INTERNATIONAL

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Standard Practice for
The Ion Exchange Separation of Uranium and Plutonium Prior to Isotopic Analysis[1]

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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:* [2]

C 698 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ((U, Pu)O_2)

C 833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets

C 859 Terminology Relating to Nuclear Materials[3]

C 1008 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets—Fast Reactor Fuel

C 1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis

C 1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis

C 1625 Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances by Thermal Ionization Mass Spectrometry

3. Terminology

3.1 *Definitions:* For definitions of terms used in this standard, refer to C 859.

4. Summary of Practice

4.1 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, sections 112.4 through 114 or method C 1625. 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 4.1.1 and 4.1.2 or by an alternative method demonstrated by the user to perform the equivalent reduction/oxidation procedure.[4]

4.1.1 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* HNO_3. Ferrous sulfate is added to reduce all plutonium (VI) to plutonium (III), then 16 *M* HNO_3 is added to oxidize plutonium (III) to plutonium (IV), and to adjust the final acid concentration to *8 M* HNO_3.

4.1.2 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* HNO_3. 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]

4.2 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* (HNO_3) 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

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[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] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Withdrawn.

[4] Reduction of all higher plutonium oxidation states to plutonium (III) by the addition of hydroxylamine or NH_2CLO_4, 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 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.

5. Significance and Use

5.1 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 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.

5.2 In those facilities where perchloric acid use is tolerated, the separation in Test Method C 698 may be used prior to isotopic abundance determination. Uranium and plutonium concentrations as well as isotopic abundances using thermal ionization mass spectrometry can be determined using this separation and following Test Method C 1625.

6. Interferences

6.1 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.

6.2 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. Organics from extraction resins may not be destroyed by this process, and will require a perchloric acid treatment, heating in a furnace at 500°C, or both.

6.3 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.

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

6.5 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.

6.6 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* HNO_3 reagent as a blank taken through the same chemical processing as the sample and computing the amount of uranium it contains.

7. Apparatus

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

7.2 *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* HNO_3 to leach uranium, rinsed in deionized water, and air or oven dried prior to use.

7.3 Infrared Heating Lamps or Hot Plate with adjustable low and high heat settings.

7.4 Transfer Pipets—Disposable.

8. Reagents

8.1 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 Society[7] 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.

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

8.3 *Nitric Acid (sp gr 1.42), 16 M*—concentrated nitric acid (HNO_3).

8.4 *Nitric Acid, 8 M*— Add 500 mL of HNO_3 (sp gr 1.42) to about 400 mL of water and dilute to 1 L.

8.5 *Nitric Acid, 4 M*— Add 250 mL of HNO_3 (sp gr 1.42) to about 700 mL of water and dilute to 1 L with water.

8.6 *Nitric Acid, 3 M*— Add 187 mL of HNO_3 (sp gr 1.42) to about 750 mL of water and dilute to 1 L with water.

8.7 *Hydrochloric Acid (sp gr 1.19), 12 M*—concentrated hydrochloric acid (HCl).

8.8 *Hydrofluoric Acid (sp gr 1.18), 29 M*—concentrated hydrofluoric acid (HF).

8.9 *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.

8.10 *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.

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

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

8.12.1 **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.

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[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.13 *Sulfuric Acid (sp gr 1.84), 18 M*—concentrated sulfuric acid (H_2SO_4).

8.14 *Ferrous Sulfate Solution (0.1 M)*—add 1.5 g of ferrous sulfate heptahydrate ($FeSO_4 \bullet 7H_2O$) to approximately 40 mL of water; add 0.3 mL (7 drops) concentrated sulfuric acid and dilute to 50 mL with water.

8.15 *Hydrogen Peroxide (H_2O_2, 30 %)*, stabilized.

9. Precautions

9.1 Strong acids are used during this analysis. Safety glasses and gloves must be worn when handling these solutions. Extreme care should be exercised in using hydrofluoric acid and other hot concentrated acids. Acid solutions are evaporated during this analysis. These operations must be conducted in a fume hood.

