Designation: C 799 – 99 (Reapproved 2005)

Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions[1]

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:

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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.

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

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[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.

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[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 Chemicals[3]

2.3 *Other Documents:*

ISO 7097 Determination of Uranium in Uranium Product Solutions and Solids with Cerium IV Oxidation Titrimetric Method[4]

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.

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[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:

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

where:

A = sample, g,
B = U_3O_8 obtained, g,
C = impurity-element oxides, g, and
D = gravimetric factor, grams of uranium/grams of U_3O_8(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 %.

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

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 HNO_3(sp gr 1.42) to 1 L with water. Standardize with sodium hydroxide solution (see 24.3).

24.2 *Potassium Oxalate ($K_2C_2O_4 \cdot H_2O$)*, 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 HNO_3 to make the sample definitely acid if the sample is neutral or acid deficient.

25.4 Add pulverized $K_2C_2O_4 \cdot H_2O$ 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 Δ^2pH/Δvol^2 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:

$$N = (A \times N_B - C \times N_A)/5 \tag{3}$$

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[5] NBS SRM 84h.

where:

A = NaOH solution used in the titration, mL
N_B = normality of the NaOH solution,
C = HNO_3 solution used in the spike, mL, and
N_A = normality of HNO_3 solution.

NOTE 2—Negative values of free acid indicate an acid deficiency.

27. Precision

27.1 The limit of error at the 95 % confidence level for a single determination is ±3 %.

DETERMINATION OF THORIUM

28. Scope

28.1 The determination of thorium by the arsenazo (III) (photometric) method has been discontinued, (see C 799-93).

28.2 As an alternative, thorium can be determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). See Test Method C 1287.

28.3 Previous sections have been deleted.

DETERMINATION OF CHROMIUM

29. Scope

29.1 The determination of chromium by the diphenyl carbazide method has been discontinued, (see C 799-93).

29.2 As an alternative, chromium can be determined using inductively coupled plasma atomic emission spectrometry (ICP-AES). Test Method C 761 can be used providing a transformation to U_3O_8 so described hereafter in sections 117–120 A direct conversion to the amonium fluoride plus nitric acid solution can also be used, (see C 761).

29.3 As an alternative, chromium can be determined using atomic absorption spectroscopy. Test Method C 761 can be used.

29.4 As an alternative, chromium can be determined using ICP-MS. Test Method C 1287 can be used.

29.5 Previous sections have been deleted.

DETERMINATION OF MOLYBDENUM

30. Scope

30.1 The determination of molybdenum by the thiocyanate (photometric) method has been discontinued, (See C 799-93).

30.2 As an alternative, molybdenum can be determined using ICP-MS. Test Method C 1287 can be used.

30.3 As an alternative, molybdenum can be determined using ICP-AES. Test Method C 761, sections 251 to 271 can be used providing a tranformation to U_3O_8 as described hereafter in sections 71-74. A direct conversion to the amonium fluoride plus nitric acid solution can also be used, (see C 761, section 251).

30.4 Previous sections have been deleted.

HALOGENS SEPARATION BY STEAM DISTILLATION

31. Scope

31.1 This test method covers the separation of the halogens by means of a steam distillation.

32. Summary of Test Method

32.1 A sample aliquot is mixed with a solution containing ferrous ammonium sulfate, sulfamic acid, phosphoric acid, and sulfuric acid. The halogens are then steam distilled at a temperature of 140°C.

33. Apparatus

33.1 *Steam Distillation Apparatus* (see Fig. 1).

33.1.1 *Distilling Flask*, 200-mL with thermometer well.

33.1.2 *Condenser*.

33.1.3 *Heating Mantle*.

33.1.4 *Steam Boiler*, 500-mL flask.

34. Reagents

34.1 *Absorber Solution (4 M Potassium Hydroxide)*—Dissolve 22.4 g KOH pellets in water and dilute to 100 mL.

34.2 *Acid Mixture*—Mix 0.2 *M* ferrous ammonium sul-fate-0.5 *M* sulfamic acid (see 34.3), phosphoric acid (85 %), and sulfuric acid (sp gr 1.84) in the ratio of 1 + 2 + 5.

34.3 *Ferrous Ammonium Sulfate Solution (0.2 M)-Sulfamic Acid (0.5 M) Solution*—Dissolve 78.4 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and 48.6 g NH_2SO_3H in H_2SO_4(5 + 95) and dilute to 1 L with H_2SO_4(5 + 95).

34.4 *Phenolphthalein Solution (10 g/L)*—Dissolve 1 g of phenolphthalein in 50 mL of ethanol and add 50 mL of water.

