



Standard Practice for The Ion Exchange Separation of Uranium and Plutonium Prior to Isotopic Analysis¹

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1. Scope

1.1 This practice is for the ion exchange separation of uranium and plutonium from each other and from other impurities for subsequent isotopic analysis by thermal ionization mass spectrometry. Plutonium-238 and uranium-238, and plutonium-241 and americium-241, will appear as the same mass peak and must be chemically separated prior to analysis. Only high purity solutions can be analyzed reliably using thermal ionization mass spectrometry.

1.2 *This standard may involve hazardous material, operations, and equipment. 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 consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

C 698 Standard Test Method for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ((U, Pu)O₂), Sections 141-149.²

C 833 Standard Specification for Sintered (Uranium, Plutonium) Dioxide Pellets.²

C 1008 Standard Specification for Sintered (Uranium, Plutonium) Dioxide Pellets - Fast Reactor Fuel.²

C 1168 Standard Practice for Preparation and Dissolution of Plutonium Materials for Analysis.²

E 267 Standard Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances.³

3. Summary of Practice

3.1 Solid samples are dissolved according to Practice C 1168 or other appropriate methods. The resulting solution is processed by this practice to prepare separate solutions of plutonium and uranium for mass spectrometric isotopic analysis using Method C 698, see Sec. 144 through 145 and 147.4

through 149 or its replacement. Appropriate aliquants are taken to provide up to 1 mg of plutonium on the ion exchange column to be separated from 10 mg or less of uranium. Valence adjustment is obtained by using one of two procedures as described in 3.1.1 and 3.1.2 or by an alternative method demonstrated by the user to perform the equivalent reduction/oxidation procedure.⁴

3.1.1 For any sample type, especially those containing large amounts of impurities, ferrous sulfate may be used for reduction. The aliquant is dissolved in 3 M HNO₃. Ferrous sulfate is added to reduce all plutonium (VI) to plutonium (III), then 16 M HNO₃ is added to oxidize plutonium (III) to plutonium (IV), and to adjust the final acid concentration to 8 M HNO₃.

3.1.2 A hydrogen peroxide reduction may be used for relatively pure samples which do not contain excessive amounts of oxidizing impurities. The aliquant is dissolved in 8 M HNO₃. Hydrogen peroxide is added to the aliquant prior to fuming to reduce plutonium (VI) to the lower oxidation states. The solution is warmed on a hot plate to destroy excess hydrogen peroxide and stabilize plutonium (IV) in solution.^{5,6}

3.2 After valence adjustment, the resulting solution is passed through an anion exchange column in the nitrate form which retains the plutonium; uranium and americium are not absorbed. The adsorbed plutonium is washed with additional 8 M nitric acid (HNO₃) to remove impurities and then stripped from the column with 0.36 M hydrochloric acid (HCl) and 0.01 M hydrofluoric acid (HF). The effluent containing the uranium and americium is converted to a HCl medium, and this solution is passed through an anion exchange column in the chloride form which retains the uranium. The adsorbed uranium is washed with additional concentrated HCl to remove the impurities and then stripped from the column with 0.1 M HCl.

4. Significance and Use

4.1 Uranium and plutonium are used in nuclear reactor fuel and must be analyzed to insure that they meet certain criteria for isotopic composition as described in Specification C 833

¹ This practice 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 12.02.

⁴ Reduction of all higher plutonium oxidation states to plutonium (III) by the addition of hydroxylamine or NH₂ClO₄, followed by oxidation to plutonium (IV) by sodium nitrite and subsequent boiling to eliminate the nitrous fumes has been found to be acceptable. This method avoids the addition of Fe, which could interfere with electrodeposition of mass spectrometric samples.

⁵ I.V. Kressin and G.R. Waterbury, *Anal. Chem.* 34(12), 1598 (1962).

⁶ C.E. Pietri, B.P. Freeman, and J.R. Weiss, *DOE/NBL-298*, September 1981.

and Specification C 1008. This standard practice is used to chemically separate the same mass peak interferences from uranium and plutonium and from other impurities prior to isotopic abundance determination by thermal ionization mass spectrometry.

