drying step to avoid loss of boron and silicon.

85.2 The greatest problem encountered is obtaining suitable material for standards, especially in the case of silicon. A satisfactory approach to obtaining acceptable base material involves making an analytical survey of various lots of UF_6 and selecting a lot which is low in boron and silicon. The amount of boron and silicon in the base material is determined by taking some of the material, making standard additions of boron and silicon, preparing spectrographic plates, and plotting the element intensities of the base material and the base material plus standards. The use of such a standard addition method makes possible suitable extrapolations of the boron and silicon in the original base material. The same study will provide an estimate of the lower limits of detection for these elements.

86. Apparatus

86.1 *Polyethylene Bottle with Cap*, 500-mL.

86.2 *Mixer-Mill Grinder*.

86.3 *Plastic Vials*, 20 mm in diameter by 51 mm long.

86.4 *Ball Pestles*, acrylic plastic 10 mm in diameter.

86.5 *Spectrograph*—A grating spectrograph with a reciprocal linear dispersion of 5 A/mm in the first order and providing wavelength coverage from 2250 to 2900 A.

86.6 *Excitation Source*, providing a 4-A d-c arc.

86.7 *Comparator-Microphotometer*—A comparator providing sufficient magnification and facility to compare spectral line density with a reference standard plate or film, and a microphotometer having a precision of ±1.0 % for transmittance values between 5 and 90 %.

86.8 *Vent-Forming Tool*, shown in Fig. 8.

86.9 *Electrodes, Graphite*:

86.9.1 *Lower*—6.15-mm rod with a cup 4.75 mm in diameter and 7.14 mm deep, high-density grade (Practice E 130, Type S-3).

86.9.2 *Boiler Cap*—7.75 mm outside diameter, 6.15 mm inside diameter with a 0.96-mm diameter vent hole. (National Carbon SPK L-3715 or equivalent.)

86.9.3 *Upper*—3.05-mm rod, 38.10 mm long, pointed (Practice E 130, Type C-1).

86.10 *Photographic Plate*, Eastman Kodak Spectrum Analysis No. 1.

86.11 *Photographic Processing Equipment*, providing developing, fixing, washing, and drying operations and conforming to the requirements of Practices E 115.

87. Reagents

87.1 *Boron-Silicon, Standard Solution*—Prepare a standard solution containing boron and silicon, each at 1000 µg/g (on a uranium basis), by adding known amounts of ammonium

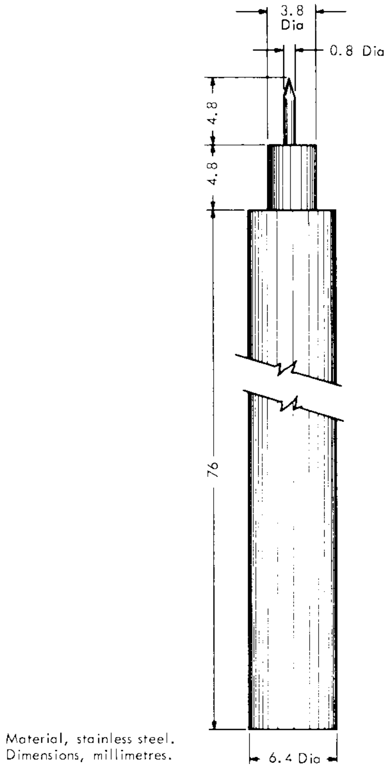

FIG. 8 Vent-Forming Tool

fluoborate (NH_4BF_4) and ammonium fluosilicate [$(NH_4)_2SiF_6$] to a known amount of boron- and silicon-free hydrolyzed UF_6(hydrolyzed in saturated ammonia water). Evaporate the hydrolyzed uranium solution to dryness on a steam bath, and blend the residue. Prepare the lower standards by making appropriate dilutions with base material that is prepared in a similar manner and blanked. Prepare a standard spectral plate using the following concentrations (µg/g): 100, 50, 20, 10, 5, 2, 1, 0.5, blank.

88. Procedure

88.1 *Sample Preparation Procedure*:

88.1.1 By means of a suitable sampling system, transfer approximately 5 g of liquid UF_6 to a tared fluorothene tube. Cool the tube in liquid nitrogen, disconnect from the sampling system, and seal with a threaded plug.

88.1.2 Weigh the filled tube to obtain the sample weight.

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

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

88.1.5 Immediately cap the bottle, and hydrolyze the contents in the fluorothene tube while shaking the bottle.

88.1.6 Transfer the slurry to a platinum dish.

88.1.7 Rinse the bottle with distilled water, and transfer the rinse solution to the platinum dish.

88.1.8 Evaporate the contents of the dish to dryness on a steam bath. Loss of boron or silicon may result if the temperature exceeds 100°C.

88.1.9 Transfer the residue to a plastic vial, add a ball pestle, and grind the mixture on the mixer-mill.

88.1.10 Weigh three 50-mg charges of the ground sample, and transfer each to an electrode.

88.1.11 Pack the sample into the bottom of the cavity by holding the electrode with a pair of forceps and tapping it briskly on the bench top.

88.1.12 Make a vent hole in the charge with the vent-forming tool shown in Fig. 8.

88.1.13 Place a boiler cap on top of the electrode.

88.2 *Spectrograph Operation Procedure*:

88.2.1 Position the plate holder containing one photographic plate on the spectrograph, and adjust the spectrograph as follows:

Slit height	3 mm
Slit width	25 µm
Timer	on and set for 45 s
Preburn timer	off
Spectral region, nm	225.0 to 290.0
Excitation	4 A dc

88.2.2 Wipe off the electrode clamps, insert the electrodes, and adjust the gap distance to 4 mm by adjusting the projected image of the gap on the target screen.

88.2.3 Turn on the d–c arc, and adjust the source to 4 A.

88.2.4 Adjust the upper electrode to maintain a 4-mm gap distance throughout the exposure.

88.2.5 At the completion of the exposure, remove the electrode, dump the charge into the scrap container, and discard both electrodes.

88.2.6 Rack the plate holder, and repeat the exposure cycle with the second and third electrodes of the sample.

88.2.7 After the sample exposures, rack the plate holder, and expose a sample of iron for 5 s at 4 A.

88.2.8 *Photographic Processing*—Process the plates in accordance with Practices E 115.

89. Photometry and Calculation

89.1 Using the comparator-microphotometer, compare the density of the elemental lines in the unknown spectrum visually with those on a standard plate to estimate the concentrations of boron and silicon. Average the results of replicate exposures. Use the following lines for the identification and estimation of boron and silicon:

Element	Wavelength, nm
Boron	249.68
Boron	249.77
Silicon	250.69
Silicon	251.61
Silicon	288.16

89.2 For a more precise value when an element concentration is measurable, measure the transmittance of the analytical line using the microphotometer. Convert this value to direct intensity, using the emulsion calibration chart, and calculate the concentration of the element from a previously prepared calibration curve which relates intensity to concentration.

90. Reliability

90.1 The precision of a single determination at the 95 % confidence level is ±2 µg/g for boron and ±3 µg/g for silicon, determined at both the 5-µg/g and 20-µg/g levels.

ATOMIC ABSORPTION DETERMINATION OF RUTHENIUM

91. Scope

91.1 A sensitive procedure for the measurement of ruthenium in UF_6 is achieved by combining distillation and solvent extraction methods for separating ruthenium, and atomic absorption for determining it. With a sample containing 5 g of uranium, 0.1 µg Ru/g U can be determined.

92. Summary of Test Method

92.1 Ruthenium is first separated by distillation as ruthenium tetroxide (RuO_4) from a concentrated sulfuric acid (sp gr 1.84)-perchloric acid (sp gr 1.76) mixture **(28).** The distilled ruthenium is reduced and then extracted with methyl isobutyl ketone (MIBK) probably as its tris (4,7-diphenyl-1,10-phenanthroline) chelate. The ruthenium in the extract is determined by atomic absorption.

92.2 Because the ruthenium-4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) complex gives an intense yellow-orange color (molar absorptivity in hexanol at 460 nm is 27 000), ruthenium can be determined spectrophotometrically **(29)**.

93. Interferences

93.1 The spectrophotometric test method is about as sensitive as the atomic absorption procedure, but it is subject to interferences from iron and technetium. For accurate analyses by the spectrophotometric method all the reagents must be free of iron contamination.

93.2 In the essentially interference-free atomic absorption procedure, the ruthenium, having been separated and concentrated by distillation and solvent extraction, is determined directly in the MIBK extract. The organic extract gives an atomic absorption sensitivity for ruthenium about twice that obtainable in dilute hydrochloric acid.

94. Apparatus

94.1 *Atomic Absorption Spectrometer* equipped with a Boling burner or equivalent.

94.2 *Distillation Apparatus* shown in Fig. 9.

94.3 *Erlenmeyer Flasks*, glass-stoppered, 250-mL.

95. Reagents

95.1 *Bathophenanthroline* (4,7-diphenyl-1,10-phenanthroline solution) (0.002 M) —Dissolve 0.0668 g of bathophenanthroline[13] in 100 mL of ethyl alcohol.

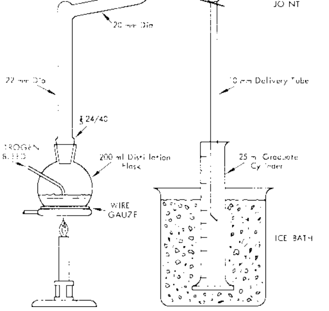

FIG. 9 Distillation Apparatus

95.2 *Hydroxylamine Hydrochloride Solution* (10 %)—Dissolve 10 g of $NH_2OH \cdot HCl$ in 100 mL of water.

95.3 *Methyl Isobutyl Ketone* (MIBK), reagent grade.

95.4 *Nitrogen*.

95.5 *Ruthenium, Standard Solution*—Prepare a stock solution containing 0.100 mg of ruthenium/mL in 0.1 *N* HCl from pure ruthenium metal or a suitable ruthenium compound, such as "Specpure"[14] ammonium aquochloro ruthenite $[(NH_4)_2RuCl_5 \cdot H_2O]$. (Analysis of this material for ruthenium by ignition in hydrogen gave 31.3 % ruthenium instead of the theoretical value of 32.15 %.) A50-fold dilution of this solution gives one containing 2.00 µg Ru/mL.

95.6 *Sodium Acetone Buffer Solution* (10 %)—Dissolve 10 g of $NaC_2H_3O_2$ in 100 mL of water.

96. Procedure

96.1 Transfer to a platinum dish a carefully measured sample aliquot of hydrolyzed UF_6 containing 5 g of uranium. Sample hydrolysis is described in 17.7 through 17.17.

96.2 Add 25 mL of concentrated H_2SO_4(sp gr 1.84), and heat the solution to fumes of H_2SO_4.

96.3 Transfer the solution, while hot, to the distillation flask shown in Fig. 9, washing the dish with concentrated H_2SO_4(sp gr 1.84).

96.4 Pipet 15 mL of 0.001 *N* HCl and 2 mL of 10 % $NH_2OH \cdot HCl$ solution into a 25-mL graduated cylinder which is used as the distillation receiver.

96.5 Add 2 mL of concentrated perchloric acid ($HClO_4$, sp gr 1.76) to the distillation flask, lubricate the glass joints with water, and assemble the apparatus as shown in Fig. 9.

96.6 Pass dry nitrogen into the distillation flask at about 5 cm^3/min while heating the contents of the flask slowly to boiling. Also, heat the glass transfer tube with a bunsen burner or resistance heating tape.

96.7 Distill the solution vigorously for 2 to 3 min.

96.8 Transfer the solution in the distillation receiver to a 150-mL beaker along with water washings of the delivery tubes and the receiver.

96.9 Evaporate the solution to about 25 mL and allow to cool to room temperature.

96.10 Add 1 mL of 10 % $NH_2OH \cdot HCl$ solution and 4 mL of 10 % $NaC_2H_3O_2$ solution to the solution, and adjust the pH of the solution to 4.8 to 5.0 with dilute NH_4OH.

96.11 Transfer the solution to a 250-mL glass-stoppered Erlenmeyer flask, and add 10 mL of 0.002 *M* bathophenanthroline solution.

96.12 Warm the solution in a water bath at 100°C for 2 h.

96.13 Cool the solution, and add 10 mL of MIBK with a pipet. Stopper the flask, and shake the solution vigorously for 3 min. Allow the phases to separate.

96.14 Analyze the organic extract by atomic absorption as follows:

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[13] Available from G. Frederick Smith Chemical Co., Box 23344, 867 McKinley Ave., Columbus, OH 43222.

[14] Sold by Johnson Mathey & Co., Ltd., London, England.

96.14.1 Prepare the instrument for ruthenium analysis as outlined in the instrument manufacturer's atomic absorption manual. Set the operating parameters as follows:

Wavelength	349.89 nm
Range	UV
Slit	0.3 mm
Source	high-intensity ruthenium hollow-cathode lamp
Lamp current	manufacturer's recommendation
Gas pressures	air—30 psig; acetylene—10 psig
Gas flowmeter settings	air—9.5; acetylene—10
Solution aspiration rate	3.5 to 4.0 mL/min
Height of absorption beam above burner	10 to 12 mm

96.14.2 Zero the instrument with pure MIBK.

96.14.3 Calibrate the instrument by preparing standards from UO_2F_2 solutions that have been spiked with 0, 5, and 10 µg of ruthenium, respectively. The standards are then extracted as outlined previously. (Calibrate each time samples are analyzed).

96.14.4 Analyze sample extracts. Determine the concentration of ruthenium in the extracts from the calibration.

97. Reliability

97.1 The precision of analyzing ruthenium at the 2 µg/g U level is± 7 % at the 95 % confidence interval.

SPECTROGRAPHIC DETERMINATION OF RUTHENIUM

98. Scope

98.1 This test method covers the spectrographic determination of ruthenium in UF_6 in concentrations from 0.1 to 10 ppm.

99. Summary of Test Method

99.1 The ruthenium in the hydrolyzed UF_6 solution **(30)** is separated from the uranium by reduction with zinc in a sulfuric acid solution after adding aluminum chloride solution to complex the fluoride. Gold is added as a gathering agent. The filtered metal precipitate is ignited, and the ignited residue is placed in a graphite electrode and excited in the d-c arc, using an argon-oxygen atmosphere. The resulting spectra are recorded on a photographic plate with a grating spectrograph. Standard spectra are placed on the same plate with the samples.

100. Apparatus

100.1 *Spectrograph*, grating, providing wave-length coverage from 225.0 to 820.0 nm with a reciprocal linear dispersion of 0.5 nm/mm in the first order.

100.2 *Excitation Stand*, conventional type with adjustable watercooled electrode holders.

100.3 *Photographic Plate Processing Unit*—Photographic processing equipment, providing developing, fixing, washing, and drying operations and conforming to the requirements of Practices E 115.

100.4 *Excitation Source* providing a 10-A-d-c arc (short-circuited).

100.5 *Comparator-Microphotometer*—A comparator providing sufficient magnification and facility to compare spectral line density with reference standard plate or film, and a microphotometer having a precision of ±1.0 % for transmittance values between 5 and 90 %.

100.6 *Calculating Equipment*—The use of a calculating board shall be optional for converting transmittance reading to ppm concentrations.

100.7 *Controlled Atmosphere Chamber*.

101. Reagents and Materials

101.1 *Aluminum Solution* (100 g Al/L)—Dissolve 100 g of 8 to 20 mesh, granular aluminum in 800 mL of concentrated HCl (sp gr 1.19) and 200 mL of distilled water. Filter the solution and dilute to 1 L with distilled water.

101.2 *Electrodes, Graphite*:

101.2.1 *Sample*—5.15-mm rod, 38.10 mm long, with a cup 4.06 mm in diameter and 3.18 mm deep with undercut 1.58 mm wide and 1.38 mm deep located 4.76 mm from the top.

101.2.2 *Counter*—3.05-mm rod, 50.8 mm long, flat end.

101.3 *Gold Solution*—Dissolve 2.500 g of gold metal in a solution made up of 3 mL of HNO_3, 18 mL of HCl, and 9 mL of water. Evaporate the solution to a paste on a steam bath; add 10 mL of HCl and evaporate again. Repeat this operation three times and if gold precipitates, add a few crystals of $NaClO_3$ to redissolve the gold. Finally, add 10 mL of HCl to the paste, and dilute the solution to 250 mL in a volumetric flask. This solution contains 10 mg Au/mL.

101.4 *Mixed Gas Cylinder*, 80 % argon and 20 % oxygen.

101.5 *Photographic Processing Solutions* as prescribed in Practices E 115.

101.6 *Ruthenium Stock Solution* (1000 µg Ru/mL)—Dissolve 0.1023 g of ruthenium trifluoride ($RuCl_3$) in 10 mL of HCl (1 + 1) and dilute to 50 mL with distilled water.

102. Procedure

102.1 *Preparation of Standards and Samples*:

102.1.1 Prepare three ruthenium standard solutions containing 10 µg Ru/mL, 1 µg Ru/mL, and 0.1 µg Ru/mL from the ruthenium stock solution (1000 µg Ru/mL). Store all ruthenium standard solutions in tightly capped polyethylene (not glass) bottles.

102.1.2 Add measured amounts of a ruthenium standard solution to aliquots of high-purity uranyl fluoride solution in 250-mL plastic beakers, each aliquot containing 3 g of uranium. Prepare five spiked uranyl fluoride solutions containing 0.3, 1, 3, 10, and 30 µg of ruthenium, respectively.

102.1.3 Likewise, place sample aliquots of hydrolyzed UF_6, each containing 3 g of uranium, in plastic beakers.

102.2 *Chemical Separation*:

102.2.1 Take samples and standards through the procedure for separating the ruthenium from the uranium in a like manner.

102.2.2 Add 50 mL of the aluminum solution to each aliquot, and adjust the volume to 125-mL volume with distilled water.

102.2.3 Add 7 mL of concentrated H_2SO_4(sp gr 1.84) and 1 mL of gold solution (10 mg Au).

102.2.4 Add 8 g of 20-mesh metallic zinc to reduce the solution and form the metal precipitate.

102.2.5 Place the solution on a steam bath and warm until the zinc reaction ceases.

102.2.6 Allow the solution to stand for several hours.

102.2.7 Add several millilitres of concentrated HCl to remove excess zinc, if any.

102.2.8 Filter the solution through a hard close–textured, double-acid–washed filter paper.[15]

102.2.9 Wash the precipitate thoroughly with (at least 200 mL) hot 2 % HCl. (Extreme care must be taken to remove all the uranium during this washing.)

102.2.10 Transfer the precipitate to a No. 1 porcelain crucible, place in a cold muffle furnace, and ignite overnight at a maximum of 500°C.

102.2.11 Break up the metal concentrate with a spatula, and transfer the entire residue to an electrode.

102.3 *Spectrochemical Requirements*:

102.3.1 Obtain spectrograms using the spectrochemical requirements in Table 5.

102.3.2 *Photographic Plate Handling Procedure*—Process the emulsion in accordance with Practice E 115.

102.4 *Visual Evaluation and Photometry*:

102.4.1 Place the sample plate in the comparator and estimate the amount of ruthenium (micrograms) present visually by comparing with a standard plate prepared previously under the same conditions.

102.4.2 When the ruthenium concentration is near 1 ppm, measure the transmission of the analytical line, and convert the transmission to intensity units.

102.4.3 Plot a working curve relating log micrograms of ruthenium versus log intensity of ruthenium from the spectrograms of the standards on the same plate with the samples.

102.4.4 Obtain the amount of ruthenium (micrograms) from the working curve. Report the ruthenium concentration in parts per million on a uranium basis.

102.4.5 The recommended ruthenium lines are as follows: 342.83 nm, 343.67 nm, 349.89 nm.

103. Reliability

103.1 The precision for a single determination by the densitometric test method is ±70 % at the 95 % confidence interval and 3-µg level.

TABLE 5 Spectrochemical Requirements

Photographic plates	2 Eastman S. A. No. 1 or equivalent
Wavelength range	235.0 to 485.0 nm in first order
External optics:	
Step filter	100-40-10 %
Filter	none
Slit width	14 µm
Slit height	3 mm
Arc gap	4 mm
Current	10 A dc on short circuit
Exposure	complete burn
Controlled atmosphere chamber	Spex No. 9027
Gas flow	4 L/min
Gas mixture	80 % argon, 20 % oxygen
Densitometer:	
Scanning speed	0.36 mm/min
Slit width	3 µm
Slit height	0.5 mm

SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM AND VANADIUM

104. Scope

104.1 Separate, but similar, procedures are provided for the spectrophotometric determination of titanium and vanadium in $^{235}UF_6$ with benzoylphenylhydroxylamine. Concentrations of 0.2 µg/g U of either element can be detected.

105. Summary of Test Method

105.1 Titanium(IV) and vanadium(V) react with benzoylphenylhydroxylamine (BPHA) in strong hydrochloric acid solutions to form highly colored extractable complexes that can be used in spectrophotometric analyses **(31, 32, 33, 34).** The yellow titanium(IV)-BPHA complex is formed in 8 *M* hydrochloric acid and extracted into chloroform; the color of the extract is measured at 420 nm. The violet vanadium(V-BPHA complex is formed and extracted with chloroform form 4 *M* hydrochloric acid, and its color is measured at 530 nm.

106. Interferences

106.1 The methods are quite selective since very few elements react with BPHA to give colored complexes under the conditions of the analysis. In the titanium method, niobium is a serious interference if its ratio to titanium is greater than 1 to 5; more than 100 µg molybdenum interferes similarly. Thorium, tungsten(VI), and zirconium interfere only in quantities of 1 mg or more. Vanadium(V) and chromium(VI) are potential interferences, but their effects are eliminated by reduction with ferrous ion in the standard procedure.

106.2 The vanadium procedure is even more selective. Molybdenum(V) at 1 mg or more interferes by consuming the BPHA; titanium interferes at 200 µg or more but, if present, it can be complexed with fluoride. Chromium(VI) interferes at 100 µg or more by oxidizing the BPHA, but it can be eliminated by volatalization as chromyl chloride before the analysis.

107. Apparatus

107.1 *Spectrophotometer* equipped with 5-cm absorption cells as described in Practice E 60.

108. Reagents

108.1 *Benzoylphenylhydroxylamine* (BPHA) *Solution*—Dissolve 0.20 g of *N*-benzoylphenylhydroxylamine[16] in 100 mL of chloroform.

108.2 *Ferrous Ammonium Sulfate Solution*—Dissolve 0.070 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in water and dilute to 100 mL.

108.3 *Potassium Permanganate Solution* (0.1 *N*)—Pre pare a 0.1 *N* solution of potassium permanganate ($KMnO_4$).

108.4 *Sodium Chloride Solution* (3.5 *M*)—Prepare a 3.5 *M* solution of sodium chloride (NaCl).

108.5 *Titanium Standard Solution*—To 0.1668 g of titanium dioxide (TiO_2) in a 250-mL beaker, add 10 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) and 0.8 g of ammonium

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[15] Whatman No. 42 filter paper has been found to be satisfactory.

[16] Eastman Kodak No. 7297, designated *N*-phenylbenzohydroxamic acid, has been found satisfactory.

sulfate [$(NH_4)_2SO_4$]. Heat the TiO_2 until it dissolves, and cool the solution to room temperature. Dilute the solution to 1 L with water. Dilute a 10-mL aliquot of this solution to 1 L with water to obtain a solution containing 1 µg Ti/mL.

108.6 *Vanadium Standard Solution*—Dissolve 0.2296 g of ammonium vanadate (NH_4VO_3) in water that has been made slightly basic with ammonium hydroxide (NH_4OH), and dilute the solution to 1 L with water. Dilute a 10-mL aliquot of this solution to 1 L with water to obtain a solution containing 1 µg V/mL.

109. Procedure for Titanium

109.1 By weight or volume, measure an aliquot of hydrolyzed UF_6 containing up to 3.00 g of uranium into a platinum dish.

109.2 Add 5 mL of concentrated H_2SO_4(sp gr 1.84), and evaporate the solution just to dryness.

109.3 Cool the residue; dissolve in 50 mL of 8 *M* HCl and transfer to a 125-mL separatory funnel using about 5 mL of 8 *M* HCl to wash the dish. Starting with 55 mL of 8 *M* HCl in a 125-mL separatory funnel, carry a reagent blank through the procedure from this point on.

109.4 Add 2 mL of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ solution to the separatory funnel; stopper and shake the funnel for 10 s.

109.5 Pipet 25 mL of the BPHA-chloroform reagent solution into the separatory funnel; stopper and shake the funnel for 5 min.

109.6 Allow the phases to separate for 1 min, and drain the organic phase through a funnel containing a plug of glass wool into a dry 50-mL centrifuge tube or a test tube.

109.7 Transfer some of the chloroform extract to a 5-cm cell, and measure the absorbance at a wavelength of 420 nm versus the reagent blank.

109.8 Determine the titanium content in the sample by reference to a calibration curve prepared by treating titanium-free uranium samples spiked with 0 to 20 µg of titanium according to the above procedure.

110. Procedure for Vanadium

110.1 Transfer a carefully measured aliquot of hydrolyzed UF_6 containing up to 5 g of uranium to a platinum dish.

110.2 Add 10 mL of concentrated $HClO_4$(sp gr 1.76), and heat the solution until the $HClO_4$ fumes in order to eliminate most of the fluoride. Transfer the solution to a 250-mL beaker using water to wash the dish; then evaporate to near dryness.

110.3 If necessary, add 1 g of solid NaCl to fume off any chromium as chromyl chloride.

110.4 Cool the solution that has been fumed to a volume of 1 to 3 mL to 70 to 100°C, and add 5 mL of water.

110.5 Then, add 0.1 *N* $KMnO_4$ solution to the sample, dropwise, until the solution remains pink.

110.6 Transfer the sample solution quantitatively to a 125-mL separatory funnel.

110.7 Add 20 mL of 3.5 *M* NaCl solution to the sample, and stir the solution.

110.8 Add 30 mL of 8 *M* HCl to the separatory funnel; stopper and shake the funnel for 10 s.

110.9 Pipet 25 mL of the BPHA-chloroform reagent solution into the separatory funnel; stopper and shake the funnel for 3 min.