35. Procedure

35.1 Place a weighed portion of about 15 mL containing approximately 5 g of uranium in the distillation flask.

35.2 Add 25 mL of the acid mixture to the distillation flask.

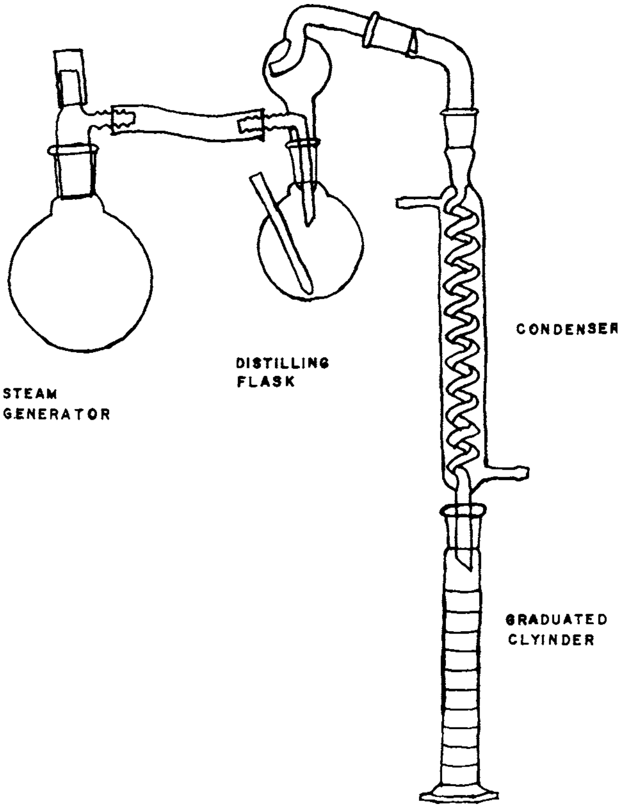

FIG. 1 Halogen Distillation Apparatus

35.3 Transfer 5 mL of the KOH solution to a 100-mL graduated cylinder and position it under the condenser tip.

35.4 Heat the distillation flask until the thermometer in the well reaches 140°C.

35.5 Pass steam through from the boiler, and maintain at a temperature of 140°C until a volume of 90 mL is collected.

35.6 Add 2 drops of phenolphthalein solution and adjust the pH of the distillate with KOH or HNO_3, to the phenolphthalein end point. Make the volume to 100 mL.

35.7 Repeat the distillation, omitting the uranium sample, to use as the matrix for the fluoride standard curve.

35.8 Reserve the distillate for the fluoride and combined halide determinations.

FLUORIDE BY SPECIFIC ION ELECTRODE

36. Scope

36.1 This test method covers the determination of as low as 2 µg F/g U in distillate containing all the halogens.

37. Summary of Test Method

37.1 An aliquot of the distillate representing 1 g of uranium is measured by specific ion electrode and compared to a standard curve prepared by spiking equivalent-size aliquots taken from a blank distillation (**4**,**5**).

38. Apparatus

38.1 *pH Meter*, expanded scale.

38.2 *Ion-Selective Electrode*, fluoride.

38.3 *Reference Electrode*, single-junction.

39. Reagents

39.1 *Buffer Solution (0.001 N)*—Dissolve 0.1 g of potassium acetate ($KC_2H_3O_2$) in water. Add 0.050 mL of acetic acid (sp gr 1.05) and dilute to 1 L.

39.2 *Fluoride Standard Solution A (1 mL = 1 mg F)*—Dissolve 0.220 g of dried sodium fluoride (NaF) in 25 mL of water and dilute to 100 mL.

39.3 *Fluoride Standard Solution B (1 mL = 5 µg F)*—Dilute 5 mL of the fluoride standard Solution A (see 39.2) to 1 L with water.

40. Procedure

40.1 Pipet a 20-mL aliquot of the sample distillate (representing about 1 g of uranium) into a 25-mL flask and make to volume with the buffer solution.

40.2 Prepare a standard curve by pipetting 20-mL aliquots from the blank distillate into 25-mL flasks and adding F^- standard solution to make 0, 5, 10, and 20 µg F^-/25 mL.

40.3 Measure all of the solutions with the fluoride ion-selective electrode.

41. Calculation

41.1 Calculate the F^- content as follows:

$$F^-, \mu g/g = A/B \qquad (4)$$

A = F^- found in the sample distillate aliquot, µg, and
B = uranium represented by the sample distillate aliquot, g.

42. Precision

42.1 The limit of error at the 95 % confidence level for a single determination is ±25 %.

HALOGEN DISTILLATE ANALYSIS: CHLORIDE, BROMIDE, AND IODIDE BY AMPEROMETRIC MICROTITRIMETRY

43. Scope

43.1 The determination of chloride, bromide and iodide by microtitrimetric method has been discontinued, (see C 799-93).

43.2 Previous sections have been deleted.

DETERMINATION OF CHLORIDE AND BROMIDE

44. Scope

44.1 Determination of bromide by the fluorescein (photometric) method has been discontinued, (see C 799-93).

44.2 As an alternative, bromide and chloride can be determined by X-Ray Fluorescence. Halogens are precipitated by silver nitrate and filtrated. The precipitate is washed and counted by X-Ray Fluorescence.

44.3 Previous sections have been deleted.

DETERMINATION OF SULFUR BY X-RAY FLUORESCENCE

45. Scope

45.1 Sulfur can be determined using X-Ray Fluorescence. See Test Method C 1296.

SULFATE SULFUR BY (PHOTOMETRIC) TURBIDIMETRY

46. Scope

46.1 This test method covers the determination of the sulfur concentration, which exists as sulfate in uranyl nitrate solutions, in the range from 100 to 1000 µg S/g of uranium.

47. Summary of Test Method

47.1 The uranium in the sample is removed by extraction with tributyl phosphate (TBP). The sulfate is then precipitated as barium sulfate ($BaSO_4$) in the presence of excess salt and acid and is held in suspension in a glycerin matrix. Sulfate is determined turbidimetrically using a spectrophotometer (**6**, **7**).

48. Interferences

48.1 Any anions that form insoluble precipitates with barium, such as phosphate, oxalate, and chromate, will interfere.

48.2 Many variables, although not classed as interferants, effect the precision of this test method. Careful control of the following parameters must be maintained to achieve the stated precision: particle size of the barium chloride ($BaCl_2$), particle size of the $BaSO_4$ formed, total ionic concentration of the final solution, degree of mixing of sample and reagents (number of times the flask is inverted), concentration of hydrogen ion in the final solution, and the length of time of standing of the supernatant before the absorbance is measured.

49. Apparatus

49.1 *Spectrophotometer*—See Practice E 60.

50. Reagents

50.1 *Barium Chloride* ($BaCl_2$), crystals. Sift the salt and use only the portion that passes through a 28-mesh screen and is retained on a 35-mesh screen.

50.2 *Sodium Chloride-Glycerin Solution (16 g/L)*—Dissolve 40 g of NaCl in 60 mL of HCl (sp gr 1.19). Add 833 mL of glycerin and dilute to 2.5 L with water.

50.3 *Sulfate Standard Solution (1 mL = 1000 µg* SO_4^{-}*)*—Dissolve 1.1813 g of K_2SO_4, dried at 110°C for 1 h, and dilute to 1 L with water.

