Designation: C1816 – 16

Standard Practice for
The Ion Exchange Separation of Small Volume Samples Containing Uranium, Americium, and Plutonium Prior to Isotopic Abundance and Content Analysis[1]

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C1008 Specification for Sintered (Uranium-Plutonium) DioxidePellets—Fast Reactor Fuel (Withdrawn 2014)[3]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.

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

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

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 (HNO_3). Ferrous sulfate is added to reduce all plutonium to plutonium (III), then 0.7 M sodium nitrite ($NaNO_2$) 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 HNO_3 for Pu and U may be written down in a simplified manner as follows:

$$\text{Pu}^{4+} + 6\text{NO}_3^{\,-} \leftrightarrow [\text{Pu}\,(\text{NO}_3)_6]^{2-}$$

$$[\text{Pu}\,(\text{NO}_3)_6]^{2-} + 2\text{NO}_3^{\,-}{}_{(5)} \leftrightarrow [\text{Pu}\,(\text{NO}_3)_6]^{2-}{}_{(5)} + 2\text{NO}_3^{\,-}$$

$$(\text{UO}_2)^{2+} + 4\text{NO}_3^{\,-} \leftrightarrow [(\text{UO}_2)(\text{NO}_3)_4]^{2-}$$

$$[(\text{UO}_2)(\text{NO}_3)_4]^{2-} + 2\text{NO}_3^{\,-}{}_{(5)} \leftrightarrow [(\text{UO}_2)(\text{NO}_3)_4]^{2-}{}_{(5)} + 2\text{NO}_3^{\,-}$$

As the nitrate concentration increases, the concentration of the hexanitrate 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 HNO_3 to remove americium and other impurities that are not adsorbed, and then washed with 3-4 M HNO_3 to remove uranium. The uranium is recovered and then the column is rinsed with a large volume of 3-4 M HNO_3 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* (NH_3OHNO_3). The plutonium is stripped from the column with a solution of 0.2 to 0.35 M HNO_3 and 1.9E-02 M *hydroxylammonium nitrate* (NH_3OHNO_3). The volume of the eluting solution needed is smaller compared to using only 0.2 to 0.35 M HNO_3, 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 ^{238}U and ^{238}Pu and from ^{241}Am and ^{241}Pu, 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 HNO_3 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 redissolving 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 ^{241}Am and ^{238}U; the most notable isobaric impurity for uranium is ^{238}Pu.

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 HNO_3 reagent as a blank taken through the same chemical processing as the sample, including the addition of ^{233}U or U^{235}, 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 HNO_3 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 Society[4] 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 HNO_3.

8.4 *Nitric Acid, 7.5 to 8 M*—Add 490 ± 15 mL of HNO_3 (*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 HNO_3 (*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 HNO_3 (*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 HNO_3 (*70.4 w/w%*) to about 750 mL of water and dilute to 1 L with water.

8.8 *Crystallized Sodium Nitrite (ACS grade)*—$NaNO_2$.

8.9 *Crystallized Ferrous Sulfate Heptahydrate (ACS grade)*—$FeSO_4$, $7H_2O$.

8.10 *Sulfuric Acid, 18 M—Concentrated* H_2SO_4 (sp gr 1.84).

8.11 *Sulfuric Acid, 0.1 M*—Add 5.6 mL of H_2SO_4 (*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* H_2O—Hydroxylammonium nitrate (NH_3OHNO_3) 2.95 M.

8.13 *Crystallized Sodium Nitrate (ACS grade)*—$NaNO_3$.

8.14 *Sodium Nitrate, 1 M*—Add 85 g of $NaNO_3$ 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 HNO_3 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 (NH_4NO_3) can form and cause an explosion risk. Additionally, nitrate form anion resin and strong concentrations of HNO_3 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 HNO_3.)**

8.16 *Preparation of the HAN Stripping Solution (0.3 M* HNO_3*, 1.9E-02 M HAN)*—Add 320 µL of hydroxylammonium nitrate to 50 mL of *~0.3 M* HNO_3.

8.17 *Preparation of Oxidation Solution (0.7 M* $NaNO_2$ *in* H_2O—Add 1.2 g of $NaNO_2$, H_2O (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.

8.18 *Preparation of Reduction Solution (0.3 M* $FeSO_4$*, 0.1 M* H_2SO_4—Add 1.67 g of $FeSO_4$, $7H_2O$ to a 20-mL volumetric flask and dilute to the mark with *0.1* M H_2SO_4. Cap the flask and agitate until the ferrous sulfate heptahydrate is dissolved completely.

NOTE 3—The reduction solution is not stable for long periods of time and should be used within 8 hours of preparation.

8.19 *Preparation of the Anion Exchange Resin*—If the resin is conditioned in a non-nitrate form, such as chloride, it must be conditioned in a nitrate form before use. Also, in order for the separation to be effective, the resin must be conditioned at *~8 M* HNO_3. Many methods are appropriate, and exact preparation can depend on the resin manufacturer, but in general the conditioning must allow for the removal of most non-nitrate ions from the resin without causing damage to the resin (some residual chloride ions may still be present after conditioning the resin, but should not affect the separation). Two example methods appropriate for use with a resin conditioned in chloride form are presented below.