4.2 In those facilities where perchloric acid use is tolerated, the ion exchange separation procedure in Test Method E 267 may be used prior to isotopic abundance determination. Also, in those facilities where perchloric acid use is tolerated and when uranium and plutonium concentrations are to be determined as well as isotopic abundances using the thermal ionization mass spectrometer, the ion exchange separation procedure in Test Method E 267 may be used.

5. Interferences

5.1 The separated heavy element fractions placed on mass spectrometric filaments must be very pure. The quantity required depends upon the sensitivity of the instrument detection system. Chemical purity of the sample becomes more important as the sample size decreases, because the ion emission of the sample is repressed by impurities.

5.2 Organics from ion exchange resin degradation products, if present, could affect the response of the mass spectrometer during the plutonium and uranium isotopic abundance measurements. Evaporation of the samples with concentrated nitric acid after the ion exchange separation has been found to destroy any resin degradation products.

5.3 The use of hydrogen peroxide for valence adjustment, when possible, avoids the addition of iron, an element which is not cleanly removed from uranium by HCl ion exchange.

5.4 Elemental impurities, especially alkali elements, tend to produce unstable ion emission and alter observed ratios in an unpredictable manner.

5.5 Isobaric impurities or contaminants will alter the observed isotopic ratios; most notable of these for plutonium are americium-241 and uranium-238; the most notable isobaric impurity for uranium is plutonium-238.

5.6 Extreme care must be taken to avoid contamination of the sample by environmental uranium. The level of uranium contamination should be measured by analyzing an aliquant of 8 M HNO₃ reagent as a blank taken through the same chemical processing as the sample and computing the amount of uranium it contains.

6. Apparatus

6.1 *Ion Exchange Columns*—Disposable, 0.9 cm id × 3 cm with a 15 mL reservoir⁷.

6.2 *Beakers or Alternate Acceptable Containers*—pretreated, 20-30 mL, borosilicate glass. To avoid cross contamination, use only new borosilicate glass containers pretreated by heating in 4 M HNO₃ to leach uranium, rinsed in deionized water, and air or oven dried prior to use.

6.3 *Infrared Heating Lamps*⁸ or Hot Plate with adjustable low and high heat settings.

6.4 *Transfer Pipets*—Disposable.

7. Reagents

7.1 Reagent grade or better chemicals should be used. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society⁹ where such specifications are available. Other grades of reagents may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of measurements made on the prepared materials. Store solutions in appropriate polyethylene or glass bottles except as noted.

7.2 *Water*—Unless otherwise indicated, references to water shall be understood to mean laboratory accepted demineralized or deionized water.

7.3 *Nitric Acid (sp gr 1.42), 15.9 M*—concentrated nitric acid (HNO₃).

7.4 *Nitric Acid, 8 M*—Add 500 mL of HNO₃ (sp gr 1.42) to about 400 mL of water and dilute to 1 L.

7.5 *Nitric Acid, 4 M*—Add 250 mL of HNO₃ (sp gr 1.42) to about 700 mL of water and dilute to 1 L with water.

7.6 *Nitric Acid, 3 M*—Add 187 mL of HNO₃ (sp gr 1.42) to about 750 mL of water and dilute to 1 L with water.

7.7 *Hydrochloric Acid (sp gr 1.19), 12.1 M*—concentrated hydrochloric acid (HCl).

7.8 *Hydrofluoric Acid (sp gr 1.18), 28.9 M*—concentrated hydrofluoric acid (HF).

7.9 *Hydrochloric Acid, 0.1 M*—Add 8 mL of HCl (sp gr 1.19) to about 900 mL of water and dilute to 1 L with water.

7.10 *Stripping solution (0.36 M HCl, 0.01 M HF)*—Add 30 mL of HCl (sp gr 1.19) and 0.4 mL HF (sp gr 1.18) to about 900 mL of water and dilute to 1 L with water.

7.11 Anion exchange resin, 50-100 mesh, wet, chloride form for uranium separation.¹⁰

7.12 Anion exchange resin, nitrate form, 50-100 mesh, wet, for plutonium separation.¹¹ The exchange capacity of the resin should be between 0.6 and 0.7 milliequivalents/gram of dry resin for optimum separation.

