Designation: C1411 – 08

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

This standard is issued under the fixed designation C1411; 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 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]

C698 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ((U, Pu)O_2)

C833 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets

C859 Terminology Relating to Nuclear Materials

C1008 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets—Fast Reactor Fuel

C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis

C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis

C1625 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 C859.

4. Summary of Practice

4.1 Solid samples are dissolved according to Practice C1168 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 C698, sections 112.4 through 114 or method C1625. 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.[3]

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.[4,5]

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

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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] 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.

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

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

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 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 C833 and Specification C1008. 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 C698 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 C1625.

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[6] 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.

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[6] *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.