



# Standard Test Method for Uranium in the Presence of Plutonium by Iron(II) Reduction in Phosphoric Acid Followed by Chromium(VI) Titration<sup>1</sup>

This standard is issued under the fixed designation C 1204; 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 covers unirradiated uranium-plutonium mixed oxide having a uranium to plutonium ratio of 2.5 and greater. The presence of larger amounts of plutonium (Pu) that give lower uranium to plutonium ratios may give low analysis results for uranium (U) **(1)**<sup>2</sup>, if the amount of plutonium together with the uranium is sufficient to slow the reduction step and prevent complete reduction of the uranium in the allotted time. Use of this test method for lower uranium to plutonium ratios may be possible, especially when 20 to 50 mg quantities of uranium are being titrated rather than the 100 to 300 mg in the study cited in Ref **(1)**. Confirmation of that information should be obtained before this test method is used for ratios of uranium to plutonium less than 2.5.

1.2 The amount of uranium determined in the data presented in Section 12 was 20 to 50 mg. However, this test method, as stated, contains iron in excess of that needed to reduce the combined quantities of uranium and plutonium in a solution containing 300 mg of uranium with uranium to plutonium ratios greater than or equal to 2.5. Solutions containing up to 300 mg uranium with uranium to plutonium ratios greater than or equal to 2.5 have been analyzed **(1)** using the reagent volumes and conditions as described in Section 10.

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.* For specific hazard statements, see Section 8.

## 2. Referenced Documents

### 2.1 ASTM Standards:

C 852 Guide for Design Criteria for Plutonium Glove boxes<sup>3</sup>

C 1128 Guide for Preparation of Working Reference Mate-

rials for Use in the Analysis of Nuclear Fuel Cycle Materials<sup>3</sup>

C 1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis<sup>3</sup>

## 3. Summary of Test Method

3.1 Samples are prepared by dissolution techniques detailed in Practice C 1168 and Ref **(2)**. Aliquants containing 20 to 300 mg of uranium, as selected by the facility procedure, are prepared by weight. The sample is fumed to incipient dryness after the addition of sulfuric acid. The sample is dissolved in dilute sulfuric acid prior to titration.

3.2 Uranium is reduced to uranium(IV) by excess ferrous (iron(II)) in concentrated phosphoric acid ( $H_3PO_4$ ) containing sulfamic acid. The excess iron(II) is selectively oxidized by nitric acid ( $HNO_3$ ) in the presence of molybdenum(VI) catalyst. After the addition of vanadium(IV), the uranium(IV) is titrated with chromium(VI) to a potentiometric end point **(3, 4)**.

3.3 A single chromium(VI) titrant delivered manually on a weight or volume basis is used. The concentration of the chromium(VI) solution is dependent upon the amount of uranium being titrated (see 7.8). Automated titrators that have comparable precisions can be used.

NOTE 1—An alternative ceric (V) sulfate or nitrate titrant may also be used, providing that the user demonstrates equivalent performance to the dichromate titrant.

3.4 For the titration of uranium alone, the precision of the modified Davies and Gray titration method has been improved by increasing the amount of uranium titrated to 1 g and delivering about 90 % of the titrant on a solid mass basis followed by titration to the end point with a dilute titrant **(5)**. This modification has not been studied for the titration of uranium in the presence of plutonium, and confirmation of its applicability should be obtained by the facility prior to its use.

3.5 The modification of the Davies and Gray titration method, as described originally in Ref **(4)**, may be used instead of the method described herein, where laboratories have demonstrated no plutonium interference at the uranium to plutonium ratios and amounts titrated at that facility. If any modification is made to the procedure in Ref **(4)** for application at the facility to uranium, plutonium mixed oxides, confirmation that the modification does not degrade the analysis

<sup>1</sup> This test method 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 Jan. 10, 2002. Published April 2002. Originally published as C 1204–91. Last previous edition C 1204–91(1996).