7.12.1 **Warning**—The dry and wet mesh size of the resins differ; for the hydrochloride form of the resin, a 100-200 mesh, dry resin is purchased to provide 50-100 mesh, wet resin. The 100-200 mesh dry hydrochloride resin may be used to prepare the 50-100 mesh, wet nitrate form of resin.

7.13 *Sulfuric Acid (sp gr 1.84), 18.0 M*—concentrated sulfuric acid (H₂SO₄).

7.14 *Ferrous Sulfate Solution (0.1 M)*—add 1.5 g of ferrous sulfate heptahydrate (FeSO₄ • 7H₂O) to approximately 40 mL of water; add 0.3 mL (7 drops) concentrated sulfuric acid and dilute to 50 mL with water.

7.15 *Hydrogen Peroxide (H₂O₂, 30 %)*, stabilized.

⁷ Available from Bodman Industries, Aston PA; catalogue number 3300-25; 70 micron frits, catalogue number 3201-00 have been found to be acceptable.

⁸ Quartz Epiradiateur Lamps Model 534 RCL, 500 watts, 120 volts, controlled by a 0-140 V variable power supply (Variac), from Atlas Electric Supplies, P.O. Box 1300, Hialeah, FL, 33011, have been found acceptable.

⁹ "Reagent Chemicals, American Chemical Society Specifications," American Chemical Society, Washington, DC.

¹⁰ Dowex[®] 1-X2 or Bio-Rad[®] AG 1-X2, chloride form has been found to be acceptable.

¹¹ Dowex[®] 1-X2 or Bio-Rad[®] AG 1-X2, nitrate form has been found to be acceptable.

8. Procedure

8.1 Plutonium Anion Exchange Separation:

8.1.1 Sample Preparation:

8.1.1.1 Dissolve solid samples according to Practice C 1168 or other appropriate methods. Aliquants of the solution containing the approximate desired quantity of element are taken; the desired quantity of element will depend upon whether or not the solution is diluted prior to filament loading. (**Warning**—No initial aliquant should contain more than 10 mg of uranium to prevent inadequate rinsing of the ion exchange resin by the volumes given, and hence, inadequate separation of uranium and plutonium.)

8.1.1.2 An aliquant containing up to 1 mg of plutonium is transferred to a new, acid leached 20-30 mL container for ion exchange preparation.

NOTE 1—From this separation, a maximum of 200 ng of plutonium or 2 µg of uranium will be loaded on a filament for thermal ionization mass spectrometric isotopic abundance determination.

8.1.1.3 Fume the aliquant just to dryness on a hot plate or under an infrared heat lamp. If the sample contains halides, add 8 M HNO₃ and dry two more times. (**Warning**—Overheating may cause polymerization of plutonium or difficulty in subsequent dissolution.)

For samples free of transition elements, proceed with 8.1.2 for ferrous sulfate reduction or with 8.1.3 for hydrogen peroxide reduction. For all other samples, proceed with 8.1.2.

8.1.2 Ferrous Sulfate Valence Adjustment:

8.1.2.1 Dissolve the residue from 8.1.1.3 in 8 mL of 3 M HNO₃.

8.1.2.2 Add 1 drop of 0.1 M FeSO₄ solution, prepared the day of the ion exchange, from a disposable pipet. Swirl to mix well. This will reduce all plutonium in higher oxidation states to plutonium (III).

8.1.2.3 Add 5 mL of 16 M HNO₃. Swirl to mix well. This will oxidize plutonium (III) to plutonium (IV) and adjust the solution concentration to 8 M HNO₃.

8.1.2.4 Proceed to 8.1.4.

8.1.3 Hydrogen Peroxide Valence Adjustment:

8.1.3.1 Dissolve the residue from 8.1.1.3 in 5 mL of 8 M HNO₃.

8.1.3.2 Add 4 drops of 30 % H₂O₂ from a disposable pipet. Place the beaker on a hot plate at low heat (80° C) for a minimum of 1.5 h while the beaker is covered with a watch glass. Gentle effervescence should occur; continue heating until the effervescence has stopped. Reduction of all plutonium (VI) to plutonium (IV) is critical to a successful ion exchange separation.

