



# Standard Test Method for Plutonium by Titanium(III)/Cerium(IV) Titration<sup>1</sup>

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 ( $\epsilon$ ) 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 Industry<sup>2</sup>

C 1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry<sup>2</sup>

C 1128 Guide for Preparation of Working Reference Materials for Use in the Analysis of Nuclear Fuel Cycle Materials<sup>2</sup>

C 1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials<sup>2</sup>

C 1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry<sup>2</sup>

C 1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials<sup>2</sup>

## 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)<sup>3</sup> 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*<sup>4</sup>:

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

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 12.01.

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

<sup>4</sup> 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*<sup>5</sup>—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*<sup>6</sup>—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.<sup>7</sup>

7.3 *Ceric Ammonium Nitrate*<sup>8</sup> (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.

<sup>5</sup> 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.

<sup>6</sup> 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.

<sup>7</sup> *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.

<sup>8</sup> 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 HNO<sub>3</sub>-3N H<sub>2</sub>SO<sub>4</sub>)*—For each litre of solution to be prepared, carefully add 83 mL of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to 350 mL of water followed by the careful addition of 500 mL of concentrated nitric acid (HNO<sub>3</sub>). 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 (NH<sub>2</sub>SO<sub>3</sub>H) for each litre of solution to be prepared.

7.9 *Titanium(III) Chloride (TiCl<sub>3</sub>)*—20 % solution, stabilized, technical grade.<sup>9</sup>

## 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 HNO<sub>3</sub>-3N H<sub>2</sub>SO<sub>4</sub> 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.

<sup>9</sup> 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.

9.9 Place the beaker on a magnetic stirrer.

9.10 Immerse the electrode into the solution.

9.11 Stir the contents of the beaker rapidly.

9.12 Add 1 mL of Ti(III) solution.

9.13 Commence titrating according to the requirements of the automated titrator after the potential stabilizes (approximately 2 min). The titration may also be done using a weight buret and a millivolt meter.

9.14 Repeat 9.4-9.13 for multiple titrations of standards to allow calculation of the precision of the standardization. A series of four titrations demonstrating an RSD of less than or equal to  $\pm 0.03\%$  is acceptable.

## 10. Preconditioning the Electrode

NOTE 5—A preconditioning of the electrode for best performance is recommended before each assay run and can be done by using approximately 1 meq (1 mL) of ferrous ammonium sulfate solution as a stand-in for plutonium. Four such initial titrations have been found to be sufficient to stabilize initial electrode performance. The results of these titrations can be ignored.

10.1 Add 1 mL of iron(II) solution to a 250-mL electrolytic beaker.

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

10.3 Add 20 mL of 8N  $\text{HNO}_3$ -3N  $\text{H}_2\text{SO}_4$  to the beaker.

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

10.5 Place the beaker on a magnetic stirrer.

10.6 Immerse the electrode into the solution.

10.7 Stir the contents of the beaker rapidly so as to form a vortex reaching at least to the stirring bar.

10.8 Add 1 mL of Ti(III) solution.

10.9 Commence titrating according to the requirements of the automated titrator when the potential stabilizes (after approximately 2 min).

## 11. Procedure

11.1 File the metal samples until the surface area exhibits a shiny luster (see Note 1 and Note 3).

11.2 Cut the metal into 210- to 240-mg samples.

11.3 Weigh the samples on a calibrated analytical balance having a sensitivity of 0.01 mg.

11.4 Proceed with sample titration exactly as described for standardization in 9.4-9.13.

NOTE 6—Titration in duplicate is recommended as a general practice with agreement criteria between results to be determined for quality control purposes.

## 12. Calculation

12.1 *Standardization:*

$$\frac{W \times f}{A \times V} = N \quad (1)$$

where:

$W$  = weight of secondary standard, mg;

$f$  = purity factor for secondary standard;

$A$  = atomic weight of plutonium;

$V$  = volume of ceric titrant, mL; and

$N$  = normality of ceric titrant.

12.2 *Samples:*

$$\frac{N \times V \times A}{W} = \frac{\text{g Pu}}{\text{g sample}} \quad (2)$$

where:

$N$ ,  $V$ , and  $A$  are as given above and

$W$  = weight of sample, mg.

12.3 Correct for uranium by subtracting 0.000 20 from the grams of plutonium per gram (g Pu/g) sample value for each 100 ppm of uranium impurity and for iron by subtracting 0.000 43 from the g Pu/g sample value for each 100 ppm of iron impurity.

NOTE 7—Laser fluorometry (6, 7) has been adapted for uranium determination in a plutonium matrix.

NOTE 8—Atomic absorption (8), inductively coupled plasma spectrometry (9), and spectrophotometry have been adapted for iron determination in a plutonium matrix.

These corrections can also be made by applying the expression:

$$\begin{aligned} \text{Corrected g Pu/g sample} = \\ \text{Titrated g Pu/g sample} - (\text{ppm U} \times 2 \times 10^{-6}) - \\ (\text{ppm Fe} \times 4.3 \times 10^{-6}) \end{aligned} \quad (3)$$

## 13. Precision and Bias

13.1 The developmental report (4, 5) for this test method states "... inexperienced technicians are capable of highly precise results with negligible bias." Results reported were as follows for data collected over ten weeks on a reference metal having a plutonium content of 0.9910 g/g as characterized by comparison to NBS 949f:

Technician	Mean, g/g	Standard Deviation, g/g
1	0.9909	0.000 23
2	0.9910	0.000 25
3	0.9908	0.000 35

13.2 At the same laboratory, two aliquots of a control metal are run with each batch of production samples. The control metal is a piece of production metal deemed to be homogenous but having no reference value. Data were collected under a full spectrum of routine production conditions between December 1988 and December 1989. The average of aliquot pairs were recorded. The standard deviation of 231 such results was 0.000 48 g/g.

13.3 This test method was developed for the assay of high purity plutonium metal. If significant amounts of impurities are present in a metal to be analyzed, the precision of the assay will depend on the precision of the impurity measurements.

13.4 This test method has not been tested at other laboratories.

## 14. Keywords

14.1 analysis; assay; automated; metal; plutonium; potentiometric; redox; test; titration

## REFERENCES

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