110.10 Allow the phases to separate for 1 min, and drain the organic phase through a funnel containing a plug of glass wool into a dry 50-mL centrifuge tube or test tube.

110.11 Transfer the chloroform extract to a 5-cm cell, and measure the absorbance at a wavelength of 530 nm versus chloroform.

110.12 Determine the vanadium content in the sample by reference to a calibration curve prepared by treating vanadium-free uranium samples spiked with 0 to 20 µg of vanadium according to the above procedure.

111. Reliability

111.1 The precision at the 95 % confidence level for determining 5 to 10 µg of titanium or vanadium is ±6 %.

SPECTROGRAPHIC DETERMINATION OF METALLIC IMPURITIES BY CARRIER DISTILLATION

112. Scope

112.1 This test method is applicable to the determination of the 32 impurity elements listed in Table 3 with their limits of detection (expressed as ppm) in the U_3O_8 residue from the ignition of hydrolyzed UF_6.

113. Summary of Test Method

113.1 The sample of UF_6 is converted to U_3O_8, blended with a selected carrier **(32, 33, 34),** placed in a Practice E 130, Type S-2, graphite anode cap, and excited on the spectrograph with a direct-current arc. The resulting spectra are recorded on a photographic plate, the plate is developed **(35),** and the concentrations of the elements sought are estimated visually by comparison with previously prepared standard plates.

113.2 As the term “carrier” implies, this procedure is a fractional distillation of the volatile impurity elements from the more refractory uranium oxide, aided by a carrier material of moderate volatility. Under proper excitation conditions, about 35 different impurities are carried into the arc while uranium, whose complex spectrum can interfere in the analysis of many elements, is nearly unaffected. There are certain limitations on the choice of a carrier, but several materials will provide satisfactory results. The carrier should be moderately volatile, free of the elements to be determined, and easily incorporated into the sample **(36).** The compounds gallium oxide, silver chloride, and mixtures of silver chloride with fluoride salts of lithium, strontium, or silver have been among those most commonly used.

113.3 Master standards are made by thoroughly mixing known ratios of pure compounds of each element and pure uranium oxide. Subsequent dilutions of these master standards with pure uranium oxide produce standards at the desired impurity levels. Standard spectral plates for visual comparison to samples are then prepared from the standards. (The U_3O_8 standard base material should be ignited at the same temperature as the uranium samples, to obtain the same bulk density.) Factors such as interelement effect and line interference are taken into account in the selection of calibration groupings and wavelengths when making standard plates.

113.4 The limits of detection are dependent upon the spectrographic equipment used, the impurities present in the electrodes and the U_3O_8 base material, and the selection and purity of the carrier. Contamination may result from handling and sampling equipment, storage and mixing equipment, or from the furnace, or a combination of these, if care is not used during the sample preparation steps.

114. Apparatus

114.1 *Spectrograph*, grating, providing wavelength coverage from 225.0 to 820.0 nm with a reciprocal linear dispersion of 0.5 nm/mm in the first order.

114.2 *Excitation Source* providing a 12-A d-c arc.

114.3 *Comparator-Microphotometer*—A comparator providing sufficient magnification and facility to compare spectral line density with a reference standard plate or film, and a microphotometer having a precision of ±1.0 % for transmittance values between 5 and 90 %.

114.4 *Mechanical Blenders* capable of blending samples.

114.5 *Polystyrene Vials*, 13 mm in diameter by 26 mm long and 20 mm in diameter by 52 mm long, with caps.

114.6 *Grinding Balls*, acrylic plastic, 10 mm in diameter.

114.7 *Mortar*, boron carbide (for standards preparation).

114.8 *Platinum Spatula*.

114.9 *Platinum Funnel*.

114.10 *Balances*, torsion-type, with capacities up to 1000 mg.

114.11 *Electrode Stand*, plastic, for 7-mm electrodes.

114.12 *Photographic Emulsion*—Eastman SA No. 1 and 1-N or equivalent.

114.13 *Electrodes*, graphite **(37):**

114.13.1 *Lower*—6.15-mm rod with a cup (4.06 mm in diameter and 7.14 mm deep) high-density-grade graphite and regular grade graphite Practice E 130, Type S-2.

114.13.2 *Upper*—3.05-mm rod, 38.10 to 50.80 mm long, pointed. Practice E 130, Type C-1.

114.13.3 *Post*—3.05-mm rod, 38.10 mm long, Practice E 130, Type S-1.

114.14 *Vent-Forming Tool* **(38)** shown in Fig. 8.

114.15 *Filters*, step.

114.16 *Photographic Processing Equipment*, providing developing, fixing, washing, and drying operations conforming to the requirements of Practices E 115.

115. Reagents

115.1 *Elemental Oxides, Carbonates, or Phosphates of High Purity*.

115.2 *Gallium Oxide* (Ga_2O_3), spectrographic grade.

115.3 *Lithium Fluoride* (LiF), spectrographic grade.

115.4 *Photographic Processing Solutions*—Formulas for processing solutions are given in Practices E 115.

115.5 *Silver Chloride* (AgCl), spectrographic grade.

115.6 *Silver Chloride-Lithium Fluoride* (AgClLiF) *Mixture* (11 + 1 by weight).

115.7 *Silver Chloride-Strontium Fluoride* ($AgCl-SrF_2$) *Mixture* (6 + 1 by weight).

115.8 *Sodium Chloride* (NaCl), spectrographic grade.

115.9 *Strontium Fluoride* (SrF_2), spectrographic grade.

115.10 *Urano-Uranic Oxide* (U_3O_8), high-purity, prepared as described in Sections 27 through 33.

116. Procedure

116.1 *Calibration Standards*:

116.1.1 Prepare three groups of standards by adding high-purity metal oxides, carbonates or (in the case of phosphorus) an alkali phosphate to high-purity uranium oxide (U_3O_8). First, produce standard stocks for a standard group containing 10 000 parts of each element per million parts of uranium (by weight). Dilute a portion of the 10 000-ppm standard with pure U_3O_8 to obtain a 1000-ppm standard. Repeat the dilutions until standards containing 100, 70, 50, 20, 10, 5, 2, 1, 0.5, 0.2, 0.1, and 0 (blank) ppm are obtained. The following are three suggested standard groups for the 32 elements:

I—Ag, Al, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sn, V, Zn
II—As, Au, Ba, Be, Bi, Ca, Co, Ge, In, P, Sb, Tl
III—Cs, K, Li, Na, Rb, Sr

116.2 *Sample Preparation Procedure*:

116.2.1 By means of a suitable sampling system, transfer approximately 7 g of liquid UF_6 to a tared fluorothene tube. Cool the tube in liquid nitrogen, disconnect from the sampling system, and seal with a threaded plug.

116.2.2 Allow the tube to warm to room temperature, and weigh the filled tube to obtain the gross weight.

116.2.3 Obtain the sample weight by the difference between the gross weight and the tare weight.

116.2.4 Cool the tube in liquid nitrogen, remove the flare connection, and place the tube into 50 mL of cold water in a platinum dish.

116.2.5 After hydrolysis of the UF_6, remove the fluoroethene tube from the dish and rinse with distilled water. Add the rinse water to the contents of the dish.

116.2.6 Measure the volume of the solution, calculate the concentration, and transfer the solution to a polyethylene bottle.

116.2.7 Transfer the aliquot of the hydrolyzed sample containing approximately 3 g of UF_6 to a platinum dish and evaporate to dryness (to uranyl fluoride) under an infrarred heat lamp.

116.2.8 Convert the uranyl fluoride sample to U_3O_8 by ignition in a pyrohydrolysis furnace at 850°C for 30 min. (Molybdenum and vanadium may be lost on prolonged ignition).

116.2.9 Weigh a 0.450-g sample of U_3O_8 and 0.050 g of the 6 + 1 $AgCl-SrF_2$ mixture into a plastic vial. Grind these together on the mechanical mixer using plastic grinding balls in the vial. Use this mixture in the determination of elements in Procedure A, Table 6 and Table 7.

116.2.10 Weigh a 0.450-g sample of the U_3O_8 and 0.050 g of the 11 + 1 AgCl-LiF mixture into a plastic vial. Grind these together on the mechanical mixer using plastic grinding balls in the vial. Use the mixture in the determination of elements in Procedure B, Table 6 and Table 7.

116.2.11 Weigh a 0.465-g sample of the U_3O_8 and 0.035 g of NaCl into a plastic vial. Grind these together on the mechanical mixer using plastic grinding balls in the vial. Use this mixture in the determination of elements in Procedure C, Table 6 and Table 7.

116.2.12 Weigh a 0.490-g sample of the U_3O_8 and 0.010 g

TABLE 6 Wavelengths and Limits of Detection for Various Carrier Procedures

Element	Limit of Detection, ppm	Suggested Wavelength, nm	Element	Limit of Detection, ppm	Suggested Wavelength, nm	Element	Limit of Detection, ppm	Suggested Wavelength, nm
Procedure A								
Aluminum	0.1	308.22	Copper	0.5	324.75	Phosphorus	20	253.40
		309.27			327.40			253.57
								255.33
Arsenic	2	228.81	Iron	5	248.33			255.50
		234.98			248.82			
		278.02			271.90	Lead	0.5	280.20
					302.06			283.31
Gold	0.5	242.80			302.11			
		267.60				Antimony	1	259.81
			Germanium	0.5	265.12			287.80
Barium	1	230.42			265.16			
		233.53			303.91	Tin	0.5	284.00
		307.16						303.41
		455.40	Indium	0.5	303.94			317.50
					325.61			326.23
Beryllium	0.01	234.86			325.86			
		313.04				Thallium	2	276.79
		313.11	Magnesium	0.5	279.55			291.83
					280.27			
Bismuth	1	289.80			285.21	Vanadium	0.5	318.34
		306.77						318.40
			Manganese	0.5	279.49			318.54
Cadmium	0.1	228.80			279.83			
		326.11			280.11	Zinc	20	330.26
								334.50
Cobalt	1	240.73	Molybdenum	0.5	313.26			334.56
		241.16			317.04			
		242.49			319.40			
		251.98						
			Nickel	0.5	300.25			
Chromium	2	283.56			300.36			
		284.33			305.08			
					310.16			
					310.19			
Procedure B								
Calcium	1	393.37	Sodium	1	589.00	Strontium	1	407.77
		396.85			589.59			460.73
		422.67						
Procedure C								
Cesium	5	852.11	Lithium	0.2	610.36	Rubinium	2	780.02
					670.78			794.76
Potassium	2	766.49						
		769.90						
Procedure D								
Silver	0.1	328.07						
		338.29						

of Ga_2O_3 into a plastic vial. Grind these together on the mechanical mixer using plastic grinding balls in the vial. Use this mixture in the determination of elements in Procedure D, Table 6 and Table 7.

116.2.13 For each excitation procedure (Table 6 and Table 7), weigh three 0.100-g charges of the appropriate mixture from 116.2.9 through 116.2.12.

116.2.14 Using a platinum funnel, transfer the charges to graphite electrodes.

116.2.15 Pack each sample into the bottom of the cavity by holding the electrode with a pair of forceps and tapping it briskly on the bench top.

116.2.16 Place a vent hole in the charge with the vent-forming tool shown in Fig. 8.

116.3 *Spectrograph Operation Procedure*:

116.3.1 To cover the complete range of elements listed, this procedure requires a series of exposures using the four sets of conditions shown in Table 7.

116.3.2 Align the electrodes, and adjust the gap width to 4 mm.

116.3.3 Adjust the appropriate spectrograph to the conditions given in Table 7, and expose the sample for the time indicated.

116.3.4 Maintain the 4-mm gap distance throughout the exposure by adjusting the electrodes as necessary.

116.3.5 At the completion of the exposure, remove and discard both electrodes.

116.3.6 Rack the spectrograph, and repeat with a second and third electrode to give triplicate exposures.

116.3.7 After the last exposure, rack the spectrograph and

TABLE 7 Spectrograph Operating Conditions for Various Carrier Procedures

	Procedure			
	A	B	C	D
Element sought	see Table 6	see Table 6	see Table 6	Ag
Wavelength range, A	2250 to 3500	3750 to 6250	6050 to 8550	2250 to 3500
Current, dc A	11	12	11	11
Preburn, s	5	5	5	5
Exposure, s	60	60	60	35
Photographic plate	SA No. 1	1-N	1-N	SA No. 1
Carrier	(6 + 1 AgCl-SrF_2), 10 %	(11 + 1 AgCl-LiF), 10 %	NaCl, 7 %	Ga_2O_3, 2 %
Internal standard	none	none	none	none
External Optics:				
Step filter, %	100-43	100-27	100-43	100-27
Filter	none	glass	Corning 3384	none
Slit width,µ m	14	14	14	20
Slit height, mm	3	2	2	3
Arc gap, mm	4	4	4	4
Electrode charge, mg	100	100	100	100

expose a sample of iron (as a wavelength indicator) for 5 s at 4Å.

116.4 *Photographic Processing*—Process the plates in accordance with Practices E 115.

117. Photometry and Calculation

117.1 Compare the density of the analytical lines visually using the comparator-microphotometer and a standard plate to estimate the concentrations of the elements in the sample. Average the results of replicate exposures. Table 6 lists the wavelengths used for the various elements.

117.2 For a more precise value when an element concentration is measurable, measure the transmittance of the analytical line using the microphotometer. Convert this value to direct intensity, and obtain the concentration of the element from a calibration curve which relates intensity to concentration. Table 6 lists the wavelengths used for the various elements.

118. Reliability

118.1 The precision of a single determination at the 95 % confidence level using the densitometer technique approximates ± 30 % of the value determined at the 20-ppm level. The precision of a single determination at the 95 % confidence level using the visual technique approximates + 100 and − 50 % of the value determined at the 50-ppm level. The visual spectrographic technique follows the logarithmic distribution rather than the normal.

SPECTROGRAPHIC DETERMINATION OF HAFNIUM, MOLYBDENUM, NIOBIUM (COLUMBIUM), TANTALUM, TITANIUM, TUNGSTEN, AND ZIRCONIUM AFTER SEPARATION FROM UF_6 WITH BPHA

119. Scope

119.1 This test method provides for the simultaneous separation of hafnium, molybdenum, niobium (columbium), tantalum, titanium, tungsten, and zirconium from UF_6 by solvent extraction and then for the spectrographic analysis of the separated elements. Using a sample aliquot containing 3 g of uranium, concentrations of the elements from 0.4 to about 100 µg/g U can be determined; this concentration range can be extended in either direction by appropriate changes in the sample size.

120. Summary of Test Method

120.1 The key step in this analysis is the separation of the elements to be determined by solvent extraction in which benzoylphenylhydroxylamine (BPHA) forms chloroform-soluble complexes with hafnium, molybdenum(VI), niobium, tantalum, titanium, tungsten(VI), and zirconium **(39, 40, 41, 42).** Vanadium(V) also forms a chloroform-soluble complex with BPHA; but in the strong hydrochloric acid medium used in the analysis, it is slowly reduced and, therefore, incompletely extracted. BPHA, a cupferron analog, has two distinct advantages over cupferron as a solvent extraction complexing agent. First, it is much more stable than cupferron, and does not need to be handled in ice-cooled solutions to prevent decomposition; second, it is more selective than cupferron which also extracts other elements including copper, iron, thorium, and rare earths.

120.2 In the procedure, 3 g of uranium from a UF_6 sample is converted to a sulfate form, and the solution is oxidized to obtain all the elements in their highest valence. Hafnium, molybdenum, niobium, tantalum, titanium, tungsten, and zirconium are then extracted from 10 *N* HCl as their BPHA complexes into chloroform, converted to oxides, dissolved, and spark-excited by the rotating-disk technique using palladium as an internal standard. The photographically recorded spectral lines are converted to micrograms of each element densitometrically using appropriate calibration curves.

121. Interferences

121.1 The only serious interferences in the analyses are spectral interferences produced when excessively large quantities of the elements molybdenum (>100 µg), vanadium (>50 µg), or zirconium (>1000 µg) are present in the sample analyzed. The presence of these elements can be anticipated by a preliminary carrier distillation analysis; however, their potential interference can be eliminated as follows:

121.1.1 Vanadium is eliminated by adding ferrous ion to the sample solution just before the extraction. Ferrous ion reduces vanadium(V) to vanadium(IV) which does not form an extractable BPHA complex.

121.1.2 Zirconium can be separated quantitatively from the sample solutions by precipitation with chloromandelic acid. The precipitate can be converted to zirconium oxide and weighed to provide a gravimetric analysis of zirconium, and the sample filtrate solution can then be analyzed spectrographically without interference.

121.1.3 Molybdenum interferences have not been studied extensively; however, an extraction procedure with diethyl ether from 10 *N* HCl has been used successfully to eliminate its interference.

122. Apparatus

122.1 *Spectrograph Grating*, providing wavelength coverage from 225.0 to 820.0 nm with a reciprocal linear dispersion of 0.5 nm/mm in the first order.

122.2 *High-Voltage Controlled-Spark Excitation Source*.

122.3 *Rotating Disk Apparatus* equipped with a platinum shaft rotating at 10 rpm.

122.4 *Electrodes*:

122.4.1 *Sample*—High-purity graphite rotating disk, 12.50 mm in diameter, 3.05 mm thick, with a 3.18-mm hole through the center, Practice E 130, Type D-1.

122.4.2 *Counter*—3.05-mm rod, 38.10 mm long (Practice E 130, Type C-6).

122.5 *Photographic Emulsion*, Eastman SA No. 1 or equivalent.

122.6 *Muffle Furnace*.

122.7 *Platinum Dishes with Lids*, 200-mL and 75-mL. Before each use, clean the dishes by fusing potassium pyrosulfate in them, rinse with water, clean with chromic acid solution, and rinse thoroughly with deionized water.

122.8 *Platinum-Tipped Tongs*.

122.9 *Infrared Heating Lamps*.

122.10 *Plastic Pipet*, 1-mL.

122.11 *Plastic Graduate*, 50-mL.

122.12 *TFE-fluorocarbon Boats*, 1.2-mL.

122.13 *Separatory Funnels with TFE-fluorocarbon Stopcocks*, 125-mL.

122.14 *Photographic Processing Equipment*, providing developing, fixing, washing, and drying operations and conforming to the requirements of Practices E 115.

123. Reagents

123.1 *Benzoylphenylhydroxylamine (BPHA) Solution (0.5 %)*—Dissolve 2.5 g of the pure reagent in 500 mL of chloroform.[17]

123.2 *Element Standard Solution*—Prepare a separate stock solution for each element, and combine portions of these solutions to give a single standard solution containing 1.00 µg of each element per millilitre. Use deionized distilled water for all dilutions.

123.2.1 For niobium, weigh 0.1431 g of pure niobium pentoxide (Nb_2O_5) into a platinum dish. Fuse the oxide with 5 g of $KHSO_4$, and cool the residue and dissolve in 200 mL of 18 % $C_4H_6O_6$ solution. Dilute the solution to 1 L in a volumetric flask with water and store in a plastic bottle.

123.2.2 Use the same procedure to prepare a tantalum solution from 0.1221 g of pure tantalum pentoxide (Ta_2O_5). Prepare solutions of zirconium and titanium in a similar manner from 0.1351 g of zirconium dioxide (ZrO_2) and 0.1668 g of titanium dioxide (TiO_2), except use warm 1 + 1 sulfuric acid (H_2SO_4) to dissolve the fusion mixes. Prepare the molybdenum solution by weighing 0.2043 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24}$], dissolving it, and diluting the solution to 1.00 L with water.

123.2.3 Some of the stock solutions may be prepared more conveniently by dissolving 0.1000-g portions of the high-purity metallic elements in a mixture of nitric acid (HNO_3) and hydrofluoric acid (HF) and diluting to 1 L with water.

123.2.4 Each of the solutions prepared as above contains 100 µg of the respective element per millilitre. Prepare the standard solutions containing 1.00 µg of each element per millilitre of solution by pipetting 10 mL of each of the above stock solutions into a 1-L volumetric flask and diluting the solution to volume with water.

123.2.5 *Photographic Processing Solutions*, as prescribed in Practices E 115.

123.3 *Ferrous Ammonium Sulfate Solution*—Prepare a 100-mg/mL solution of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in water.

123.4 *Palladium Chloride Solution*—Prepare a 0.1-mg/mL solution of $PdCl_2$ in 2 *N* hydrochloric acid (HCl).

123.5 *Potassium Bisulfate* ($KHSO_4$).

123.6 *Potassium Permanganate Solution*—Prepare a 3-mg/mL solution of $KMnO_4$ in water.

123.7 *Potassium Pyrosulfate* ($K_2S_2O_7$).

123.8 *Tartaric Acid* ($C_4H_6O_6$) *Solution* (18 %).

124. Procedure

124.1 *Preparation and Extraction of the Sample*:

124.1.1 Transfer an accurately measured aliquot of hydrolyzed UF_6 containing 3.0 g of uranium to a 200-mL platinum dish.

124.1.1.1 With each sample or group of samples, weigh a control sample of 3.5 g of pure U_3O_8 in a 200-mL platinum dish. Analyze this sample along with the unknown samples to establish the reliability of the previously prepared calibration curve.

124.1.1.2 Dissolve the oxides in 10 mL of 8 *N* HNO_3, cover the dish with a platinum lid, and heat gently to dissolve the sample.

124.1.1.3 Remove the platinum lid and rinse back into the dish with water.

124.1.1.4 Spike the pure uranium control sample with 2.0, 3.0, and 5.0 mL of the element standard solution.

124.1.1.5 Add 10 mL of concentrated HF (sp gr 1.17) and 10 mL of concentrated H_2SO_4(sp gr 1.84) to the dish. Swirl the solution gently to mix the contents thoroughly.

124.1.2 Add 10 mL of concentrated H_2SO_4(sp gr 1.84) to the UF_6 sample aliquot, and evaporate both the sample and control solutions to dryness under an infrared lamp or on a hot plate.

NOTE 14—Overnight heating with the lamp 102 mm above the dish is recommended to assure the removal of fluorides that prevent the quantitative extraction of titanium.

124.1.3 Rinse the sides of the dish with water, add a few drops of concentrated perchloric acid ($HClO_4$, sp gr 1.76) and evaporate the solution to near dryness.

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[17] Arsenazo III is available from the J. T. Baker Chemical Co. as Item No. B577.

NOTE 15—If the use of $HClO_4$ is inconvenient, the highest oxidation states of these elements can be assured by the dropwise addition of dilute permanganate solution to the water solution of the residue in 124.1.4 until a permanent pink color is obtained. Treatment of this solution with the appropriate amount of concentrated HCl (sp gr 1.19) then yields the 60-mL volume of 10 *N* HCl solution indicated in 124.1.5.

124.1.4 Dissolve the residue by heating gently with 10 mL of water. Use a platinum spatula to break up the solids, if necessary.

124.1.5 Transfer the solution to a 125-mL separatory funnel, rinsing the dish with 50 mL of 12 *N* HCl to give a total volume of 60 mL.

NOTE 16—If a large amount of vanadium (that is, more than 10 µg/g U) is known or suspected to be present, add 2 mL of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ solution to the separatory funnel to reduce the vanadium to a valence state of four and prevent its extraction.

124.1.6 Add 20 mL of 0.5 % BPHA-chloroform solution to each separatory funnel, and stopper and shake the funnel for 5 min.

124.1.7 Allow the phases to separate for 5 min and drain all but a small portion of the chloroform layer into a second 125-mL separatory funnel.

124.1.8 Repeat the extraction in the first funnel with 15 mL of BPHA solution, shake for 5 min, and combine the extracts. Discard the aqueous layer into a suitable salvage container.

124.1.9 Wash the combined chloroform extracts by shaking for 20 s with 25 mL of 10 *N* HCl. Allow the layers to separate for at least 10 min.

124.1.10 Drain the chloroform layer into a 75-mL platinum dish, leaving the last few drops in the separatory funnel.

124.1.11 Add 5 mL of chloroform to the extraction funnel and, without shaking, drain all but a small portion of it into the 75-mL platinum dish.

124.1.12 Evaporate the chloroform solution to dryness under an infrared lamp.

124.1.13 Moisten the residue with a few millilitres of 8 *N* HNO_3 and heat gently under an infrared lamp.

124.1.14 Digest the residue with 3 mL of concentrated HNO_3(sp gr 1.42) and a few drops of concentrated H_2SO_4(sp gr 1.84), and evaporate the solution to dryness.

124.1.15 Cover the dish and carefully heat to 500°C in a muffle furnace; then, ignite it until the carbon is burned off (3 to 4 h or overnight for convenience).

124.1.16 Add 5 mL of 5 + 1 concentrated HCl-HF (sp gr 1.19 - sp gr 1.17) solution and 1 mL of the palladium internal standard solution to each dish.

124.1.17 Place the solution on a warm hot plate and evaporate slowly until just dry.

124.1.18 Add 1 mL of the HCl-HF solution and warm gently for a few seconds to redissolve the solids without evaporating the solution. Swirl the solution in the dish to mix it thoroughly and pour into a 1.2-mL TFE-fluorocarbon boat.

124.2 *Spectrographic Analysis*:

124.2.1 Place the rotating disk assembly in the electrode clips.

124.2.2 Set the electrical parameters as follows:

Capacitance, µF	0.005
Inductance, µH	300
Resistance,Ω	residual
Primary voltage, V	195
Spark power	2
No. of discharges/half cycle	5
Prespark, s	40
Rf, A	5.5

124.2.3 Set the spectrograph as follows:

Slit width, µm	20
Turret lens, 8	100/10 % transmission
Wavelength range, nm	236.0 to 336.0
Exposure index	40 % transmission of the Pd 311.4 nm line

NOTE 17—With the conditions and equipment indicated, a 90-s exposure gives the desired exposure index.