<sup>2</sup> The boldface numbers in parentheses refer to the list of references at the end of this test method.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 12.01.

technique as stated should be demonstrated prior to its use.

#### 4. Significance and Use

4.1 Factors governing selection of a method for the determination of uranium include available quantity of sample, sample purity, desired level of reliability, and equipment availability.

4.2 This test method determines 20 to 300 mg of uranium, is applicable to fast breeder reactor (FBR)-mixed oxides having a uranium to plutonium ratio of 2.5 and greater, is tolerant towards most metallic impurity elements usually specified for FBR-mixed oxide fuel, and uses no special equipment.

4.3 The ruggedness of the titration method has been studied for both the volumetric (6) and the weight (7) titration of uranium with dichromate.

#### 5. Interferences

5.1 Interfering elements are not generally present in significant quantities in mixed uranium, plutonium oxide product material. However, elements that cause an error when present in milligram quantities are silver (Ag), vanadium (V), plutonium (Pt), ruthenium (Ru), osmium (Os), and iodine (I). Interference from tin (Sn), arsenic (As), antimony (Sb), molybdenum (Mo), manganese (Mn), fluorine (F), chlorine (Cl), and bromine (Br) are eliminated when the preparation procedure is followed as given (4, 8, 9, 10, 11, 12) in this titrimetric method. Of the metallic impurity elements usually included in specifications for FBR-mixed oxide fuel, silver, manganese, lead (Pb), and vanadium interfere.

5.2 Other interfering metallic elements are gold (Au), mercury (Hg), iridium (Ir), and palladium (Pd). Elimination of their interference requires their separation from uranium by such techniques as ion exchange and solvent extraction (13, 14).

5.3 An initial fuming with sulfuric acid removes such impurity elements as the halides and volatile metallic elements.

5.4 The effects of impurities and their removal are listed in Table A1.1 of Annex A1, and the details are given in Refs (4, 8, 9, 10, 11, 12, 13, 14, 15).

#### 6. Apparatus

6.1 *Buret*—Polyethylene bottle (preparation instructions can be found in Appendix X1), glass weight, or volumetric.

6.2 *pH Meter*, with indicator (platinum has been found to be satisfactory) and reference (saturated calomel has been found to be satisfactory) electrodes.

NOTE 2—The indicator electrode should be changed or cleaned if there is a titration problem such as less distinct than normal end point break or end point drift, or, if desired, prior to use when more than a week has passed since its last use. Suggested cleaning procedures for platinum electrodes are detailed in Appendix X2.

NOTE 3—The reference electrode should be covered with a rubber tip or submerged in a solution (saturated potassium chloride solution for the calomel electrode) for overnight storage.

#### 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 conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>4</sup> Other grades of reagents 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 laboratory accepted demineralized or deionized water.

7.3 *Ferrous Sulfate (1.0 M)*—Add 100 mL of sulfuric acid ( $H_2SO_4$ , sp gr 1.84) to 750 mL of water as the solution is stirred. Add 280 g of ferrous sulfate heptahydrate ( $FeSO_4 \cdot 7H_2O$ ), and dilute the solution to 1 L with water. Prepare ferrous sulfate reagent fresh on a weekly basis. See Note 6 on combination of this reagent.

7.4 *Nitric Acid ( $HNO_3$ ), 8 M*—Add 500 mL of  $HNO_3$  (sp gr 1.42) to less than 500 mL of water and dilute to 1 L.

7.5 *Nitric Acid (8 M)-Sulfamic Acid (0.15 M)-Ammonium Molybdate (0.4 %)*—Dissolve 4 g of ammonium molybdate [ $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ] in 400 mL of water, and add 500 mL of nitric acid ( $HNO_3$ , sp gr 1.42). Mix and add 100 mL of 1.5 M sulfamic acid solution (see 7.9) and mix.

7.6 *Orthophosphoric Acid ( $H_3PO_4$ ), 85 %*—Test and treat for reducing substances prior to use (see Annex A2).

