



Standard Guide for Determination of Plutonium and Neptunium in Uranium Hexafluoride by Alpha Spectrometry¹

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1. Scope

1.1 This method covers the determination of plutonium and neptunium isotopes in uranium hexafluoride by alpha spectroscopy. The method could also be applicable to any matrix that may be converted to a nitric acid system.

1.2 *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 requirements prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

C 787 Specification for Uranium Hexafluoride for Enrichment²

C 996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ²³⁵-U²

C 1163 Test Method for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride²

C 1475 Guide for the Determination of Neptunium-237 in Soil²

D 1193 Specification for Reagent Water³

D 3084 Practice for Alpha-Particle Spectrometry of Water⁴

D 3648 Practices for the Measurement of Radioactivity⁴

3. Terminology

3.1 *reagent blank*—DI water processed the same as the samples; used in the determination of the minimum detectable activity.

3.2 *region-of-interest (ROI)*—the channels, or region, in the alpha spectra in which the counts due to a specific radioisotope appear on a functioning calibrated alpha spectrometry system.

4. Summary of Test Method

4.1 An aliquot of hydrolyzed uranium hexafluoride equivalent to approximately 0.5 g of uranium is converted to an oxalic acid-nitric acid system and the uranium is selectively removed via solid phase extraction. Plutonium and neptunium are further purified by additional solid phase extractions. The plutonium and neptunium are then co-precipitated with neodymium as the fluorides and counted by alpha spectrometry.

4.2 Tracer recoveries using this method are typically between 75 and 90 %. The resolution of the tracer is typically less than 40 keV full-width at half-maximum.

4.3 The minimum detectable activity will vary with tracer recovery, sample size, instrument background, and counting efficiency.

5. Significance and Use

5.1 The method is applicable to the analysis of materials to demonstrate compliance with the specifications set forth in Specifications C 787 and C 996.

6. Interferences

6.1 Incomplete removal of U-234 from the neptunium fraction could result in a false positive for the Np-237 analysis. The method has been shown to adequately remove uranium at enrichments up to 5 %. If the method is used for the analysis of materials at greater than 5 % enrichment, a blank consisting of uranium at the same enrichment as the samples should be analyzed to show adequate removal of the U-234.

6.2 A Pu tracer is used to monitor the chemical recovery of the Np. Spiked analyses should be performed to confirm the appropriateness of this correction; fractionation of Np and Pu during the separation could lead to incorrect test results.

7. Instrumentation

7.1 *Alpha Spectrometry System*—See Practices D 3084 and D 3648 for a description of the apparatus.

8. Apparatus

8.1 *Ion Exchange Columns*, able to hold a 10 mL resin bed and 15 mL solution washes.

¹ This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on 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.

⁴ *Annual Book of ASTM Standards*, Vol 11.02.

8.2 *Filter Paper*, 0.1 µm pore size, 25-mm diameter, compatible with HF.⁵

9. Reagents and Materials

9.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁶

9.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined in Specification D 1193.

9.3 *Ammonium Oxalate (0.1M)*—Dissolve 12.4 g ammonium oxalate in approximately 500 mL of water and dilute to 1 L.

9.4 *Ascorbic Acid Solution (Saturated)*—Add ascorbic acid to 2M nitric acid while stirring until no more ascorbic acid will dissolve. Prepare fresh when needed for use.

9.5 *Ethanol*, ethyl alcohol, absolute (200 proof), denatured.

9.6 *Hydrochloric Acid (HCl)*, specific gravity 1.19, concentrated.

9.7 *Hydrochloric Acid, 9M*—Add 750 mL concentrated HCl to 100 mL of water, dilute to a final volume of 1 L.

9.8 *Hydrochloric Acid, 4M*—Add 333 mL of concentrated HCl to 500 mL of water; dilute to a final volume of 1 L.

9.9 *Hydrochloric Acid, 1.5M*—Add 125 mL of concentrated HCl to 500 mL of water; dilute to a final volume of 1 L.

9.10 *Hydrochloric Acid, 1M*—Add 83 mL of concentrated HCl to 500 mL of water; dilute to a final volume of 1 L.

9.11 *Hydrofluoric Acid (HF)*, concentrated HF, minimum assay 48 %.

9.12 *Iron (III) Nitrate (10 mg Fe/mL)*—Dissolve 18.0 g of Fe(NO₃)₃·9H₂O in 250 mL of water.

9.13 *Neodymium Chloride (10 mg Nd/mL)*—Add 25 mL concentrated HCl to 1.17 g neodymium oxide and heat at 100°C until dissolved. Allow solution to cool and dilute to 100 mL with water.