124.2.4 Place the sample boat on the rotating disk platform.

124.2.5 Insert the electrodes, and turn on the rotating disk drive motor.

NOTE 18—All rotating disk electrodes are presparked for 20 s using the following electrical parameters:

Capacitance, µF	0.0025
Inductance, µH	600
Resistance,Ω	3
Primary voltage, V	130
No. of discharges/half cycle	3

124.2.6 Set the analytical gap at 3 mm, and spark the sample.

124.2.7 Process the emulsion in accordance with Practices E 115.

124.3 *Photometric Methods and Calculations*:

124.3.1 Use the densitometer to measure the percentage of transmission of each of the lines listed in Table 8 for both standards and samples.

124.3.2 Convert the transmission readings to intensities using an emulsion calibration curve that has been transposed on a calculating board.

124.3.3 Determine the ratio of the intensity of each line measured to that of the appropriate palladium line.

124.3.4 From standard curves, determine the amount (micrograms) of each element present.

124.3.5 Calculate the concentration of each element on a uranium basis.

124.4 *Preparation of a Standard Curve*—Prepare a standard curve by treating samples of pure U_3O_8 with 2 to 20 µg of hafnium, molybdenum, niobium, tantalum, titanium, tungsten, and zirconium from the standard solutions and analyzing them by the procedure given. Plot the intensity ratios against micrograms of the element taken, on log-log graph paper for each element to obtain the standard curves.

TABLE 8 Photometric Data

Element	Wavelength, nm	Palladium Internal Standard Line, nm	Micrograms of Element to Be Detected
Hafnium	246.42	248.89	2–10
Molybdenum	267.18	248.89	2–10
	278.00	248.89	2–15
Niobium	267.36	248.89	3–15
	309.42	311.40	1–10
Tantalum	268.51	248.80	2–10
Titanium	308.80	311.40	1–5
	253.12	248.89	3-10
Tungsten	239.71	248.89	4–10
Zirconium	256.89	248.89	4–15

125. Reliability

125.1 The precision at the 95 % confidence level in determining 0.7 to 3 µg/g U of each element is ±25 %.

SPECTROGRAPHIC DETERMINATION OF HAFNIUM, MOLYBDENUM, NIOBIUM, TANTALUM, TITANIUM, TUNGSTEN, VANADIUM, AND ZIRCONIUM AFTER SEPARATION FROM UF_6 AS CUPFERRIDES

126. Scope

126.1 This test method is applicable to the determination of microgram quantities of hafnium, molybdenum, niobium, tantalum, titanium, tungsten, vanadium, and zirconium in UF_6. The limit of detection for the individual elements depends on the sample size; the following limits (expressed as µg/g) are attainable on 10 g of uranium:

Hafnium	1.0
Molybdenum	0.1
Niobium	0.2
Tantalum	0.5
Titanium	0.3
Tungsten	0.5
Vanadium	0.3
Zirconium	0.5

127. Summary of Test Method

127.1 Hafnium, molybdenum, niobium, tantalum, titanium, tungsten, vanadium, and zirconium are separated from hexavalent uranium by extraction as the cupferrides with isoamyl alcohol-chloroform solvent **(3, 31)**. After evaporation of the solvent and ignition of the residue, the residue is dissolved; palladium internal standard solution is added; the sample is sparked by the rotating disk technique; and the spectrum is recorded photographically. Intensity ratios of analytical lines to internal standard lines are determined, and the concentrations are obtained from established curves.

127.2 The above elements are separated completely from uranium (VI) with cupferron, the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N{\cdot}NO{\cdot}ONH_4$.

127.3 The precipitation is carried out in a strong acid solution. Nitric acid solutions cannot be treated, however, because oxidizing agents destroy the reagent **(43)**.

127.4 The reagent is used as an 8 % aqueous solution which should be made up fresh, being unstable for periods longer than a month. Precipitation is always made in the cold, as cupferron is decomposed on heating. Sufficient reagent should be added to form completely the curdy precipitate of the metallic derivative of cupferron and to give a precipitate of white needles of free phenylnitrosohydroxylamine **(44)**. The washing solutions must be cold and should contain a little cupferron. Among the interfering elements are antimony(III), bismuth, cerium, copper, iron(III), thallium(III), thorium, and tin.

127.5 The rotating-disk-electrode system used in the procedure has been found to be the most reproducible method of exciting the sample. The use of spark excitation minimizes interferences from small amounts of uranium that may be carried into the organic phase.

128. Apparatus

128.1 *Refrigerated Bath*.

128.2 *Spectrograph*—A grating spectrograph with a reciprocal linear dispersion of 5 A/mm in the first order and providing wavelength coverage from 2350 to 3200 A.

128.3 *High-Voltage Controlled-Spark Excitation Source*.

128.4 *Rotating Disk Assembly and Drive*.

128.5 *Comparator-Microphotometer*—A comparator providing sufficient magnification and facility to compare spectral line density with a reference standard plate or film, and a microphotometer having a precision of ±1.0 % for transmittance values between 5 and 90 %.

128.6 *TFE-Fluorocarbon Dish*, 0.8-mL capacity, 4 mm deep, to accommodate the rotating disk.

128.7 *Photographic Processing Equipment*, providing developing, fixing, washing, and drying operations and conforming to the requirements of Practices E 115.

128.8 *Electrodes*:

128.8.1 *Lower*—High-purity graphite disk, 12.50 mm in diameter, 3.05 mm thick, with a 3.18-mm hole through the center, Practice E 130, Type D-1.

128.8.2 *Upper*—High-purity graphite rod, 3.05 mm in diameter, Practice E 130, Type C-6.

128.9 *Photographic Plates*, Eastman Kodak Spectrum Analysis No. 1.

129. Reagents

129.1 *Cupferron Solution* (80 g/L)—Dissolve 80 g of cupferron in water and dilute to 1 L.

129.2 *Isoamyl Alcohol-Chloroform Solution* (*7 + 3*)—Mix 7 volumes of isoamyl alcohol and 3 volumes of chloroform. Saturate the mixture with 3 *M* sulfuric acid (H_2SO_4) by shaking in a separatory funnel.

129.3 *Palladium Solution* (0.40 mg Pd/mL)—Dissolve 0.34 g of palladium chloride ($PdCl_2$) in a minimum amount of concentrated hydrochloric acid (HCl, sp gr 1.19) and dilute to 500 mL.

129.4 *Photographic Processing Solutions*—Formulas for processing solutions are given in Practices E 115.

129.5 *Potassium Permanganate Solution* (0.1 *N*)—Prepare a 0.1 *N* solution of potassium permanganate ($KMnO_4$).

130. Procedure

130.1 *Calibration*—Prepare a set of eight standards containing 0 (blank), 1, 2, 5, 10, 20, 50, and 100 µg of each of the group metals by adding measured amounts of fluoride solutions of the metallic oxide reagents to aliquots of high-purity UO_2F_2 solution, each containing 10 g of uranium. Take these standard solutions through the analysis procedure, and make a standard spectral plate. Prepare element calibration curves after measuring the transmittances with the comparator-microphotometer.

130.2 *Sample Preparation Procedure*:

130.2.1 By means of a suitable sampling system, transfer approximately 9 g of liquid UF_6 to each of two tared fluorothene tubes. Cool the tubes in liquid nitrogen, disconnect from the sampling system, and seal with threaded plugs.

130.2.2 Warm the tubes to room temperature and weigh to obtain the gross weight.

130.2.3 Obtain the sample weight from the difference between the gross weight and the tare weight.

130.2.4 Immerse the tubes in liquid nitrogen, remove the flare connections, and place both tubes in 100 mL of cold water in a polyethylene beaker.

130.2.5 After hydrolysis of the UF_6, remove the fluorothene tubes from the beaker and rinse with distilled water. Add the rinse water to the contents of the beaker.

130.2.6 Measure the volume of the solution, calculate the concentration, and transfer the solution to a polyethylene bottle.

130.2.7 Transfer an aliquot of the hydrolyzed UF_6 sample containing 10 g of uranium to a platinum dish.

130.2.8 Add 20 mL of concentrated H_2SO_4(sp gr 1.84).

130.2.9 Place the sample on a hot plate and fume to dryness.

130.2.10 Cool the sample, and add 50 mL of 3 *M* H_2SO_4.

130.2.11 Place the solution on a hot plate and heat to dissolve the residue. While the solution is hot, add a slight excess of $KMnO_4$ solution (two drops after the pink color has developed).

130.2.12 Transfer the solution to a 250-mL separatory funnel, place in a refrigerated bath, and cool to 5°C.

130.2.13 Add 10 mL of 8 % cupferron solution to precipitate the cupferrides; then shake the mixture well.

130.2.14 Add 20 mL of isoamyl alcohol-chloroform mixture to the separatory funnel and shake until most of the precipitate is dissolved (the precipitate will not dissolve completely on the first extraction). Allow 10 min for the phases to separate.

130.2.15 Drain the aqueous phase into another funnel, and repeat the extraction with several 20-mL quantities of isoamyl alcohol-chloroform mixture until all the cupferrides are removed (organic phase becomes colorless). Combine the collected organic phases.

130.2.16 Wash the combined extracts once with a mixture of 20 mL of 1 *M* H_2SO_4 and 2 mL of cupferron solution. Allow 10 min for the phases to separate, and discard the washings.

130.2.17 Transfer the isoamyl alcohol-chloroform extract to a platinum dish and evaporate to dryness. Ignite the residue for 30 min at 500°C.

130.2.18 Dissolve the ignited residue in a mixture of 5 mL of concentrated HCl (sp gr 1.19) and 1 mL of 48 % HF. Add 400 µg of palladium as internal standard, and evaporate the mixture to 0.5 ± 0.2–mL volume for spectrographic analysis.

130.3 *Spectrograph Operation Procedure*:

130.3.1 Place the 3-mm counter electrode in the upper electrode holder of the spectrograph.

130.3.2 Fit a disk electrode onto the platinum mandrel and insert into the rotating disk assembly as the lower electrode.

130.3.3 Adjust the electrodes to give a 3-mm gap, centered about the optical axis of the spectrograph.

130.3.4 Position a TFE-fluorocarbon sample dish (0.8 mL) under the disk electrode, and transfer the sample into it with a plastic pipet.

130.3.5 Position the plate holder containing one photographic plate on the spectrograph, and adjust the spectrograph as follows:

Spectral region, nm	237.5 to 320.0
Slit width, µm	25
Slit length, mm	4
Preburn, s	15
Exposure, s	120

130.3.6 Excite the standards and samples with the spark discharge, using the following parameters:

Capacitance, µF	0.005
Inductance, µH	310
Resistance in series with gap	residual
Primary voltage, V	205
Radio-frequency current, A	5.5
Discharge breaks per half cycle	4

130.4 *Photographic Plate Handling Procedure*—Process the emulsion in accordance with Practices E 115.

NOTE 19—If the sample is known to be of high purity, thus containing very low levels of these specification elements, this procedure may be simplified; at the laboratory's discretion, one may reduce sample size, employ fewer extractions, add bismuth for a bulk gathering agent, and excite with a d-c arc (for more sensitivity) after adding silver fluoride (AgF) or fluorinated graphite as a carrier. The results will be less quantitative, but of a quality adequate for determination of impurities well below Federal Register specification levels.

131. Photometry and Calculation

131.1 Using the comparator-microphotometer, measure the transmittances of the analytical and internal standard lines listed in Table 9 for both the standard samples and the unknown samples.

131.2 Convert the transmittances of the analytical and internal standard lines of the sample to log intensity ratios with the aid of the emulsion calibration charts. Obtain the concentration of the element in micrograms per gram of uranium from the appropriate calibration curve.

132. Reliability

132.1 The precision of a single determination at the 95 % confidence level is ±30 % for the elements of this group, determined at the 2-µg/g level with a 10-g sample.

SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN

133. Scope

133.1 A test method is described for the spectrophotometric determination of tungsten in uranium compounds **(45)**. The test method uses thiocyanate to develop a yellow color with tungsten(V) and can detect 0.5 µg tungsten in a gram of uranium.

TABLE 9 Analytical Line Pairs

Element		Analytical Line, nm	Palladium Internal Standard Line, nm	Concentration Range, µg/g U
Hafnium (Hf)	Hf	282.02	311.40	1 to 10
Molybdenum (Mo)	Mo	267.18	259.33	0.1 to 10
	Mo	281.62	311.40	<0.1 to 3
Niobium (Nb)	Nb	267.36	259.33	0.2 to 10
	Nb	309.42	311.40	<0.1 to 3
Tantalum (Ta)	Ta	268.51	259.33	0.5 to 10
Titanium (Ti)	Ti	253.13	259.33	0.1 to 10
	Ti	308.80	311.40	<0.1 to 3
Tungsten (W)	W	239.71	259.33	0.5 to 10
Vanadium (V)	V	269.02	259.33	0.1 to 10
	V	309.31	311.40	<0.1 to 2
	V	292.46	311.40	<0.1 to 5
	V	292.04	311.40	1 to 30
Zirconium (Zr)	Zr	256.76	259.33	0.5 to 10

134. Summary of Test Method

134.1 This test method is based on the formation and solvent extraction of the yellow complex produced by reaction of thiocyanate and tungsten(V) **(46, 47).** The quantitative formation of tungsten(V) in the presence of uranium requires a strong, high-capacity reductant, since all the uranium must first be reduced at least to a valence of four. Amalgamated bismuth in 9 to 12 *M* HCl is a suitable reductant. After the reduction, the HCl concentration is reduced below 8 *M* to prevent thiocyanate decomposition and kept above 6 *M* to prevent reoxidation of the tungsten. Thus, an acid concentration of 7 to 7.5 *M* HCl is used in developing and extracting the tungsten(V)-thiocyanate complex.

135. Interferences

135.1 Very few elements interfere in the test method **(46).** About 10 µg of niobium or vanadium and about 200 µg of molybdenum are equivalent to 1 µg of tungsten. The effect of molybdenum, a likely contaminant in UF_6, is essentially eliminated in the standard procedure by the addition of H_2SO_4 before reducing the tungsten and by measuring the absorbance of the extracted tungsten and molybdenum thiocyanates at 505 as well as 405 nm. At 505 nm, the molybdenum thiocyanate complex has the same absorbance as at 405 nm, while the tungsten thiocyanate has practically no absorbance. The reading at 505 nm thus can be used to make a correction for the molybdenumthiocyanate contribution at 405 nm. Molybdenum interference can also be reduced by pyrohydrolysis of hydrolyzed UF_6 samples at 900°C. Under these conditions, most of the molybdenum is apparently vaporized with no loss of tungsten.

136. Apparatus

136.1 *Spectrophotomter*, equipped with 1 and 5-cm absorption cells as described in Practice E 60.

137. Reagents

137.1 *Bismuth Metal*, 6 to 20-mesh granules.

137.2 *Bismuth Amalgam* (6.3 %)—Weigh 100 g of bismuth metal in a 250-mL beaker and wash with 7 *M* HCl. Add 0.5 mL of mercury from a buret, and stir until the bismuth is thoroughly covered with mercury. Store it in dilute HCl.

137.3 *Butyl Acetate*, purified.

137.4 *Mercury*, triple-distilled.

137.5 *Potassium Thiocyanate Solution* (30 %)—Dissolve 30 g of KSCN in water, and dilute the solution to 100 mL. Make this reagent fresh daily. If high blanks occur with new reagent, recrystallize the solid from ethyl alcohol and dry in a nitrogen atmosphere.

137.6 *Stannous Chloride Solution* (20 %)—Dissolve 50 g of $SnCl_2 \cdot 2H_2O$ in concentrated hydrochloric acid (HCl, sp gr 1.19), and dilute the solution to 250 mL with concentrated HCl (sp gr 1.19).

137.7 *Tungsten Standard*—Fuse 0.6305 g of WO_3 in a platinum dish with Na_2CO_3. Dissolve the melt with deionized water and dilute to 1 L. Dilute 10 mL of this solution to 1 L with deionized water. This solution contains 5 µg W/mL.

138. Procedure

138.1 Transfer an accurately measured sample aliquot of hydrolyzed $UF_6(UO_2F_2$ solution) containing up to 2.0 g of uranium to a platinum dish.

138.2 Evaporate the solution to dryness.

138.3 Dissolve the residue in 3 *M* HCl, and transfer the solution to a 100-mL beaker with 3 *M* HCl.

138.4 Evaporate the solution to dryness to eliminate most of the fluoride.

138.5 Cool the beaker, and dissolve the residue with 12 mL of concentrated HCl (sp gr 1.19) added with a pipet.

138.6 Add about 0.5 to 1.0 mL of concentrated H_2SO_4(sp gr 1.84), 5 mL of 20 % $SnCl_2$ in HCl, and 3 to 5 mL of bismuth amalgam to the sample.

138.7 Cover the beaker with a watch glass and heat gently for 20 min.

138.8 Cool the beaker in a water bath to room temperature, and dilute the sample to 45 mL with 7 *M* HCl.

NOTE 20—When more than one sample is to be analyzed, the samples should be diluted and carried through the rest of the procedure individually.

138.9 Pipet 5 mL of 30 % KSCN solution into each sample and mix thoroughly.

138.10 After 1 min (± 10 s), pipet 5 mL of 20 % $SnCl_2$ in HCl into the mixture, and transfer the sample to a separatory funnel containing 25.0 mL of butyl acetate.

138.11 Rinse the beaker with 7 *M* HCl into the separatory funnel, and dilute the solution to 75 to 80 mL with 7 *M* HCl.

138.12 Shake the funnel for 1 min to extract the tungsten complex.

138.13 Allow the aqueous layer containing the uranium to separate; then transfer the butyl acetate layer to a 50-mL centrifuge tube and centrifuge for 2 min.

NOTE 21—In the case of samples containing more than 100 µg of copper, iron, or nickel along with the uranium, it is necessary to wash the butyl acetate extract with a solution consisting of 40 mL of 7 *M* HCl, 5 mL of 20 % $SnCl_2$ solution, and 5 mL of 30 % KSCN solution. This solution should be prepared as needed.

138.14 Transfer the butyl acetate extract to a 1 or 5-cm absorption cell, and determine its absorbance at wavelengths of 405 and 505 nm against a reagent blank.

138.15 Subtract the absorbance at 505 nm from the absorbance at 405 nm to correct for any molybdenum present in the sample.

138.16 Determine the quantity of tungsten in the aliquot from the adjusted absorbance at 405 nm, using a calibration curve prepared by analyzing pure uranium solutions spiked with 0, 5, 10, 25, and 50 µg of tungsten by the preceding procedure.

138.17 Calculate the tungsten concentration in the uranium from the quantity of uranium taken in the aliquot.

139. Reliability

139.1 Twenty-five micrograms of tungsten can be determined with a precision of ±5 % at the 95 % confidence level.

SPECTROPHOTOMETRIC DETERMINATION OF THORIUM

140. Scope

140.1 This test method provides a rapid and reliable analysis of thorium in UF_6. Using a sample aliquot containing 0.5 g of uranium, the test method can detect 2 µg Th/g U. This range can easily be extended to a much lower level by use of a larger sample size.

141. Summary of Test Method

141.1 Thorium is separated from uranium by a rapid ion exchange procedure in which the uranium is adsorbed on a strongly basic anion exchange resin from 8 *M* HCl **(48).** The thorium-bearing effluent is treated directly with oxalic acid to complex any zirconium and with Arsenazo III to develop the blue thorium-Arsenazo III complex which has a molar absorptivity of 116 000 in about 5 *M* HCl solution **(49, 50).** The test method is nearly specific for thorium since the potential interferences of uranium, and up to about 200 µg zirconium, are eliminated by the standard procedure. Rare earths at levels about 50 times the thorium also interfere.

141.2 This test method can be adapted to handling a large volume of samples by reducing the sample aliquot to a quantity small enough to contain 0.1 g of uranium. Ten samples can be passed through the ion exchange column before it is necessary to elute the uranium. Under these conditions the limit of detection becomes 10 µg Th/g U, which is adequate for most purposes.

142. Apparatus

142.1 *Ion Exchange Columns*, Fig. 10.

142.2 *Spectrophotometer*, with 1-cm cells as described in Practice E 60.

142.3 *Platinum Dishes*, 100-mL.

143. Reagents

143.1 *Arsenazo III[o-(1,8-dihydroxy-3,6-disulfo- naphthylene - 2,7 - bisazo)-bisbenzenearsonic acid, disodium salt] Solution (0.2 %)*—Dissolve 0.2 g of Arsenazo III in water, add 1 mL of 5 % sodium carbonate (Na_2CO_3) to the solution, and adjust the volume to 100 mL with distilled water.[17]

143.2 *Dowex 1-X8* (50 to 100 mesh), a strongly basic anion exchange resin. Treat new resin with at least 100 mL of 8 *M* HCl before use, and discard the resin after it has been used three times.

143.3 *Oxalic Acid Solution* (5 %)—Dissolve 5 g of $H_2C_2O_4$ in distilled water and dilute to 100 mL.

143.4 *Thorium Standard*—Weigh 0.2393 g of thorium nitrate [$Th(NO_3)_4 \cdot 4H_2O$] into a 250-mL beaker and fume to dryness three times with 5-mL portions of concentrated HCl (sp gr 1.19). Dissolve the residue in 0.1 *M* HCl and dilute to 1 L with 0.1 *M* HCl to give a solution containing 100 µg Th/mL. Dilute an aliquot to the appropriate volume to give a solution containing 5 µg Th/mL.

144. Procedure

144.1 Measure a sample aliquot of hydrolyzed UF_6 containing no more than 0.5 g of uranium and up to 50 µg of thorium by weight or volume into a 100-mL platinum dish.

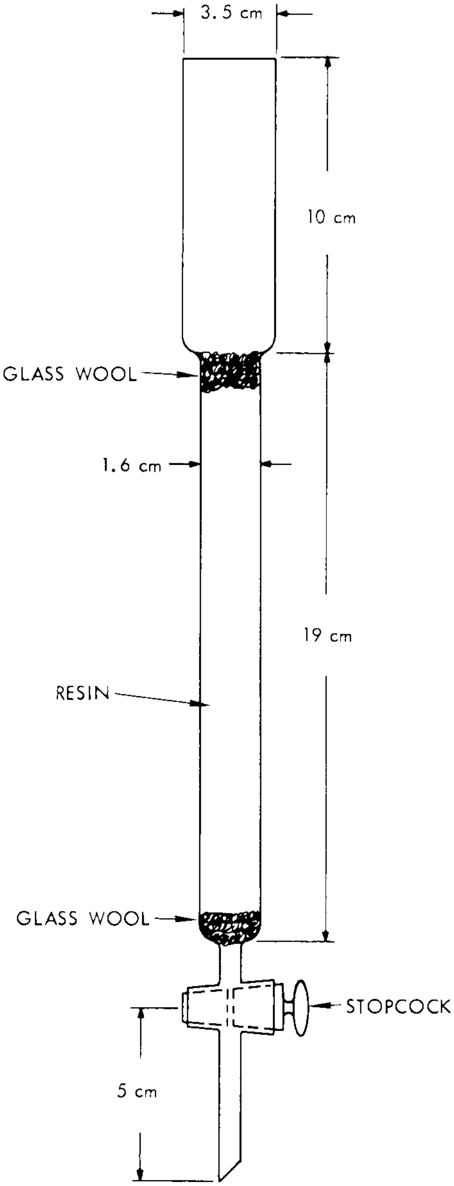


FIG. 10 Adsorption Column

144.2 Fume the solution to dryness four times with 10-mL portions of concentrated HCl (sp gr 1.19) to remove fluoride.

144.3 Dissolve the residue in 2 to 3 mL of concentrated HCl (sp gr 1.19) using heat if necessary.

144.4 Dilute the solution to about 10 mL with 8 *M* HCl and transfer to the ion exchange column.

144.5 Rinse the beaker with a minimum quantity of 8 *M* HCl (about 5 mL), and add the rinse solution to the column.

144.6 Open the stopcock, and drain the column into a suitable graduated cylinder at a rate of 3 to 4 mL/min.

144.7 Discard the first 7 mL of effluent, and collect the remaining effluent in a 50-mL, volumetric flask.

144.8 Wash the resin with two 5-mL and two 10-mL portions of 8 *M* HCl; collect all the effluents in the 50-mL flask.

144.9 Add 1 mL of 5 % $H_2C_2O_4$ to the flask to complex any zirconium.

144.10 Add 2 mL of Arsenazo III solution to the flask, and dilute the solution to volume with distilled water and mix thoroughly.

144.11 Within 30 min, measure the absorbance of the solution in a 1-cm cell at 665 nm against a blank solution containing all reagents.

144.12 Determine the concentration of thorium from a calibration curve prepared previously as in the above procedure. This calibration curve is prepared from solutions having a concentration range from 0 to 100µ g Th/50 mL.

NOTE 22—It is necessary to run the calibration standards through the ion-exchange column.

144.13 Elute the uranium from the exchange column with 200 mL of 0.1 *M* HCl at the rate of 3.0 to 3.5 mL/min. Then, pass 50 mL of 8 *M* HCl through the column to prepare it for the next sample.

NOTE 23—The test method can be adapted to handling a large volume of samples by taking sample aliquots containing 0.1 g of uranium and eluting the uranium from the column after ten sample aliquots have been passed through the column. When the column is used in this manner, it should be washed with an extra 50 mL of 8 *M* HCl between successive samples.

145. Reliability

145.1 The precision at the 95 % confidence level in determining 200µ g Th/g U by the standard procedure is ±5 %.

SPECTROGRAPHIC DETERMINATION OF THORIUM AND RARE EARTHS

146. Scope

146.1 This test method is applicable to the determination of microgram quantities of the rare earth elements and thorium in UF_6. The elements determined by the test method and their limits of detection are listed in Table 10.

147. Summary of Test Method

147.1 The elements listed in Table 10 are separated from the uranium by precipitation as fluorides **(51)**. Calcium and lead are partially precipitated but do not interfere with the method. Due to the gelatinous nature of the rare earth precipitates, this separation is rarely used for large amounts of the elements. However, for trace amounts the test method is excellent, and no difficulty is experienced in the filtration of the precipitate.