50.4 *Tributyl Phosphate Solution (3 + 7)*—Dilute 300 mL of TBP with 700 mL of kerosine and equilibrate with 8 *M* HNO_3.

51. Procedure

51.1 Transfer a weighed aliquot of sample that contains approximately 1 g of uranium to a 60-mL separatory funnel. Adjust the nitric acid concentration to 4 to 5 *M* and the volume to 5 mL.

51.2 Add 10 mL of TBP solution (see 50.4) and equilibrate the solutions.

51.3 Allow the layers to separate and transfer the aqueous layer to 50-mL volumetric flask containing 30 mL of distilled water. Use a minimum volume of 1 *N* HNO_3 wash solution to ensure quantitative transfer of the aqueous layer to the 50-mL flask.

51.4 Pipet 10 mL of NaCl-glycerin solution into the 50-mL flask and dilute to volume with water.

51.5 Add 0.50 g of $BaCl_2$(see 50.1), stopper the flask, and invert the solution 20 times to dissolve the $BaCl_2$.

NOTE 3—The conditions of mixing and the time of standing prior to measuring the absorbance *must* be the same for sample and standards.

51.6 Allow the solution to stand 60 ± 5 min; then measure the absorbance at 450 nm in 5-cm cells with a blank containing all of the reagents except sample as the reference.

51.7 Prepare a calibration curve by transferring 0.200, 0.500, 1.000, 1.500, and 2.000-mL aliquots of the standard sulfate solution into 60-mL separatory funnels that contain 5 mL of 4 to 5 *M* nitric acid and process in accordance with 51.2-51.6.

52. Calculation

52.1 Calculate the sulfur content in micrograms per gram of uranium as follows:

$$\text{Sulfur, µg/g} = (A \times B)/C \qquad (5)$$

A = SO_4 = found in the sample solution,µ g,
B = 0.334, the gravimetric factor converting SO_4 = to S, and
C = uranium in the sample solution aliquot, g.

53. Precision

53.1 The limit of error at the 95 % confidence level for a single determination is ±3 %.

PHOSPHORUS BY THE MOLYBDENUM BLUE (PHOTOMETRIC) METHOD

54. Scope

54.1 This test method covers determination of phosphorus in nuclear-grade uranyl nitrate solutions. Appropriate dilution may be made to facilitate obtaining samples containing 0 to 60 µg P.

55. Summary of Test Method

55.1 Phosphorus is determined by the formation of heteropoly molybdophosphoric acid and its subsequent reduction to molybdenum blue. Sodium molybdate is used to complex the P in an acid solution containing the sample. The yellow complex is then extracted into isobutanol. After the excess molybdate is washed out with water, the organic phase is contacted with an acid solution of stannous chloride to reduce the complex. The resulting molybdenum blue is read at 725 nm using a spectrophotometer (**8**).

56. Interferences

56.1 The molybdenum blue reaction is not specific for phosphorus; however, adjustment of the acidity to above 0.9 *N* avoids the formation of molybdosilicic acid.

56.2 Fluoride and chloride must be fumed off before the heteropoly acid is formed.

57. Apparatus

57.1 *Spectrophotometer*—See Practice E 60.

58. Reagents

58.1 *Isobutanol*.

58.2 *Phosphorus Standard Solution A (1 mL = 100 µg P)*—Dissolve 0.4393 g of KH_2PO_4, which has been dried at 110°C for 1 h, in 1 L of water.

58.3 *Phosphorus Standard Solution B (1 mL = 10 µg P)*—Dilute 10.0 mL of Solution A to 100 mL with water.

58.4 *Sodium Molybdate Solution (10 g/L)*—Dissolve 25 g of $Na_2MoO_4 \cdot 2\,H_2O$ in 250 mL of water. Filter if turbid and store in a polyethylene bottle.

58.5 *Stannous Chloride Solution (2 N in HCl)*—Dissolve 2.38 g of $SnCl_2 \cdot 2\,H_2O$ in 170 mL of HCl (sp gr 1.19), and dilute to 1 L with water. Store in a polyethylene bottle containing 1 to 2 g of tin metal pellets or granules.

59. Procedure

59.1 Transfer a weighed portion of sample solution containing 0.1 g of uranium or an appropriate dilution to a 150-mL beaker.

59.2 Add 3 mL of $HClO_4$ (72 %) or H_2SO_4 (sp gr 1.84) to the beaker and heat to strong fumes.

59.3 Add 40 mL of water and 5 mL of $Na_2MoO_4 \cdot 2\,H_2O$ solution and let stand 5 min.

59.4 Transfer to a 125-mL separatory funnel.

59.5 Add 40 mL of isobutanol and extract for 1 min.

59.6 Discard the aqueous layer.

59.7 Wash the organic layer with two 25-mL portions of water and discard the aqueous layers.

59.8 Add 25 mL of $SnCl_2$ solution and shake for 15 s.

59.9 Discard the aqueous layer.

59.10 Drain the organic layer into a 50-mL volumetric flask. Wash the funnel with isobutanol and add the washings to the flask.

59.11 Make to volume with isobutanol and read at 725 nm in 1-cm cells with isobutanol as the reference.

59.12 Prepare a standard curve by carrying 0 to 60 µg P through the procedure (59.2-59.11).

60. Calculation

60.1 Calculate the phosphorus content as follows:

$$\text{Phosphorus, µg/g} = A/B \tag{6}$$

where:

A = phosphorus found in the sample solution, µg, and

B = uranium contained in the sample solution, g.