9.14 *Neodymium Chloride (100 µg Nd/mL)*—Dilute 1 mL of the 10 mg Nd/mL solution to 100 mL with water.

9.15 *Nitric Acid (HNO₃)*, concentrated nitric acid, specific gravity 1.42.

9.16 *Nitric Acid (3M)*—Add 188 mL concentrated nitric acid to 500 mL of water; dilute to a final volume of 1 L.

9.17 *Nitric Acid (2M)*—Add 125 mL of concentrated nitric acid to 500 mL of water; dilute to a final volume of 1 L.

9.18 *Oxalic Acid in 1M HCl (0.1M)*—Dissolve 12.6 g oxalic acid dihydrate in 500 mL of 1M HCl; dilute to a final volume of 1 L with 1M HCl.

9.19 *Oxalic Acid in 2M HNO₃ (0.1M)*—Dissolve 12.6 g oxalic acid dihydrate in 500 mL of 2M HNO₃; dilute to a final volume of 1 L with 2M HNO₃.

9.20 *Pu-236 or Pu-242 Tracer*, traceable to a national or international standard.

9.21 *Sodium Nitrite (100 mg/mL)*—Dissolve 500 mg NaNO₂ in 5 mL water. Prepare fresh when using.

9.22 *Extraction Chromatography Resin*, containing octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP) as the immobilized extractant.^{7,8}

9.23 *Extraction Chromatography Resin*, containing diamyl amylphosphonate (DAAP) as the immobilized extractant.^{9,10}

10. Calibration and Standardization

10.1 The alpha spectrometry units should be calibrated for energy, resolution and efficiency according to the manufacturers instructions. The background counting rate for the instrument should be measured at a frequency determined by the user. See Practices D 3084 and D 3648 for additional information.

11. Procedure

11.1 Uranium Removal:

11.1.1 Pipette an aliquot of hydrolyzed UF₆ sample equivalent to 0.5 g uranium into a beaker. Add the Pu tracer to the sample and evaporate to dryness. Add 10 mL concentrated nitric acid and evaporate to dryness. *Option:* Neptunium-239 can be added as an independent tracer for the Np-237; see Guide C 1475 for its use.

11.1.2 Prepare 2 DAAP extraction columns per sample by adding resin slurred in water to the column. Allow the water to drain to obtain a 10 mL bed volume. Condition the columns by adding 15 mL of the oxalic acid in 2M nitric acid solution. Allow the solution to pass through the columns.

11.1.3 Dissolve the sample residue in the beaker above by adding 15 mL of the oxalic acid in 2M nitric acid solution. Heat gently to complete the dissolution. Add the sample to the first of the extraction columns and collect the load solution in a clean beaker. Add an additional 15 mL of the oxalic acid in 2M nitric acid solution to the column and collect the rinsate in the same beaker.

NOTE 1—The column retains the U; Pu and Np will pass through in the load and rinse solutions.

11.1.4 Add the combined solutions from the two steps above to the second DAAP extraction column. Collect the load solution in a clean beaker. Rinse the column with 15 mL of the oxalic acid in 2M nitric acid solution and collect in the same beaker.

11.1.5 Evaporate the combined solution from above to dryness. Add 10 mL of concentrated nitric acid to the beaker and evaporate to dryness.

NOTE 2—Elute the uranium from the DAAP columns by adding 40 mL of 0.1M ammonium oxalate. Dispose of the eluant containing the uranium according to site specific disposal procedures.

⁷ Horwitz, E. P., Chiarizia, R., Dietz, M. L., Diamond, H., and Nelson, D., "Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography," *Analytica Chimica Acta*, 281, 1993, pp. 361-372.

⁸ TRU resin from EIChroM Industries, Darien IL, USA, has been found to be acceptable.

⁹ Horwitz, E. P., Dietz, M. L., Chiarizia, R., Diamond, H., Essling, A. M., and Graczyk, D., "Separation and Preconcentration of Uranium from Acidic Media by Extraction Chromatography," *Analytica Chimica Acta*, 266, 1992, pp. 25-37.

¹⁰ U-TEVA resin from EIChroM Industries, Darien IL, USA, has been found to be acceptable.

⁵ The Gelman Metrical filter has been found to be acceptable.

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington DC.

11.2 Preparation of Plutonium and Neptunium for Counting:

11.2.1 Dissolve the residue from above in 10 mL of 3M nitric acid by gently heating. Add 1 mL of the 10 mg Fe/mL solution and 2.5 mL of the saturated ascorbic acid solution to the sample.