7.7 *Potassium Dichromate Solution (2 %)*—Dissolve 2 g of  $K_2Cr_2O_7$  in water, and dilute to 100 g with water.

7.8 *Potassium Dichromate Titrant (0.0045 M and 0.045 M)*—Dissolve 2.65 g of reagent grade or purer grade  $K_2Cr_2O_7$  in water; transfer this solution to a pre-weighed, 2-L volumetric flask and dilute to volume; this solution is for use in titration of 20 to less than 100 mg uranium aliquants. Dissolve 26.5 g of reagent grade or purer grade  $K_2Cr_2O_7$  in water; transfer this solution to a pre-weighed, 2-L flask and dilute to volume; this solution is for use in titration of 100 to 300 mg uranium aliquants.

7.8.1 If National Institute of Standards and Technology (NIST) standard reference material dichromate (SRM 136e or equivalent) was used, proceed as in 7.8.1.1 and 7.8.1.2 before going to 7.8.3; otherwise go to 7.8.2.

7.8.1.1 Allow the solution to equilibrate to room temperature, weigh the solution, and compute the uranium equivalent titration factor after correcting the weight of dichromate for buoyancy (see 11.1.1) and for oxidizing power (see 11.1.2).

7.8.1.2 Verify the preparation accuracy of the dichromate or ceric titrant solution by titration with a standard uranium solution (see 7.12) within laboratory accepted error limits.

7.8.2 If a reagent grade dichromate or ceric titrant was used, allow the solution to equilibrate to room temperature and standardize the dichromate solution against CRM uranium (see 7.12).

7.8.3 Store the dichromate solution in one or more borosilicate glass bottles with poly-seal tops, or equivalent containers,

<sup>4</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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

to prevent concentration changes due to evaporation.

7.9 *Sulfamic Acid* (1.5 M)—Dissolve 146 g of sulfamic acid ( $\text{NH}_2\text{SO}_3\text{H}$ ) in water, filter the solution, and dilute to 1 L.

7.10 *Sulfuric Acid* (1 M)—Add 56 mL of  $\text{H}_2\text{SO}_4$  (sp gr 1.84) to water, while stirring, and dilute to 1 L with water.

7.11 *Sulfuric Acid* (0.05 M)—Add 2.8 mL of  $\text{H}_2\text{SO}_4$  (sp gr 1.84) to water, while stirring, and dilute to 1 L with water.

7.12 *Uranium Reference Solution*—Guide C 1128, Section X3.4 may be used to prepare working reference solutions, or solutions may be prepared with appropriate in-house procedures from certified uranium metal.<sup>5</sup>

7.12.1 Clean the surface of the uranium metal, New Brunswick Laboratory CRM 112-A or its replacement,<sup>5</sup> following the instructions on the certificate.

7.12.2 Weigh the metal by difference to 0.01 mg making buoyancy and purity corrections detailed in 11.1.1 and 11.1.2, respectively.

7.12.3 Prepare the uranium standard solution in accordance with Guide C 1128 or by the procedure approved for use by your facility. There are many methods of uranium metal dissolution that are successful; methods that reproduce the uranium assay value on the certificate are acceptable. An example of an acceptable dissolution method is given in Appendix Appendix X4.

7.12.4 Equilibrate the uranium solution to room temperature, and weigh the solution to give the same number of significant figures as the metal weight.

7.12.5 Calculate the solution concentration in mg uranium/g uranium solution using the calculation in 11.2.2.

7.13 *Vanadyl Sulfate Dihydrate in Solution* (0.0038 M vanadium(IV)-0.18 M  $\text{H}_2\text{SO}_4$ )—Add 20 mL concentrated sulfuric acid (sp gr 1.84) to less than 980 mL water with stirring and equilibrate to room temperature. Weigh 1.5 g of vanadyl sulfate dihydrate ( $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ ) crystals, mix the solid with the temperature equilibrated sulfuric acid, and dilute the solution to 2 L. The vanadyl sulfate concentration should provide 75 to 125 mg  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$  per titration, but the concentration is not critical (see Refs (6) and (7)).

