Standard Guide for Determination of Neptunium-237 in Soil[1]

This standard is issued under the fixed designation C 1475; 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 guide covers the determination of neptunium-237 in soil by means of radiochemical separations and alpha spectrometry. This guide provides options in the selection of sample preparation, separation, and measurement. Although neptunium-237 is not a component of global fallout, it is a product of production reactors and spent fuel processing. This guide is designed for analysis of ten grams of soil previously collected and treated in accordance with Practices C 998 and C 999. Larger-size samples of environmental soil may also be analyzed, as long as the concentrations of interferences such as uranium and thorium are at or near environmental concentrations. Depending on the choice of a sample dissolution method, all chemical forms of neptunium may not be completely solubilized. This guide should allow the determination of neptunium-237 concentrations from sub becquerel per gram levels to applicable standards depending on count time, sample size, detector efficiency, background, and tracer yield.

1.2 *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 limitations prior to use.* Specific precautionary statements are given in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

C 998 Practice for Sampling Surface Soil for Radionuclides[2]
C 999 Practice for Soil Sample Preparation for the Determination of Radionuclides[2]
C 1000 Test Method for Radiochemical Determination of Uranium Isotopes in Soil by Alpha Spectrometry[2]
C 1001 Test Method for Radiochemical Determination of Plutonium in Soil by Alpha Spectroscopy[2]
C 1163 Test Method for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride[2]
C 1284 Practice for Electrodeposition of the Actinides for Alpha Spectrometry[2]
C 1317 Practice for Dissolution of Silicate or Acid-Resistant Matrix Samples[2]
C 1342 Practice for Flux Fusion Sample Dissolution[2]
C 1387 Guide for Determination of Technetium-99 in Soil[2]
C 1412 Practice for Microwave Oven Dissolution of Glass Containing Radioactive and Mixed Wastes[2]
D 1193 Specification for Reagent Water[3]
D 1890 Test Method for Beta Particle Radioactivity of Water[4]
D 3084 Practice for Alpha-Particle Spectrometry of Water[4]
D 4962 Practice for NaI(TI) Gamma-Ray Spectrometry of Water[4]
IEEE/ASTM SI-10 Standard for the Use of the International System of Units (SI): The Modern Metric System[5]

3. Summary of Guide

3.1 This guide may be used to determine neptunium-237 in soil at potential release sites. A neptunium-239 yield monitor is added to the soil aliquot and the sample solubilized by one of several methods, such as those described in Guide C 1387. The neptunium is separated from the resulting solution using an extraction chromatography column. A valence adjustment is performed prior to loading the sample onto the conditioned chromatography column. The sample is passed through the column, which retains the neptunium in the +4 oxidation state. The column is washed to remove interferences and selectively eluted with dilute acid. The samples are prepared for measurement by neodymium fluoride co-precipitation or electrodeposition, and the neptunium-237 content determined by alpha spectrometry. The neptunium-239 yield monitor is determined by beta or gamma-ray counting.

4. Significance and Use

4.1 A soil sampling and analysis program provides a direct means of determining the concentration and distribution of radionuclides in soil. The presence and extent of neptunium-237 is of particular interest because it is one of the more mobile transuranics in terms of migration and plant uptake. Since soil is an integrator and a reservoir on long-lived radionuclides, and serves as an intermediary in several pathways of potential importance to humans, knowledge of the concentration of neptunium-237 in soil is essential.

---

[1] This guide 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 10, 2000. Published August 2000.

[2] *Annual Book of ASTM Standards*, Vol 12.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 11.02.

[5] *Annual Book of ASTM Standards*, Vol 14.04.

5. Interferences

5.1 Phosphates present in the sample matrix will interfere with the separation chemistry. Aluminum nitrate may be added to the load solution to minimize this problem.

5.2 High concentrations of uranium or thorium can overload the column, resulting in low recoveries of neptunium or spectral interferences. A preliminary separation may be required to avoid spectral interference from uranium, see Test Method C 1000. The presence of uranium-233 and uranium-234 could cause spectral interferences with the neptunium-237 determination.

6. Apparatus

6.1 Apparatus for the sample dissolution and measurement are identified within the selected test method.

6.2 *Extraction Columns*, with a bed volume of several millilitres for the extraction chromatography resin.[6]

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[7] Other grades 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 the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined in Specification D 1193.