8.1.3.3 Cool solution to room temperature.

8.1.4 Anion Exchange:

8.1.4.1 Fill the ion exchange column with a water slurry of the nitrate resin to a settled height of 1-2 cm. Pass 10 mL of 8 M HNO₃ through the resin, and then add 5 mL of 8 M HNO₃ and drain just before the sample is added. The column should be prepared the same day as the ion exchange is done to prevent degradation of the resin in the acid.

8.1.4.2 Place a new, acid leached, labeled container under the prepared ion exchange column to collect the uranium fraction, and then transfer the sample from 8.1.2.4 or 8.1.3.3 to

the column. Rinse the sample beaker with at least 3 mL of 8 M HNO₃ and transfer to the column; repeat rinse.

8.1.4.3 Add enough 8 M HNO₃ to the column to collect 10 to 15 mL of eluate in the uranium fraction container, and set the eluate aside for uranium recovery in 8.2.

8.1.4.4 Place a beaker to collect waste under the column. Wash the ion exchange column with successive 5 mL portions of 8 M HNO₃ until 30 mL have been used. Collect the washings in the waste beaker and discard them to appropriate waste containers. Plutonium (IV) is adsorbed by the resin.

8.1.4.5 When the last portion of 8 M HNO₃ wash solution drains to the top of the resin bed, place a new, acid leached, labeled beaker under the column to collect the plutonium fraction. Add 5 mL of the HCl/HF stripping solution to the column slowly, using a transfer pipet, and collect the plutonium fraction. Discard the column and resin to waste. (**Warning**—If large amounts of uranium are present, > 10 000 parts of uranium to 1 part of plutonium, 8.1.1.3-8.1.4.5 may need to be repeated for complete purification of the plutonium.)

8.1.4.6 Place the container of plutonium on a hot plate or under an infrared heat lamp, and evaporate the solution to dryness. (**Warning**—Overheating may cause polymerization of plutonium or difficulty in subsequent dissolution.)

8.1.4.7 Cool the container to room temperature, add sufficient concentrated HNO₃, dropwise, to dissolve the sample, and repeat the evaporation to dryness.

8.1.4.8 Cool the beaker to room temperature, place a Parafilm[®] or alternate cover over the container, and store the sample for plutonium isotopic analysis by Method C 698; Sections 144 through 145 and 147.4 through 149; or its replacement.

8.2 Uranium Anion Exchange Separation:

8.2.1 Evaporate the uranium/amerium fraction from 8.1.4.3 to dryness on a hot plate or under an infrared heat lamp.

8.2.2 Dissolve the dry salts with 5 mL of 12 M HCl.

8.2.3 Fill the ion exchange column with a water slurry of anion exchange resin, chloride form, to a settled height of 1 to 2 cm.

8.2.4 To prepare the column, pass 10 mL of concentrated HCl through the resin before the sample is added.

8.2.5 Transfer the uranium/amerium chloride solution from 8.2.2 to the prepared ion exchange column.

8.2.6 Wash the column with successive 10 mL portions of concentrated HCl until 30 mL have been added, collected, and discarded.

8.2.7 Place a new, acid leached, labeled container under the column, and elute the uranium with 5 mL of 0.1 M HCl which is added slowly using a transfer pipet. Discard the column and resin to waste.

8.2.8 Evaporate the uranium solution to dryness on a hot plate or under an overhead infrared heat lamp.

8.2.9 Cool to room temperature, add 5 mL concentrated HNO₃ to dissolve the salts, and evaporate to dryness on a hot plate or under an overhead infrared heat lamp.

8.2.10 Cool to room temperature, cover with Parafilm[®] or an alternate cover, and reserve the sample for uranium isotopic analysis by Standard Method C 698, Sections 144 through 145 and 147.5 through 149, or its replacement.

9. Keywords

9.1 ion exchange separation of uranium and plutonium; mass spectrometry; plutonium isotopic analysis; sample prepa-

ration for mass spectrometry; thermal ionization mass spectrometry; uranium isotopic analysis

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