



Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions¹

This standard is issued under the fixed designation C 799; 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 These test methods cover procedures for the chemical, mass spectrometric, spectrochemical, nuclear, and radiochemical analysis of nuclear-grade uranyl nitrate solution to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

	Sections
Determination of Uranium	7
Specific Gravity by Pycnometry	15-20
Free Acid by Oxalate Complexation	21-27
Determination of Thorium	28
Determination of Chromium	29
Determination of Molybdenum	30
Halogens Separation by Steam Distillation	31-35
Fluoride by Specific Ion Electrode	36-42
Halogen Distillate Analysis: Chloride, Bromide, and Iodide by Amperometric Microtitrimetry	43
Determination of Chloride and Bromide	44
Determination of Sulfur by X-Ray Fluorescence	45
Sulfate Sulfur by (Photometric) Turbidimetry	46
Phosphorus by the Molybdenum Blue (Photometric) Method	54-61
Silicon by the Molybdenum Blue (Photometric) Method	62-69
Carbon by Persulfate Oxidation-Acid Titrimetry	70
Conversion to U_3O_8	71-74
Boron by Emission Spectrography	75-81
Impurity Elements by Spark Source Mass Spectrography	82
Isotopic Composition by Thermal Ionization Mass Spectrometry	83
Uranium-232 by Alpha Spectrometry	84-90
Total Alpha Activity by Direct Alpha Counting	91-97
Fission Product Activity by Beta Counting	98-104
Entrained Organic Matter by Infrared Spectrophotometry	105
Fission Product Activity by Gamma Counting	106
Determination of Arsenic	107
Determination of Impurities for the EBC Calculation	108
Determination of Technetium 99	109
Determination of Plutonium and Neptunium	110

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.* Specific precautionary statements are given in Section 5.

¹ These test methods are under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and are the direct responsibility of Subcommittee C26.05 on Methods of Test.

Current edition approved June 1, 2005. Published October 2005. Originally approved in 1975. Last previous edition approved in 1999 as C 799 – 99¹.

2. Referenced Documents

2.1 ASTM Standards:²

- C 696 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets
- C 761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride
- C 788 Specification for Nuclear-Grade Uranyl Nitrate Solution
- C 1219 Test Methods for Arsenic in Uranium Hexafluoride
- C 1233 Practice for Determining Equivalent Boron Contents of Nuclear Materials
- C 1254 Test Method for the Determination of Uranium in Mineral Acids by X-Ray Fluorescence
- C 1267 Test Method for Uranium by Iron (II) Reduction in Phosphoric Acid Followed by Chromium (VI) Titration in the Presence of Vanadium
- C 1287 Test Method for Determination of Impurities in Uranium Dioxide by Inductively Coupled Plasma Mass Spectrometry
- C 1295 Test Method for Gamma Energy Emission from Fission Products in Uranium Hexafluoride and Uranyl Nitrate Solution
- C 1296 Test Method for the Determination of Sulfur in Uranium Oxides and Uranyl Nitrate Solutions by X-Ray Fluorescence (XRF)
- C 1380 Test Method for Determination of Uranium Content and Isotopic Composition by Isotope Dilution Mass Spectrometry
- C 1413 Test Method for Isotopic Analysis of Hydrolysed Uranium Hexafluoride and Uranyl Nitrate Solutions by Thermal Ionization Mass Spectrometry
- D 1193 Specification for Reagent Water
- E 12 Terminology Relating to Density and Specific Gravity

² 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.

of Solids, Liquids, and Gases

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals

2.2 *American Chemical Society Specification:*

Reagent Chemicals³

2.3 *Other Documents:*

ISO 7097 Determination of Uranium in Uranium Product Solutions and Solids with Cerium IV Oxidation Titrimetric Method⁴

3. Significance and Use

3.1 Uranyl nitrate solution is used as a feed material for conversion to the hexafluoride as well as for direct conversion to the oxide. In order to be suitable for this purpose, the material must meet certain criteria for uranium content, isotopic composition, acidity, radioactivity, and impurity content. These methods are designed to show whether a given material meets the specifications for these items described in Specification **C 788**.

3.1.1 An assay is performed to determine whether the material has the specified uranium content.

3.1.2 Determination of the isotopic content of the uranium is made to establish whether the effective fissile content is in accordance with the purchaser's specifications.

3.1.3 Acidity, organic content, and alpha, beta, and gamma activity are measured to establish that they do not exceed their maximum limits.

3.1.4 Impurity content is determined to ensure that the maximum concentration limit of certain impurity elements is not exceeded. Impurity concentrations are also required for calculation of the equivalent boron content (EBC), and the total equivalent boron content (TEBC).

4. Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades 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.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification **D 1193**.

5. Safety Precautions

5.1 Use of this standard does not relieve the user of the obligation to be aware of and to conform to all health and safety requirements.

5.2 The user should also be cognizant of and adhere to all federal, state, and local regulations for processing, shipping, or in any way using uranyl nitrate solutions.

6. Sampling

6.1 Criteria for sampling this material are given in Specification **C 788**.

DETERMINATION OF URANIUM

7. Scope

7.1 Uranium can be determined using iron (II) reduction and dichromate titration. Test Method **C 1267** can be used.

7.2 Uranium can also be determined using cerium (IV) oxidation titrimetry. **ISO 7097** Test Method can be used.

7.3 Uranium can also be determined by X-Ray Fluorescence using Test Method **C 1254**.

7.4 Previous sections have been deleted.

URANIUM BY IGNITION GRAVIMETRY

8. Scope

8.1 This test method covers the determination of uranium in nuclear-grade uranyl nitrate solution. Appropriate size sample aliquots are chosen to obtain 5 to 10 g of U_3O_8 .