147.2 In practice, a small amount of yttrium is added to a solution of hydrolyzed UF_6 to serve as a collector for the trace quantities involved; a large excess of hydrofluoric acid is added, and the solution is allowed to stand for a time sufficient to effect precipitation and coagulation. The precipitate is separated by filtration, and the paper and precipitate are ignited; the residue is placed in a graphic electrode and excited with a direct current arc in a controlled atmosphere chamber **(52)** in a mixture of argon and oxygen. The controlled atmosphere is used to minimize interference from cyanogen bands.

TABLE 10 Limits of Detection for Thorium and Rare Earths

Element	Limit of Detection, ppm^A	Element	Limit of Detection, ppm^A
Ce	0.4	Nd	0.2
Dy	0.2	Pr	0.2
Er	0.2	Sm	0.2
Eu	0.2	Tb	0.2
Gd	0.2	Th	1
Ho	0.2	Tm	0.2
La	0.2	Yb	0.2
Lu	0.2	Y	0.2^B

[A] Limits based on 5-g uranium sample using yttrium gathering agent; if improved sensitivity is desired, a larger sample should be processed.

[B] Limits based on 5-g uranium sample using lanthanum as the gathering agent.

147.3 The spectrum is recorded photographically, and a visual comparison is made with standard spectra to determine element concentration. A more precise estimate may be made by measuring line intensities, using yttrium as an internal standard.

148. Apparatus

148.1 *Spectrograph, Grating*, providing wavelength coverage from 225.0 to 820.0 nm with a reciprocal linear dispersion of 0.5 nm/mm in the first order.

148.2 *Excitation Source*, providing a 11-A d-c arc.

148.3 *Arc Chamber*, controlled atmosphere, shown in Fig. 11.

148.4 *Filter*, plate glass with mount.

148.5 *Comparator-Microphotometer*—A comparator providing sufficient magnification and facility to compare spectral line density with reference standard plate or film, and a microphotometer having a precision of ±1.0 % for transmittance values between 5 and 90 %.

148.6 *Filtering Funnels*, polyethylene plastic.

148.7 *Beakers and Reagent Containers*, polyethylene plastic or platinum.

148.8 *Photographic Processing Equipment* providing developing, fixing, washing, and drying operations and conforming to the requirements of Practices E 115.

148.9 *Photographic Plates*, Eastman Kodak Spectrum Analysis No. 1 or equivalent.

148.10 *Electrodes, Graphite:*

148.10.1 *Lower*—5.15-mm rod with a cup 4.06 mm in diameter and 3.18 mm deep with undercut 1.59 mm wide and 1.39 mm deep located 4.76 mm from the top.

148.10.2 *Upper*—Rod, 3.22 mm in diameter, 101.60 mm long, pointed.

149. Reagents

149.1 *Argon Supply*.

149.2 *Graphite Powder*, highest purity, conducting grade.

149.3 *Hydrofluoric Acid Solutions* (2.5 *M* and 48 %).

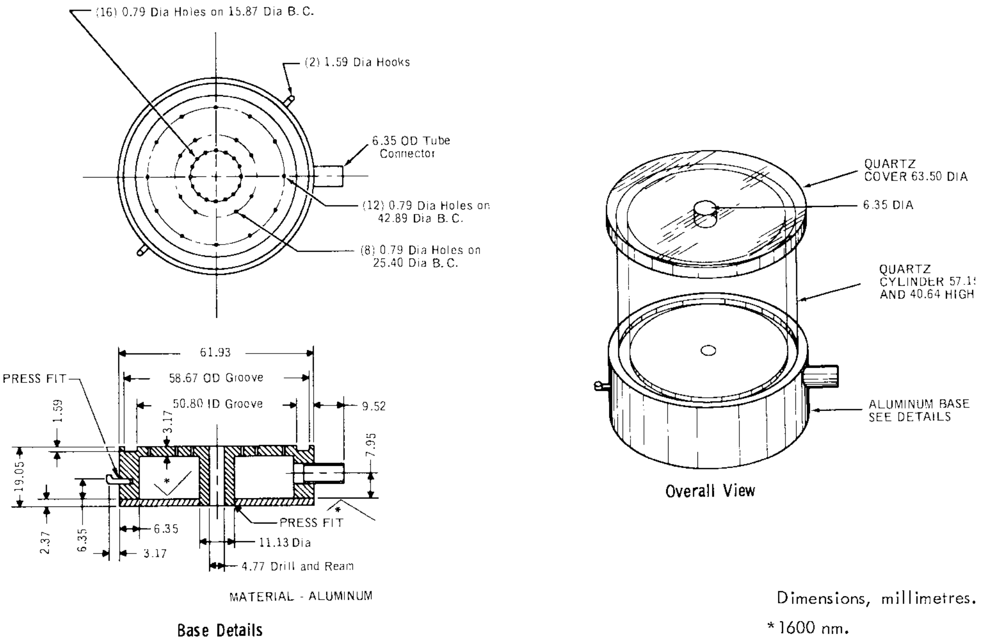
149.4 *Oxygen Supply*.

149.5 *Photographic Processing Solutions*, as prescribed in Practices E 115.

149.6 *Yttrium Solution*—Dissolve 0.6350 g of high-purity yttrium oxide (Y_2O_3) in a minimum volume of HNO_3 and dilute to 100 mL with water. This solution contains 5 mg Y/mL.

150. Procedure

150.1 *Calibration*—Prepare a set of six standards by adding measured amounts of standard solutions of the group metals (generally nitrate solutions of the oxides) to aliquots of UO_2F_2 solution, each containing 5 g of uranium. Take the spiked



Base Details

Overall View

Dimensions, millimetres.

*1600 nm.

FIG. 11 Arc Chamber

TABLE 11 Elements in UF$_6$ and Spark Source Detection Limits

Element	Detection Limit, wt ppm	
	Instrument	Method
Li	0.004	0.4
Na	0.001	1
Mg	0.01	1
Al	0.003	0.5
P	0.02	0.7
K	0.01	2
Ca	0.01	3
Ti	0.03	0.4
V	0.02	0.02
Cr	0.02	0.1
Mn	0.02	0.2
Fe	0.02	2
Co	0.02	0.02
Ni	0.03	0.3
Cu	0.03	0.8
Zn	0.03	0.6
Sr	0.04	0.04
Zr	0.1	0.1
Nb	0.05	0.05
Mo	0.3	0.3
Sn	0.2	0.2
Sb	0.1	0.1
Ba	0.05	0.05
Sm	0.3	0.3
Gd	0.5	0.5
Dy	0.3	0.3
Ta	0.1	0.3
W	0.4	0.4
Pb	0.1	0.2
Bi	0.1	0.1
Th	1	1

standards through the analysis procedure for separating these elements from uranium. Make standard spectral plates with the residues. Prepare standards which contain 0 (blank), 0.5, 1, 2, 5, and 10 µg/g for each element.

150.2 *Analysis*:

150.2.1 *Sample Preparation Procedure*:

150.2.1.1 Prepare the sample as described in the hydrolysis procedure, 17.7 to 17.17.

150.2.1.2 From the hydrolyzed UF$_6$ sample, take duplicate portions each containing 5 g of uranium and transfer to platinum dishes. Add 10 mL of concentrated HNO$_3$(sp gr 1.42) to each portion and boil. (Prepare duplicate samples since two spectrographic settings are required for the determination of the entire group of elements. Perform the following preparation steps on both samples.) Table 11

150.2.1.3 Evaporate the uranium solution to near dryness on a hot plate.

150.2.1.4 Dissolve the uranium residue in 180 mL of distilled water and transfer to a plastic or platinum container; then add 20 mL of 48 % HF.

150.2.1.5 Add 2 mL of yttrium solution to the sample, mix well, and allow to stand for 2 h or longer.

150.2.1.6 Filter the solution through a close–textured, double–acid–washed filter paper[16] using a plastic filter funnel.

150.2.1.7 Wash the precipitate with 100 mL of 2.5 *M* HF.

150.2.1.8 Allow the rinse solution to drain. Transfer the filter paper and precipitate to a clean 30-mL platinum crucible. Ignite the contents of the crucible at 1000°C in a muffle furnace until the carbon is removed.

150.2.1.9 Transfer the residue to a 5.15-mm undercut electrode, and add 5 mg of graphite powder.

150.2.2 *Spectrograph Operation Procedure*:

150.2.2.1 Position the plate holder containing two photographic plates on the spectrograph, and make adjustments as follows:

Slit height, mm	3
Slit width, µm	30
Timer	on and set for 120 s
Wavelength range, nm	225.0 to 350.0
Excitation	current regulator set at 11 A dc
Step filter	medium step

150.2.2.2 Wipe off the electrode clamps, and place the controlled-atmosphere chamber on the lower electrode holder.

150.2.2.3 Insert the electrodes, adjust the gap distance to 4 mm, and position the cover on the chamber.

150.2.2.4 Meter the argon and oxygen to give a 12-standard ft^3/h flow of a 70 % argon-30 % oxygen mixture.

150.2.2.5 Turn the d-c arc on; adjust the source to 11 A and excite for 120 s.

150.2.2.6 Maintain the 4-mm gap distance throughout the exposure by adjusting the electrodes as necessary.

150.2.2.7 At the completion of the exposure, remove the electrodes and discard.

150.2.2.8 Repeat the exposure cycle for the duplicate sample, using the same conditions as above, with the following changes:

Condensing lens	none
Filter	glass
Wavelength range, nm	312.5 to 437.5

150.2.3 *Photographic Processing*—Process the emulsion in accordance with Practices E 115.

151. Photometry and Calculation

151.1 Using the comparator-microphotometer, visually compare the density of the lines with those on a standard plate to determine the concentration of elements sought in the sample.

151.2 For a more precise value, when an element concentration is measurable, measure the transmittance of the analytical line and of the internal standard. Convert the value to direct intensity, calculate the ratio, and obtain the concentration of the element from a calibration curve which relates intensity ratio to concentration.

151.3 The lines listed in Table 12 are suggested for use in the identification and estimation of the rare earth elements.

152. Reliability

152.1 The 95 % confidence limits of a single visual measurement are + 100 % and − 50 % of the value, at concentrations just above the limit of detection. The visual estimation follows the logarithmic distribution rather than the normal.

TABLE 12 Suggested Lines for Use in the Identification and Estimation of the Rare Earth Elements

Element	Wavelength, nm				
Ce	418.66	429.66	...	...	...
Dy	317.00	338.50	339.36	340.78	...
Er	323.06	326.48	...	...	...
Eu	266.83	272.78	290.67	292.50	...
Gd	310.05	335.05	335.86	342.25	...
Ho	339.90	345.60	...	...	...
La	324.51	333.75	338.09	...	...
Lu	261.54	289.48	290.03	291.14	307.76
Nd	430.35	...	...	...	...
Pr	422.30	422.53	...	...	...
Sm	327.35	425.64	426.27	427.97	428.08
Tb	322.00	329.31	332.44	...	...
Th	285.13	289.97	308.85	310.83	311.95
	318.02	323.59	323.81	326.27	329.17
	329.25	...	...	...	...
Tm	313.13	313.39	315.10	315.73	336.26
Yb	289.14	328.94	...	...	...
Y(Internal Standard)	318.24	320.03	320.33	321.67	324.23
	332.79	340.99	...	...	...

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM

153. Scope

153.1 The thiocyanate spectrophotometric test method for analyzing molybdenum **(53, 54)** employs the molybdenum(V)-thiocyanate complex which is first fully developed and then extracted with an organic solvent. The method presented is capable of detecting 0.2 µg molybdenum in a sample containing 1 g of uranium.

154. Summary of Test Method

154.1 This test method is based on the formation and solvent extraction of the amber-colored complex produced when thiocyanate and molybdenum(V) react in a dilute H_2SO_4 solution. The color of the extract is measured spectrophotometrically at 470 nm, and the quantity of molybdenum present is determined from a calibration curve.

154.2 Stable complex formation and complete color development depend upon the efficient reduction of molybdenum(VI) to molybdenum(V) and the subsequent stabilization of the pentavalent state of the molybdenum **(47).**

154.3 Stannous ion is commonly used for reduction of molybdenum(VI) to molybdenum(V); however, large excesses of stannous ion will cause the color of the molybdenum(V)-thiocyanate complex to fade, probably by reducing part of the molybdenum to lower valence states. Crouthamel and Johnson **(47)** found that cuprous ion produced a stable solution of molybdenum(V) ion, which in turn gave a rapid and complete color development with thiocyanate. On the basis of this work, a small amount of cuprous ion (50 µg Cu(I)/mL) was added to the stannous chloride reducing solution. This addition made color development of the molybdenum-thiocyanate complex in uranium sulfate solutions more rapid and stable **(55).** Within a wide range of H_2SO_4 concentrations (1.8 to 7.2 *N*), there is no effect on the formation of the complex, the stability of color, or the extraction of the complex. Concentration of the cuprous ion must be controlled because cuprous thiocyanate is relatively insoluble. The molar absorptivity of the molybdenum thiocyanate complex obtained with the following procedure is about 19 600 L/mol cm, a value which approximates the maximum values reported in the literature **(47, 53).**

154.4 This procedure is very specific when the molybdenum-thiocyanate complex is extracted. Uranium gives no interference even in 1-g quantities. Niobium, tantalum, titanium, tungsten, and vanadium at 200µ g each give no interference. There are no likely interferences in relatively pure UF_6. Technetium(VI) can interfere in irradiated UF_6, but its interference can be eliminated by evaporating the hydrolyzed UF_6 to dryness in the presence of a strong oxidant.

155. Apparatus

155.1 *Platinum Dish*, 200 or 300 mL.

155.2 *Spectrophotometer*, equipped with 1-cm and 5-cm cells as described in Practice E 60.

156. Reagents

156.1 *n-Butyl Acetate*, purified.

156.2 *Molybdenum, Standard Solution*—Dissolve 0.1840 g of ammonium molybdate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$ in 50 mL of

10 % H_2SO_4, and dilute the solution to volume in a 1-L volumetric flask with distilled water. Dilute 20 mL of this solution to volume in a 1-L volumetric flask to obtain a solution containing 2 µg molybdenum per millilitre.

156.3 *Potassium Thiocyanate* (20 % w/v)—Dissolve 200 g of KSCN in water and dilute to 1 L with water.

156.4 *Stannous Chloride—Cuprous Chloride Solution*—Dissolve 100 g of $SnCl_2{\cdot}2H_2O$ and 0.039 g of Cu_2Cl_2 in 250 mL of concentrated HCl (sp gr 1.19) and dilute to 500 mL with water. After mixing, add 1 g of tin shot to the solution. Keep the solution in a well-stoppered container. (Do not use this solution if the tin metal is completely dissolved.)

157. Procedure

157.1 Hydrolyze a weighed portion of UF_6(6 to 10 g) with about 100 mL of water in a 200-mL platinum dish.

157.2 Evaporate the solution to dryness under a heat lamp. If technetium is suspected to be present, add 5 mL of concentrated H_2SO_4(sp gr 1.84) to the solution before evaporating.

157.3 Dissolve the UO_2F_2 residue with 5 mL of H_2SO_4; and transfer the solution to a 100-mL volumetric flask, then dilute to volume with water.

157.4 Pipet an aliquot containing up to 40 µg of molybdenum from the 100-mL flask into a 125-mL separatory funnel.

157.5 Add 10 mL of 50 % H_2SO_4 to the aliquot. Dilute the solution in the funnel to about 50 mL.

157.6 Add 2 mL of $SnCl_2$-Cu_2Cl_2 solution to the funnel, stopper, and shake for a few seconds.

157.7 Add 2 mL of 20 % KSCN solution to the funnel, stopper, and shake for a few seconds.

157.8 Pipet 25 mL of butyl acetate into the funnel, stopper, and shake for 1 min. Allow the layers to separate, and drain the aqueous layer.

NOTE 24—If an emulsion forms, add several drops of 50 % H_2SO_4, and shake the solution again.

157.9 Add 50 mL of 10 % H_2SO_4, 2 mL of KSCN solution, and 2 mL of $SnCl_2$–Cu_2Cl_2 solution to the separatory funnel, and shake again for 1 min.

157.10 Allow the layers to separate, and discard the bottom layer, allowing a few mililitres of butyl acetate to pass through.

157.11 Drain the remainder of the butyl acetate layer into a 50-mL centrifuge tube and centrifuge for 1 min.

157.12 Read the absorbances of the butyl acetate solutions in 1 or 5-cm cells (depending on intensity of the color) with the spectrophotometer at 470 nm, using pure *n*-butyl acetate in the reference cell.

157.13 Calculate the molybdenum content from a previously prepared calibration curve prepared with standards analyzed as follows:

157.13.1 Prepare standard aliquots containing 1.0-g portions of molybdenum-free uranium and 0, 10, 20, 30, 40, and 50 µg of molybdenum, respectively. Follow the extraction procedure outlined above.

157.13.2 Plot a graph of absorbance versus micrograms molybdenum in 25 mL of butyl acetate.

158. Reliability

158.1 The precision of analyzing molybdenum at the 5-µg level is± 5 % at the 95 % confidence level.

ATOMIC ABSORPTION DETERMINATION OF METALLIC IMPURITIES

159. Scope

159.1 A test method is presented for the analysis of 14 metallic elements in uranium compounds by atomic absorption spectroscopy **(56, 57).** The test method has been shown to be applicable to the analysis of aluminum, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, potassium, sodium, and zinc.

160. Summary of Test Method

160.1 The uranium in a sample is separated by solvent extraction with tributylphosphate (TBP) from 6 to 8 *N* HNO_3**(58).** The HNO_3 solution containing the elements to be determined is evaporated to dryness and the residue redissolved in 0.2 *N* HCl. Any or all of the elements can then be determined in this one solution by standard atomic-absorption spectrometry procedures with little or no matrix effects in the usual type of sample.

160.2 Direct atomic-absorption analysis of several elements in uranium solutions is sometimes satisfactory **(59, 60)** but it has several disadvantages: (*1*) uranium concentration of the solutions must be known and controlled because the uranium absorbs some radiation and contributes to density and viscosity changes in the solution; (*2*) uranium suppresses the absorption of several elements; and (*3*) direct aspiration of uranium solutions presents radioactive contamination problems.

160.3 The uranium is extracted with pure TBP from 6 *N* HNO_3. The aqueous layer is then washed with 20 % TBP in chloroform. A total of 99.9 % of the uranium is removed, leaving a nearly residue-free solution when the HNO_3 solution is evaporated to dryness. Since all atomic absorption analyses are then made in exactly the same medium, that is, 0.2 *N* HCl solution, standards preparation is simplified, and conditions for maximum precision and accuracy are ideal.

160.4 In relatively pure UF_6 that is usually analyzed by this test method, there is usually no problem with anionic interference. Fluoride can interfere with the extraction, but it is easily removed before the extraction by pyrohydrolysis or by fuming the sample with HNO_3. Sulfate and phosphate are possible interferences in the extraction, but they are rarely present in significant quantities.

160.5 Where more than one element is to be analyzed, the atomic absorption procedure requires substantially less labor per analysis than spectrophotometric methods. Furthermore, for some elements such as magnesium, potassium, and sodium, no satisfactory spectrophotometric methods are available. Compared to the carrier distillation spectrographic method, the atomic absorption procedure, though longer, provides better sensitivity and range, and much better precision and accuracy.

161. Apparatus

161.1 *Atomic Absorption Spectrophotometer*, as described in Proposed Recommended Practices for Atomic Absorption Spectrometry.[4]

162. Reagents

162.1 *Carbon Tetrachloride, Reagent Grade*—Wash 1 L of

CCl_4 with 100 mL of 0.1 N HNO_3 and then with 100 mL of deionized water.

NOTE 25—**Caution:** Carbon tetrachloride must be handled with due safety precautions. It should be handled in a hood to avoid breathing its vapor.

162.2 *Hexane, Reagent Grade*—Wash 1 L of C_6H_{14} with 100 mL of 0.1 N HNO_3 and then with 100 mL of deionized water.

162.3 *Hydrochloric Acid, Purified*—Distill and determine the normality as for HNO_3.

162.4 *Hydrochloric Acid* (0.2 N)—Prepare by appropriate dilution of purified HCl with deionized water.

162.5 *Lanthanum Chloride* (*$LaCl_3$*), *Purified* (50 mg/mL)—Transfer 200 mL of saturated lanthanum nitrate [$La(NO_3)_3$], 400 mL of 2.0 N aluminum nitrate [$Al(NO_3)_3$], and 300 mL of purified TBP to a 1-L separatory funnel. Shake the solution vigorously for 2 min to extract lanthanum. Discard the aqueous layer, and wash the TBP phase twice with 100 mL of deionized water. Discard these washings. Transfer the TBP phase to a 1-L beaker. Add about 500 mL of calcium-free acetone or ethanol and 50 mL of water. Distill NH_4OH into this solution until precipitation of lanthanum hydroxide [$La(OH_3)_3$] is complete. Filter the precipitate and wash with deionized water. Ignite the precipitate at 800°C to form lanthanum oxide (La_2O_3). Dissolve the La_2O_3(58.64 g) in purified HCl, and dilute to 1 L with deionized water.

162.6 *Nitric Acid* (*HNO_3*), *Purified*—Distill approximately 1700 mL of concentrated HNO_3(sp gr 1.42) into a 2-L plastic bottle containing 400 mL of deionized water. A quartz still is preferable for the distillation, but if one is not available, borosilicate glassware is satisfactory. Determine the specific gravity of the distilled HNO_3, and calculate the normality.

162.7 *Nitric Acid* (6.0 N)—Prepare by appropriate dilution of purified HNO_3 with deionized water.

162.8 *Standard Stock Solution, 100 µg/mL of Each Element*—Prepare a stock solution containing all elements to be determined by dissolving 0.100 g ± 0.1 mg each of the pure metals in purified HNO_3 or HCl. Convert the nitrate solutions to chloride when feasible by digestion with HCl. Add lead as the nitrate. Dilute the stock solution to 1 L with 0.2 N HCl. After a preliminary analysis has been made on an unknown sample to determine the approximate concentration of impurities, dilute aliquots of the stock solution to give concentrations that bracket the sample.

162.9 *n-Tributylphosphate (TBP), Purified*—Wash 500 mL of purified TBP with at least four 500-mL portions of deionized water to remove sodium and orthophosphate.

NOTE 26—For determining low concentrations of sodium (for example, <5 µg/g U), special purification steps such as vacuum distillation in a quartz system may be required.

162.10 *Urano-Uranic Oxide* (U_3O_8)—Hydrolyze redistilled UF_6 in deionized water to form uranyl fluoride (UO_2F_2). Evaporate the solution to dryness in a plantinum dish and pyrohydrolyze the residue at 900°C for 6 to 8 h with occasional mixing to form U_3O_8.

163. Procedure

163.1 Hydrolyze enough UF_6 to contain the desired amount of uranium (5 to 20 g) with deionized water.

163.2 Evaporate the solution to dryness under heat lamps, and convert the UO_2F_2 to U_3O_8 by pyrohydrolysis at 900°C for 45 min. (U_3O_8 produced in the gravimetric analysis of uranium in UF_6 is suitable.)

NOTE 27—If elements that form volatile fluorides are to be analyzed by atomic absorption, the UO_2F_2 solution should be digested with HNO_3 several times to remove fluoride and obtain a suitable $UO_2(NO_3)_2$ solution for the extraction.

163.3 Weigh enough U_3O_8 to give the desired weight of uranium (to the nearest milligram) into a platinum dish or a TFE-fluorocarbon beaker.

163.4 Dissolve the sample in purified concentrated HNO_3(sp gr 1.42, 1 mL acid per gram of oxide), and evaporate the solution to near dryness.

NOTE 28—When uranium fluorides containing chromium are pyrohydrolyzed, a nitric acid-insoluble compound, probably $CrUO_4$, is formed. Consequently, samples to be analyzed for chromium must be fumed with perchloric acid ($HClO_4$) *after* dissolution with HNO_3 to dissolve this uranium-chromium compound. Add a few drops of 30 % hydrogen peroxide (H_2O_2) to reduce chromium (VI) to chromium (III) before extraction of the uranium.

163.5 Dissolve the residue in 6 N HNO_3, and dilute the solution to 100 mL with 6 N HNO_3.

NOTE 29—Blanks containing all reagents *must* be run through the entire procedure.

163.6 Transfer the sample solution containing up to 10 g of uranium to a 250-mL separatory funnel, using 6 N HNO_3 to rinse the beakers. Use a 500-mL separatory funnel for samples containing 10 to 20 g of uranium. (Plastic separatory funnels are preferred.)

163.7 Add 50 mL of purified TBP to the separatory funnel for each 4 g of uranium.

163.8 Shake the separatory funnel vigorously for 2 min to extract the uranium.

163.9 Allow the phases to separate completely (this requires about 15 min).

NOTE 30—When the extracted sample contains 15 to 20 g uranium, the density of the TBP phase is greater than the density of the aqueous phase. Add 50 mL hexane *after the extraction* to reduce the density of the TBP phase. (If the hexane were added before the extraction, the resulting TBP-hexane mixture would have a lower extraction efficiency.)

163.10 Transfer the aqueous phase to a second separatory funnel. Wash the TBP phase with two 30-mL portions of 6 N HNO_3, and add the washings to the second separatory funnel.

163.11 Wash the aqueous phase with 50 mL of 20 % TBP in CCl_4. After separation, drain off the organic phase.

163.12 Wash the aqueous phase twice with 25-mL portions of CCl_4.

163.13 Transfer the aqueous phase to a TFE-fluorocarbon beaker or platinum dish, and evaporate the solution to dryness.

163.14 Dissolve the residue in 0.2 N HCl and dilute to a desired volume according to the following tabulation:

Impurity, µg/g U	Wt of Uranium, g	Volume, mL
0.1–0.5	20	10
0.5–1	20	25
1–5	10	25
5–50	10	50–100

>50	5	100

163.15 Determine the desired elements by standard atomic absorption techniques, comparing the sample measurements to those of known standards in the same concentration ranges.

NOTE 31—Samples to be analyzed for calcium or magnesium require the addition of lanthanum or strontium to eliminate suppression. Pipet an aliquot of the sample into a volumetric flask, and add sufficient lanthanum or strontium chloride to give 10 mg of lanthanum or strontium per millilitre. Dilute the solution to volume with 0.2 *N* HCl and analyze by comparison to known standards also containing lanthanum or strontium.

