



Standard Test Method for Plutonium by Titanium(III)/Cerium(IV) Titration¹

This standard is issued under the fixed designation C 1235; 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 test method is applicable to the assay or purity determination of plutonium metal of 98 % purity or higher. Uranium and iron are known interferences and must be determined separately. Their respective corrections must then be made to the assay value.

1.2 The recommended amount of plutonium determined in the titration is 210 to 240 mg.

1.3 *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:

C 1009 Guide for Establishing a Quality Assurance Program for Analytical Chemistry Laboratories Within the Nuclear Industry²

C 1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry²

C 1128 Guide for Preparation of Working Reference Materials for Use in the Analysis of Nuclear Fuel Cycle Materials²

C 1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials²

C 1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry²

C 1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials²

3. Summary of Test Method

3.1 In a redox titration, as titrant is added, the change in concentration of the redox couple is monitored. This change in concentration of the redox couple can be monitored by measuring the potential difference between a platinum indicator electrode and a reference electrode (such as a saturated

calomel electrode) in contact with the solution or by other equivalent methods of endpoint determination. The endpoint of the titration is usually chosen to be the point at which the rate of change in concentration of the redox couple is greatest per increment of titrant added. The concentration of analyte is calculated from the volume or mass of titrant added to reach the endpoint, the concentration of the titrant, and the mass of the sample titrated. Lingane (1)³ discusses the principles of automatic potentiometric titrations, and Meites (2) lists numerous examples of potentiometric redox titrations.

3.2 This test method is an adaptation of the Coppel and Regnaud method (3) in which the plutonium in solution is reduced to Pu(III) with titanium(III) chloride, excess Ti(III) is destroyed with nitric acid, and finally, the reduced plutonium is oxidized to Pu(IV) with ceric titrant using ferroin indicator. However, this adaptation substitutes a potentiometric endpoint for the indicator endpoint and uses commercial titration instrumentation (4, 5).

3.3 This test method was developed for production support and has distinct advantages when a large number of samples are to be analyzed. It is largely automated, accomplishing a titration approximately every 2 min when optimizing step-wise operations. Variations on this test method, such as manual titration with visual or photometric endpoint detection or use of a weight buret would, no doubt, provide quality data, but at the expense of limiting sample throughput.

4. Significance and Use

4.1 This test method is designed to determine the plutonium content of plutonium metal.

4.2 *Committee C-26 Safeguards Statement*⁴:

4.2.1 The material (plutonium metal) to which this test method applies is subject to nuclear safeguards regulations governing its possession and use. Materials for use by the commercial nuclear community must also meet compositional specifications.

4.2.2 The analytical method in this test method both meets U.S. Department of Energy guidelines for acceptability of a measurement method for generation of safeguards accountability measurement data and also provides data that may be used

¹ This test method is under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

Current edition approved Jan. 10, 1999. Published February 1999. Originally published as C 1235 – 93. Last previous edition C 1235 – 93a.

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

³ The boldface numbers in parentheses refer to the list of references at the end of this test method.

⁴ Based upon Committee C-26 Safeguards Matrix (C 1009, C 1068, C 1128, C 1156, C 1210, and C 1297).

to demonstrate specification compliance in buyer-seller interactions.

5. Interferences

5.1 Interference is caused by any substance that can be reduced by titanium(III) chloride and, subsequently, oxidized by Ce(IV) during the titration. The only elements normally present in high-purity plutonium metal that interfere are iron and uranium. Corrections for these two interferences are based upon iron and uranium content determined by other methods and by stoichiometry of the titration reaction.

6. Apparatus

6.1 *Automated Titrator*⁵—An instrument capable of delivering titrant and recognizing the redox titration endpoint. Alternatively, a weight buret and a millivolt meter could be used for manual titration.

6.2 *Combination Electrode or Endpoint Indicator*⁶—A combination platinum-calomel reference electrode or appropriate endpoint indicator.

6.3 *Analytical Balance*—A calibrated balance having a sensitivity of 0.01 mg for weighing plutonium samples.

6.4 *Bottle-Top Dispensers*—A variety of fixed volume or adjustable dispensers for delivering reagents to the titration beaker.

7. Reagents

7.1 All reagent solutions are to be prepared using laboratory demineralized or deionized water.

7.2 Reagent grade chemicals are used unless otherwise specified.⁷

7.3 *Ceric Ammonium Nitrate*⁸ (0.051N)—For each litre of solution to be prepared, dissolve 28.0 g of ceric ammonium nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ in 950 mL of water. When the reagent has dissolved, add 27 mL of concentrated sulfuric acid. When cool, dilute the resulting solution to 1 L with water, and mix thoroughly. Standardize as discussed in Section 9.