7.3 *Aluminum Nitrate Hydrate* [$Al(NO_3)_3 \cdot 9H_2O$].

7.4 *Extraction Chromatography Resin*.[6]

7.5 *Ferrous Sulfamate* [$Fe(SO_3NH_2)_2$], 1.0 *M*—Dissolve 38.8 g of sulfamic acid (NH_2SO_3H) and 11.6 g of iron powder in approximately 150 mL of water. Stir while heating until dissolved and then dilute to 200 mL with water. Prepare fresh each week or keep under a nitrogen blanket to minimize oxidation.

7.6 *Hydrofluoric Acid* (48 to 51 %)—Concentrated hydrofluoric acid (HF).

7.7 *Iron Powder*.

7.8 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

7.9 *Nitric Acid,* 3.0 *M*—Mix 189 mL of concentrated nitric acid with water and dilute to 1.0 L.

7.10 *2.5 M Nitric Acid-0.5 M Aluminum Nitrate*—Dissolve 187.6 g of aluminum nitrate in about 500 mL of water, add 159 mL of concentrated nitric acid, and dilute to 1.0 L.

7.11 *0.02 M Nitric Acid-0.02 M Hydrofluoric Acid*—Mix 1.25 mL of concentrated nitric acid and 0.7 mL of concentrated hydrofluoric acid in water and dilute to 1.0 L.

7.12 *Radiometric Yield Tracer*—Neptunium-239 is normally used as a yield monitor in the determination of neptunium-237. Where beta counting is used to determine the neptunium-239 yield, a relatively low amount of activity, for example, 5 to 15 Bq, is typically required to obtain the desired precision with a 60-min count duration. Another option is the addition of a known quantity of americium-243, in secular equilibrium with neptunium-239, directly to the sample. This approach has the advantage of allowing the use of americium-243 solutions of NIST-traceable activity. Where gamma-ray counting is used to determine the neptunium-239 yield, a larger amount of activity, for example, 120 to 1200 Bq, may be required to obtain the desired precision with a 10-min count duration dependent on the use of a NaI(TI) or HPGe detector. In this situation, it may be preferred to obtain the neptunium-239 from an americium-243 ′cow.'[8] This approach has the advantage of conserving the americium-243 parent with the neptunium-239 activity being replenished over time. However, it has the disadvantage that the neptunium-239 activity of the milked solution must be determined with high precision in order to not adversely impact the precision of the sample neptunium-237 activity determination.

7.13 *Sodium Nitrite ($NaNO_2$)*.

7.14 *Sodium Nitrite*, 3.0 *M*—Dissolve 2.1 g of sodium nitrite in 10 mL of water. Prepare fresh daily.

7.15 If prepacked columns are not available, prepare the resin by combining it with an equal volume of water, mix well, and allow to settle overnight. Decant the supernatant water and add a fresh volume of water prior to storage. Replace the water with a fresh aliquot before each use. Prepare a column for each sample by pouring resin into each column. Adjust the settled resin bed volume to approximately 2 mL.

8. Precautions

8.1 Refer to the laboratory's chemical hygiene plan and other applicable guidance for handling chemical and radioactive materials and for the management of radioactive, mixed, and hazardous waste.

8.2 Hydrofluoric acid is a highly corrosive acid that can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid. 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. Due to the serious consequences of hydrofluoric acid burns, prevention of exposure or injury of personnel is the primary goal. Utilization of appropriate laboratory controls (hoods) and wearing adequate personal protective equipment to protect from skin and eye contact is essential.

---

[6] Prepacked columns of TEVA Spec resin from EIChroM Industries, Darien, IL, have been found to be satisfactory for this purpose.

[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] Information on the generation and use of americium-243 cows to obtain neptunium-239 can be obtained from: Garraway, J., and Wilson, P. D., "Preparation of Np-239 by Separation from the Parent Am-243," *Journal of the Less-Common Metals*, 91, 1983, L13-L16, and Bubernak, J., Lew, M. S., and Matlack, G. M., "Ion Exchange Extraction, Separation and Radiochemical Determination of Neptunium-237 in Plutonium-238," *Analytica Chemica Acta*, 48, 1969, pp. 233-241.