163.16 Table 13 gives the operating parameters for the atomic-absorption analysis of the elements, using an atomic-absorption spectrometer equipped with a Boling burner for all elements except aluminum, which must be analyzed with the nitrous oxide burner. Adjust the burner settings for a maximum absorption with copper and leave at those settings for the rest of the analyses.

164. Reliability

164.1 At the 1 to 10 µg/g U level, all the elements except aluminum can be determined with a precision of ±10 % at the 95 % confidence interval. The precision for the aluminum analysis is ±30 % at the 95 % confidence interval.

IMPURITY DETERMINATION BY SPARK SOURCE MASS SPECTROGRAPHY

165. Scope

165.1 This test method covers the spark-source mass-spectrographic analysis of UF_6 for the 31 elements listed in Table 8 with their detection limits. *Instrument* limits can be attained if the blank corrections are zero. *Method* limits include observed blank corrections. Several other elements probably can be determined. Elements not determinable include boron, silicon, ruthenium, and cadmium.

166. Summary of Test Method

166.1 A sample of the UF_6 is hydrolyzed, an internal standard and H_2SO_4 are added, and the sample is converted to U_3O_8. The U_3O_8 is compacted with silver and sparked in a mass spectrograph. The optical densities of the standard and impurity spectral lines on a photographic plate are measured, and the concentrations of the impurities are calculated.

TABLE 13 Operating Parameters for the Atomic-Absorption Analysis of the Elements

Element	Concentration Range, µ g/mL	Wavelength, nm	Recommended Flows	
			Fuel	Air
Al	10–200	309.27	>15[A]	8 (N_2O)
Ca	0–20	422.67	≈9[A]	7.5
Cd	0.5–5	228.80	9	9
Co	4–20	240.73	9	9
Cr	2–20	357.87	≈9[A]	7.5
Cu	2–20	324.75	9	9
Fe	2–20	248.33	9	9
K	1–10	766.48	9	9
Mg	0–2	285.21	≈9	7.5
Mn	2–20	279.48	9	9
Na	0.3–3	589.00	9	9
Ni	2–25	232.00	9	9
Pb	0–40	217.00	9	9
Zn	0–5	213.86	9	9

[A] Fuel adjusted to maximum percentage of absorption.

167. Apparatus

167.1 *Spark-Source Mass Spectrograph* [18], if the ion-source exit slit is 0.127 mm (0.005 in.). The ion source plates are tantalum except for the No. 2 plate (first grounded plate) which is silver. The electrode holders are silver with spring loaded clamps.

167.2 *Photographic Plates.* [19]

167.3 *Photographic Processing Equipment*, providing developing, fixing, washing, and drying operations and conforming to the requirements of Practices E 115.

167.4 *Microphotometer*.

167.5 *Muffle Furnace*.

167.6 *Plastic Vial*, 12.7 mm in diameter by 25.4 mm long.

167.7 *Plastic Ball*, 9.5 mm in diameter.

167.8 *Shaker.* [20]

167.9 *Polyethylene Slug,* [21] 11.1–mm diameter by 15.9 mm long. Drill two parallel holes, 2.4 mm diameter by 9.5 mm deep, diametrically in the slugs. Clean the drilled slugs in 4 *M* HNO_3, rinse in deionized water, and dry.

167.10 *Molding Die.* [22]

167.11 *Laboratory Press,* [23] 11 000-kg.

167.12 *Polytetrafluoroethylene (PTFE) Tape*, 0.075 mm thick by 12.7 mm wide.

167.13 *Platinum-Tip Forceps*.

167.14 *V-Shaped Platinum Pan*—Bend a platinum sheet, 0.012 mm thick, 25.4 mm wide, and 50.8 mm long, 90° at midlength.

167.15 *Platinum Rod*, 3.2 mm diameter by 50.8 mm long.

167.16 *Platinum Dishes*, 20 mL.

168. Reagents

168.1 *Hydrolyzed High-Purity UF_6 Solution* (1 g = known uranium weight of approximately 0.1 g).

168.2 *Impurity-Element, Standard Solutions* (1 mL = 20 µg)—Prepare the solutions from the elements, or from oxides, fluorides, sulfates, or nitrates of the elements using HF, H_2SO_4, or HNO_3 as necessary.

168.3 *Photographic Processing Solutions*—The processing solutions shall be as given in Practices E 115.

168.4 *Silver Powder* (99.999 % purity and 100-mesh).

168.5 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

168.6 *Yttrium, Standard Solution* (1 mL = 20 µg)—Dissolve 0.254 g of Y_2O_3 in 1 *M* HNO_3 and dilute to 100 mL. Dilute 1 mL of this solution to 100 mL.

169. Sample Preparation

169.1 Hydrolyze a weighed sampled of 5 to 10 g of UF_6, sampled in accordance with 10.1.1 to 10.2.11, and dilute to a known uranium concentration of approximately 0.1 g/g of solution.

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[18] Associated Electrical Industries Model MS 702 has been found satisfactory.

[19] Ilford Q2 photographic plates have been found satisfactory.

[20] Spex Industries mechanical mixer has been found satisfactory.

[21] Associated Electrical Industries slugs have been found satisfactory.

[22] Associated Electrical Industries Molding Die has been found satisfactory.

[23] Carver Laboratory Press has been found satisfactory.

169.2 Place an aliquot of the solution containing 0.5 g of uranium in a 20-mL platinum dish.

169.3 Add 0.25 mL of yttrium solution for 10 ppm of yttrium on a uranium basis.

169.4 Add 0.25 mL of H_2SO_4.

169.5 Evaporate the solution and ignite the residue at 850°C for 10 min.

169.6 Break up the solid with a platinum rod and transfer it to a plastic vial.

169.7 Add 0.5 g of silver powder and a plastic ball.

169.8 Cap the vial and shake it on a shaker for 3 min.

169.9 Using a V-shape platinum pan for containing and directing the powder mixture, pour it into the two holes in a polyethylene slug until the holes are approximately half full.

169.10 Cover the holes with PTFE tape, and insert the slug into a molding die.

169.11 Place the die in a laboratory press and apply 11 000 kg of force for 30 s.

169.12 Discard the pressed material, fill the holes with the powder mixture, and repeat 169.10 and 169.11, forming sample electrodes.

170. Procedure

170.1 *Sparking the Sample*:

170.1.1 Install the sample electrodes in the mass spectrograph using platinum-tip forceps for handling the electrodes.

170.1.2 When the source and analyzer pressures are 1×10^{-6} torr and 2×10^{-8} torr, respectively, prespark the electrodes with 30 kV for 3 min, at a pulse rate of 300 pulses/s and a pulse length of 200 µs.

170.1.3 Set the accelerating voltage and magnet current for a mass range from 7 to 240.

170.1.4 Obtain 14 graded exposures on a photographic plate from 1×10^{-3} nanocoulombs (nC) to 100 nC at alternate intervals of 3 and 3.33 times the preceding exposure, plus intermediate exposures of 5.5 and 17 nC, and a final exposure of 200 nC. Begin with a pulse rate of 10 pulses/s and a pulse length of 25 µs, and increase them between exposures as necessary to maintain a 20 to 50 % scale reading on the ion-current monitor.

170.2 *Photographic Processing*—Process the photographic plate in accordance with Practices E 115.

170.3 *Relative-Sensitivity-Factor Determination*:

170.3.1 Using a solution of hydrolyzed high-purity UF_6, prepare four samples, beginning with 169.2, adding 0.25 mL of each standard impurity-element solution to each sample for 10 ppm of the element on an uranium basis, and proceeding as for an unknown sample.

170.3.2 Calculate the relative sensitivity factor for each element in accordance with 172.1, except substituting 10 ppm for C_i in the equation in 172.3, assuming $B_i = 0$, and solving the equation for F_i. Average the results for each element.

170.4 *Blank-Correction Determination*—Analyze four samples of a solution of hydrolyzed high-purity UF_6, beginning with 169.2. Average the results for each element.

170.5 *Multiple-Charge-Factor Determination*:

170.5.1 Measure the optical densities of the single- and applicable multiple-charge lines of the pertinent element, selecting exposures which give optical densities of less than 0.3.

170.5.2 Calculate the multiple-charge factor in accordance with 172.4.

171. Photometry

171.1 Measure the optical densities of the yttrium line at m/e 89 for exposures giving optical densities from 0.01 to 0.5.

171.2 Measure the optical densities of a line of each impurity element. Use the single-charge, most abundant isotope line, if it is free of interfering lines; if not, use a less abundant isotope, or a multiple-charge line. Select an exposure which gives an optical density of less than 0.3, so as to be within the linear portion of the calibration curve as obtained in 172.1.

172. Calculations

172.1 Plot optical density versus exposure for the yttrium line on 2-cycle by 2-cycle logarithmic graph paper. From visual estimation, draw the best-fit straight line through the points below approximately 0.3 optical density, forming a calibration curve.

172.2 From the calibration curve, obtain the yttrium exposures (E_y) corresponding to the optical densities of the impurity lines.

172.3 Calculate the concentrations of the impurities as follows:

$$C_i = (0.11\, E_y W_i / E_i A_i F_i M_i) - B_i \tag{26}$$

where:

i = impurity,
y = yttrium,
C = concentration, wt ppm (U basis),
E = exposure, nC,
A = isotopic fraction,
F = relative sensitivity factor,
M = multiple-charge factor,
W = atomic weight,
B = blank correction, wt ppm, and
0.11 = $(C_y/W_y) = (10/89)$.

172.4 Calculate multiple-charge factors as follows:

$$M_i = E_s D_m / E_m D_s \tag{27}$$

where:

M_i = multiple-charge factor,
E_s = exposure for single-charge line,
E_m = exposure for multiple-charge line,
D_s = optical density of single-charge line, and
D_m = optical density of multiple-charge line.

173. Reliability

173.1 The relative standard deviation ranges between ± 12 and ± 60 %, depending on the element and the concentration, with an average of ±33 % at 10 ppm.

DETERMINATION OF BORON-EQUIVALENT NEUTRON CROSS SECTION

174. Scope

174.1 This test method is applicable to the calculation of the thermal neutron absorption of specified impurity elements as equivalent parts of boron per million parts of uranium. As described, the test method is applicable to relatively pure uranium and its compounds.

175. Summary of Test Method

175.1 The boron-equivalent cross section is found by totaling the slow-neutron absorption cross sections of selected impurity elements, computed from their spectrographic or chemical analyses, or both, and the relation of each element's cross section to that of boron.

176. Procedure

176.1 Multiply the concentration of each impurity element by its EBC factor, as shown in Table 2, Specification C 753, which converts the weight concentration to its boron equivalent.

176.2 The sum of these values should not exceed the boron-equivalent limit stated in the specifications.

177. Reliability

177.1 A precision of ±30 % at the 95 % confidence interval for a single determination was established from the analysis of four samples by each of four laboratories participating in the *Umpire Certification Program* **(61).**

DETERMINATION OF URANIUM-233 ABUNDANCE BY THERMAL IONIZATION MASS SPECTROMETRY

178. Scope

178.1 This test method is applicable to the determination of the absolute isotopic abundance of^{233}U in UF_6. Abundances as low as 1 ppm are determined when the^{235}U abundance is less than 5 %.

179. Summary of Test Method

179.1 The UF_6 sample is hydrolyzed, and the solution is evaporated on filaments which are then installed in a thermal-ionization mass spectrometer. The filaments are heated, ionizing the uranium. The U^+ ions are accelerated through a magnetic analyzer, resolving the isotopes. The spectrum is scanned, the ion currents are amplified and recorded, and the ^{233}U abundance is calculated from the peak heights.

180. Apparatus

180.1 *Mass Spectrometer*—Use a 304-mm radius, magnetic scanning instrument with 5 to 10-kV ion acceleration potential. The ion detection and measuring system should include an electrometer (or combination electron multiplier-electrometer) capable of measuring ion currents of 1×10^{-17} A to 3×10^{-11} A, and a strip-chart recorder.

180.1.1 The triple-filament ion source includes a rhenium ionizing filament and two tungsten or rhenium sample filaments, each 0.03 mm thick and 1 mm wide. Tungsten is not suitable for the ionizing filament because a potassium impurity produces ions at *m/e* 234 and 236. Tungsten is preferred for the sample filaments, however, because it better resists corrosion by hot nitrate solutions, the potassium impurity not being evident at the relatively low sample-filament temperature.

180.1.2 The vacuum system should maintain ion source and analyzer pressures of 3×10^{-7} torr and 3×10^{-8} torr, respectively, during an analysis. Although not required, a vacuum-lock filament changer and ion source cold finger enable more rapid attainment of operating vacuum following a sample change.

180.1.3 The resolving power, mass divided by peak width in mass units at 5 % peak height, should be greater than 350 at mass 238.

180.1.4 The abundance sensitivity, ratio of the peak height of a major peak at mass *M* to the background at *M*-1, should be greater than 40 000 at mass 238.

180.2 *UF_6 Subsampling System*—Vacuum system, 10-µm, with provision for attaching and isolating 6-mm diameter polyethylene tubing.

180.3 *Filament Drying Unit*—Power supply, 110 V ac, 5 A, with variable transformer, current meter, and connector for filament.

181. Sample Preparation

181.1 Attach one end of a 102 mm long, 6 mm diameter polyethylene tube to the UF_6 subsampling system and the other end to a sample cylinder of the UF_6 to be analyzed.

181.2 Evacuate the polyethylene tube and valve off the vacuum system.

181.3 Cover the middle 26 to 39 mm of the tube with crushed dry ice. Open the sample cylinder valve for approximately 2 s, then close the valve.

181.4 Allow 10 s for all of the UF_6 to solidify; then remove the tube and rinse the UF_6 into a 10-mL beaker.

181.5 Add 1 mL of HNO_3 and evaporate the solution to dryness.

181.6 Dissolve the residue in 2 mL of water.

182. Procedure

182.1 Place a small drop of the solution, which contains approximately 50 mg U/mL, on one of the mass spectrometer sample filaments.

182.2 Connect the filament to the filament drying unit, and pass sufficient current through it to dry it and to change the color of the residue from yellow to orange.

182.3 Repeat 182.1 and 182.2 on the other sample filament.

182.4 Install the loaded filaments in the mass spectrometer.

182.5 When the source pressure is 1×10^{-5} torr, increase the sample-filament current gradually to outgas the sample.

182.6 When the source pressure is 1×10^{-6} torr, turn on the ion accelerating voltage and the other electronic components required in the analysis.

182.7 Set the ionizing-filament current for efficient ionization of uranium, and adjust the magnet current to collect the major uranium isotope ions (U^+).

182.8 Adjust the source potentials for maximum signal.

182.9 Increase the sample-filament current until the largest measurable ion current is obtained.

182.10 Scan the mass region from *m/e* 230 to 225 for hydrocarbon peaks; if present, allow additional pumping time until they have disappeared.

182.11 Adjust the magnet current for *m/e* 233, and adjust the sample-filament current until a measurable^{233}U peak is obtained.

182.12 Scan and record the following isotopes in the order

^{233}U,^{234}U,^{234}U,^{233}U, selecting electrometer shunts for maximum on-scale peaks.

182.13 Repeat 182.12 until eight peaks have been recorded for each isotope.

182.14 Adjust the magnet current to collect the major uranium isotope, and adjust the sample-filament current until the signal is 80 % of the highest electrometer scale.

182.15 Scan and record the following isotopes in the order ^{234}U,^{235}U,^{236}U,^{238}U, ^{238}U,^{236}U,^{235}U,^{234}U, selection electrometer shunts for maximum on-scale peaks.

182.16 Repeat 182.15 until eight peaks have been recorded for each isotope.

182.17 Decrease the filament currents to zero, and record the zeros of the electrometer on the shunts used in the scans.

183. Calculation

183.1 Measure the heights of the recorded peaks, and subtract the respective shunt zeros to obtain the net peak heights (NPH). The NPH of a small peak is the vertical distance from the peak top to the extrapolated tail of any interfering large peak.

183.2 Obtain the average NPH ($\overline{N}\ \overline{H}\ \overline{P}$) of each isotope.

183.3 Multiply each $\overline{N}\ \overline{H}\ \overline{P}$ by its respective electrometer shunt to obtain the real peak height (RPH) of each isotope.

NOTE 32—Although a mass bias correction is usually applied to a complete analysis of all isotopes, the mass correction for 233 is small relative to the reliability of the method when used for ppm abundances and is, therefore, ignored.

183.4 From the ^{233}U through ^{234}U recording, divide the RPH of ^{233}U by the RPH of ^{234}U to obtain the ratio of ^{233}U to ^{234}U.

183.5 From the ^{234}U through ^{238}U recording, divide the RPH of each isotope by the RPH of ^{238}U to obtain the ratio of each isotope to ^{238}U.

183.6 Multiply the ratio of ^{233}U to ^{234}U by the ratio of ^{234}U to ^{238}U to obtain the ratio of ^{233}U to ^{238}U (R_3).

183.7 Calculate the isotopic abundance of ^{233}U as follows:

$$A_3 = (R_3W_3/\Sigma R_iW_i) \times 10^6 \qquad (28)$$

A_3 = micrograms of ^{233}U/g U,
R_3 = ratio of ^{233}U to ^{238}U,
R_i = ratio of isotope to ^{238}U (R_8 = 1),
W_3 = atomic weight of ^{233}U, and
W_i = atomic weight of isotope.

184. Reliability

184.1 The 95 % confidence limit for one analysis and one filament loading is ±0.8 µg/g at an abundance of 3.0 µg/g, based on 26 determinations by three laboratories **(61).**

DETERMINATION OF URANIUM-232 BY ALPHA SPECTROMETRY

185. Scope

185.1 This test method is applicable to the determination of uranium-232 in uranyl fluoride solutions, in concentrations as low as 0.05 ppb^{232}U/U.

186. Summary of Test Method

186.1 Uranyl fluoride solutions are evaporated to dryness, and the uranium is converted to the oxide. A weighed portion of the oxide is dissolved in HNO_3 and electroplated on a stainless steel disk. The alpha activities from ^{232}U with energies of 5.28 and 5.32 MeV and ^{238}Th with energies of 5.34 and 5.42 MeV are measured with a pulse height analyzer. The two ^{232}U energy peaks are summed and corrected for the unresolved ^{238}Th 5.34 MeV. The counts are converted to disintegration rate and divided by the specific alpha activity of ^{232}U to determine the weight of ^{232}U on the disk.

187. Apparatus

187.1 *Multiple-cell Electroplating Apparatus* **(26)** with four cells operating independently of each other and the current within each cell automatically controlled to 3 A at 32 V dc. The speed of the stirrers shown in Fig. 12 is 500 rpm.

187.2 *Silicon Surface Barrier Detector*, or equivalent.

187.3 *Multichannel Alpha Spectrometer* with surface-barrier detector.

188. Reagents

188.1 *Ammonium Oxalate Solution*, (0.4 *M*)—Dissolve 56.8 of $(NH_4)_2C_2O_4{\cdot}H_2O$ in warm distilled water and dilute to 1 L.

188.2 *Gas Mixture*—Ionizing gas for Frisch grid ionization chamber; 90 % argon, 10 % methane.

188.3 *Plutonium Standard*—^{238}Pu and ^{239}Pu, with an activity approximately 10 000 cpm, deposited on a 52-mm diameter stainless steel disk.

188.4 *Neptunium Standard*—Electroplate ^{237}Np on a 25-mm diameter stainless steel disk for an alpha activity of 50 000 to 100 000 disintegrations per minute. Have the activity measured and certified by the National Institute of Standards and Technology.

189. Procedure

189.1 *Sample Preparation*:

189.1.1 Evaporate the uranyl fluoride (UO_2F_2) solution, obtained by hydrolysis of a UF_6 subsample, to dryness; ignite to U_3O_8 in a platinum dish; and weigh the oxide.

189.1.2 Dissolve a sample containing 25 mg of uranium in 1 mL of 8 *N* HNO_3 and dilute to 500 mL.

189.1.3 Place a nickel disk (Grade A, cold-rolled, smooth finish, 52–mm diameter) in the center depression of the electroplating cell base plate, and a rubber gasket on a fluorothene or glass cell stack. (High-luster 300 series stainless steel can be substituted for nickel.)

189.1.4 Place the cell stack and gasket, as a unit, on a nickel or stainless steel disk which serves as the bottom and cathode of the electroplating cell.

189.1.5 Fasten the cell stack to the base plate, making a leak-proof seal between the disk and the cell stack.

189.1.6 Add 10 mL of 0.4 *M* $(NH_4)_2C_2O_4$ solution to the cell, then add a volume of sample containing 0.5 mg of uranium.

189.1.7 Adjust the volume of the solution to 25 mL with distilled water.

189.1.8 Place the cell in a water bath, between 75 and 85°C, on the electroplating apparatus.

189.1.9 Turn on the electroplating apparatus, and lower the platinum anode into the solution until the anode is about 10 mm above the disk.

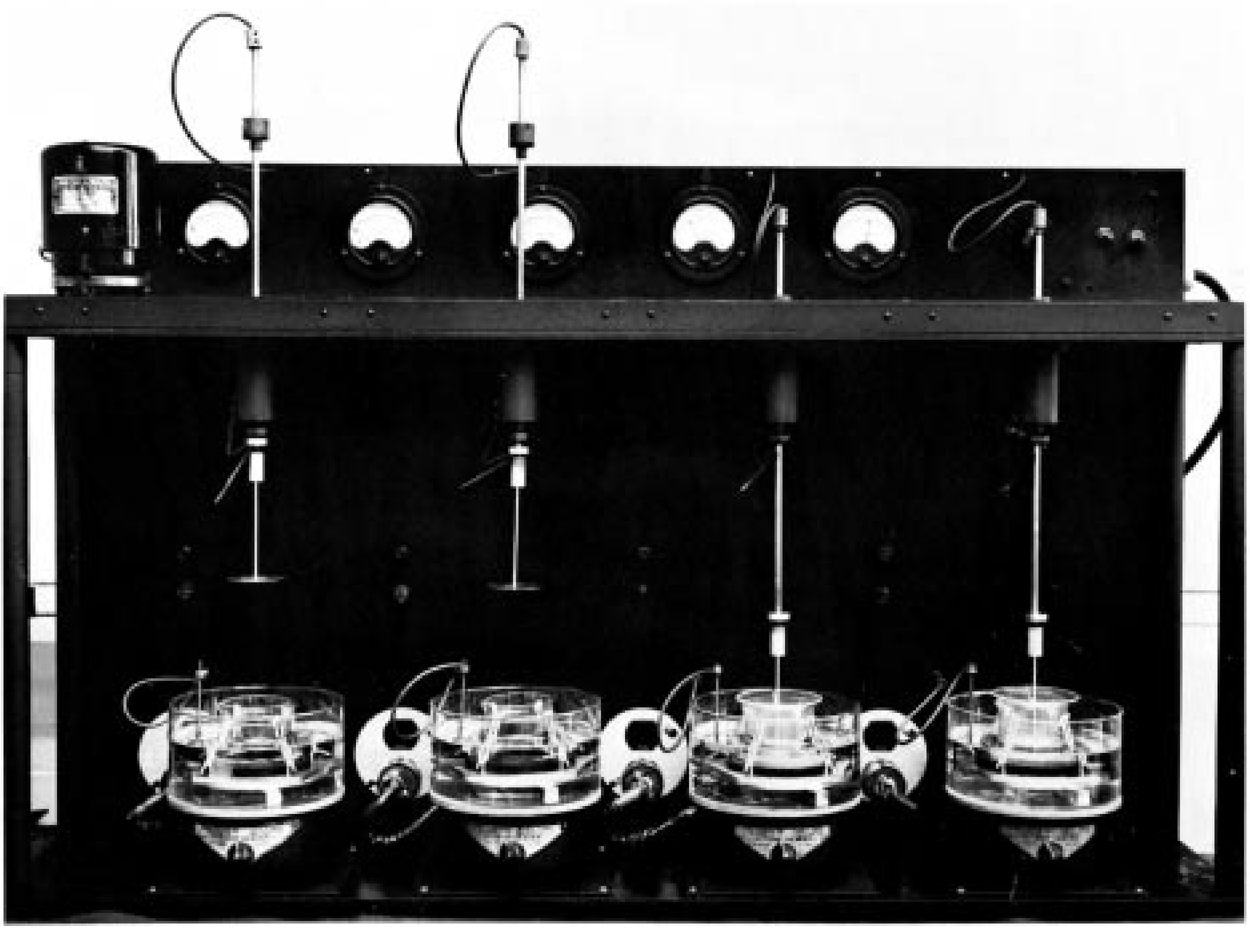

FIG. 12 Multiple-Cell Electroplating Apparatus

189.1.10 Add distilled water to replace the water evaporated during electroplating.

189.1.11 After 45 min, remove the cell from the electroplating apparatus, and quickly pour out the electrolyte.

189.1.12 Rinse the cell with approximately 15 mL of ethyl alcohol to dry the film.

189.1.13 Disassemble the cell stack, and heat the uranium on the disk in a furnace at 425°C for 10 min.

189.2 *Counting*:

189.2.1 Place the ^{238}Pu and ^{239}Pu standard in the surface barrier detector chamber under the active area of the detector.

189.2.2 Connect the surface-barrier detector through the preamplifier and amplifier to the analyzer.

189.2.3 Turn on the vacuum pump connected to the detector chamber, and pump the chamber to a pressure of approximately 15 µm.

189.2.4 Adjust the detector bias voltage to the voltage specified for the detector.

189.2.5 Adjust the amplifier to cover a spectrum area approximately 3.7 to 7.0 MeV, and measure the alpha emissions 10 min to determine the resolution at 5.14 and 5.48 MeV. The resolution must not exceed 0.050 MeV.

189.2.6 Turn the bias voltage to zero.

189.2.7 Close the vacuum line, vent the detector chamber, and remove the plutonium standard.

189.2.8 Place the neptunium standard under the detector; adjust the vacuum and bias voltage as in 189.2.3 and 189.2.4, and alpha count 20 min to determine the counter efficiency factor. The activity of the standard has been determined on a parallel-plate alpha counter of known counter efficiency.

