



Standard Test Method for Uranium by Iron (II) Reduction in Phosphoric Acid Followed by Chromium (VI) Titration in the Presence of Vanadium¹

This standard is issued under the fixed designation C 1267; 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, commonly referred to as the Modified Davies and Gray technique, covers the titration of uranium in product, fuel, and scrap materials after the material is dissolved. The test method is versatile and has been ruggedness tested. With appropriate sample preparation, this test method can give precise and unbiased uranium assays over a wide variety of material types (**1**, **2**).² Details of the titration procedure in the presence of plutonium with appropriate modifications are given in Test Method **C 1204**.

1.2 Uranium levels titrated are usually 20 to 50 mg, but up to 200 mg uranium can be titrated using the reagent volumes stated in this test method.

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 safeguard and safety precaution statements, see Section 4.

2. Referenced Documents

2.1 ASTM Standards:³

C 696 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets

C 799 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions

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

C 1204 Test Method for Uranium in the Presence of Plu-

onium by Iron(II) Reduction in Phosphoric Acid Followed by Chromium(VI) Titration

C 1346 Practice for Dissolution of UF₆ from P-10 Tubes

C 1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis

2.2 *NIST Standard:*⁴

SRM 136e Potassium Dichromate (Oxidimetric Standard)

2.3 *NBL Standard:*⁵

CRM 112A Uranium Metal Standard

3. Summary of Test Method

3.1 Samples are prepared by dissolution techniques detailed in Practices **C 1346**, **C 1347**, or Refs (**2**), (**3**), and (**4**). Appropriate uncertainties for sampling and weight determination should be applied to the overall precision and bias calculations for the final result. Aliquants containing 20 to 200 mg of uranium are prepared by weight. The sample is fumed to dryness after the appropriate acid treatment. The sample is dissolved in dilute nitric acid or water prior to titration.

3.2 Uranium is reduced to uranium(IV) by excess 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 a molybdenum(VI) catalyst. After the addition of a vanadium(IV) solution, the uranium(IV) is titrated with chromium(VI) to a potentiometric end point.

3.3 The chromium(VI) titrant may be delivered manually on a weight or on a volumetric basis as specified by the facility titration procedure.

3.3.1 If the titrant is delivered on a volumetric basis, corrections to the volume of titrant may be needed to adjust for the difference between the temperature of preparation and the ambient temperature.

3.3.2 Automated titrators are facility specific and are not explicitly addressed in this test method. However, automated titrators which have comparable bias and precision may be used.

3.3.3 There is an alternate, high precision (~0.005 % RSD) modified Davies and Gray titration, which is similar to the

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 standard.

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.

⁴ Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, <http://www.nist.gov>.

⁵ New Brunswick Laboratory (NBL) Certified Reference Materials Catalog (U.S. Department of Energy), <http://www.nbl.doe.gov>.

method covered in this procedure. In the high precision method, the amount of uranium titrated is increased and about 90 % of the titrant is delivered on a solid weight basis followed by titration to the end point with a dilute titrant. Details of this alternate method are available in Ref (5).

4. Significance and Use

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

4.2 This uranium assay method is referenced in the Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets (Test Methods C 696) and in the Test Methods for Chemical, Mass Spectrometric, and Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions (Test Methods C 799). This uranium assay method may also be used for uranium hexafluoride and uranium ore concentrate. This test method determines 20 to 200 mg of uranium; is applicable to product, fuel, and scrap material after the material is dissolved; is tolerant towards most metallic impurity elements usually specified in product and 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.

4.4 Committee C26 Safeguards Statement:

4.4.1 The materials (nuclear grade uranium in product, fuel, and scrap) to which this test method applies are subject to nuclear safeguard regulations governing their possession and use. The analytical method in this standard meets U.S. Department of Energy guidelines for acceptability of a measurement method for generation of safeguards accountability measurement data.

4.4.2 When used in conjunction with the appropriate certified reference materials (SRM⁶ or CRM), this procedure can demonstrate traceability to the national measurement base. However, use of the 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 assure that its application to safeguards has the approval of the proper regulatory authorities.

5. Interferences

5.1 Interfering elements are not generally present in product and fuel material in quantities which cause interference in the titration.