9.2 Hydrofluoric acid is a highly corrosive and toxic acid that can severly burn skin, eyes, and mucous membranes. Hydrofluoric acid differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers. Unlike other acids that are rapidly neutralized, hydrofluoric acid reactions with tissue may continue for days if left untreated. Utilization of appropriate laboratory controls and wearing adequate personal protective equipment to protect from skin and eye contact is essential.

10. Procedure

10.1 *Plutonium Anion Exchange Separation*:

10.1.1 *Sample Preparation*:

10.1.1.1 Dissolve solid samples according to Practice C 1168, C 1347, 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 that 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.)

10.1.1.2 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.

10.1.1.3 Fume the aliquant just to dryness on a hot plate or under an infrared heat lamp. If the sample contains halides, add *8 M* HNO_3 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 10.1.2 for ferrous sulfate reduction or with 10.1.3 for hydrogen peroxide reduction. For all other samples, proceed with 10.1.2.

10.1.2 *Ferrous Sulfate Valence Adjustment*:

10.1.2.1 Dissolve the residue from 10.1.1.3 in 8 mL of *3 M* HNO_3.

10.1.2.2 Add 1 drop of *0.1 M* $FeSO_4$ 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).

10.1.2.3 Add 5 mL of *16 M* HNO_3. Swirl to mix well. This will oxidize plutonium (III) to plutonium (IV) and adjust the solution concentration to *8 M* HNO_3.

10.1.2.4 Proceed to 10.1.4.

10.1.3 *Hydrogen Peroxide Valence Adjustment*:

10.1.3.1 Dissolve the residue from 10.1.1.3 in 5 mL of *8 M* HNO_3.

10.1.3.2 Add 4 drops of 30 % H_2O_2 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.

10.1.3.3 Cool solution to room temperature.

10.1.4 *Anion Exchange*:

10.1.4.1 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* HNO_3 through the resin, and then add 5 mL of *8 M* HNO_3 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.

10.1.4.2 Place a new, acid leached, labeled container under the prepared ion exchange column to collect the uranium fraction, and then transfer the sample from 10.1.2.4 or 10.1.3.3 to the column. Rinse the sample beaker with at least 3 mL of *8 M* HNO_3 and transfer to the column; repeat rinse.

10.1.4.3 Add enough *8 M* HNO_3 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 10.2.

10.1.4.4 Place a beaker to collect waste under the column. Wash the ion exchange column with successive 5 mL portions of *8 M* HNO_3 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.

10.1.4.5 When the last portion of *8 M* HNO_3 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, 10.1.1.3-10.1.4.5 may need to be repeated for complete purification of the plutonium.)

10.1.4.6 Place the container with the 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.)

10.1.4.7 Cool the container to room temperature, add sufficient concentrated HNO_3, dropwise, to dissolve the sample, and repeat the evaporation to dryness.

10.1.4.8 Cool the beaker to room temperature, place a Parafilm (trademarked) or alternate cover over the container, and store the sample for plutonium isotopic analysis by Method C 698 or Test Method C 1625.

10.2 *Uranium Anion Exchange Separation*:

10.2.1 Evaporate the uranium/americium fraction from 10.1.4.3 to dryness on a hot plate or under an infrared heat lamp.

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

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

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

10.2.5 Transfer the uranium/americium chloride solution from 10.2.2 to the prepared ion exchange column.

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

10.2.7 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.

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

10.2.9 Cool to room temperature, add 5 mL concentrated HNO_3 to dissolve the salts, and evaporate to dryness on a hot plate or under an overhead infrared heat lamp.

10.2.10 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.

11. Keywords

11.1 ion exchange; mass spectrometry; plutonium; plutonium isotopic analysis; thermal ionization mass spectrometry; uranium; uranium isotopic analysis

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