7.13.1 The vanadyl sulfate solution is not stable (16);  $\text{H}_2\text{SO}_4$  stabilizes the vanadium(IV) oxidation state, but the  $\text{H}_2\text{SO}_4$  concentration is not critical. The  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$  solution should be prepared at suitable intervals to prevent vanadium(V) interference (24-h intervals for preparation are suggested).

7.13.2 Alternatively, crystalline vanadyl sulfate dihydrate (75 to 125 mg per titration) may be used with a water diluent in place of the solution (see 10.13).

## 8. Hazards

8.1 Since plutonium- and uranium-bearing materials are radioactive and toxic, adequate laboratory facilities, gloved boxes, fume hoods, etc., along with safe techniques, must be used in handling samples containing these materials. A detailed discussion of all precautions necessary is beyond the scope of this test method. However, personnel who handle radioactive

materials should be familiar with such safe handling practices as are given in Guide C 852 and Refs (17) and (18).

8.2 *Committee C-26 Safeguards Statement:*

8.2.1 The materials (nuclear grade mixed oxides (U, Pu) $\text{O}_2$  powders and pellets) to which this test method applies are subject to nuclear safeguard regulations governing their possession and use. The analytical method in this test method meets U.S. Department of Energy guidelines for acceptability of a measurement method for generation of safeguards accountability measurement data.

8.2.2 When used in conjunction with the appropriate standard or certified reference materials (SRMs or CRMs), this procedure can demonstrate traceability to the national measurement base. However, use of this test method does not automatically guarantee regulatory acceptance of the resulting safeguards measurements. It remains the sole responsibility of the user of this test method to ensure that its application to safeguards has the approval of the proper regulatory authorities.

## 9. Calibration

9.1 If NIST standard potassium dichromate (SRM 136e or equivalent) is used, only solution preparation, verification titrations are needed.

9.1.1 The potassium dichromate should be prepared as instructed on the certificate, weighed to 0.01 mg, and corrected for buoyancy and purity using the calculations in 11.1.1 and 11.1.2.

9.1.2 The dichromate solution concentration is calculated in mg  $\text{K}_2\text{Cr}_2\text{O}_7$ /g solution using the calculation in 11.2.1.

9.1.3 The titration factor (mg uranium/g dichromate solution) is calculated for the dichromate solution using the calculation in 11.3.1.

9.2 If reagent grade potassium dichromate or ceric titrant is used, the solution must be standardized against a primary uranium standard (CRM 112-A or its replacement) for traceability to the national measurement base.

9.2.1 Analyze individually dispensed aliquants of the uranium reference solution in accordance with 10.3-10.14.4. See Appendix X3 for analysis control recommendations.

9.2.2 Calculate the uranium titration factor (mg uranium/g dichromate solution) for the standardized potassium dichromate solution using the calculation in 11.3.2.

## 10. Procedure

NOTE 4—Satisfactory analysis results will only be attained if the temperature of the reagents (usually at room temperature) used are  $>23^\circ\text{C}$  ( $74^\circ\text{F}$ ).

10.1 Weigh the sample (0.5 g or more) to 0.1 mg. Dissolve the sample following the procedures in Ref (2) and Practice C 1168.

10.2 Quantitatively transfer the weighed, dissolved sample to a weighed bottle for mixing prior to sample splitting. See 10.2.1 for plastic bottles or 10.2.2 for glass bottles.

10.2.1 A low-density polyethylene narrow mouth bottle, with a one-piece polypropylene special seal-ring screw closure to prevent leakage, may be used, or any other leak-proof bottle. If polyethylene bottles are used, long-term (weeks and months)

<sup>5</sup> New Brunswick Laboratory Certified Reference Materials Catalog, current issue, U.S. Department of Energy.