8.19.1 *Example 1: Resin Chloride to Nitrate Conversion and Conditioning at ~8 M* HNO_3 *in a Beaker:*

8.19.1.1 Place 250 g of resin conditioned in chloride form into a 5-L beaker.

8.19.1.2 Add 2 L of deionized water to the beaker and agitate the mixture for 1.5 hours.

8.19.1.3 Let the resin solution settle for 2 hours and then decant the supernatant.

8.19.1.4 Repeat steps 8.19.1.2 to 8.19.1.3 at least two additional times (a total of 6 L deionized water) or until the addition of silver nitrate to the decanted supernatant reveals no silver chloride precipitate.

8.19.1.5 Add 2 L of *~0.3 M* HNO_3 from 8.7 to the beaker and agitate the mixture for 1.5 hours.

8.19.1.6 Let the resin solution settle for 2 hours and then decant the supernatant.

8.19.1.7 Repeat steps 8.19.1.5 to 8.19.1.6 one additional time (a total of 4 L *~0.3 M* HNO_3).

8.19.1.8 Add 2 L of *3.4 to 4 M* HNO_3 from 8.5 to the beaker and agitate the mixture for 1.5 hours.

8.19.1.9 Let the resin solution settle for 2 hours and then decant the supernatant.

8.19.1.10 Repeat steps 8.19.1.8 to 8.19.1.9 one additional time (a total of 4 L *3.4 to 4 M* HNO_3).

8.19.1.11 Add 2 L of *7.5 to 8 M* HNO_3 from 8.4 to the beaker and agitate the mixture for 1.5 hours.

8.19.1.12 Let the resin solution settle for 2 hours and then decant the supernatant.

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[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.

8.19.1.13 Repeat steps 8.19.1.11 to 8.19.1.12 one additional time (a total of 4 L *7.5 to 8 M* HNO_3).

8.19.1.14 If the resin is not used immediately, add 2 L of deionized water and agitate the mixture for 1.5 hours. Let the resin solution settle for 2 hours and then decant the supernatant. Transfer the resin to a clean bottle for storage. The resin may be safely stored for an extended period of time submerged in deionized water in a cool storage location with low light exposure.

8.19.1.15 If the resin has been stored, decant the supernatant, and repeat steps 8.19.1.5, 8.19.1.6, 8.19.1.8, 8.19.1.9, 8.19.1.11, and 8.19.1.12.

8.19.2 *Example 2: Resin Chloride to Nitrate Conversion and Conditioning at ~8 M* HNO_3 *in a Column:*

8.19.2.1 Transfer the chloride form resin for conversion into a column for washing.

8.19.2.2 Wash the resin bed with 10 bed volumes of *1 M* $NaNO_3$ from 8.13 to exchange chloride for nitrate.

8.19.2.3 Rinse the excess $NaNO_3$ and residual sodium chloride (NaCl) from the resin bed with ~6 bed volumes of deionized water.

NOTE 4—Column conversion of chloride form resin to nitrate form resin by similar process has been demonstrated to be highly effective at removing chloride (Cl < 250 µg/g dry resin).

8.19.2.4 Condition the resin bed with six bed volumes of *7.5 to 8 M* HNO_3 from 8.4.

8.19.2.5 If the resin is not used immediately, rinse the resin bed with six bed volumes of deionized water. Transfer the nitrate form resin to a clean bottle for storage. The resin may be safely stored for an extended period of time if it is submerged in deionized water or damp in a closed bottle in a cool storage location with low light exposure.

8.19.2.6 If the resin has been stored, transfer the resin into a column and repeat steps 8.19.2.4 and 8.19.2.5.

8.19.3 *Preparation of the Polyethylene Ion Exchange Columns*—Place a small glass wool pad at the bottom of a clean, new polyethylene ion exchange column. Add the prepared anion exchange resin to a height of 10 mm (approximately 2 mL of resin). Place another glass wool pad over the resin and pack the resin gently into the separation column.

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 hot concentrated acids. Acid solutions are evaporated during this analysis. These operations must be conducted in a fume hood or a glovebox.

9.2 Use of HAN with moderate to high concentration HNO_3 can cause the formation of ammonium nitrate (NH_4NO_3), which is an explosion hazard, if these solutions are allowed to dry. Precautions should be taken to avoid storing or discarding mixtures of high concentration HNO_3 and HAN, such as in used resin, etc.

10. Procedure

10.1 *Plutonium/Uranium Anion Exchange Separation:*

10.1.1 *Sample Preparation:*

10.1.1.1 Dissolve solid samples according to Practice C1168, C1347, or other appropriate methods. Aliquots 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 aliquot should contain more than 0.5 mg of uranium to prevent inadequate rinsing of the ion exchange resin by the volumes given, and hence, inadequate separation of uranium and plutonium. If the uranium-to-plutonium ratio is much greater than 100:1 then 10.1.3.1 – 10.1.3.10 may need to be repeated to ensure complete purification of the plutonium, or Test Method C1415 can be used on the single separation fraction to measure the plutonium-238.)**

10.1.1.2 Approximately 1 mL of solution containing approximately 5 µg of plutonium in 1 M HNO_3 is transferred to a new, acid leached (if necessary) 10-mL container for ion exchange preparation.