5.1.1 Of the metallic impurity elements usually included in specifications for product and fuel, silver, manganese, and vanadium (in the V oxidation state) interfere when present in amounts of 10 mg or greater of impurity per 100 mg of uranium (2, 8).

5.1.2 Silver and vanadium (in the V oxidation state) cause positive bias when present in milligram quantities in the sample. The aliquant treatment adjusts the oxidation state of

any vanadium(V) present in the sample (2). To remove silver, the sample must be treated prior to titration (8).

5.1.3 Manganese was originally found to cause a negative bias (2), but this bias is eliminated when the titration aliquant preparation procedure is followed as given (9, 10) in this titrimetric method.

5.2 Interferences with the Modified Davies and Gray titration, which may be present in some uranium materials, have been systematically studied.

5.2.1 The non-interference of copper, titanium, cobalt, nickel, cerium, and samarium was demonstrated (11) at the 50 mg impurity level for 100 mg of uranium.

5.2.2 The effects of the following elements in milligram quantities were studied: silver, gold, lead, iodine, arsenic, antimony, and bismuth (8).

5.2.2.1 Gold, lead, arsenic(V), antimony(V), and bismuth do not interfere when present in amounts of 10 mg for 100 mg of uranium.

5.2.2.2 Silver, iodine, arsenic(III), and antimony(III) interfere seriously in the determination of uranium and must be eliminated prior to titration.

5.2.3 The effects of impurities on the titration of uranium continued with the platinum metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum), chloride, bromide (12), fluoride (13), and technetium (14).

5.2.3.1 Ruthenium, palladium, osmium, iridium, and platinum cause serious positive errors in the determination of uranium. Rhodium alone among the platinum metals does not cause any significant error.

5.2.3.2 Chloride and bromide interfere with the assay through their effect on the platinum indicator electrode.

5.2.3.3 Small amounts of fluoride, less than 400 mg as hydrofluoric acid (HF) or 600 mg if HNO₃ is present, can be tolerated by the titration.

5.2.3.4 Technetium, found in high temperature reactor grade recycle (htgr) fuel, interferes with the titration and must be removed before titration.

5.3 The removal of certain interferences in the modified Davies and Gray titration has also been studied.

5.3.1 The initial fuming of titration aliquants with sulfuric acid removes impurity elements such as the halides and volatile metallic elements (2, 12, 13).

5.3.2 Arsenic(III) and antimony(III) can be eliminated in the H₃PO₄ by potassium dichromate (K₂Cr₂O₇) oxidation prior to its addition to the titration medium (8).

5.3.3 Elimination of interferences in the titration by mercury, platinum, and palladium by means of a copper column was evaluated (15).

5.3.4 Elimination of interferences by solvent extraction of the uranium from the impurities has also been studied (16).

5.4 A list of impurities with brief references to their treatment for elimination is given in Table A1.1 in Annex A1, and the details are given in Refs 2, 8, 9, 10, and 12-16.

6. Apparatus

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

⁶ SRM is a registered trademark.

6.2 *pH Meter*, with indicator (a 16-gauge platinum wire has been found to be satisfactory) and reference (saturated calomel has been found to be satisfactory) electrodes.

6.2.1 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 wire electrodes are detailed in [Appendix X2](#).

6.2.2 Asbestos and glass bead tipped saturated calomel electrodes can be placed directly in the titration solution. Glass frit tipped saturated calomel electrodes may have a faster leak rate and may need to be used with a separator tube containing the electrolyte to prevent titration problems due to chloride.

6.2.3 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.

6.3 *Magnetic Stirrer and TFE-Fluorocarbon Coated Magnet*.

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.⁷ 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 Heptahydrate* ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$, 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 $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$, and dilute the solution to 1 L with water. Prepare the $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ reagent fresh, weekly. See the [Note 5](#) in [10.8](#) on combination of this reagent with the H_3PO_4 .