7.4 *Ferrous Ammonium Sulfate Solution* (approximately 0.92N in approximately 0.5N HCl)—First add 20 mL of concentrated hydrochloric acid (HCl) to 400 mL of water in a graduated 500-mL beaker and stir. Weigh 180 g of ferrous ammonium sulfate hexahydrate $(\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O})$ crystals and pour slowly into the dilute hydrochloric acid. Stir until dissolved. Finally, add water to the 500-mL mark and continue stirring until mixed. Transfer the contents to a 500-mL storage bottle. This amount represents a convenient volume for extended use.

⁵ The Mettler DL40 Memotitrator with the DV910 10-mL polypropylene and glass buret with Mettler GA40 or GA44 printer, available from Mettler Instrument Corp., Box 71, Hightstown, NJ 08520, has been found satisfactory.

⁶ The Mettler DM140 combination platinum ring with calomel reference electrode and 3N KCl filling solution, available from Mettler Instrument Corp., Box 71, Hightstown, NJ 08520, has been found satisfactory.

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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁸ The G. F. Smith Primary Standard has been found to be satisfactory and has a minimum purity of 99.9 %. Reagent grade ceric ammonium nitrate can be as low as 99 % pure and its use is not recommended.

7.5 *Hydrochloric Acid Solution (6N)*—For each litre of solution to be prepared, carefully add 500 mL of concentrated hydrochloric acid (HCl) to 500 mL of water and mix thoroughly.

7.6 *Nitric Acid-Sulfuric Acid Solution (8N HNO₃-3N H₂SO₄)*—For each litre of solution to be prepared, carefully add 83 mL of concentrated sulfuric acid (H₂SO₄) to 350 mL of water followed by the careful addition of 500 mL of concentrated nitric acid (HNO₃). When cool, dilute the resulting solution to 1 L and mix thoroughly.

7.7 *Potassium Chloride Solution (3N)*—Dissolve 22.37 g of potassium chloride (KCl) crystals in 100 mL of water. This amount represents a convenient volume for extended use.

7.8 *Sulfamic Acid Solution* (approximately 0.5 % by weight)—Dissolve 5 g of sulfamic acid (NH₂SO₃H) for each litre of solution to be prepared.

7.9 *Titanium(III) Chloride (TiCl₃)*—20 % solution, stabilized, technical grade.⁹

8. Preparation of the Automated Titrator

8.1 Commercially available automated titrators and electrode systems generally require performance optimization. The operating manual will provide instructions for instrument setup and checkout.

8.2 The parameters specific for the Mettler DL40 Autotitrator are found in Ref (5).

9. Standardization

NOTE 1—A well-characterized plutonium metal is used as a secondary standard, traceable to NBL-CRM 126 or its equivalent. Secondary standards can also be included with the sample run as quality assurance checks.

NOTE 2—Multiple titrations are recommended to establish a precise standardization of the titrant and will precede sample titrations to permit direct calculation of sample results.

9.1 File the secondary standard metal to a shiny luster. Other cleaning procedures may be as effective though not as fast.

NOTE 3—**Warning:** Plutonium metal is pyrophoric. Filing of plutonium will generate sparks. To prevent a fire, avoid having other plutonium metal, particularly turnings, in the immediate vicinity.

9.2 Cut metal to be used for standardization into 210- to 240-mg pieces.

9.3 Weigh the metal on a calibrated analytical balance having a sensitivity of 0.01 mg.

9.4 Transfer the metal to a 250-mL electrolytic beaker.

9.5 Add 4 mL of 6N HCl to the beaker.

NOTE 4—The metal dissolves rapidly with effervescence. Sample loss is prevented by the tall sides of the beaker.

9.6 Swirl the beaker until the metal is entirely dissolved.

9.7 Add 20 mL of 8N HNO₃-3N H₂SO₄ to the beaker.

9.8 Add 0.5 % sulfamic acid solution from a squeeze bottle to the beaker, rinsing the sides, to a total volume of approximately 125 mL.

⁹ Fisher Scientific is the sole domestic supplier; their product number is ST43-500. This product is necessary for proper titration characteristics because of its concentration and the fact that it is stabilized with phosphoric acid.