61. Precision

61.1 The limit of error at the 95 % confidence level for a single determination is ±3 %.

SILICON BY THE MOLYBDENUM BLUE (PHOTOMETRIC) METHOD

62. Scope

62.1 This test method covers the determination of up to 20 µg Si (2 to 200 µg Si/g U) in uranyl nitrate solutions.

63. Summary of Test Method

63.1 Silicon is determined by the formation of B-silicomolybdic acid and subsequent reduction to molybdenum blue. Ammonium molybdate is used to complex the silicon in an acid solution of the sample. Oxalic acid and sodium sulfite are added to prevent phosphorus interference and to stabilize the complex. Reduction to molybdenum blue is carried out with stannous chloride. Measurement is made at 820 nm using a spectrophotometer **(9, 10, 11).**

64. Interferences

64.1 Phosphorus also forms a heteropoly acid with molybdate; however, oxalic acid is used to decompose it.

65. Apparatus

65.1 *Plastic Beakers.*

65.2 *Polyethylene Pipets.*

65.3 *Spectrophotometer*—See Practice E 60

66. Reagents

66.1 *Ammonium Molybdate Solution (65 g/L)*—Dissolve 65 g of $(NH_4)_6Mo_7O_{24}·4H_2O$ in water, dilute to 1 L, and store in a plastic bottle.

66.2 *Hydrochloric Acid (1 + 9)*—Mix 100 mL of HCl (sp gr 1.19) with 900 mL water and store in a plastic bottle.

66.3 *Oxalic Acid Solution (100 g/L)*—Dissolve 25 g of HO_2CCO_2H in 250 mL of water and store in a plastic bottle.

66.4 *Silicon, Standard Solution A (1 mL = 100 µg Si)*—Fuse 0.0214 g of silicon dioxide (SiO_2) with 1 g of Na_2CO_3 until a clear melt is obtained. Dissolve the cooled melt in water and dilute to volume in a 100-mL polyethylene volumetric flask.

66.5 *Silicon, Standard Solution B (1 mL = 2 µg Si)*—Dilute 2 mL of standard silicon Solution A (see 66.4) to 100 mL in a polyethylene volumetric flask.

66.6 *Sodium Carbonate (Na_2CO_3)*, anhydrous powder.

66.7 *Sodium Sulfite Solution (150 g/L)*—Dissolve 30 g of Na_2SO_3 in 200 mL of water and store in a plastic bottle.

66.8 *Stannous Chloride Solution A (100 g/L)*—Dissolve 50 g of $SnCl_2·2H_2O$ in 100 mL of HCl (sp gr 1.19) and 50 mL of water. Heat, if necessary, to dissolve. Dilute to 500 mL with water and store in a plastic bottle containing 1 g of metallic tin (Sn).

66.9 *Stannous Chloride Solution B*—Dilute 10 mL of stannous chloride Solution A (see 66.8) to 100 mL with water. Make fresh daily.

66.10 *Sulfuric Acid (1 + 3)*—Add 125 mL of H_2SO_4(sp gr 1.84) slowly to 375 mL of water. Cool and store in a plastic bottle.

67. Procedure

67.1 Pipet 5 mL of $(NH_4)_6Mo_7O_{24}·4H_2O$ solution and 4 mL of HCl (1 + 9) into a 100-mL plastic beaker.

67.2 Transfer a weighed portion of sample solution containing 2 to 3 drops of HF (48 %) or an appropriate dilution into the beaker and swirl to mix.

67.3 Dilute to 35 mL with water and let stand 15 to 30 min.

67.4 Add, in order and swirling after each addition, 2 mL of oxalic acid solution, 2 mL of sodium sulfite solution, and 5 mL of sulfuric acid (1 + 3), and let stand 3 min.

67.5 Add 1 mL of stannous chloride Solution B, dilute to 100-mL volume with water, and let stand 5 min.

67.6 Read at 820 nm in 5-cm cells with water as a reference.

67.7 Prepare a standard curve by carrying 0 to 20 µg Si through the procedure (67.1-67.6).

NOTE 4—Uranium does not contribute to a blank when present in 100-mg amounts or less.

68. Calculation

68.1 Calculate the silicon content as follows:

$$\text{Silicon, µg/g} = A/B \tag{7}$$

where:

A = silicon found in the sample solution, µg, and

B = uranium contained in the sample solution, g.

69. Precision

69.1 The limit of error at the 95 % confidence level for a single determination is ±5 %.

CARBON BY PERSULFATE OXIDATION-ACID TITRIMETRY

70. Scope

70.1 Determination of carbon by the persulfate oxidation titrimetry method has been discontinued, (see C 799-93).

70.2 Previous sections have been deleted.

CONVERSION TO U_3O_8

71. Scope

71.1 This test method is specifically designed for the conversion of uranyl nitrate to U_3O_8.

72. Summary of Test Method

72.1 Uranyl nitrate is evaporated to dryness and baked on a hot plate to yield uranium trioxide (UO_3). The UO_3 is transferred to a platinum crucible and ignited at 900°C for 2 h to obtain U_3O_8 which is used for the spectrographic analysis.

73. Apparatus

73.1 *Beaker*, TFE-fluorocarbon, 100-mL.

73.2 *Crucible*, platinum, 50-mL capacity.

73.3 *Heat Lamp*, infrared.

73.4 *Hot Plate*.

73.5 *Muffle Furnace*.

73.6 *Plastic Balls*, poly(methyl methacrylate), 9.52 mm (3⁄8 in.) in diameter.

73.7 *Plastic Vial*, 19.05 by 50.8 mm (3⁄4 by 2 in.).

73.8 *Shaker*, [6] heavy-duty.

73.9 *Spatula*, long-handle, platinum or tantalum.

74. Procedure

74.1 Transfer 5 g of uranyl nitrate solution to a clean 100-mL TFE-fluorocarbon beaker.

74.2 Evaporate the solution to crystallization under an infrared lamp.

74.3 Transfer the beaker and contents to a hot plate having a surface temperature of approximately 300°C. (At this temperature, the uranyl nitrate crystals convert to a mixture of UO_3 and nitrates.)

74.4 Remove the beaker from the hot plate and cool when the uranium mixture is an orange-colored solid.

74.5 Transfer the orange UO_3 to a clean 50-mL platinum crucible using a platinum or tantalum spatula. (All of the samples must be removed from the beaker for impurity analysis.)