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

7.5 HNO_3 , 1 M—Add 64 mL of HNO_3 (sp gr 1.42) to <900 mL of water, and dilute to 1 L.

7.6 HNO_3 (8 M)—Sulfamic Acid ($\text{NH}_2\text{SO}_3\text{H}$, 0.15 M)—Ammonium Molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 0.4 %)—Dissolve 4 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 400 mL of water, and add 500 mL of HNO_3 (sp gr 1.42). Mix and add 100 mL of 1.5 M $\text{NH}_2\text{SO}_3\text{H}$ solution (see [7.10](#)) and mix.

7.7 *Orthophosphoric Acid* (H_3PO_4), 85 %—Test for reducing substances prior to use (see [Annex A2](#)).

7.8 *Potassium Dichromate* ($\text{K}_2\text{Cr}_2\text{O}_7$) Solution (2 %)—Dissolve 2 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in water, and dilute to 100 g with water.

7.9 $\text{K}_2\text{Cr}_2\text{O}_7$ (0.0045 M)—Dissolve 2.65 g of reagent grade or purer grade $\text{K}_2\text{Cr}_2\text{O}_7$ in water; transfer this solution to a pre-weighed, 2-L volumetric flask or suitable alternative and dilute to volume, or use equivalent weight/volume ratios for larger quantities of solution.

7.9.1 If National Institute of Standards and Technology (NIST) standard reference material $\text{K}_2\text{Cr}_2\text{O}_7$ (SRM 136e or its equivalent) was used, proceed as in [7.9.1.1](#) and [7.9.1.2](#) before going to [7.9.3](#); otherwise go to [7.9.2](#).

7.9.1.1 Allow the solution to equilibrate to room temperature, obtain the weight of the solution. Compute the dichromate concentration ([11.2.2](#)) and the uranium titration factor ([11.3.2](#)) after correcting the weight of dichromate for buoyancy ([11.1.2](#)) and for purity ([11.1.3](#)).

7.9.1.2 As a good quality practice, a check on the material handling of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution within laboratory accepted uncertainties may be done by titration with a working reference uranium solution. For guidance in the preparation of a working reference uranium solution, see [Guide C 1128](#). If the titrations do not agree within laboratory accepted uncertainties, verification titrations for SRM 136e or its equivalent may be done using New Brunswick Laboratory (NBL) CRM 112-A uranium metal or its equivalent,⁵ prepared in [7.12](#), or the $\text{K}_2\text{Cr}_2\text{O}_7$ solution should be discarded.

7.9.2 If a reagent grade $\text{K}_2\text{Cr}_2\text{O}_7$ was used, allow the solution to equilibrate to room temperature and standardize the $\text{K}_2\text{Cr}_2\text{O}_7$ solution against CRM 112-A uranium metal or its equivalent prepared in [7.12](#) (see [Appendix X3](#)). Compute the uranium titration factor as in [11.3.3](#).

7.9.3 Store the $\text{K}_2\text{Cr}_2\text{O}_7$ solution in one or more borosilicate glass bottles with a poly-seal top or an equivalent container to prevent concentration changes due to evaporation.

7.10 $\text{NH}_2\text{SO}_3\text{H}$ (1.5 M)—Dissolve 146 g of $\text{NH}_2\text{SO}_3\text{H}$ in water, filter the solution, and dilute to 1 L.

7.11 *Sulfuric Acid* (H_2SO_4 , 1 M)—Add 56 mL of H_2SO_4 (sp gr 1.84) to water, while stirring, and dilute to 1 L with water.

7.12 *Uranium Standard (CRM) Solution*:

7.12.1 Clean the surface of the uranium metal (CRM 112-A or its equivalent) following the instructions on the certificate.

7.12.2 Obtain the weight of the metal by difference to 0.01 mg making buoyancy and purity corrections detailed in [11.1.2](#) and [11.1.3](#), respectively.

7.12.3 Prepare the uranium standard solution. There are many successful methods of uranium metal dissolution (none is specified on the CRM 112-A certificate); methods which reproduce the uranium assay value on the certificate are acceptable. An example of an acceptable method is given in [Appendix X4](#).

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

7.12.4.1 Calculate the solution concentration in mg U/g uranium solution using the calculation in [11.2.3](#).

7.12.4.2 As a good quality practice, a check on the material handling of the uranium solution within laboratory accepted

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.