



Designation: **C1816—15 C1816 – 16**

Standard Practice for The Ion Exchange Separation of Small Volume Samples Containing Uranium, Americium, and Plutonium Prior to Isotopic Abundance and Content Analysis¹

This standard is issued under the fixed designation C1816; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This practice is an alternative to Practice **C1411** for the ion exchange separation in small mass samples (~5 μg of plutonium and up to 0.5 mg of uranium in 1 mL of solution) of uranium and plutonium from each other and from other impurities for subsequent isotopic abundance and content analysis by thermal ionization mass spectrometry (TIMS). In addition to being adapted to smaller sample sizes, this practice also avoids the use of hydrochloric acid (HCl) and hydrofluoric acid (HF) and does not require the use of two anion exchange columns as required in Practice **C1411**.

1.2 In chemically unseparated samples isobaric nuclides at mass 238 (^{238}U and ^{238}Pu), and mass 241 (^{241}Pu and ^{241}Am) will be measured together thus compromising the accuracy of the results of isotopic composition of Pu. Therefore, chemical separation of elements is essential prior to isotopic analyses. Concentrations and volumes given in the paragraphs below can be modified for larger sample sizes, different types of anion exchange resin, etc.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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.*

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C1008 Specification for Sintered (Uranium-Plutonium) Dioxide Pellets—Fast Reactor Fuel (Withdrawn 2014)³

C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis

C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis

C1411 Practice for The Ion Exchange Separation of Uranium and Plutonium Prior to Isotopic Analysis

C1415 Test Method for ^{238}Pu Isotopic Abundance By Alpha Spectrometry

C1625 Test Method for Uranium and Plutonium Concentrations and Isotopic Abundances by Thermal Ionization Mass Spectrometry

C1672 Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer

D1193 Specification for Reagent Water

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology **C859**.

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. Current edition approved June 1, 2015. Published July 15, 2016. Originally approved in 2015. Last previous edition approved in 2015 as C1816 – 15. DOI: 10.1520/C1816-15.10.1520/C1816-16.

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.

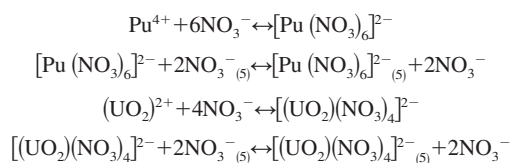
³ The last approved version of this historical standard is referenced on www.astm.org.

4. Summary of Practice

4.1 Solid samples are dissolved according to Practices **C1168** or **C1347** or other appropriate methods. The resulting solution is processed by this practice to prepare separate solutions of plutonium and uranium for mass spectrometric isotopic abundance analysis using Test Method **C698**, **C1625**, or **C1672**. Appropriate portions are taken to provide up to 5 µg of plutonium on the ion exchange column to be separated from 0.5 mg or less of uranium. All dilutions should be performed by mass to ensure the smallest uncertainty possible. This practice can be used for higher uranium to plutonium ratios, but column rinsing volumes should be adjusted accordingly (see **10.1.3.8**). Using the volumes proposed in this practice leads to a separation efficiency of at least 99.999 % between uranium and plutonium. Valence adjustment is obtained by using the procedure described in **4.1.1** or by an alternative method demonstrated by the user to perform the equivalent reduction/oxidation procedure.

4.1.1 For any sample type, especially those containing large amounts of impurities, ferrous sulfate may be used for reduction. The sample is diluted in 1 M nitric acid (HNO₃). Ferrous sulfate is added to reduce all plutonium to plutonium (III), then 0.7 M sodium nitrite (NaNO₂) is added to oxidize plutonium (III) to plutonium (IV).

4.2 After oxidation state adjustment, the resulting solution is passed through an anion exchange column in the nitrate form, which retains negatively-charged complexes of Pu(IV), U(VI), U(IV), etc. The process of complex formation and sorption in solutions of HNO₃ for Pu and U may be written down in a simplified manner as follows:



As the nitrate concentration increases, the concentration of the hexanitrato complex increases and the maximum adsorption is attained at an acidity of about 7.7 M.

The adsorbed plutonium is washed with 7-8 M HNO₃ to remove americium and other impurities that are not adsorbed, and then washed with 3-4 M HNO₃ to remove uranium. The uranium is recovered and then the column is rinsed with a large volume of 3-4 M HNO₃ to remove the residual uranium. Two mechanisms are used in the desorption of tetravalent plutonium from the anion exchanger. One is to shift the complex formation equilibrium by decreasing the concentration of nitrate ions in the eluent. The second mechanism consists of reducing Pu(IV) to Pu(III) by addition of the reducing agent *hydroxylammonium nitrate* (NH₃OHNO₃). The plutonium is stripped from the column with a solution of 0.2 to 0.35 M HNO₃ and 1.9E-02 M *hydroxylammonium nitrate* (NH₃OHNO₃). The volume of the eluting solution needed is smaller compared to using only 0.2 to 0.35 M HNO₃, and the solution obtained after purification is more concentrated.

5. Significance and Use

5.1 Uranium and plutonium are used in nuclear reactor fuel and must be analyzed to ensure that they meet acceptance criteria for isotopic composition as described in Specifications **C833** and **C1008**. The criteria are set by mutual agreement between the manufacturer and end user (or between buyer and seller). This standard practice is used to separate chemically the isobaric interferences from ²³⁸U and ²³⁸Pu and from ²⁴¹Am and ²⁴¹Pu, and from other impurities prior to isotopic abundance determination by TIMS.