74.6 Place the platinum crucible in the muffle furnace and ignite at 900°C for 2 h.

74.7 Remove the sample of U_3O_8 from the furnace and cool.

74.8 Transfer the sample to a 19.05 by 50.8-mm (3⁄4 by 2-in.) plastic vial containing one 9.52-mm (3⁄8-in.) plastic ball.

74.9 Close the plastic vial and seal the lid with masking tape.

74.10 Place the vial and its contents in the heavy-duty shaker and lock it into its holder.

74.11 Set the shaker timer for 2 min and start.

74.12 Examine the blend for uniformity of particles after the shaker has stopped. If it is lumpy, or different in texture from the standards, blend for an additional 2 min.

74.13 If the blend is uniform in size then the sample is ready for spectrochemical impurity analysis as described in Test Methods C 696 or Test Methods C 761.

BORON BY EMISSION SPECTROGRAPHY[7]

75. Scope

75.1 This test method covers the determination of 0.05 to 33 µg B/g of uranium.

76. Summary of Test Method

76.1 Boron is separated from uranium in dilute nitric acid by cation exchange. Mannitol complexing is used to prevent boron losses during evaporation of the effluent to dryness prior to the spectrographic determination **(12).**

77. Apparatus

77.1 *Ion-Exchange Column*, 1.0 cm^2 by 14 cm.

77.2 *Beaker*, TFE-fluorocarbon.

78. Reagents

78.1 *Boron Standard Solution (1 mL = 100 µg B)*—Dissolve 0.5724 g of boric acid (H_3BO_3)[8] in 0.2 *N* HNO_3 and dilute to 1 L with 0.2 *N* HNO_3.

78.2 *Boron Working Standard Solutions*— Pipet 1, 2, 5, 10, 50, and 100-mL aliquots of the boron standard solution (see 78.1) into 100-mL flasks and dilute to volume with 0.2 *N* HNO_3.

78.3 *Cation Exchange Resin*, [9]*H^+ form (200–400 mesh)*—Wash the resin free of "fines," residual color, and any boron contamination, and prepare a resin bed 80 mm in length. Wash the bed with 50 mL of 1 *N* HNO_3, then 150 mL of 0.2 *N* HNO_3 immediately prior to use.

NOTE 5—The resin column can only be used once.

78.4 *Electrodes*, ASTM C-1 cathode and ASTM S-1 pedestal with anode cap.[10] Seal the caps with two applications of 5 drops each of 2 % polychlorotrifluorethylene grease in carbon tetrachloride (CCl_4). Evaporate the solvent completely after each application.

78.5 *Indium Oxide (In_2O_3)*, boron-free.

78.6 *Mannitol*, powder, reagent grade.

78.7 *Zinc Internal Standard Solution (1 mL = 4 mg Zn)*—Dissolve 1.2448 g of high-purity ZnO (99.99 + %) in 0.2 *N* HNO_3 and dilute to 250 mL with 0.2 *N* HNO_3.

79. Procedure

79.1 Determine a blank on each prepared ion-exchange column by adding 10 mL of 0.2 *N* HNO_3.

79.2 Adjust the flow rate at about 0.3 to 0.5 mL/min and collect the effluent in a TFE-fluorocarbon dish.

79.3 Wash the column with 50 mL of 0.2 *N* HNO_3 when the level of solution reaches the top of the resin bed.

79.4 Add 25 mg of mannitol to the effluent in the dish.

79.5 Dissolve the mannitol and slowly evaporate the solution to dryness under heat lamps but do not bake.

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[6] A Spex Industries mixer is suitable for this purpose.

[7] As an alternative, boron can be determined using ICP-MS. Test Method C 1287 can be used.

[8] NBS SRM 951.

[9] Dowex 50W-X10.

[10] National Carbon Co. No. L-4030.

79.6 Cool the dish and dissolve the residue in 500 µL of the zinc internal standard solution.

79.7 Pipet 100-µL aliquots of this solution onto each of four sealed electrodes containing 2.5 mg of In_2O_3 as spectrographic matrix and dry under heat lamps.

79.8 Pipet 5 mL of the sample solution into a platinum dish and evaporate to near dryness on a steam bath.

79.9 Add 10 mL of 0.2 *N* HNO_3 and transfer to a column. Continue with 79.2-79.7.

79.10 Make exposures of each sample under the following excitation conditions:

Exposure:	10 s
Current:	25 d-c A
Gap:	4 mm
Entrance Slit:	25 µm
Spectral Range:	2300 to 2900 Å
Photographic Plates:	[A]

[A] Eastman SA-1.

79.11 Measure the boron 2497.73 Å and zinc 2756.45Å analytical lines on the processed photographic plates with a microphotometer.

79.12 Prepare an analytical working curve by pipetting 100-µL aliquots of the standard boron solutions onto sealed graphite electrodes containing 5 mg of mannitol and 2.5 mg of In_2O_3. Dry the electrodes and add 100 µL of the zinc internal standard solution to each, dry again, and excite the electrode following the above procedure.

80. Calculation

80.1 Plot the relative log intensity ratios of the boron -zinc pair against the concentration of the boron standards; then determine the concentration of boron in the sample from the curve (no background corrections to the measured intensities are necessary):

$$\text{Boron, µg/g} = (A \times 5)/C \quad (8)$$

where:

A = boron found in each 100 µL of sample solution,µ g, and
C = uranium contained in a total sample solution, g.

81. Precision

81.1 A relative standard deviation of ±9 % can be obtained with a boron range from 0.1 to 30 µg/g.

IMPURITY ELEMENTS BY SPARK SOURCE MASS SPECTROGRAPHY

82. Scope

82.1 The determination of impurities by spark source mass spectrography method has been discontinued, (see C 799-93).

82.2 Previous section have been deleted.

ISOTOPIC COMPOSITION BY THERMAL IONIZATION MASS SPECTROMETRY

83. Scope

83.1 The determination of isotopic composition using a single collector thermal ionisation mass spectrometer has been discontinued, (see C 799-93 and C 696).

83.2 As an alternative, the isotopic composition can be measured using a multi- collector thermal ionisation spectrometer. Test Method C 1413 can be used.