9. Sampling

9.1 Collect the sample in accordance with Practice C 998.

9.2 Prepare the sample for analysis in accordance with Practice C 999.

10. Sample Solubilization

10.1 Weigh 10.00 g of dried and prepared soil and add neptunium-239 yield monitor in either a separated form or in secular equilibrium with americium-243. As indicated in 7.12, either beta counting using Test Method D 1890 or gamma-ray spectrometry using Practice D 4962 may be utilized for counting the neptunium-239 yield monitor. The amount of neptunium-239 yield monitor activity utilized is dependent on the selected counting technique, the efficiency of the counting technique, and the desired counting duration. Obtaining approximately 10 000 net counts from neptunium-239 by whatever counting technique is used will produce a Poisson counting uncertainty of about 1 % at one standard deviation. Given the short half-life of neptunium-239, delay in its counting will reduce the number of counts obtained with resulting increase in counting uncertainty.

10.2 A number of methods are available to solubilize soil samples to prepare them for radiochemical analysis. Three frequently used techniques are acid leaching, fusion, and microwave digestion. Leaching procedures are described in Test Methods C 1000 and C 1001. A general overview of all three methods is provided in Guide C 1387 along with references to detailed procedures. Other methods include procedures for dissolution of silicates or acid-resistant matrix samples in Practice C 1317, dissolution of solid samples by fusion in Practice C 1342, and the microwave dissolution of glass in Practice C 1412. The choice of specific dissolution method is left to the laboratory conducting this analysis.

11. Procedure

11.1 Prepare any blanks, spikes, duplicates, or other samples required by the laboratory protocols as part of this analysis in accordance with 10.2.

11.2 Evaporate the samples to near dryness on a hot plate set at 110°C.

11.3 Remove the sample beakers from the hot plate and allow them to cool to room temperature.

11.4 Add 5 mL of 2.5 M HNO_3-0.5 M $Al(NO_3)_3$ to each beaker and swirl to dissolve the residue.

11.5 Add 0.4 mL of 1.0 M ferrous sulfamate solution to each beaker.

11.6 Add 0.5 mL of 3.0 M sodium nitrite to each sample beaker.[9]

11.7 Allow the samples to sit at room temperature for 30 to 40 min. The sample beakers should be swirled occasionally to facilitate the reaction.[10]

11.8 During the 30-min incubation period, prepare the extraction chromatography columns.

11.9 For prepackaged columns, break off the tip and allow the water to drip through into an appropriate waste container.

11.10 For either column type, condition the columns by adding 5 mL of 3.0 M nitric acid. Collect the column wash as waste.

11.11 After the samples have reacted for 30 to 40 min,[10] load the samples on the columns using disposable transfer pipettes. Collect the effluent as waste.

11.12 Rinse the sample beaker with 5 mL of 3.0 M nitric acid, pass this rinse through the column, and collect the rinse as waste.

11.13 Repeat 11.12.

11.14 Elute the neptunium by passing 15 mL of 0.02 M HNO_3-0.02 M HF through each column. Collect the column strip solutions in clean, labeled teflon containers.

11.15 Prepare the samples for alpha spectrometry by either co-precipitating with neodymium fluoride in accordance with Test Method C 1163 or by electrodeposition in accordance with Practice C 1284.

12. Measurement and Calculation

12.1 The radiochemical recovery of the method is determined by measurement of the neptunium-239 yield monitor.

12.2 The determination of neptunium-237 in separated samples is typically conducted by alpha spectrometry. A standard practice for the measurement and calculation of separated actinides is available in Practice D 3084. The result should be provided to the requestor after all laboratory quality control procedures have been conducted.

13. Precision and Bias

13.1 This guide only addresses the separation steps in the overall preparation and measurement of neptunium-237 in soil samples and thus does not produce any measurements. Hence a statement of precision and bias is not applicable.

14. Keywords

14.1 alpha spectroscopy; americium-243; beta counting; extraction chromatography; gamma-ray spectroscopy; neptunium-239; neptunium-237 determination; soil analysis

---

[9] When the sodium nitrite solution is added, a reaction should occur indicated by the observation of gas bubbles.

[10] Thirty minutes is required to allow the reaction in the sample solution to proceed to a point where the resin bed will not be adversely affected; however, it is critical that the waiting period not exceed 40 min, or the chemical recovery will be greatly reduced.