



Designation: C1267 – 17 (Reapproved 2022)

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 C1267; 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 C1204.

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

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific safeguard and safety precaution statements, see Section 5.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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.

2. Referenced Documents

2.1 ASTM Standards:³

C696 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets

C799 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions

C859 Terminology Relating to Nuclear Materials

C1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry

C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials

C1204 Test Method for Uranium in Presence of Plutonium by Iron(II) Reduction in Phosphoric Acid Followed by Chromium(VI) Titration

C1346 Practice for Dissolution of UF₆ from P-10 Tubes

C1347 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. Terminology

3.1 Except as otherwise defined herein, definitions of terms are as given in Terminology C859.

4. Summary of Test Method

4.1 Samples are prepared by dissolution techniques detailed in Practices C1346, C1347, or Refs (2), (3), and (4). Appropriate uncertainties for sampling and weight determination

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://science.energy.gov/nbl>.

should be applied to the overall precision and bias calculations for the final result. Aliquants containing 20 mg 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.

4.2 Uranium is reduced to uranium(IV) by excess 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 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.

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

4.3.1 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.

4.3.2 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.

4.3.3 There is an alternate, high precision ($\sim 0.005\%$ RSD) modified Davies and Gray titration, which is similar to the 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).

5. Significance and Use

5.1 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.

5.2 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 C696) and in the Test Methods for Chemical, Mass Spectrometric, and Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions (Test Methods C799). This uranium assay method may also be used for uranium hexafluoride and uranium ore concentrate. This test method determines 20 mg 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.

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

5.4 *Fitness for Purpose of Safeguards and Nuclear Safety Application*—Methods intended for use in safeguards and nuclear safety applications shall meet the requirements specified by Guide C1068 for use in such applications.

5.4.1 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.

6. Interferences

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

6.1.1 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).

6.1.2 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).

6.1.3 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.

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

6.2.1 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.

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

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

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

6.2.3 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).

6.2.3.1 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.

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

6.2.3.3 Small amounts of fluoride, less than 400 mg as hydrofluoric acid (HF) or 600 mg if HNO_3 is present, can be tolerated by the titration.

⁶ SRM is a registered trademark.