83.3 As an alternative, the isotopic composition can be measured using isotope dilution mass spectormetry. Test Method C 1380 can be used.

83.4 Previous section have been deleted.

URANIUM-232 BY ALPHA SPECTROMETRY

84. Scope

84.1 This test method covers the determination of uranium-232 in nuclear-grade uranyl nitrate solutions, in concentrations as low as 0.05 ng $^{232}U/^{235}U$.

85. Summary of Test Method

85.1 A weighed portion of uranyl nitrate solution is electroplated on a stainless steel disk. The alpha activities from ^{232}U with energies of 5.28 and 5.32 Mev and ^{228}Th with energies of 5.34 and 5.42 Mev are measured with a surface barrier detector and a pulse height analyzer. The two ^{232}U energy peaks are summed and corrected for the unresolved ^{228}Th 5.34 Mev. The counts are converted to disintegration rate and divided by the specific alpha activity of ^{232}U to determine the weight of ^{232}U on the disk. Self-absorption corrections are avoided by maintaining the same deposit thickness for sample and standard.

86. Apparatus

86.1 *Multiple-Cell Electroplating Apparatus* with four cells operating independently of each other and the current within each cell automatically controlled to 3 A at 32 V d-c. The speed of the stirrers shall be 500 rpm (see Fig. 2).

86.2 *Silicon Surface Barrier Detector*, or equivalent.

86.3 *Multichannel Analyzer*.

87. Reagents and Materials

87.1 *Ammonium Oxalate Solution (0.4 M g/L)*—Dissolve 56.8 g of $(NH_4)_2C_2O_4 \cdot H_2O$ in warm distilled water and dilute to 1 L.

87.2 *Disk*, 52 mm in diameter. Use Grade A, cold-rolled, smooth finish nickel or 300 series high-luster stainless steel.

87.3 *Uranium Standard*—Electroplate 0.5 mg of natural uranium on a 50-mm diameter stainless steel disk.

88. Procedure

88.1 *Sample Preparation*—Take a sample containing 25 mg of uranium and dilute to 500 mL.

88.1.1 Place a disk in the center depression of the electroplating cell base plate, and a rubber gasket on a fluorothene or glass cell chimney.

88.1.2 Place the cell chimney and gasket, as a unit, on the disk which serves as the bottom and cathode of the electroplating cell.

88.1.3 Fasten the cell chimney to the base plate, making a leak-proof seal between the disk and the cell chimney.

88.1.4 Add 10 mL of 0.4 *M* $(NH_4)_2C_2O_4$ solution to the cell; then add an aliquot of sample containing 0.5 mg of uranium.

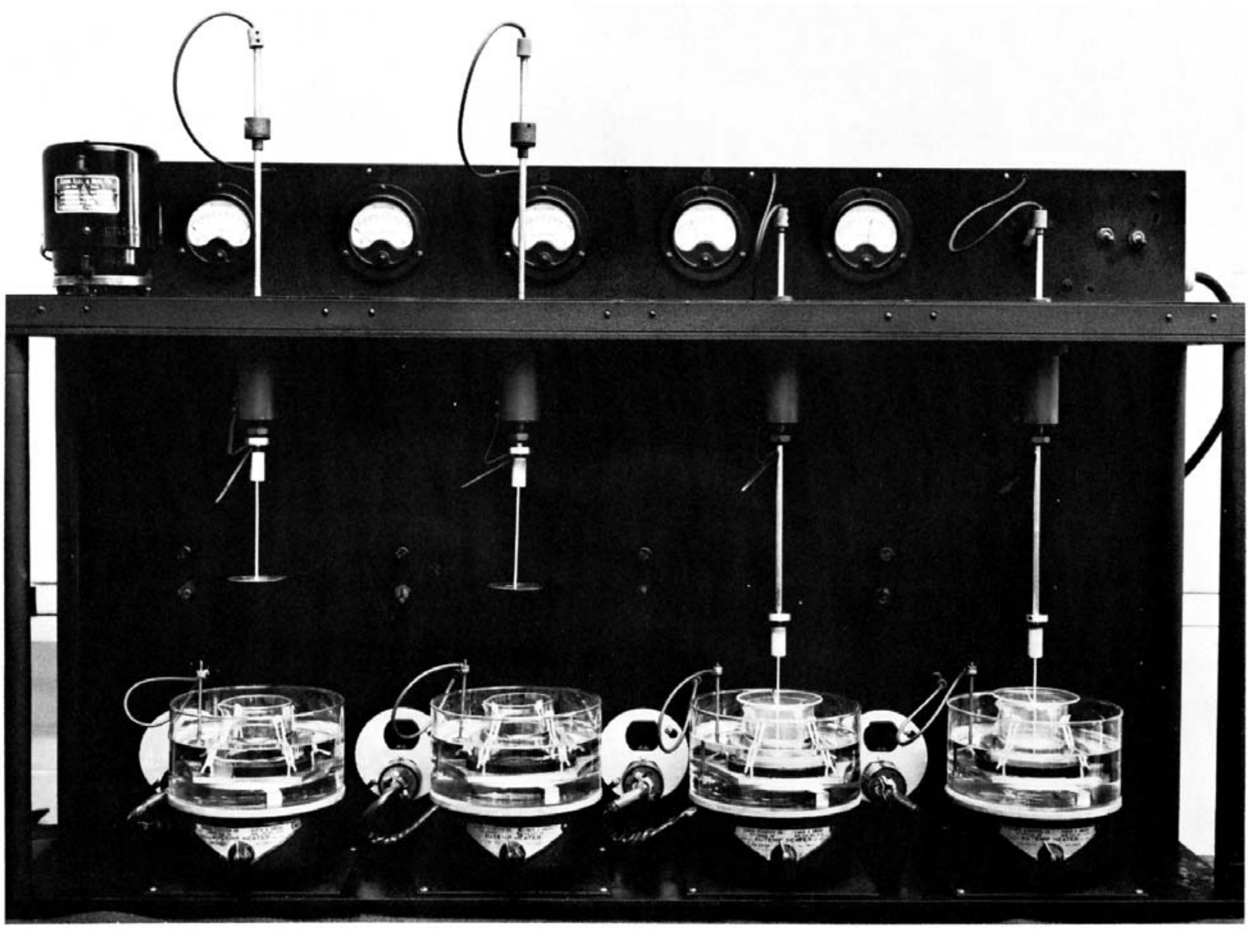

FIG. 2 Multiple-Cell Electroplating Apparatus

88.1.5 Adjust the volume of the solution to 25 mL with distilled water.

88.1.6 Place the cell in a water bath (75 to 85°C), on the electroplating apparatus.

88.1.7 Turn on the electroplating apparatus, and lower the platinum anode into the solution until the anode is about 10 mm above the disk.