189.2.9 Remove the neptunium standard as in 189.2.7.

189.2.10 Place the uranium sample under the detector; adjust the vacuum and bias voltage as in 189.2.3 and 189.2.4, and count the sample 40 min. Lower the counting time if the sample contains a significant amount of ^{232}U.

189.2.11 Obtain the sum of all counts in the 5.3 MeV peak (which includes the ^{232}U at 5.32 and 5.28 MeV plus the unresolved ^{228}Th at 5.34 MeV). Also, determine the sum of the ^{228}Th counts in the 5.42–MeV peak.

190. Calculation

190.1 Convert total counts to net ^{232}U counts per minute as follows:

$$^{232}C = (C_{5,3} - 0.394C_{5,42})/t \tag{29}$$

where:

^{232}C = net ^{232}U counts per minute,

$C_{5,3}$ = total counts in 5.32 and 5.27 MeV of ^{232}U peak and 5.34–MeV peak of ^{228}Th corrected for background,

$C_{5,42}$ = ^{228}Th counts in 5.42–MeV peak corrected for background,
t = time in minutes for $C_{5,3}$ and $C_{5,42}$, and
0.394 = known ratio of ^{228}Th counts at 5.34 MeV to counts at 5.42 MeV.

190.2 Determine the ^{232}U disintegration rate of the sample as follows:

$$D = {}^{232}C/E \quad (30)$$

where:
D = sample disintegrations per minute, and
E = counter efficiency obtained by dividing the net counting rate obtained on a neptunium standard by the known disintegration rate for the standard.

190.3 Calculate the amount of ^{232}U in nanograms per gram of ^{235}U as follows:

$$^{232}\text{U}/^{235}\text{U, ng/g} = D/4.65 \times 10^4\, WF \quad (31)$$

where:
D = sample disintegrations per minute,
4.65×10^4 = alpha activity of ^{232}U in disintegrations per minute per nanogram,
W = weight of sample aliquot counted, g U, and
F = weight fraction ^{235}U in sample.

191. Reliability

191.1 A 95 % confidence limit of ±16 % for a single determination has been obtained by analyzing eight separate aliquots from a uranium solution containing 100 µg/g ^{232}U/^{235}U.

DETERMINATION OF FISSION PRODUCT ACTIVITY BY BETA AND GAMMA COUNTING

192. Scope

192.1 This test method covers the measurement of the fission product activity in UF_6.

193. Summary of Test Method

193.1 The uranium with its thorium daughters is extracted into a tributylphosphate (TBP)-Stoddard solvent solution **(62),** after adding aluminum nitrate as a salting agent, citric acid to complex the zirconium and prevent its extraction into the organic solvent, and hydroxylamine hydrochloride to keep the ruthenium in a reduced valence state which will not be extracted into an organic phase.

193.2 The gamma activity of the fission products and the ^{232}U daughters below ^{238}Th is measured in the aqueous solution in a high-pressure ionization chamber, and the ^{232}U daughter activity is measured by gamma spectrometry and subtracted. The fission-product beta activity is measured by counting aliquots of the aqueous solution in a proportional counter and correcting for the activity of the ^{232}U daughters.

193.3 The beta and gamma activity from the ^{232}U daughters below ^{238}Th is determined by measuring the ^{208}Tl peak, in the aqueous portion, on the pulse height analyzer and correlating it with the measurements of a sample of known ^{232}U daughter activity measured on the pulse-height analyzer, the beta counter, and the high-pressure ionization chamber.

194. Apparatus

194.1 *High-Pressure Ionization Chamber* (HPIC)—267-mm deep, 51-mm diameter well with 3-mm steel walls; for 600-psig (4.15–MPa) argon pressure; with a vibrating reed electrometer and recorder **(63, 64).**

194.2 *Proportional Counter* with a 2-mg/cm^2 mica window.

194.3 *Pulse-Height Analyzer (4096 channel)* with sodium iodide detector.

195. Reagents

195.1 *Hydroxylamine Hydrochloride Solution* (10 %)—Dissolve 10 g of $NH_2OH{\cdot}HCl$ in 100 mL of distilled water.

195.2 *TBP-Stoddard Solvent* (50 %)—Dilute 1 L of TBP with 1 L of Stoddard solvent. Purify the TBP by washing it with an equal volume of 0.1 M Na_2CO_3 solution to remove traces of DBP.

196. Procedure

196.1 *Sample and Standard Preparation*:

196.1.1 *UF_6 Sample*:

196.1.1.1 Weigh the sealed fluorothene tube containing UF_6 subsample obtained in 10.1.1 through 10.3.8.

196.1.1.2 Freeze the UF_6 by immersing the sealed tube in liquid nitrogen for 10 min.

196.1.1.3 Remove the plug, gasket, and flare nut quickly from the frozen tube, and place each on its side in a 200-mL platinum dish or fluorothene beaker containing 150 mL of distilled water at <5°C. Rinse the gasket with distilled water.

196.1.1.4 When sample hydrolysis is complete, remove the tube, rinse with distilled water, dry, and weigh.

196.1.1.5 Add 2 mL of $NH_2OH{\cdot}HCl$ solution to the volume of sample solution containing 10.000 g of uranium and heat about 10 min. (If the volume is over 50 mL, evaporate the sample under an infrared heat lamp to 50 mL.)

196.1.1.6 Allow the sample to cool and then transfer to an extraction cell.

196.1.2 *Natural Uranium Reference Standards*:

196.1.2.1 Weight two 11.792-g samples of U_3O_8(natural uranium in equilibrium with ^{234}Th) into beakers, and add 50 mL of 4 N HNO_3 to each beaker.

196.1.2.2 Cover the beakers with watch glasses, heat on a hot plate until all the U_3O_8 is dissolved, and allow to cool.

196.1.2.3 Transfer one sample, in equal portions, to two 250-mL test tubes. Dilute the solution in each tube to 100 mL with distilled water and use as a permanent gamma-activity reference standard.

196.1.2.4 Transfer the other natural uranium sample to a 200-mL flask and dilute to volume with 4 N HNO_3.

196.1.2.5 Shake the flask thoroughly, and pipet 500-µL aliquots into three beta-counting dishes. Evaporate the samples to dryness under heat lamps.

196.1.2.6 Allow the dishes to cool, cover with thin, adhesive, cellulose acetate tape, and use as reference standards for beta activity. Prepare a standard from the flask each time the beta activity of a sample is measured.

196.1.3 *Separation of Fission Products and ^{232}U Daughters from Uranium and Thorium*:

196.1.3.1 Add 1 g of citric acid and 45 g of aluminum nitrate [$Al(NO_3)_3$] to the sample in the extraction cell.

196.1.3.2 Cool and extract the sample with 50 mL of a 50 % TBP-Stoddard solvent solution.

196.1.3.3 Drain the aqueous portion into a beaker, and wash the TBP-Stoddard solvent with approximately 10 mL of 4 *N* HNO_3 which is also drained into the beaker.

196.1.3.4 Add 2 mL of $NH_2OH·HCl$ solution to the aqueous portion in the beaker; heat this on a hot plate about 5 min (to keep the ruthenium in a reduced state).

196.1.3.5 Add 10 g of $Al(NO_3)_3$ to the sample, and extract the second time with 50 mL of 50 % TBP-Stoddard solvent.

196.1.3.6 Drain the aqueous portion into a beaker and wash the TBP-Stoddard solvent with approximately 10 mL of 4 *N* HNO_3 which is also drained into the beaker.

196.1.3.7 Repeat 196.1.3.5 and 196.1.3.6 until seven extractions are completed. Add 2 mL of $NH_2OH·HCl$ after every other extraction.

196.1.3.8 Transfer the aqueous portion containing the fission products and^{232}U daughters below ^{232}Th into a 200-mL flask and dilute to volume.

196.1.3.9 Pipet three 500-µL aliquots from the flask into separate beta-counting dishes.

196.1.3.10 Evaporate the aliquots to dryness under infrared heat lamps.

196.1.3.11 Allow the dishes to cool then cover with cellulose acetate tape for beta counting. Hold the remaining portion of the aqueous solution for gamma-activity measurements (see 196.2.1.4).

196.1.4 *Separation of ^{232}U Daughters from Uranium and Thorium for ^{232}U Correction Factor*:

196.1.4.1 Spike 10 g of natural uranium as UO_2F_2 with a known quantity of ^{232}U (to approximate 20 % of the activity of the uranium).

196.1.4.2 Extract it with TBP-Stoddards solvent as in 196.1.3.

196.1.4.3 Transfer the aqueous portion containing the^{232}U daughters into a 200-mL flask and dilute to volume.

196.1.4.4 Pipet three 500-µL aliquots from the flask into separate beta-counting dishes.

196.1.4.5 Evaporate the aliquots to dryness under infrared heat lamps.

196.1.4.6 Allow the dishes to cool then cover with cellulose acetate tape for beta counting. Hold the remaining portion of the aqueous solution for gamma activity measurements, (see 196.2.2.4).

196.2 *Counting*:

196.2.1 *Measurement of Beta and Gamma Activity from Fission Products and ^{232}U Daughters*:

196.2.1.1 Place the beta sample dishes containing fission products and ^{232}U daughters below ^{238}Th in the sample changer of the beta proportional counter, and obtain 1000 or more counts for each dish.

196.2.1.2 Calculate the average counting rate for the three dishes and correct for counter background.

196.2.1.3 Count the three dishes from the reference standard in the same manner.

NOTE 33—An alternative test method of correcting for ^{232}U daughters can be used by holding the beta and gamma sample dishes and the standard dishes, and recounting in the same manner 87 h later. The half-life of ^{234}Ra (a ^{232}U daughter) which determines the decay rate of the^{232}U daughters is 87 h.

196.2.1.4 Place the 200-mL flask containing fission products and ^{232}U daughters below ^{238}Th from 196.1.3.11, on a sodium iodide detector connected to a pulse-height analyzer and measure the gamma activity from 0 to 4 MeV for 15 min.

196.2.1.5 Remove the sample, and with the analyzer in the subtract mode, measure the background for 15 min, using a 200-mL flask filled with distilled water.

196.2.1.6 Print out the counts, showing the 2.6-MeV peak with the minima counts on either side of the peak.

196.2.1.7 Extrapolate the printout values from the minima on either side to find the background count rate.

196.2.1.8 Subtract the background count rate from the total count rate and divide by 15 to obtain the net count rate per minute.

196.2.1.9 Transfer the sample into two 250-mL test tubes in equal portions for total gamma activity measurements on the high-pressure ionization chamber.

196.2.1.10 Record the background counting rate of the ionization chamber for 3 min on the stripchart recorder. Use the average reading for the third minute as the background.

196.2.1.11 Place one of the tubes containing the fission products and ^{232}U daughters below ^{238}Th in the counting chamber, and record the counting rate for 3 min. Average the reading (in millivolts) for the last minute, and subtract the background. Obtain a reading on the second tube in the same manner. Add the readings for the two tubes.

196.2.1.12 Obtain a reading on the reference standard in the same manner as on the sample.

196.2.1.13 Repeat 196.2.1.10, 196.2.1.11, and 196.2.1.12 and record (Note 33).

196.2.2 *Measurement of Beta and Gamma Activity from ^{232}U Daughters* **(65)** *Below ^{228}Th:*

196.2.2.1 Place the beta sample dishes containing ^{232}U daughters below ^{228}Th in the sample chamber of the beta proportional counter, and obtain 1000 or more counts for each dish.

196.2.2.2 Calculate the average counting rate for the three dishes and correct for counter background.

196.2.2.3 Count the three dishes from the reference standard in the same manner.

196.2.2.4 Place the 200-mL flask containing ^{232}U daughters below ^{228}Th, from 196.1.4.6, on a sodium iodide detector connected to a pulse height analyzer, and measure the gamma activity from 0 to 4 MeV for 15 min.

196.2.2.5 Remove the sample, and, with the analyzer in the subtract mode, measure the background for 15 min, using a 200-mL flask filled with distilled water.

196.2.2.6 Print out the counts showing the 2.6-MeV peak with the minima on either side of the peak.

196.2.2.7 Extrapolate the printout values from the minima on either side to find the background count rate.

196.2.2.8 Subtract the background count rate from the total count rate and divide by 15 to obtain the net count rate per minute in the thallium peak at 2.6 MeV.

196.2.2.9 Transfer the sample into two 250-mL test tubes in equal portions for total gamma activity measurements on the high-pressure ionization chamber.

196.2.2.10 Record the background counting rate of the ionization chamber for 3 min on the strip-chart recorder. Use the average reading for the third minute as the background.

196.2.2.11 Place one of the tubes containing the ^{232}U daughters below ^{228}Th in the counting chamber, and record the counting rate for 3 min. Average the reading (in millivolts) for the last minute, and subtract the background. Obtain a reading on the second tube in the same manner. Add the readings for the two tubes.

196.2.2.12 Repeat 196.2.2.10 and 196.2.2.11 and record as total gamma activity from^{232}U daughters below ^{228}Th.

197. Calculation

197.1 Determine the^{232}U correction factors as follows:

$$\beta_c = {}^{232}\text{U, cpm}/{}^{208}\text{Tl, cpm} \quad (32)$$

and

$$\gamma_c = {}^{232}\text{U, mV}/{}^{208}\text{Tl, cpm} \quad (33)$$

where:

β_c = beta correction factor for^{232}U daughters below ^{228}Th,
γ_c = gamma correction factor for^{232}U daughters below ^{228}Th,
^{232}U, cpm = beta counts per minute from ^{232}U daughters below ^{228}Th after extraction from ^{232}U spiked solution, measured on a beta counter,
^{232}U, mV = total gamma activity from ^{232}U daughters below ^{228}Th after extraction from ^{232}U spiked solution, measured on HPIC as millivolts, and
^{208}Tl, cpm = gamma activity from ^{208}Tl after extraction from ^{232}U spiked solution, measured on a gamma spectrometer at 2.6 MeV.

197.2 Determine fission product beta and gamma activity as follows:

$$\beta_{frp} = [\beta_s - ({}^{208}\text{Tl} \times \beta_c)]/\beta_n \times 100 \quad (34)$$

and

$$\gamma_{frp} = [\gamma_t - ({}^{082}\text{Tl} \times \gamma_c)]/\gamma_n \times 100 \quad (35)$$

where:

β_{frp} = fission-product beta activity expressed as a percentage of the activity of natural uranium in equilibrium with ^{234}Th,
γ_{fp} = fission-product gamma activity expressed as a percentage of the activity of natural uranium in equilibrium with ^{234}Th,
β_s = beta activity in sample, measured on a beta proportional counter as counts per minute,
^{208}Tl, cpm = gamma activity from ^{208}Tl after extraction from sample, measured on a gamma spectrometer at 2.6 MeV.
β_n = beta activity from natural uranium reference standard, measured on a beta proportional counter as counts per minute,
γ_n = gamma activity from natural uranium reference standard, measured on HPIC as millivolts, and
γ_t = total gamma activity from fission products and^{232}U daughters, measured on the HPIC.

197.3 Determine fission product beta and gamma activity by an alternative test method as follows:

$$\beta_{frp} = \beta_1 - 2(\beta_1 - \beta_2) \quad (36)$$

and

$$\gamma_{frp} = \gamma_1 - 2(\gamma_1 - \gamma_2) \quad (37)$$

where:

β_{fp} = fission-product beta activity expressed as a percentage of the beta activity of natural uranium in equilibrium with ^{234}Th,
γ_{fp} = fission-product beta activity expressed as a percentage of the beta activity of natural uranium in equilibrium with ^{234}Th,
β_1 = first beta measurement of fission product and ^{232}U daughter below ^{228}Th activity in the sample, expressed as a percentage of the beta activity of natural uranium in equilibrium with ^{234}Th,
β_2 = second beta measurement made in the same manner as the first but 87 h later,
γ_1 = first gamma measurement of fission product and^{232}U daughter below^{228}Th activity in the sample, expressed as a percentage of the gamma activity of natural uranium in equilibrium with^{234}Th, and
γ_2 = second gamma measurement made in the same manner as the first but 87 h later.

198. Reliability

198.1 A 95 % confidence limit of ±10 % for a single gamma determination has been obtained by analyzing eight separate aliquots from a uranium solution containing 20 % fission product gamma activity.

198.2 A 95 % confidence limit of 20 % for a single beta determination has been obtained by analyzing eight separate aliquots from a uranium solution containing 4 % fission product beta activity.

DETERMINATION OF PLUTONIUM BY ION EXCHANGE AND ALPHA COUNTING

199. Scope

199.1 This test method **(66)** provides for the efficient carrier-free separation of plutonium activity from uranium. The separated plutonium activity can then be determined by alpha counting. Plutonium alpha activities of 300 d·m/g of uranium can be detected, and at the 3000-d·m/g of uranium level the method has a precision of about 15 to 20 %.

200. Summary of Test Method

200.1 Plutonium is commonly separated from uranium and most other elements by precipitation with fluoride using lanthanum as a carrier **(67).** For uranium of high-specific alpha activity (for example, more than 1 %^{234}UU or ^{233}UU in isotopic composition), this method does not give satisfactory separation from uranium alpha activity. When this precipitation procedure is combined with the anion exchange procedure described by Wish and Rowell **(68),** a complete separation from uranium activity is achieved, and the plutonium is provided in a carrier-free residue that gives excellent counting characteristics.

200.2 Since the method combines two separation processes, based on entirely different principles, elements interfering in one are not likely to interfere in the other. Elements that can be carried down with plutonium in the flocculent lanthanum fluoride precipitate include: barium, neptunium, and thorium. Uranium is not precipitated but is carried along mechanically.

200.3 Of these elements, only neptunium and uranium will absorb along with the plutonium from 12 *M* HCl on a strongly basic anion-exchange resin. Barium and thorium will not absorb. Of the absorbed elements, only the plutonium is reduced and removed with the eluting agent; that is, ammonium iodide and hydroxylamine hydrochloride in 12 *M* HCl.

200.4 Evaporation of this eluate with HNO_3 leaves behind a very small, adhesive residue, that is ideally suited to alpha counting.

201. Apparatus

201.1 *Ion-Exchange Column*—The bottom half of a 10-mL pipet serves satisfactorily for this purpose.

201.2 *Proportional Counter*.

201.3 *Motor-Driven Stirrer*, made from a platinum wire sealed in a glass rod.

202. Reagents

202.1 *Dowex-1, X-8*, 500 to 100 mesh.

202.2 *Hydroxylamine Hydrochloride* (4 *M*)—Prepare a 4 *M* solution of hydroxylamine hydrochloride ($NH_2OH·HCl$).

202.3 *Lanthanum Nitrate Solution* (0.05 *M*)—Prepare a 0.05 *M* solution of lanthanum nitrate ($La(NO_3)_3$).

202.4 *Nitric Acid-Hydrochloric Acid Wash Solution* (1 *N* HNO_3 and 5 *N* HF).

202.5 *Plutonium Nitrate [$Pu(NO_3)_6$] Standard Solution*, pure, of known alpha activity of about 6000 d·m/mL.

202.6 *Potassium Hydroxide* (KOH) 50 %, carbonate-free.

202.7 *Reducing Solution*—Concentrated HCl (sp gr 1.19), saturated with $NH_2OH·HCl$; the resulting solution is made 0.1 *M* with respect to ammonium iodide (NH_4I).

203. Procedure

203.1 Fume an aliquot containing up to 0.1 g of uranium with concentrated H_2SO_4(sp gr 1.84) to remove the fluoride ion and nitrate ion.

203.2 Transfer the aliquot to a 15-mL centrifuge tube.

203.3 Add 2 mL of $NH_2OH·HCl$ solution, and heat the solution for 20 min at 80°C.

203.4 Add 1 mL of the $La(NO_3)_3$ solution, and mix the plutonium solution thoroughly.

203.5 Add 1 mL of 1 + 1 HF and stir.

203.6 Centrifuge the mixture for 2 min, and decant the supernatant liquid. Wash the precipitate with 1 mL of HNO_3-HF solution with the aid of the motor-driven stirrer. Then centrifuge the solution, decant the supernate, and repeat the washing process.

203.7 Add 1 mL of KOH solution, and wash the precipitate. Centrifuge the solution for 2 min, and decant the supernatant part. Wash the precipitate and centrifuge again with the caustic solution, and then wash once with water to remove excess KOH.

203.8 Dissolve the precipitate with 2 to 3 mL of concentrated HCl (sp gr 1.19) containing a trace of HNO_3[one drop of concentrated HNO_3(sp gr 1.42) per 15 mL of concentrated HCl (sp gr 1.19)].

203.9 Prepare an ion-exchange column with Dowex-1 by pouring enough resin slurry into the column to give a resin bed about 15 cm high. Pass 10 mL of concentrated HCl (sp gr 1.19) through the column.

203.10 Pass the solution of the dissolved precipitate through the ion-exchange column at 4 drops/min (a slight vacuum will be required to maintain this rate of flow). Wash the resin with 5 mL of concentrated HCl (sp gr 1.19).

203.11 Elute the absorbed plutonium with 10 mL of reducing solution.

203.12 Add 2 to 3 drops of concentrated HNO_3 (sp gr 1.42) to the eluate, and evaporate it to dryness. Dissolve the residue with 2 to 3 drops of concentrated HNO_3(sp gr 1.42), and rinse the sides of the beaker with 1 mL of water.

203.13 Transfer the solution to a counting planchet and evaporate to near dryness. Rinse the beaker twice with 1 mL of water; transfer the washings to the planchet and evaporate to dryness.

203.14 Alpha count the residue on a proportional counter.

203.15 Convert the alpha counts to disintegrations using a geometry and recovery factor determined by analyzing known amounts of plutonium activity by the above procedure. Recoveries of 90 to 100 % of 600 dis/min of plutonium activity should be achieved.

DETERMINATION OF PLUTONIUM BY EXTRACTION AND ALPHA COUNTING

204. Scope

204.1 This thenoyltrifluoroacetone (TTA) test method covers the determination of total plutonium in UF_6. Plutonium can be quantitatively and selectively extracted from an aqueous solution into a TTA-xylene solution.

205. Summary of Test Method

205.1 Plutonium-bearing UF_6 is hydrolyzed using a nitric acid-aluminum nitrate solution. The plutonium is then reduced with hydroxylamine hydrochloride to Pu^{+3}, oxidized to Pu^{+4} with sodium nitrite, and extracted into TTA. Removal from TTA is with nitric acid. The plutonium-bearing aqueous phase is then evaporated to dryness on appropriate surfaces for counting gross alpha. Counting rates are compared to those of known standards to determine total plutonium.

206. Interferences

206.1 There is no appreciable interference due to uranium and thorium; however, neptunium is not quantitatively separated from the plutonium in the extraction procedure. If prepared sample disks have appreciable alpha counts, an alpha energy analysis should be performed and a neptunium correction applied when necessary. For samples counting near the detectability level, the alpha energy scan is useless since sensitivity is inadequate to distinguish between neptunium and plutonium.

207. Apparatus

207.1 *Alpha Counter* with a background counting rate of 5 cpm or less is recommended. Either a proportional counter or parallel-plate alpha counter is suitable.

207.2 *Alpha Energy Analyzer* is optional for checking the selectivity of the extraction process.

207.3 *Equipment for Agitating Solutions* is desirable. A variable-speed laboratory shaker or a bank of extraction cells and stirrers will suffice.

208. Reagents

208.1 *Thenoyltrifluoroacetone (TTA) Solution (0.5 M)*—Dissolve 111 g of TTA in 1 L of xylene.

208.2 *Hydroxylamine Hydrochloride Solution* (1*M*)—Dissolve 69.5 g of $NH_2OH \cdot HCl$ in 1 L of water.

208.3 *Sodium Nitrite Solution* (1*M*)—Dissolve 69 g of $NaNO_2$ in 1 L of water (prepare daily).

208.4 *Aluminum Nitrate* (2 *M*)—Dissolve 187.5 g of $Al(NO_3)_3 \cdot 9H_2O$ in 250 mL of 2 *M* HNO_3.

208.5 *Nitric Acid* (6 *M)-Aluminum Nitrate* (0.1 *M) Solution*—Add 375.5 mL of HNO_3 and 37.51 g of $Al(NO_3)_3$ to 1 L of water.

209. Procedure

209.1 *Hydrolysis*:

209.1.1 Hydrolyze a sample aliquot containing 5 g of uranium as UF_6 using 250 mL of 6 *M* HNO_3-0.1 *M* $Al(NO_3)_3$ solution.

209.1.2 Hydrolyze a standard of plutonium-free UF_6 with the above solution, using 50 mL of the hydrolyzing solution per gram of uranium.

209.2 *Extraction*:

209.2.1 Transfer duplicate 50-mL aliquots from the prepared sample solution to 150-mL beakers. (For each group of samples, prepare a blank and a spike solution from the plutonium-free uranium standard. The blank is a 50-mL aliquot of the uranium standard in a 150-mL beaker. The spike is a similar aliquot spiked with 2400-dpm plutonium.)

209.2.2 Evaporate sample, blank, and spike solutions to dryness slowly on a hot plate and treat identically throughout the remainder of the procedure.

209.2.3 Flame the solid residue to eliminate fluorides.

209.2.4 Use approximately 10 mL of 2 *N* HNO_3 to put the solid residue back in solution.

209.2.5 Add 4 mL of 2 *M* $Al(NO_3)_3$-2 *M* HNO_3.

209.2.6 Add 2 mL of 1 *M* $NH_2OH \cdot HCl$ solution.

209.2.7 Stir the solution and allow to stand in a water bath at 80°C for 5 min.

209.2.8 Remove the sample from the water bath, and add 8 mL of 1 *M* $NaNO_2$ solution cautiously. Stir the solution, allow to stand for 5 min, and then transfer to an extraction cell.

209.2.9 Add 20 mL of 0.5 *M* TTA solution in xylene, and stir the solution for 15 min.

209.2.10 Discard the aqueous phase.

209.2.11 Wash the organic phase four times with approximately 15 mL of 2 *M* HNO_3. Perform the washings by adding wash solution, stirring a few seconds, and discarding the aqueous phase.

