



Designation: C1204 – 14

Standard Test Method for Uranium in Presence of Plutonium by Iron(II) Reduction in Phosphoric Acid Followed by Chromium(VI) Titration¹

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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)², 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 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.* For specific hazard statements, see Section 8.

¹ 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.

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

2. Referenced Documents

2.1 ASTM Standards:³

C852 Guide for Design Criteria for Plutonium Gloveboxes
C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials
C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis

3. Summary of Test Method

3.1 Samples are prepared by dissolution techniques detailed in Practice C1168 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 (H₃PO₄) containing sulfamic acid. The excess iron(II) is selectively oxidized by nitric acid (HNO₃) 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 significantly 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 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.

3.5 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 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 is suitable for samples between 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 bias 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.⁴ 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 potassium dichromate traceable to a national standards laboratory (for example the National Institute of Standards Technology (NIST) in the U.S. or the Federal Institute for Materials Research and Testing (BAM) in Germany) was

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.