88.1.8 Add distilled water to replace the water evaporated during electroplating.

88.1.9 Remove the cell from the electroplating apparatus after 45 min, and quickly pour out the electrolyte.

88.1.10 Rinse the cell with approximately 15 mL of ethanol to dry the film.

88.1.11 Disassemble the cell chimney, and heat the uranium on the disk in a furnace at 425°C for 10 min.

88.2 *Counting*:

88.2.1 Position the uranium standard (with a known disintegration rate) under the surface barrier detector; adjust the vacuum and bias voltage, then alpha count 20 min to determine the counter efficiency factor.

88.2.2 Position the uranium sample under the surface barrier detector; adjust the vacuum and bias voltage, then count the sample 40 min. Decrease the counting time if the sample contains a significant amount of ^{232}U.

88.2.3 Integrate the counts in the 5.3-Mev peak (which includes the ^{232}U at 5.32 and 5.28 Mev plus the unresolved ^{228}Th at 5.34 Mev). Also, integrate the ^{228}Th counts in the 5.42-Mev peak.

89. Calculation

89.1 Convert integrated counts to net ^{232}U counts per minute as follows:

$$^{232}C = \frac{(C_{5.3} - B_{5.3}) - 0.394\,(C_{5.42} - B_{5.42})}{t} \tag{9}$$

where:

^{232}C = net ^{232}U counts per minute,

$C_{5.3}$ = integrated counts in 5.32 and 5.27 Mev ^{232}U peak and 5.34 Mev ^{228}Th peak,

$C_{5.42}$ = integrated count in 5.42-Mev ^{228}Th peak, $B_{5.3}$ and $B_{5.42}$ integrated background counts in 5.3-Mev peak and 5.42-Mev peak, respectively,

t = time in minutes for $C_{5.3}$ and $C_{5.42}$, and

0.394 = known ratio of ^{228}Th counts at 5.34 Mev to counts at 5.42 Mev.

89.2 Calculate the counter efficiency, as follows:

$$E = {}^{235+\ 238}C/A \tag{10}$$

where:
C = net counts per minute of the standard, and
A = disintegration rate of the standard.

89.3 Determine the ^{232}U disintegration rate of the sample as follows:

$$D = {}^{232}C/E \quad (11)$$

where:
C = net counts per minute of the sample,
D = sample disintegrations per minute, and
E = counter efficiency.

89.4 Calculate the amount of ^{232}U in nanograms per gram of ^{235}U, as follows:

$$^{232}U/^{235}U, \text{ ng/g} = \frac{D}{4.65 \times 10^4 (W)(F)} \quad (12)$$

where:
4.65×10^4 = alpha activity of ^{232}U in disintegrations per min per ng,
W = weight of sample aliquot counted, g,
D = sample disintegrations per minute, and
F = weight fraction of ^{235}U in sample.

90. Precision

90.1 The limit of error at the 95 % confidence level for a single determination is ±10 %.

TOTAL ALPHA ACTIVITY BY DIRECT ALPHA COUNTING

91. Scope

91.1 This test method covers the determination of the sum of all alpha-emitting nuclides in uranyl nitrate solutions.

92. Summary of Test Method

92.1 An aliquot of uranyl nitrate solution containing less than 1 mg of uranium is deposited on an electropolished stainless steel counting disk. The solution is evaporated to dryness then ignited to the oxide. The alpha activity is measured with a surface barrier detector. The counts are converted to disintegration rate using a standard alpha source of known activity. The total alpha activity of the sample is then related to the amount of uranium on the disk to obtain disintegrations per minute per gram of uranium.

93. Apparatus

93.1 *Burner*, Meker type.

93.2 *Heat Lamp*, infrared.

93.3 *Surface Barrier Detector*.

93.4 *Scaler* suitable for use with the surface barrier detector.

94. Reagents

94.1 *Disk*, electropolished stainless steel of suitable dimensions to fit the counter chamber.

95. Procedure

95.1 Measure the efficiency of the proportional counter by counting a standard alpha source of known activity (in terms of disintegration per minute) and relating it to the counts per minute obtained.

95.2 Transfer a weighed portion of sample solution containing 0.5 g of uranium to a 100-mL volumetric flask and dilute to volume with distilled water.

95.3 Pipet 100 µL of the diluted solution into the center of a disk, and carefully dry under a heat lamp.

95.4 Heat the disk to a dull red color for 1 min over a Meker burner; then cool.

95.5 Measure the background count using a clean disk.

95.6 Measure the alpha activity of the sample disk by accumulating at least 10 000 counts.

95.7 Normalize the background and sample counts to counts per minute, and subtract the background from the sample to obtain net counts per minute.

96. Calculation

96.1 Calculate the total alpha activity, A_t, as follows:

$$A_t, \text{ disintegrations/min/g} = \frac{C}{E \times G} \quad (13)$$

where:
C = net counts per minute of the sample,
E = efficiency factor expressed as a ratio of counts per minute to disintegrations per minute, and
G = uranium on the disk, g.

97. Precision

97.1 The limit of error at the 95 % confidence level for a single determination is ±5 %.

FISSION PRODUCT ACTIVITY BY BETA COUNTING

98. Scope

98.1 This test method covers the measurement of the beta emitters fission product activity of nuclear-grade uranyl nitrate solutions.