209.2.12 Add 4 mL of 8 *M* HNO_3 to the organic phase. (8 *M* HNO_3 may be replaced with 0.6 *M* HF for extracting plutonium out of the organic phase.)

209.2.13 Stir the solution for 15 min.

209.2.14 Withdraw the aqueous phase containing plutonium.

209.2.15 Pipet a 1-mL aliquot of plutonium-bearing solution onto a stainless steel alpha-counting disk, and evaporate to dryness under a heat lamp. (Stainless steel disks may be replaced by stainless steel dishes.)

209.2.16 Heat the disk over open flame to red heat and cool.

209.3 *Counting*:

209.3.1 Count the sample, blank, and spike disks for gross alpha.

209.3.2 In case of doubt concerning selectivity of extraction, perform an alpha energy scan to assure that the sample count is due to plutonium.

210. Calculations

210.1 Since each sample aliquot contains 1 g of uranium, the following expressions hold:

$$\text{Pu alpha cpm/gU} = A_0/GF \times (S - B)/(A_s - B) \tag{38}$$

where:

A_O = alpha disintegrations per minute in spike aliquot,
GF = geometry factor,
A = alpha cpm from sample disk,
B = alpha cpm from blank disk, and
A_s = alpha cpm from spike aliquot disk.

210.2 Plutonium alpha activity in disintegrations per minute per gram of uranium may be obtained by multiplying the result in Eq 38 by a geometry factor that is found by counting a plutonium standard of known disintegration rate. With most plates, this factor is 2.

210.3 Calculate parts per billion plutonium as follows:

$$\text{ppb Pu} = ((\text{Pu alpha cpm})/\text{gU})/(136)/\text{GF}) \tag{39}$$

where:

ppb Pu = parts per billion plutonium on a uranium basis, and
136 = specific activity for one nanogram of ^{239}Pu.

211. Reliability

211.1 The procedure as described has a 95 % symmetrical confidence level of ±10 % at alpha rates greater than about 136 dpm/g uranium.

211.2 By using larger sample aliquots and plating more than 1 mL of extracted solution, concentrations as low as 8 dpm/g of uranium may be measured to a 95 % symmetrical confidence interval of ±20 % of the value.

DETERMINATION OF NEPTUNIUM BY EXTRACTION AND ALPHA COUNTING

212. Scope

212.1 The thenoyltrifluoroacetone (TTA) test method covers to the determination of^{237}Np in UF_6. Neptunium can be selectively extracted from an aqueous solution into a TTA-xylene solution, and a ^{239}Np tracer technique can be used to measure extraction losses; thereby, eliminating the need for a more laborious quantitative extraction.

213. Summary of Test Method

213.1 Neptunium-bearing UF_6 is hydrolyzed using a nitric acid-aluminum nitrate solution. The resulting solution is spiked with a ^{239}Np tracer, brought to dryness, and flamed to rid the residue of fluorides. Residue is dissolved with hydrochloric acid, the neptunium reduced to Np^{+4}, and extracted into TTA. Neptunium is recovered from TTA in nitric acid as the Np^{+5} ion. The neptunium-bearing solution is evaporated to dryness on appropriate counting disks, and the necessary counting is performed.

214. Interferences

214.1 There is no radiochemical interference of consequence. Uranium, thorium, and plutonium are essentially removed in the extraction procedure. An alpha energy scan is optional to preclude interference.

215. Apparatus

215.1 *Alpha Counter* with a background counting rate less than 5 cpm is recommended. Either a proportional counter or a parallel-plate alpha counter is suitable.

215.2 *Gamma Scintillation Spectrometer*, required for the ^{239}Np tracer. A single-channel analyzer is adequate, with a multichannel instrument being optional.

215.3 *Alpha Energy Analzyer*, optional for checking the selectivity of the extraction process.

215.4 *Equipment for Agitating Solutions*, desirable. Extraction cells or separatory funnels will suffice.

216. Reagents

216.1 *Hydrochloric Acid* (1 *M*)—Prepare a 1 *M* solution of hydrochloric acid (HCl).

216.2 *Nitric Acid* (*HNO_3*) (6 *M*)*—Aluminum Nitrate* [*$Al(NO_3)_3$*] *(0.1 M) Solution.*

216.3 *Reducing Solutions*—150 mL of 5 *M* hydroxylamine hydrochloride ($NH_2OH\cdot HCl$) + 250 mL of 2 *M* hydrochloric acid (HCl) + 100 mL of 1.5 *M* ferrous chloride ($FeCl_2$). The solution is unstable, therefore, store it in a dark bottle and prepare every two weeks.

216.4 *Thenoyltrifluoroacetone* (*TTA*) (0.5 *M*)—Dissolve 111 g of TTA in 1 L of xylene solution.

217. Procedure

217.1 *Preparation of ^{239}Np Tracer*:

217.1.1 Encapsulate aliquots of 100 mg normal or depleted U_3O_8 in high-silica ampules and expose for 10 min to a nominal neutron flux of 2×10^{14}n/cm^2·s.

217.1.2 Break the ampules and put the contents in solution with 6 *M* HNO_3.

217.1.3 The extraction procedure for ^{239}Np tracer is the same as that for extracting ^{237}Np from sample solutions (see 216.3).

217.1.4 With a ^{239}Np half-life of 2.3 days, the usable life of a batch of tracer is about 2 weeks. (The tracer technique gives greater accuracy and precision with a minimum of analytical effort; however, the analysis can be performed without ^{239}Np. If tracer is not used, ^{237}Np standards should be run through the extraction procedure to determine a loss correction and the procedural steps performed methodically to assure uniform losses.)

217.2 *Preparation of Sample*:

217.2.1 Hydrolyze a sample aliquot containing 5 g of uranium as UF_6 using 250 mL of 6 *M* HNO_3-0.1 *M* $Al(NO_3)_3$ solution.

217.2.2 Transfer duplicate 50-mL aliquots from the hydrolyzed solution to 150-mL beakers.

217.2.3 Add 2 mL of tracer solution to each aliquot (adjust the concentration of ^{239}Np tracer solution by appropriate dilution to give about 1000 cpm/mL when the scintillation counter is accepting photons from the 0.28-MeV gamma peak).

217.3 *TTA Extraction*:

217.3.1 Bring the spiked sample aliquots to dryness slowly on a hot plate to prevent spattering.

217.3.2 Heat each residue over an open flame until it becomes burnt orange color to remove fluorides and nitrates.

217.3.3 Cool the residue and put in solution with approximately 30 mL of 1 *M* HCl.

217.3.4 Add approximately 15 mL of reducing solution, and allow the solution to digest for 5 to 10 min.

217.3.5 Transfer the sample to an extraction cell, add 15 mL of TTA-xylene, and stir the resulting mixture for 20 min. (Replace xylene by benzene if desired.)

217.3.6 Discard the aqueous phase.

217.3.7 Wash the organic phase three times with 1 *M* HCl. Wash by adding HCl, stir ½ min, and discard the aqueous phase.

217.3.8 Add 5 to 10 mL of 8 *M* HNO_3 to the organic phase, and stir the resulting mixture for 20 min.

217.3.9 Withdraw the aqueous phase, containing neptunium, and bring to dryness on a hot plate.

217.3.10 Repeat 217.3.3 through 217.3.7.

217.3.11 Wash the organic phase twice as in 217.3.7 except with 0.05 *M* HNO_3.

217.3.12 Add 4 mL of 8 *M* HNO_3 to the organic phase, and stir the resulting mixture for 20 min.

217.3.13 Withdraw the aqueous phase, containing neptunium.

217.4 *Sample and Tracer Disk Preparation*:

217.4.1 *Sample Disk*:

217.4.1.1 Pipet 2 mL of the sample solution onto a stainless steel disk and allow to dry under a heat lamp.

217.4.1.2 Heat the disk to red heat over an open flame and cool.

217.4.2 *Tracer Disk*:

217.4.2.1 Pipet 1 mL of tracer solution onto a stainless steel disk and allow to dry under a heat lamp.

217.4.2.2 Heat the disk to red heat over an open flame and cool.

217.5 *Counting*:

217.5.1 Count the sample disks to determine net alpha counts per minute.

217.5.2 Count the sample and tracer disks to determine net gamma activity (counts/min) due to the 0.28-MeV ^{239}Np peak.

217.5.3 An alpha energy scan is optional to certify that all alpha activity is due to ^{237}Np.

218. Calculations

218.1 Each sample aliquot contains 1 g of uranium. If A equals the net ^{237}Np alpha count per minute on the sample disk, B equals the net gamma count of the ^{239}Np spike, and C equals the net ^{239}Np gamma count extracted; the following equation gives ^{237}Np alpha concentration in sample.

$$^{237}\text{Np alpha cpm/gU} = AB/C \tag{40}$$

218.2 Neptunium alpha activity in disintegrations per minute per gram of uranium may be obtained by multiplying the result in Eq 40 by a geometry factor that is found by counting a neptunium standard of known disintegration rate. With most standard plates or disks, this factor is 2. Calculate as follows:

$$\text{ppm Np} = ((\text{Np alpha cpm})/\text{gU})/((1562)/(GF)) \tag{41}$$

where:

ppm Np = parts per million neptunium on a uranium basis,
1562 = specific activity for 1 µg of ^{237}Np, and
GF = geometry factor.

219. Reliability

219.1 The procedure has a 95 % symmetrical confidence interval of ± 10 % at alpha rates greater than about 156 dpm/g of uranium.

219.2 At 16 dpm/g uranium, the confidence interval is ± 30 %.

219.3 The lower limit of detectability is about 4 dpm/g of uranium.

ATOMIC ABSORPTION DETERMINATION OF CHROMIUM SOLUBLE IN URANIUM HEXAFLUORIDE

220. Scope

220.1 A test method is presented for the determination of chromium, soluble in UF_6, in the concentrations of 0.2 to 100 µg/g (uranium basis).

221. Summary of Test Method

221.1 The UF_6 is filtered through a porous filter (see procedure on subsampling, Sections 6 to 9), and the filtered sample is hydrolyzed in deionized water. The chromium in the hydrolyzed UF_6 solution is separated from the uranium, with or without prior concentration, with an *n*-tributyl phosphate (TBP)-xylene mixture, leaving the chromium in the aqueous phase. The chromium is then determined by atomic absorption spectroscopy after dilution to a standard volume. Combining atomic absorption spectroscopy with solvent extraction of the chromium has two advantages: (*1*) uranium matrix effects are eliminated from the atomic absorption spectrometry and (*2*) radioactivity contamination problems arising from aspirating uranium solutions are eliminated.

221.2 Two extraction techniques are presented. In Method A, a sample solution containing 1 g of uranium is used and does not include a concentration step prior to extraction. Therefore, the detection limit is not as low as Method B, that includes a 5-g uranium sample and a concentration step prior to the extraction. Method A, that has a detection limit of 2 µg/g (uranium basis), is the preferred method because of its simplicity. However, if a lower detection limit is required, Method B should be used. Method B has a detection limit of 0.2 µg/g (uranium basis).

221.3 Boric acid is used in both Method A and Method B to form a complex with the fluoride prior to the extraction. A TBP-xylene mixture is used in both methods to extract the uranium, leaving the chromium in the aqueous phase, in which the final atomic absorption determination is made.

222. Interferences

222.1 In relatively pure UF_6, that is normally analyzed by this method, there is usually no problem with interferences.

223. Apparatus

223.1 *Atomic Absorption Spectrophotometer*, as described in Proposed Recommended Practices for Atomic Absorption Spectrometry.

224. Reagents

224.1 *Boric Acid* (H_3BO_3), reagent grade.

224.2 *Boric Acid Solutions*, saturated. Prepare by dissolving reagent-grade boric acid in deionized water until an excess of boric acid crystals remains undissolved.

224.3 *Chromium, Stock Solution, 1000 µg/mL*—Dissolve 3.7349 g of potassium chromate (K_2CrO_4) in 1 L of deionized water or use commercially[24] available standard solutions.

224.4 *n-Tributyl Phosphate*, purified.

224.5 *n-Tributyl Phosphate-Xylene Mixture (1 + 2)* —Mix 1 volume of TBP with 2 volumes of reagent-grade xylene.

224.6 *Xylene* (C_8H_{10}), reagent grade.

225. Procedure

225.1 *Method A*:

225.1.1 Hydrolyze the filtered UF_6 sample with chilled deionized water in accordance with 17.1 to 17.14.2.

225.1.2 Transfer an aliquot of the sample that contains 1 g of uranium to a 125-mL separatory funnel.

225.1.3 Add 10 mL of saturated boric acid solution and enough concentrated HNO_3 to make the solution 2.5 M in HNO_3.

225.1.4 Add 25 mL of the (1 + 2) TBP-xylene mixture and shake for 30 s.

225.1.5 Allow the layers to separate, and transfer the bottom (aqueous) layer to a second 125-mL separatory funnel.

225.1.6 Repeat 225.1.4 with the aqueous portion in the separatory funnel.

225.1.7 Allow the layers to separate and collect the aqueous layer in a 50-mL volumetric flask.

225.1.8 Dilute to volume with water.

225.2 *Method B*:

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[24] Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219 is a suggested vendor.

225.2.1 Hydrolyze the filtered UF_6 sample with chilled deionized water in accordance with 17.1 to 17.14.2.

225.2.2 Weigh 3 g of boric acid into a 100-mL beaker.

225.2.3 Transfer an aliquot of the sample that contains 5 g of uranium to the beaker, and concentrate the mixture to less than 15 mL on a hot plate.

225.2.4 Add 10 mL of concentrated HNO_3, and transfer with minimum water to a 125-mL separatory funnel.

225.2.5 Add 50 mL of the (1 + 2) TBP-xylene mixture and shake for 30 s.

225.2.6 Allow the layers to separate, and transfer the lower (aqueous) layer to a second 125-mL separatory funnel.

225.2.7 Repeat 225.2.5 with the aqueous portion. Allow the layers to separate.

225.2.8 Transfer the lower (aqueous) layer to a 25-mL volumetric flask, and dilute to volume with water.

225.3 Analyze the aqueous extract by atomic absorption as follows:

225.3.1 Prepare the instrument for chromium analysis as outlined in the instrument manufacturer's atomic absorption manual.

225.3.2 Zero the instrument with deionized water.

225.3.3 Calibrate the instrument by preparing standards from UO_2F_2 solutions that have been spiked with known amounts of chromium. The standards are then extracted as outlined above. (Calibration is performed each time samples are analyzed.)

225.3.4 Analyze the sample extracts. Determine the concentration of chromium in the extracts from the calibration.

226. Precision and Bias

226.1 The relative standard deviation of a single analysis by this test method is approximately 10 % at the 2-µg/g concentration level, and the bias is + 1.5 % (relative). (A minimum of ten replicate measurements were used to determine the standard deviation and the bias of the test method.)

ATOMIC ABSORPTION DETERMINATION OF CHROMIUM INSOLUBLE IN URANIUM HEXAFLUORIDE

227. Scope

227.1 A test method is presented for the determination of chromium, insoluble in UF_6, by atomic absorption spectroscopy. The detection limit achieved using this technique is dependent upon the amount of sample filtered through the filter. A detection limit of 0.5µ g/g has been obtained using a 10-g sample.

228. Summary of Test Method

228.1 The liquid UF_6 sample is filtered through a porous nickel filter (see Sections 6 to 9), and both the filter and the residue are dissolved in dilute nitric acid for the analysis. The amount of UF_6 filtered is determined by the detection limit required. The usual sample will vary between 10 and 50 g. The dissolved solution is diluted so as to contain a final nickel concentration of 1 % and an ammonium chloride concentration of 2 %. The chromium is then determined by atomic absorption spectrophotometry.

228.2 In the atomic absorption analysis, nickel suppresses the chromium response. To minimize this effect, it is necessary to add ammonium chloride. To further compensate for this and other matrix effects, it is necessary to prepare standard chromium solutions that contain both 1 % nickel and 2 % ammonium chloride. The concentration range of the standards prepared should bracket the expected concentrations in the samples.

229. Interferences

229.1 The interference of nickel and other metallic elements is controlled by the addition of ammonium chloride to suppress ionization.

230. Apparatus

230.1 *Atomic Absorption Spectrophotometer,* as described in Proposed Recommended Practices for Atomic Absorption Spectrometry.

231. Reagents

231.1 *Ammonium Chloride Solution*, 20 %—Dissolve 200 g of ammonium chloride, reagent grade, in deionized water and dilute to 1 L.

231.2 *Chromium Standard Solutions*—Prepare 100-mL quantities of a 1 % nickel solution containing 50, 30, 20, 10 and 5µ g of chromium. Add 10 mL of the ammonium chloride stock solution to each standard solution before diluting to volume.

231.3 *Chromium Stock Solution*, 1000 µg/mL—Dissolve 3.7349 g of potassium chromate (K_2CrO_4) in 1 L of deionized water or use commercially[21]available standard solutions.

231.4 *Nickel Solution*, 10 %—Dissolve 100 g of spectrographically pure nickel powder in 500 mL of deionized water and 50 mL of concentrated HNO_3. Heat until dissolution is complete and dilute to 1 L with deionized water.

232. Procedure

232.1 Filter sufficient UF_6 to obtain the desired detection limit (see Sections 6 to 9).

NOTE 34—The detection limit of the atomic absorption technique is 0.05 µg chromium/mL in a 1 % nickel solution. When a 1-g filter is dissolved and diluted to 100 mL, the weight of chromium needed in the determination to report a positive value is in excess of 5 µg. -g uranium sample at this level would show 0.5 µg/g chromium, while a 50-g uranium sample would show 0.1 µg/g chromium.

232.2 Dissolve the filter and residue in a minimum amount of (1 + 1) HNO_3(about 10 mL).

232.3 Transfer the solution to a 100-mL volumetric flask (for a 1-g filter), add 10 mL of the ammonium chloride solution, and dilute to volume with deionized water.

NOTE 35—For filters weighing other than 1 g, make appropriate dilution so that the final solution will contain 1 % nickel and 2 % ammonium chloride.

232.4 Analyze the diluted sample by atomic absorption as follows:

232.4.1 Prepare the instrument for chromium analysis as outlined in the instrument manufacturer's atomic absorption manual.

232.4.2 Zero the instrument with a blank 1 % nickel solution which contains 2 % ammonium chloride.

232.4.3 Determine the chromium by standard atomic absorption techniques, comparing the sample measurements to those of the prepared standards in the same concentration region.

233. Precision and Bias

233.1 The relative standard deviation of a single analysis using this test method is approximately 10 %. (Ten replicate measurements were made to determine the standard deviation of the procedure. A bias could not be computed, since no certified standard was available.)

DETERMINATION OF TECHNETIUM-99 IN URANIUM HEXAFLUORIDE

234. Scope

234.1 This test method is applicable to the determination of technetium-99 (^{99}Tc) in UF_6, after hydrolyzing it to uranyl fluoride.

235. Summary of Test Method

235.1 The sample, to which a nonradioactive rhenium carrier has been added, is dissolved in HNO_3 and the solution is evaporated almost to dryness at low temperature (do not boil). A solution of potassium carbonate (K_2CO_3) and hydrogen peroxide (H_2O_2) is added, and the technetium is extracted into methyl ethyl ketone. The ketone is evaporated, and the residue of perrhenate and pertechnetate is dissolved in water. Stable cerium, cesium, ruthenium, and strontium are added to the residual solution to dilute any radioactive trace quantities of these elements that may precipitate with the^{99}Tc. The technetium and rhenium are precipitated with tetraphenyl arsonium chloride, weighed in a tared stainless steel dish, and beta counted. The beta counting rate is corrected for the recovery indicated by the rhenium carrier, and compared to that of a^{99}Tc standard.

236. Apparatus

236.1 *Automatic Low-level Beta Counter*.

236.2 *Counter Standard*, known activity of ^{90}Sr-^{90}Y, or some other well-characterized beta standard.

236.3 *Centrifuge*.

236.4 *Stainless Steel Dish*, 25 mm in diameter and 6.4 mm deep.

236.5 *Separatory Funnel*, 250 mL.

237. Reagents

237.1 *Ammonium Hydroxide (NH_4OH),* concentrated.

237.2 *Boric Acid Solution*, saturated.

237.3 *Ferric Nitrate Solution*—Dissolve 18 g of $Fe(NO_3)_3 \cdot 9H_2O$ in distilled water and dilute to 250 mL.

237.4 *Hydrochloric Acid* (*HCl*), reagent grade, concentrated.

237.5 *Hydrogen Peroxide (H_2O_2),* 30 %.

237.6 *Methyl Ethyl Ketone*, reagent grade.

237.7 *Methyl Orange Indicator Solution*.

237.8 *Potassium Carbonate*, 3 *M*—Dissolve 414.6 g of K_2CO_3 in distilled water and dilute to 1 L.

237.9 *Potassium Perrhenate*—Dissolve 2 g of $KReO_4$ in distilled water and dilute to 1 L.

237.10 *Stable Solution of Cerium, Cesium, Ruthenium, and Strontium*—Dissolve 7.75 g of $Ce(NO_3)_3 \cdot 6H_2O$, 6.25 g of $RuCl_3$, 7.50 g of $SrCl_2 \cdot 6H_2O$, and 2.75 g of $CsNO_3$ in distilled water and dilute to 1 L.

237.11 *Technetium Standard in a Basic Aqueous Solution*.

237.12 *Tetraphenyl Arsonium Chloride (TPA)* —Dissolve 4 g of $(C_6H_5)_4AsCl$ in distilled water and dilute to 250 mL.

238. Procedure

238.1 *Sample Preparation*:

238.1.1 *Hydrolyzed UO_2F_2 Sample Preparation*:

238.1.1.1 Pipet 3 mL of $KReO_4$ solution into a beaker.

NOTE 36—**Caution:** The final precipitate of $(C_6H_5)_4AsReO_4$ must not exceed 14 mg to prevent shielding of^{99}Tc.

238.1.1.2 Pipet 10 mL of the sample into the same beaker.

238.1.1.3 To complex the fluorides present, add 3 mL of saturated boric acid solution per gram of UO_2F_2.

238.1.1.4 Make basic by adding 10 mL of 3 *M* K_2CO_3 solution, and stir until the precipitate dissolves. (Uranyl hydroxide is soluble in K_2CO_3.) Add 2 mL of 30 % H_2O_2 to oxidize technetium to + 7. (Technetium must be present as Tc (+ 7) before extracting into ketone **(69)**.)

238.1.2 *Control Sample Preparation*:

238.1.2.1 Pipet 3 mL of KR_eO_4 solution into a beaker.

NOTE 37—**Caution:** The final precipitate of $(C_6H_5)_4AsReO_4$ must not exceed 14 mg to prevent shielding of^{99}Tc.

238.1.2.2 Pipet 10 mL of a^{99}Tc solution of known activity level (100 dis/min/mL) into the same beaker.

238.1.2.3 Make basic by adding 10 mL of 3 *M* K_2CO_3 solution. Add 2 mL of 30 % H_2O_2 to oxidize the technetium to (+ 7) valence. (Technetium must be present as Tc (+ 7) before extracting into ketone.)

238.1.3 *Extraction*:

238.1.3.1 Transfer a sample in accordance with 238.1.1.1 and 238.1.2.1 to a separatory funnel, wash the beaker in accordance with 238.1.1.1 and 238.1.2.1 with approximately 10 mL of 3 *M* K_2CO_3, and drain the washings into the separatory funnel.

238.1.3.2 Add approximately 50 mL of methyl ethyl ketone to the separatory funnel and shake for about 2 min. Release the pressure after several seconds of agitation.

238.1.3.3 Drain the aqueous phase into a salvage container, and save the ketone that contains the rhenium and technetium.

238.1.3.4 Wash the sides of the separatory funnel by shaking twice with 10-mL portions of 3 *M* K_2CO_3, and discard the washings.

238.1.3.5 Drain the ketone into a beaker.

238.1.3.6 Add 10 mL of distilled water to the same beaker in accordance with 238.1.3.5 and evaporate the ketone under heat lamps. (The water prevents the sample from going to dryness and the possible loss of Tc.)

238.1.4 *Precipitation*:

238.1.4.1 Transfer the solution to a 50-mL centrifuge tube. Wash the beaker with distilled water, and transfer the rinse solution to the tube.

238.1.4.2 Add three drops of concentrated HCl, five drops of the stable cerium, cesium, ruthenium, and strontium solution, and five drops of the ferric nitrate solution. Agitate slightly after each addition.

238.1.4.3 Precipitate $Fe(OH)_3$ by adding several drops of concentrated NH_4OH until the solution is basic to pH paper.

238.1.4.4 Filter the solution through No. 41 Whatman filter paper into another 50-mL centrifuge tube and discard the precipitate. (Technetium must be as Tc (+ 7) or else it will coprecipitate with the $Fe(OH)_3$.)

238.1.4.5 Add one drop of methyl orange indicator to the filtrate, and add HCl until the indicator turns red. Then add five extra drops of HCl.

238.1.4.6 Cool for 5 to 10 min in an ice bath, add 2 mL of TPA and stir **(69).**

238.1.4.7 Remove the solution from the ice bath, and centrifuge for 1 min at 3000 r/min.

238.1.4.8 Pour off the supernatant liquid. Wash the precipitate twice with approximately 10 mL of ice water.

238.1.4.9 Pour off the supernatant and dissolve the precipitate in 1 mL of acetone. Transfer the solution to a counting dish that has been weighed to ±0.1 mg.

238.1.4.10 Evaporate the precipitate to dryness under a heat lamp.

238.1.4.11 Weigh the dish, and calculate the net weight of the residual tetraphenyl arsonium perrhenate, $(C_6H_5)_4AsReO_4$.

238.1.4.12 Cover each dish with a layer of cellophane tape to prevent loss of the residue.

239. Counting

239.1 Beta count the counter standard until 30 000 counts are registered. Calculate the counting rate; it must be within ±2.5 % of the posted mean for the standard. (A typical value is 20 000 counts per minute (cpm).)