5.2 In facilities where perchloric acid use is authorized, the separation in Test Method **C698** may be used prior to isotopic abundance determination. Uranium and plutonium content as well as isotopic abundances using TIMS can be determined by using this separation practice and by following Test Methods **C698**, **C1625**, or **C1672**.

6. Mass Spectrometry Interferences Resolved by this Separation Practice

6.1 The separated heavy element fractions placed on mass spectrometric filaments must be 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 Organic compounds from the degradation of ion exchange resin, if present, could affect the response of the mass spectrometer during the plutonium and uranium isotopic abundance measurements. Evaporation of the samples in concentrated HNO₃ after the ion exchange separation will destroy resin degradation products.

NOTE 1—The sample should not be evaporated using heat above approximately 170°C to avoid oxide formation that will make re-dissolving the sample difficult.

6.3 Elemental impurities, especially alkali elements, tend to produce unstable ion emission that alter the observed plutonium and uranium isotope ratios in an unpredictable manner.

6.4 Isobaric impurities or contaminants will alter the observed isotope ratios; most notable of these for plutonium are ²⁴¹Am and ²³⁸U; the most notable isobaric impurity for uranium is ²³⁸Pu.

6.5 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, including the addition of ²³³U, ²³⁵U or U²³⁵, and computing the amount of uranium it contains.

7. Apparatus

7.1 *Polyethylene Ion Exchange Columns*—Disposable, 0.9 cm id × 3 cm with a 15-mL reservoir (or other column with sufficient volume for operation).

7.2 *Laboratory Balance*—Precision ±0.1 mg.

7.3 *Beakers or Alternate Acceptable Containers*—Pretreated, 10-30 mL, borosilicate glass. To avoid cross contamination, use only new borosilicate glass containers. Depending on the need, containers can be pretreated by heating in 4 M HNO₃ to leach uranium, and then rinsed in deionized water, and air or oven dried prior to use.

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

7.5 *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 Society⁴ where such specifications are available. Other grades of reagents may be used, provided it is first ascertained that the reagent is of sufficient 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 in conformance with Specification **D1193**, Type 1.

8.3 *Nitric Acid, 70.4 w/w%*—concentrated HNO₃.

8.4 *Nitric Acid, 7.5 to 8 M*—Add 490 ± 15 mL of HNO₃ (70.4 w/w%) to about 400 mL of water and dilute to 1 L.

8.5 *Nitric Acid, 3.4 to 4 M*—Add 234 ± 20 mL of HNO₃ (70.4 w/w%) to about 700 mL of water and dilute to 1 L with water.

8.6 *Nitric Acid, 1 M*—Add 63 mL of HNO₃ (70.4 w/w%) to about 750 mL of water and dilute to 1 L with water.

8.7 *Nitric Acid, ~0.3 M*—Add 19 mL of HNO₃ (70.4 w/w%) to about 750 mL of water and dilute to 1 L with water.

8.8 *Crystallized Sodium Nitrite (ACS grade)*—NaNO₂.

8.9 *Crystallized Ferrous Sulfate Heptahydrate (ACS grade)*—FeSO₄ · 7H₂O.

8.10 *Sulfuric Acid, 18 M*—Concentrated H₂SO₄ (sp gr 1.84).

8.11 *Sulfuric Acid, 0.1 M*—Add 5.6 mL of H₂SO₄ (sp gr 1.84) to about 750 mL of water and dilute to 1 L with water.

8.12 *Hydroxylammonium nitrate (HAN) (sp gr 1.18), 24 wt.% in H₂O*—Hydroxylammonium nitrate (NH₃OHNO₃) 2.95 M.

8.13 *Crystallized Sodium Nitrate (ACS grade)*—NaNO₃.

8.14 *Sodium Nitrate, 1 M*—Add 85 g of NaNO₃ to about 750 mL of water, agitate until the sodium nitrate is completely dissolved and then dilute to 1 L with water.

8.15 *Anion Exchange Resin*—1 × 4 100 – 200 mesh, dry resin, conditioned in 8 M HNO₃ to achieve 50 – 100 mesh, wet resin. **(Warning—Never allow anion exchange resin conditioned in strong concentrations of acid with HAN to dry, as ammonium nitrate (NH₄NO₃) can form and cause an explosion risk. Additionally, nitrate form anion resin and strong concentrations of HNO₃ can undergo a chemical reaction under certain conditions and can self-heat and undergo an autocatalytic reaction. To avoid these hazards ensure that the resin is rinsed with a solution capable of removing the nitrate from the resin, for example <0.5 M HNO₃.)**

8.16 *Preparation of the HAN Stripping Solution (0.3 M HNO₃, 1.9E-02 M HAN)*—Add 320 µL of hydroxylammonium nitrate to 50 mL of ~0.3 M HNO₃.

8.17 *Preparation of Oxidation Solution (0.7 M NaNO₂ in H₂O)*—Add 1.2 g of NaNO₂, H₂O (ACS grade) to a 20-mL volumetric flask and dilute to the mark with water. Cap the flask and agitate until the sodium nitrite is dissolved completely.

NOTE 2—The oxidation solution is not stable for long periods of time and should be used within 8 hours of preparation.

⁴ *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.