NOTE 3—The ascorbic acid reduces the Fe from [+3] to [+2]; the Fe then serves to reduce the Pu from [+4] to [+3] and the Np from [+5] to [+4].

11.2.2 Prepare one CMPO-TBP extraction column per sample by loading 2 mL of resin per column.¹¹ Condition the column by adding 5 mL of 3M nitric acid to the column and allowing it to drain completely through.

11.2.3 Add the sample to the column and allow it to pass through the column. Rinse the column with 5 mL of 3M nitric acid. Discard all the rinses.

11.2.4 Add 0.1 mL of the 100 mg/mL sodium nitrite solution to 5 mL of 2M nitric acid and swirl to mix. Add this solution to the column.

NOTE 4—The sodium nitrite oxidizes the Pu from [+3] to [+4].

11.2.5 Rinse the column with 10 mL of 2M nitric acid.

11.2.6 Rinse the column, in succession, with 5 mL 9M HCl (crossover solvent), 10 mL 4M HCl (elutes Am) and 35 mL 1.5M HCl (elutes Th). Discard all the rinses.

11.2.7 Place a PTFE beaker under the column. Elute the plutonium and neptunium by adding 15 mL of the oxalic acid in 1M HCl solution.

11.3 Preparation for Counting:

NOTE 5—Refer to Test Method C 1163 for additional guidance.

11.3.1 Add 0.5 mL of the 100 µg Nd/mL solution and 1 mL of concentrated HF to the Np and Pu fraction from above and mix. Allow the sample to sit for 30 min.

11.3.2 Place a 0.1 µm, 25-mm diameter filter on a vacuum flask. Rinse the filter first with ethanol and then with water.

11.3.3 Pour the sample through the filter. After the sample solution has passed through the filter rinse the filter with water and then with ethanol, allowing each solution to pass com-

pletely prior to the next one. Remove the filter from the flask and dry under a heat lamp.

11.3.4 Count the sample in a calibrated alpha spectrometry system for an appropriate amount of time.

11.3.5 Confirm the removal of uranium by examining the U-238 region of the alpha spectrum. If detectable uranium remains the Np-237 must be corrected for the U-234 in the same region, or the sample should be re-extracted.

12. Calculations

12.1 Calculation of Tracer Yield:

$$Y = (G_t - B_t) / (E \cdot A_t) \quad (1)$$

where:

Y = chemical yield,

G_t = gross counts per second in the Pu tracer ROI,

B_t = background counts per second in the Pu tracer ROI,

E = detector counting efficiency (cps/dps), and

A_t = activity of the Pu tracer in Bq (dps).

12.2 Calculation of Activity:

The following equation is used to calculate the activity in the sample including any possible reagent blank:

$$A_i = [(G_i - B_i) / (G_r - B_r)] \cdot [A_r / (AB_i \cdot W)] \quad (2)$$

where:

A_i = activity of isotope of interest in Bq per gram U (Pu-238, Pu-239+240, Np-237),

G_i = gross counts per second in the analyte ROI,

B_i = background counts per second in the analyte ROI,

AB_i = abundance of alpha decay in ROI, expressed as a fraction, and

W = weight of U analyzed, g.

Additional calculations, including reagent blank subtraction, can be found in Practice D3084.

12.3 Calculation of Minimum Detectable Activity:

$$MDA_i = (4.65 \cdot S_B + 2.71) / (E \cdot Y \cdot T \cdot AB_i \cdot W) \quad (3)$$

where:

MDA = minimum detectable activity (Bq/g),

S_B = standard deviation of the reagent blank counts, and

T = counting time, s.

13. Keywords

13.1 alpha spectrometry; neptunium; plutonium; uranium hexafluoride

¹¹ The prepacked TRU column available from EIChroM Industries has been found to be acceptable.

APPENDIX

(Nonmandatory Information)

X1.

X1.1 This method does not have sufficient data to be qualified as a Standard Method for ASTM but is offered as a Guide for those wishing options for the analysis of Pu and Np in UF₆. At present there are no Certified Reference Materials available from the national standards bodies to provide a complete Precision and Bias statement, however the information below is offered as an example of data produced following this Guide.

X1.2 Twenty samples of UF₆ were spiked at the 0.01 Bq/g (0.27 pCi/g) level with Np-237 and with Pu-239 and analyzed to give an indication of the precision and bias. The relative standard deviation of the 20 results was determined to be 15 % and 14 % for Np-237 and Pu-239, respectively, as an indication of precision. The percent recovery was 103 % and 98 % for Np-237 and Pu-239, respectively, as an indication of bias.

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