239.2 Beta count the sample and control sample.

239.3 Subtract the counter background (cpm) from both the sample and control sample counting rates to obtain the net cpm.

240. Calculations

240.1 Calculate rhenium carrier yield (y) for the sample and control sample as follows:

$$y = a/(b)(2.19) \tag{42}$$

where:
a = net sample weight in beta counting dish, mg, and
b = net weight of $KReO_4$ added, mg.

(If 1 mg of $KReO_4$ is precipitated with tetraphenyl arsonium chloride, 2.19 mg of $(C_6H_5)_4AsReO_4$ is formed.)

240.2 Calculate the geometry factor (GF) as follows:

$$GF = d/c \tag{43}$$

where:
d = disintegrations per minute (dpm) of ^{99}Tc control sample, and
c = net cpm of control sample corrected for yield.

240.3 Calculate the ^{99}Tc in the sample as follows:

$$\text{micrograms } ^{99}\text{Tc/grams sample} = \frac{(s)(GF)/(y)}{(37\ 807)(\text{grams sample})} \tag{44}$$

where:
s = net cpm of sample,
GF = geometry factor,
y = yield fraction of sample, and
37 807 = specific activity of ^{99}Tc in dpm/microgram.

241. Precision and Bias

241.1 The relative standard deviation of an analysis is 25 % of the value in the range 0.01 to 0.05 µg^{99}Tc/g sample. A minimum of ten replicate measurements was performed.

242. Sensitivity

242.1 The lower limit of detection is 0.001 µg ^{99}Tc with the Omni/Guard Low Background beta counter.

METHOD FOR THE DETERMINATION OF GAMMA-ENERGY EMISSION RATE FROM FISSION PRODUCTS IN URANIUM HEXAFLUORIDE

243. Scope

243.1 This proposed test method is applicable to the measurement of gamma fission products in solutions of uranium prepared by the hydrolysis of uranium hexafluoride. It is an alternative to a specifications method **(70)** requiring radiochemical separation of the uranium and ion-chamber measurement of the fission products.

244. Summary of Test Method

244.1 The fission products in a uranium sample are measured nondestructively, with a multichannel energy analyzer, using a germanium-lithium (Ge-Li) or germanium (Ge) detector.

244.2 A solution of the uranium sample is scanned on an energy analyzer and the fission-product peaks are summed. The counts under the peaks are converted to gamma-ray emissions per minute, that are then multiplied by the energy to convert to energy release. These products are summed and divided by the weight of uranium in the sample to calculate total emission in MeV/min/g of uranium.

245. Apparatus

245.1 *Multichannel Energy Analyzer*, 2000 or more channels.

245.2 *Ge-Li or Ge Detector*, with 10 % efficiency (relative to NaI detector) or higher, and resolution of 2.3 keV or less (full width, half maximum) using 1.33 MeV photons. (A sodium iodide detector lacks the resolution required for this method.)

245.3 *Lead Shield for the Detector and Sample*.

245.4 *Printer*.

246. Standards

246.1 Use energy standards to calibrate the efficiency of the detector from 88 to 1836 keV. Suitable standard mixtures of isotopes in units of gamma per minute are available from the National Institute of Standards and Technology.

247. Procedure

247.1 Prepare the sample for counting.

247.2 Scan the sample on an energy analyzer.

247.3 Sum each fission product energy peak and convert the counts to gamma-ray emissons per minute. Determine gamma-ray emissions for each fission product by dividing the count rate of each fission product energy peak by the efficiency of the counting system. Determine the efficiency of the counting system by use of energy calibration standards. A calibration energy curve is plotted as counts per minute per gammas per minute, cpm/γpm, versus energy in keV. The samples should be in solution for best results, but the volume of the sample, type of container, and the distance from the detector must be determined for specific equipment and samples.

247.4 The energies of the fission product^{95}Nb (766 keV) and the^{234}Pa (767 keV) daughter of^{238}U are not resolved. The following method is suggested as a test for the presence of ^{95}Nb:

247.4.1 Measure a sample of aged natural uranium (ANU), at least 8 months old, under the same conditions that a test sample is measured. Sum the counts under the 767 and 1001-keV peaks of ^{234m}Pa. Divide the counts under the 767-keV peak by the counts under the 1001-keV peak to obtain a ratio. Repeat several times for an average ratio.

247.5 The energies of the fission product ^{141}Ce at 145 keV and ^{235}U at 144 keV are not resolved. The following method is suggested to test for the presence of ^{141}Ce:

247.5.1 Measure a sample of ANU under the same conditions that a test sample is measured. Sum the counts under the 186 and 144-keV peaks of ^{235}U. Divide the counts under the 144-keV peak by the counts under the 186-keV peak to obtain a ratio. Repeat several times for an average ratio.

248. Calculation

248.1 The fission-product energy release, F, in MeV per minute per gram of uranium is calculated from:

$$F = \sum_{i=1}^{i=n} D_i \times E_i / G \quad (45)$$

where:

D_i = gamma-ray emissions per minute at energy E_i,
E_i = energy, MeV per photon, and
G = sample weight, g U.

For rapid and efficient calculations, the system should be computer programmed.

248.2 Sum the counts under the 767 and 1001-keV peaks of the test sample and calculate N, the counts due to ^{95}Nb, as follows:

$$N = m - (ay) \quad (46)$$

where:

m = counts under 767-keV peak in test sample,
y = counts under 1001-keV peak in test sample, and
a = average ratio of 767-keV peak to 1001-keV peak in ANU (see 247.4).

248.3 If N is greater than zero, convert N to gamma-ray emissions per minute, and include in the summations in 248.1.

248.4 Sum the counts under the 144 and 186-keV peaks of the test sample and calculate C, the counts due to ^{141}Ce, as follows:

$$C = T - (LH) \quad (47)$$

where:

T = counts under the 144-keV peak in test sample,
L = ratio of 144-keV peak to 186-keV peak in ANU (see 247.5), and
H = counts under the 186-keV peak in test sample.

248.5 If C is greater than zero, convert C to gamma-ray emissions per minute, and include in the summation in 248.1.

249. Precision and Bias

249.1 Insufficient analyses have been made using this proposed test method to enable an appraisal of the precision and bias of the test method.

250. Sensitivity

250.1 The lower limit of detection for the five most probable fission-produce nuclides (^{141}Ce, ^{144}Ce, ^{106}Ru, ^{95}Nb, and^{95}Zr) is expected to be about 500 MeV per minute per gram of uranium. This is equal to about 3 % of the gamma emission rate of ANU. The sensitivity will vary somewhat according to the mass of sample and detector-to-sample distance.

METALLIC IMPURITIES BY ICP-AES

251. Scope

251.1 This test method is applicable to the determination of metallic impurities in uranium hexafluoride.

251.2 The elements determined are aluminum (Al), barium (Ba), beryllium (Be), bismuth (Bi), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), antimony (Sb), tin (Sn), vanadium (V), tungsten (W), zinc (Zn), and zirconium (Zr).

251.3 The detection limits range from 0.01 µg/gU to 0.6 µg/gU depending on the element.

251.4 This test method is also applicable to determination of metallic impurities in U_3O_8 and U-metal with no additional procedure changes.

252. Summary of Test Method

252.1 Uranium oxide, U_3O_8, generated in the pyrohydrolysis of uranium hexafluoride is dissolved in a solution of ammonium fluoride and nitric acid. The uranium is separated from the metallic impurities by solvent extraction using tri (2-ethylhexyl) phosphate diluted with heptane. The aqueous phase containing the metallic impurities is nebulized directly into the inductively coupled argon plasma and the metals are measured by emission spectroscopy **(71, 72)**.

253. Interferences

253.1 Uranium is a spectral interference and must be separated from the elements of interest. A uranium concentration of <100 µg/mL in the analyte solution can be tolerated.

254. Instrumentation and Apparatus

254.1 *Instrumentation*:

254.1.1 *Inductively Coupled Plasma-Emission Spectrometer*—Direct reading (simultaneous) or scanning (sequential) with a spectral bandpass of 0.05 nm or less. Either pneumatic or ultrasonic aerosol generators may be used to introduce the sample solution to the plasma source. An interactive computer based data and control system may be used.

254.1.2 The nebulizer and spray chamber should be resistant to hydrofluoric acid. These should be made of TFE fluorocarbon or polypropylene. A TFE-fluorocarbon-lined sample introduction tube with a sapphire tip is required in the torch assembly.

254.2 *Apparatus*:

254.2.1 *Peristaltic pump*.

254.2.2 *Beakers and lids*, TFE-fluorocarbon, 50 mL.

254.2.3 *Sample analysis tubes*, graduated, plastic, 50 mL.

254.2.4 *Separatory funnels*, TFE-fluorocarbon, 125 mL.

255. Reagents

255.1 *Argon*—High purity gas derived from the head space gas over the liquid in a liquid argon cylinder is recommended.

255.2 *Ammonium Fluoride (1 % W/V)*—Dissolve 1.0 g of ammonium fluoride in 100 mL of water. Store in a plastic bottle.

255.3 *Nitric Acid (sp. gr. 1.42)*—Concentrated nitric acid (HNO_3).

255.4 *Nitric Acid (8M)*—Add 1 volume of concentrated HNO_3 to an equal volume of water.

255.5 *Nitric Acid (1.6M)*—Add 1 volume of concentrated HNO_3 to 9 volumes of water.

255.6 *Tri(2-ethylhexyl) phosphate* $[(C_8H_{17}O)_3PO]$—Technical grade (TEHP).

255.7 *Heptane* $[CH_3(CH_2)_5CH_3]$.

255.8 *TEHP-Heptane Solution (1:1 V/V), purified*—Add 25 mL TEHP to a 250 mL separatory funnel and dilute with 25 mL heptane. Add 75 mL of 8M HNO_3 to the funnel, stopper, and shake for 2 min. Discard the acid layer and retain the TEHP-heptane in the separatory funnel. This purification step is carried out immediately before use.

255.9 *Calibration Solutions*—Prepare several compatible multi-element standard solutions in 4M nitric acid by adding appropriate volumes of single element stock solutions prepared by dissolving metals or metal salts of high purity. Commercial stock solutions may be used but should be verified. Calibration solutions with Zr should contain 1 % hydrofluoric acid by volume. Element concentration range of the solution should be 1 to 100 µg/mL.

NOTE 38—To avoid precipitation of alkaline earth fluorides, do not mix multielement standard solutions with Zr solutions. Compatibility of mixing commercial stock solution should be verified.

255.10 *Uranium Oxide Standards*—U_3O_8 standards containing metallic impurities.

255.11 *Uranium Oxide* (U_3O_8)—High purity to be used as a blank. See Appendix X3for preparation procedure.

256. Preparation of Apparatus

256.1 A set of suggested instrument operating parameters are given in Table 14. Operating parameters will vary with the type of instrument and the manufacturer's instructions should be followed.

TABLE 14 Suggested Instrument Operating Parameters for ICP-AES Analysis

Argon Gas Flows	Coolant 21 L/min Plasma 0.6 L/min Nebulizer 0.4 L/min
RF Power	Forward 1100 W Reverse <10 W
Vertical Observation Zone	16 mm above the load coil
Integration Time	2 × 7 s on-line 1 × 7 s on-background
Nebulizer	Fixed cross flow Solution uptake 1 mL/min
Peristaltic Pump	Solution uptake 1.1 mL/min

256.2 A set of suggested analytical wavelengths is given in Table 15.

257. Calibration

257.1 *Calibration*:

257.1.1 Nebulize the multielement standard solutions, (see 255.9) to calibrate the instrument.

NOTE 39—The linear dynamic range should be established for each analytical channel and should cover the range expected in the samples.

257.1.2 Prepare calibration curves if automatic data processing equipment is not available.

258. Procedure

258.1 *Sample Preparation*:

258.1.1 Weigh a U_3O_8 sample containing 2 g of uranium to 0.001 g into a 50 mL TFE-fluorocarbon beaker.

NOTE 40—U_3O_8 sample from the pyrohydrolysis of UF_6 as described in 17.33.

258.1.2 Add 10 mL of concentrated HNO_3 and 3 mL of 1 % NH_4F solution to the sample.

TABLE 15 Suggested Wavelengths for ICP Analysis

Element	Wavelength, nm	Alternate Wavelength, nm
Al	308.2	...
Ba	455.4	493.4
Be	313.0	...
Bi	223.1	...
Ca	393.3	317.9
Cd	228.8	226.5
Co	228.6	...
Cr	205.6	267.7
Cu	324.8	...
Fe	259.9	...
Mg	279.6	280.3
Mn	257.6	...
Mo	202.0	204.6
Na	589.0	...
Nb	316.3	...
Ni	231.6	...
Pb	220.4	...
Sb	217.6	...
Sn	190.0	...
Ta	222.2	228.9
Ti	334.9	...
V	292.4	...
W	207.9	224.9
Zn	213.9	...
Zr	343.8	339.2

258.1.3 Cover the beaker with a TFE-fluorocarbon lid and heat the sample at 100°C for 10 min. After the sample dissolves, cool the solution.

258.1.4 Add 10 mL of water and mix the solution. Transfer the sample to a 125 mL separatory funnel containing 50 mL of the purified TEHP-heptane solution. Wash the beaker with 1 to 2 mL of 8M HNO_3 and add the washings to the separatory funnel.

258.1.5 Stopper the separatory funnel and shake the funnel for 2 min. Allow the phases to separate.

258.1.6 Drain the aqueous phase into another 125 mL separatory funnel containing 50 mL of purified TEHP-heptane. Stopper and shake for 2 min. Allow the phases to separate.

258.1.7 Drain the aqueous phase into a graduated analysis tube and dilute to 40 mL with water. Cap the tube and mix thoroughly.

258.1.8 Run a series of U_3O_8 standards and a U_3O_8 blank using the above procedure.

258.2 *Measurement*:

258.2.1 Nebulize the extracted uranium blank and standards to verify chemical preparation and extraction efficiency and to establish a reagent blank.

258.2.2 Nebulize extracted sample solutions from 258.1.7.

259. Calculation

259.1 If automatic data processing is not available to calculate the metal concentrations on a uranium basis the calculation is as follows:

$$\text{Metal, µg/gU} = A \times 40/W(0.848) \tag{48}$$

where:

A = micrograms of metal per mL of the measured solution corrected for reagent blank,

W = weight of U_3O_8, in g.

260. Precision and Bias

260.1 *Precision*—The single operator and within laboratory precision of this method are shown in Table 16. Two precision estimates were made using the same U_3O_8 standard. The first estimate was based on eight separate determinations and the second estimate was based on five separate determinations.

TABLE 16 Analysis of Mallinckrodt U_3O_8—Standard A by ICP-AES

Element	µg Element/g U				
	Certified Value	Mean and Standard Deviation			
		Run 1		Run 2	
Al	64	64	8	64	2
Ba	61	61	3	63	2
Be	4.9	4.9	0.4	5.4	0.2
Bi	4.9	4.9	0.3	4.5	0.4
Ca	53	53	3	59	2
Cd	0.6	0.6	0.1	0.7	0.2
Cr	47	47	3	50	3
Cu	7.8	7.8	0.9	8.9	1
Fe	43	43	2	48	2
Mg	10	10	0.8	12	2
Mn	5	4.9	0.5	5.2	0.4
Ni	69	69	4	75	4
Sn	30	28	6	26	3
Zn	13	13	3	19	3

260.2 *Bias*—A New Brunswick Laboratory reference material set (CRM No. 123, 18 Element Impurity Standard) was analyzed by this test method. Single analyses were made on CRM 123 (1-3) and duplicate analyses were made on CRM 123 (4-6). A comparison of the results to the reference values are shown in Table 17 and Table 18. Although the data are insufficient to establish an estimate of bias for the test method, the results compare very well with the reference values and fall within the range established by an inter-laboratory measurement program **(73)**.

MOLYBDENUM, NIOBIUM, TANTALUM, TITANIUM, AND TUNGSTEN BY ICP-AES

261. Scope

261.1 This test method is applicable to the determination of molybdenum, niobium, tantalum, titanium, and tungsten in uranium hexafluoride.

261.2 The limit of detection for each element is 0.1 µg/gU.

262. Summary of Test Method

262.1 Molybdenum, niobium, tantalum, titanium, and tungsten are separated from uranium by solvent extraction as their benzoylphenylhydroxylamine (BPHA) complexes into chloroform **(17)**. The extract is evaporated to dryness and then wet ashed with nitric acid and sulfuric acid. The residue is ignited at 600°C and then dissolved in a mixture of hydrochloric and hydrofluoric acids and diluted with water. The solution is nebulized into an inductively coupled argon plasma and the metals are measured by emission spectroscopy **(74, 71)**.

263. Interferences

263.1 Uranium is a spectral interference and must be separated from the elements of interest. A uranium concentration of <100 µg/mL in the analyte solution can be tolerated.

264. Instrumentation and Apparatus

264.1 *Instrumentation*:

264.1.1 *Inductively Coupled Plasma-Emission Spectrometer*—Direct reading (simultaneous) or scanning (sequential) with a spectral bandpass of 0.05 nm or less. Either

TABLE 17 Analysis of NBL-CRM 123, U_3O_8 by ICP-AES

Element	Standard, µg Element/gU					
	123-1		123-2		123-3	
	Ref.	Found	Ref.	Found	Ref.	Found
Al	205	200	105	110	55	65
B	5.1	4.8	2.6	2.5	1.1	1.0
Cd	5.2	4.5	2.7	2.3	1.2	0.9
Ca	200	213	100	113	51	58
Cr	102	114	52	60	22	25
Cu	50	50	25	26	10.4	11
Fe	210	206	110	114	60	60
Pb	51	50	26	26	10.8	11
Mg	101	100	51	60	21	26
Mo	100	95	50	48	20	19
Ni	202	211	102	110	52	54
Na	400	362	200	187	100	99
Sn	51	50	26	26	11	10
V	50	48	25	24	10	9
Zn	202	223	102	116	52	58

TABLE 18 Analysis of NBL-CRM 123, U_3O_8 by ICP-AES

Element	Standard, µg Element/gU					
	123-4		123-5		123-6	
	Ref.	Found	Ref.	Found	Ref.	Found
Al	24	28	14	17	9	9
B	0.7	0.6	0.4	0.3	0.3	0.4
Cd	0.5	0.4	0.25	0.2	0.1	0.25
Ca	20	28	10	15	5	8
Cr	15	14	10	8	7	5
Cu	5	5	2.5	2.8	1	1
Fe	28	30	18	20	13	14
Pb	5	5	2.5	3	1	1.3
Mg	10	14	5	8	2	4
Mn	5	6	2.5	2.9	1	1
Ni	20	22	10	12	5	6
Na	30	43	20	19	10	12
Sn	5	7	2.5	2.5	1	1.5
V	5	4	2.5	1.8	1	0.4
Zn	20	22	10	12	5	6
Zr	20	24	10	12	5	7

pneumatic or ultrasonic aerosol generators may be used to introduce the sample solution to the plasma source. An interactive computer based data and control system may be used.

264.2 *Apparatus*:

264.2.1 *Peristaltic pump*,

264.2.2 *Platinum dishes with lids*, 75 and 250 mL

264.2.3 *Separatory funnels with TFE-fluorocarbon stopcocks*, 250 mL

264.2.4 *Beakers and lids*, TFE-fluorocarbon, 250 mL

264.2.5 *Graduates*, plastic, 50 mL

264.2.6 *Sample analysis tubes*, graduated, plastic, 50 mL

264.2.7 *Automatic shaker with clamps*, to hold 250 mL separatory funnels.

265. Reagents

265.1 *Boric Acid Solution (10 %)*—Dissolve 100 g of boric acid, H_3BO_4, in 800 mL of hot water and dilute to one liter with water. Store this solution at 60°C.

265.2 *Ethyl Alcohol (C_2H_5OH)*, absolute.

265.3 *N-Phenylbenzohydroxamic Acid Solution (2 %)*—Dissolve 20 g n-phenylbenzohydroxamic acid (BPHA) in 1 L of ethyl alcohol.

265.4 *Chloroform ($CHCl_3$).*

265.5 *Hydrochloric Acid (sp. gr. 1.19)*—Concentrated hydrochloric acid (HCl).

265.6 *Hydrofluoric Acid (48 %)*—Concentrated hydrofluoric acid (HF).

265.7 *Hydrofluoric Acid (2M)*—Add 83 mL of concentrated HF to 1 L with water. Store in a plastic bottle.

265.8 *Nitric Acid (sp. gr. 1.42)*—Concentrated nitric acid (HNO_3).

265.9 *Sulfuric Acid (sp. gr. 1.84)*—Concentrated sulfuric acid (H_2SO_4).

265.10 *Hydrochloric Acid—Hydrofluoric Acid Solution (1:5 V/V)*—Add one volume of concentrated hydrochloric acid (HCl) to five volumes of concentrated hydrofluoric acid (HF).

265.11 *Element Standard Stock Solutions (100µ g/mL)*—Dissolve 0.1000 g of high purity metal powder in 5 mL concentrated HF. Add concentrated HNO_3 dropwise to aid the dissolution. Dilute to 1.00 liter with 2*M* HF.

265.12 *Element Standard Solutions (10 µg/mL)*—Aliquot 100 mL of each standard stock solution into a one liter plastic volumetric flask and dilute to volume with 2*M* HF.

265.13 *Element Calibration Standards (0.1, 0.5, 1.0, and 5.0µ g/mL)*—Aliquot 1, 5, 10, and 50 mL of each element standard stock solutions into 4 one-liter plastic volumetric flasks. Add 25 mL of concentrated HNO_3 to each flask and dilute to volume with water.

265.14 *Uranium Standard Solution (100 g U/L)*—Dissolve 117.9 g of pure U_3O_8 with 100 mL of 8*M* HNO_3. Dilute to 1 L with water.

266. Preparation of Apparatus

266.1 A set of suggested instrument operating parameters are shown in Table 14. Operating parameters will vary with the type of instrument and the manufacturer's instructions should be followed.

266.2 A set of suggested analytical wavelengths are given in Table 15.

267. Calibration and Standardization

267.1 *Uranium Calibration Standards*:

267.1.1 Pipet two 50-mL aliquots of the 100 gU/L uranium standard solution into separate 250-mL TFE fluoro-carbon beakers.

267.1.2 Spike one uranium aliquot with 1 mL of the 10 µg/mL element standard solution, 146.12. The other uranium aliquot will be used as a blank.

267.1.3 Add 10 mL of concentrated HF to each solution.

267.1.4 Follow the procedure from 268.1.2 through 268.1.13.

267.2 *Calibration*:

267.2.1 Nebulize the multi-element standards 265.13 to calibrate the instrument.

NOTE 41—The linear dynamic range should be established for each analytical channel and should cover the range expected in the samples.

267.2.2 Prepare calibration curves if automatic data processing equipment is not available.

267.3 *Measurement*:

267.3.1 Nebulize the extracted uranium blank and standard to verify the chemical preparation, extraction and to establish a reagent blank.

267.3.2 Nebulize the extracted sample solutions.

268. Procedure

268.1 *Sample Preparation*:

268.1.1 Transfer an aliquot of UO_2F_2 solution containing 10 g of U to a 250 mL TFE fluorocarbon beaker.

NOTE 42—UF_6 sample hydrolyzed as described in 10.6.

268.1.2 Add 50 mL of 10 % boric acid solution to the beaker and mix thoroughly.

268.1.3 Transfer the sample solution to a 250 mL separatory funnel.

268.1.4 Add 5 mL of the 2 % BPHA-ethyl alcohol solution and mix. Allow the solution to stand for 10 min.

268.1.5 Add 20 mL of chloroform, stopper, and shake for 10 min using an automatic shaker.

268.1.6 Allow the layers to separate and drain the chloroform layer into a 75 mL platinum dish.

268.1.7 Evaporate the chloroform extract to dryness on a hot plate at about 80°C.

NOTE 43—Direct a gentle stream of air over the surface to aid evaporation and keep the solution from creeping.

268.1.8 Add 2 to 3 mL of concentrated HNO_3 to the residue. Wait until the residue turns black.

268.1.9 Add 0.5 mL of concentrated H_2SO_4 and evaporate to dryness.

268.1.10 Cover the platinum dish with a lid and ignite the residue at 600°C for 1 h.

268.1.11 Dissolve the residue in 1 mL the HCl-HF mixture by heating the solution gently.

268.1.12 Transfer the solution to a 50 mL analysis tube.

268.1.13 Add 1 mL of concentrated HNO_3 and dilute to 40 mL with water.

269. Calculation

269.1 If automatic data processing is not available, calculate the metal concentrations on a uranium basis. The calculation is as follows:

$$\text{Metal } \mu\text{g/gU} = \frac{A \times 40}{W} \qquad (49)$$

where:

A = micrograms of metal per mL of the measured solution corrected for reagent blank.

W = weight of U in UO_2F_2 aliquot (147.1.1).

270. Precision and Bias

270.1 *Precision*—The single operator and within laboratory precision of this method is shown in Table 19. These estimates are based on four separate analyses on uranyl fluoride solutions containing 10 g of U spiked at two levels.

270.2 *Bias*—Since there is no accepted reference material for determining bias in these test methods for measuring Mo, Nb, Ta, Ti, and W in UF_6, no statement of bias is being made.

271. Keywords

271.1 analytical methods; mass spectrometry; radiochemistry; uranium hexafluoride

TABLE 19 Precision Estimates for ICP-AES Analysis

Concentration	Relative Standard Deviation, %				
µ g/gU	Mo	Nb	Ta	Ti	W
1.0	6.0	7.3	6.2	9.3	7.4
2.0	3.4	5.4	4.4	3.4	5.6

APPENDIX

(Nonmandatory Information)

X1. LIST OF ALTERNATIVE STAND ALONE ASTM TEST METHODS

C 1219 Arsenic in UF_6

C 1287 Impurities in UO_2 by ICP-MS

Elements measured include Li, Be, Mg, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Ru, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Rh, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, Tc-99, B, Na, Si, P, K, and Ca

C 1295 Gamma Energy Emission from Fission Products in Uranium Hexafluoride

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