10.1.2 *Ferrous Sulfate/Sodium Nitrite Valence Adjustment:*

10.1.2.1 Add 1 mL of the Reduction Solution (*0.3 M* $FeSO_4$*, 0.1 M* H_2SO_4) from 8.18, from a disposable pipette to the 10-mL beaker containing the sample. Swirl for five minutes to mix well. This will reduce all plutonium in higher oxidation states to plutonium (III).

10.1.2.2 Add 1 mL of the Oxidation Solution (*0.7 M* $NaNO_2$ *in* H_2O) from 8.17, from a disposable pipette to the 10-mL beaker containing the portion of solution. Swirl for five minutes to mix well. This will oxidize plutonium (III) to plutonium (IV).

10.1.2.3 Adjust the acidity of the sample by adding 3 mL of *70.4 w/w%* concentrated HNO_3.

10.1.3 *Separation of Americium, Uranium, and Plutonium:*

10.1.3.1 Use an ion exchange column prepared in step 8.19.3. Place a 30-mL waste beaker under the prepared ion exchange column and pass 10 mL of *7.5 to 8 M* HNO_3 from 8.4 through the resin, and drain just before the sample is added.

10.1.3.2 Keeping the waste beaker under the column, transfer the entire sample from 10.1.2.3 to the resin column. Plutonium (IV) and uranium (VI) are adsorbed to the column, and americium (III) is not adsorbed to the column. Small residual amounts of americium (III) remain in the column and must be removed by rinsing.

10.1.3.3 Rinse the remaining americium and a fraction of the uranium from the column by adding 3 mL of *3.4 to 4 M* HNO_3 from 8.5 and collect the eluate in the waste container, and discard.

10.1.3.4 Place a new acid leached (if necessary) 10-mL beaker under the column to collect the uranium fraction and elute uranium with 2 to 8 mL (depending on the amount of uranium in the sample) of *3.4 to 4 M* HNO_3 from 8.5.

NOTE 5—Steps 10.1.3.5 and 10.1.3.6 can be performed concurrently with steps 10.1.3.7 – 10.1.3.11.

10.1.3.5 Place the container with the uranium on a hot plate or under an overhead infrared heat lamp, and evaporate the solution to dryness. (**Warning—Overheating may calcinate the uranium and make it difficult to dissolve**.)

10.1.3.6 Cool the container to room temperature, add sufficient *~0.3 M* HNO_3 from 8.7, dropwise, to dissolve the sample.

Approximately 0.2 mL should be sufficient. Place a paraffin film or alternate cover over the container and reserve the sample for uranium isotopic abundance analysis by Test Method C698, C1625, or C1672.

10.1.3.7 Place a 50-mL waste beaker under the column.

10.1.3.8 Wash the ion exchange column with 30 mL (depending on the amount of uranium in the sample) of *3.4 to 4 M* HNO_3 from 8.4 to remove most of the remaining uranium from the column. Allow all 30 mL of the washing solution to collect in the waste beaker.

NOTE 6—This volume (30 mL) works well for uranium to plutonium ratios of up to 100:1. Higher ratios may require larger rinsing volumes of washing solution.

10.1.3.9 With the waste beaker from 10.1.3.8 still under the column, add 2 mL of *~0.3 M* HNO_3 from 8.7 to reduce the concentration of nitrates. This desorbs a fraction of the plutonium ions from the resin with the last remaining amounts of uranium. Most of the plutonium (IV) is still adsorbed by the resin. Discard the waste solution to an appropriate waste container.

10.1.3.10 Place a new, acid leached (if necessary) 10-mL beaker under the column to collect the plutonium fraction. Add 3 mL of the HAN stripping solution from 8.16 to the column slowly, using a transfer pipet, and collect the pure plutonium fraction.

NOTE 7—Steps 10.1.3.11 and 10.1.3.12 can be performed concurrently with step 10.1.3.13.

10.1.3.11 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 calcinate the plutonium and make it difficult to dissolve**.)

10.1.3.12 Cool the container to room temperature, add sufficient *~0.3 M* HNO_3, dropwise, to dissolve the sample. Approximately 0.2 mL should be sufficient. Place a paraffin film or alternate cover over the container, and store the sample for plutonium isotopic abundance analysis by Test Method C698, C1625, C1672.

10.1.3.13 Rinse the column with *0.3 M* HNO_3 from 8.7, then discard the effluent in the appropriate waste container and dispose of the column and resin. (**Warning—Ensure that the resin has been rinsed with a solution capable of removing the nitrate from the resin, for example <0.5 M HNO_3**.)

11. Keywords

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