9. Summary of Test Method

9.1 The uranyl nitrate solution is evaporated to dryness, ignited to U_3O_8 , and weighed. Corrections are made for any impurities present (**1, 2**).

10. Interferences

10.1 The weight of U_3O_8 is corrected for the nonvolatile impurities present as determined by spectrographic analysis.

10.2 Volatile anions that are difficult to decompose require an extended ignition period.

11. Apparatus

11.1 *Heat Lamp*, infrared.

11.2 *Hot Plate*.

11.3 *Muffle Furnace*.

12. Procedure

12.1 Transfer a weighed portion of uranyl nitrate solution containing 5 to 10 g of uranium into a preweighed platinum dish and add 2 drops of HF (48 %).

12.2 Position the dish under the heat lamp and evaporate the solution to dryness.

12.3 Place the dish on a hot plate with a surface temperature of about 300°C and heat until most of the nitrate has decomposed.

12.4 Transfer the dish to a muffle furnace and ignite for 2 h at 900°C.

12.5 Remove the dish to a desiccator and allow to cool to room temperature.

12.6 Weigh the dish; then repeat **12.4-12.6** until a constant weight is obtained.

³ *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.

⁴ Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

13. Calculation

13.1 Calculate the uranium content as follows:

$$\text{Uranium, g/g} = ((B - C)/A) D \quad (1)$$

where:

A = sample, g,

B = U₃O₈ obtained, g,

C = impurity-element oxides, g, and

D = gravimetric factor, grams of uranium/grams of U₃O₈(varies according to uranium enrichment).

14. Precision

14.1 The limit of error at the 95 % confidence level for a single determination is ±0.03 %.

SPECIFIC GRAVITY BY PYCNOMETRY

15. Scope

15.1 This test method covers the determination of the specific gravity of a solution of uranyl nitrate to ±0.0004.

16. Summary of Test Method

16.1 A known volume of the solution adjusted at a controlled temperature is weighed and compared to the weight of water measured in the same container (Terminology E 12).

17. Apparatus

17.1 *Volumetric Flasks*, 50-mL, Class A.

17.2 *Water Bath*, temperature controlled to ±0.1°C at a temperature slightly above normal room temperature, and provided with clips for holding volumetric flasks.

18. Procedure

18.1 Weigh the clean, dry volumetric flask and its stopper to the nearest 0.1 mg.

18.2 Fill the volumetric flask with the uranyl nitrate solution to a point close to the volume mark, using a thinstemmed funnel and a glass dropper.

18.3 Place the stoppered volumetric flask in the water bath for 30 min.

18.4 Use a finely drawn glass dropper to adjust the liquid volume to the mark.

18.5 Leave the flask in the water bath an additional 10 min to make sure that the bath temperature has been reached.

18.6 Dry and weigh the flask to the nearest 0.1 mg.

18.7 Repeat 18.2-18.6 using boiled and cooled distilled water instead of the uranyl nitrate solution.

19. Calculation

19.1 Very accurate determinations of specific gravity require that vacuo corrections be made, but if a median correction figure in terms of grams per grams of sample is applied to the solution weights in all cases the resulting error will not exceed 0.05 %.

$$\text{Sp gr} = \frac{B - A + 0.0007(B - A)}{C - A + 0.0010(C - A)} \quad (2)$$

where:

B = sample plus flask in air, g,

A = flask in air, g,

C = water plus flask in air, g,

0.0007 g/g = correction factor applicable for densities of 1.3 to 1.5, and

0.0010 g/g = correction factor for water.

20. Precision

20.1 The limit of error at the 95 % level for a single determination is ±0.03 %.

FREE ACID BY OXALATE COMPLEXATION

21. Scope

21.1 This test method covers the determination of the free acid content of uranyl nitrate solutions that may contain a ratio of up to 5 moles of acid to 1 mole of uranium.

22. Summary of Test Method

22.1 To a diluted solution of uranyl nitrate, solid, pulverized potassium oxalate is added until a pH of about 4.7 is reached. The solution is then titrated with standard NaOH solution by the delta pH method to obtain the inflection point (3).

23. Apparatus

23.1 *pH Meter*, with glass and calomel electrodes.

23.2 *Buret*, Class A, 50-mL.

24. Reagents

24.1 *Nitric Acid (2.0 N)*—Dilute 130 mL of HNO₃(sp gr 1.42) to 1 L with water. Standardize with sodium hydroxide solution (see 24.3).

24.2 *Potassium Oxalate (K₂C₂O₄·H₂O)*, crystals.

24.3 *Sodium Hydroxide Solution (0.3 N)*—Dissolve 12.0 g of NaOH in 1 L of water. Standardize with acid potassium phthalate.⁵

25. Procedure

25.1 Transfer a 5-mL sample aliquot into a 250-mL beaker.

25.2 Add 100 mL of distilled water or such volume that the uranium concentration will be between 7 and 50 g/L.

25.3 Add a spike of sufficient 2.0 N standard HNO₃ to make the sample definitely acid if the sample is neutral or acid deficient.

25.4 Add pulverized K₂C₂O₄·H₂O slowly and with constant stirring until a pH of 4.7 to 4.9 is reached.

25.5 Immerse the titration beaker in an ice bath. (Titrations made at room temperature are possible but are less sharp.)

25.6 Titrate with 0.3 N NaOH using 0.20-mL increments and determine the inflection point by the delta pH or “analytical” method.

NOTE 1—This test method of locating the end point depends on the fact that the second derivative Δ²pH/Δvol² is zero at the point where the slope ΔpH/Δvol is a maximum.

26. Calculation

26.1 Calculate the free acid normality, *N*, as follows:

$$N = (A \times N_B - C \times N_A)/5 \quad (3)$$

⁵ NBS SRM 84h.