99. Summary of Test Method

99.1 Uranium in the sample is separated from its thorium daughters and the various fission products by a liquid-liquid extraction (**40**). Acid-deficient aluminum nitrate is used as the salting agent and tributyl phosphate (TBP)-kerosine solution as the extractant. Citric acid and hydroxylamine hydrochloride are added to complex zirconium and keeps ruthenium in a reduced valence state, thereby preventing their extraction.

99.2 Correction factors for the beta activity from the ^{232}U daughters below ^{228}Th are determined by measuring the ^{208}Tl peak in a portion of the aqueous phase on the pulse-height analyzer and correlating it with measurements of a standard of known ^{232}U daughter activity taken on the pulse-height analyzer and the beta counter.

99.3 The fission product beta activity is measured by counting aliquots of the aqueous phase in a proportional counter, then using the factor to correct for the activity of the ^{232}U daughters.

100. Apparatus

100.1 *Proportional Counter* with a 2-mg/cm^2 mica window.

100.2 *Pulse-Height Analyzer* with sodium iodide (NaI) or lithium drifted germanium (Ge(Li)) detector.

101. Reagents

101.1 *Aluminum Nitrate [$A1(NO_3)_3 \cdot 9 H_2O$]*, crystal.

101.2 *Citric Acid*, anhydrous crystal.

101.3 *Hydroxylamine Hydrochloride (100 g/L)*—Dissolve 10 g of $NH_2OH \cdot HCl$ in distilled water and dilute to 100 mL.

101.4 *Tributyl Phosphate (TBP) Solution (1 + 1)*—Purify the TBP by washing it with an equal volume of 0.1 *M* Na_2CO_3 solution to remove traces of DBP. Dilute 1 L of TBP with 1 L of kerosine.

102. Procedure

102.1 *Standard Preparation*:

102.1.1 Weigh three 11.792-g samples of U_3O_8(natural uranium in equilibrium with ^{234}Th) into beakers, and add 50 mL of 4 *N* HNO_3 to each beaker.

102.1.2 Cover the beakers with watchglasses, heat on a hot plate until all the U_3O_8 is dissolved, and allow to cool.

102.1.3 Transfer one standard, in roughly equal portions, to two 250-mL test tubes. Dilute the solution in each tube to 100 mL with distilled water.

102.1.4 Transfer another standard to a 200-mL flask and dilute to volume with 4 *N* HNO_3.

102.1.5 Shake the flask thoroughly, and pipet 500-µL aliquots into three beta-counting dishes. Evaporate the samples to dryness under heat lamps.

102.1.6 Allow the dishes to cool, cover with thin, adhesive, cellulose acetate tape, and use as reference standards for beta activity. Prepare a standard from the flask each time the beta activity of a sample is measured.

102.1.7 Spike the third standard with a known quantity of ^{232}U (to approximately 20 % of the activity of the uranium) and transfer it to a 125-mL separatory funnel.

102.2 *Sample Preparation*:

102.2.1 Weigh a portion of the sample solution containing about 10 g of uranium into a platinum dish and evaporate until the sample has crystallized.

102.2.2 Add 25 mL of water and 2 mL of $NH_2OH \cdot HCl$ and warm for about 10 min.

102.2.3 Cool the sample and transfer to a 125-mL separatory funnel.

102.3 *Separation of Fission Products and ^{232}U Daughters*—Separate samples and standards at the same time.

102.3.1 Add 1 g of citric acid and 45 g of $(NO_3)_3 \cdot 9 H_2O$ to each separatory funnel.

102.3.2 Cool and extract with 50 mL of TBP solution.

102.3.3 Drain the aqueous portion into a beaker, and wash the TBP-kerosine with approximately 10 mL of 4 *N* HNO_3 which is also drained into the beaker.

102.3.3.1 Add 2 mL of $NH_2OH \cdot HCl$ to the aqueous portion in the beaker; heat this on a hot plate about 5 min (to keep the ruthenium in a reduced state).

102.3.4 Add 10 g of $Al(NO_3)_3 \cdot 9 H_2O$ and extract a second time with 50 mL of TBP solution.

102.3.5 Drain the aqueous portion into a beaker and wash the TBP kerosine with approximately 10 mL of 4 *N* HNO_3 which is also drained into the beaker.

102.3.6 Repeat 102.3.4 and 102.3.5 until seven extractions are completed. Add 2 mL of $NH_2OH \cdot HCl$ after every other extraction.

102.3.7 Transfer the aqueous portion containing the fission products and ^{232}U daughters below ^{228}Th into a 200-mL flask and dilute to volume.

102.3.8 Pipet three 500-µL aliquots from the flask into separate beta-counting dishes.

102.3.9 Evaporate the aliquots to dryness under infrared heat lamps.

102.3.10 Allow the dishes to cool then cover with cellulose acetate tape for beta counting. Retain the remaining portion of the aqueous solution for gamma activity measurements.

102.4 *Counting*:

102.4.1 Place the three dishes of the spiked uranium standard in the sample changer of the beta proportional counter and obtain 1000 or more counts on each dish.

102.4.2 Calculate the average count rate for the three-dish set, correct for counter background, and normalize to Bq.

102.4.3 Place the 200-mL flask on a NaI or Ge(Li) detector connected to the pulse height analyzer and measure the activity from 0 to 4 Mev for 15 min.

102.4.4 Change the analyzer to the subtract mode and measure the background for 15 min using a 200-mL flask containing distilled water.

102.4.5 Print out the 2.6-Mev ^{208}Tl peak with the minimum counts on either side of the peak.

102.4.6 Extrapolate the printout from the minimum to obtain the Compton background count.

102.4.7 Correct the total peak count for the Compton background and normalize to obtain cpm.

102.4.8 Repeat 102.4.1 and 102.4.2 for the natural uranium standard dishes.

102.4.9 Repeat 102.4.1-102.4.7 for the sample.

NOTE 6—An alternative method for correcting for the ^{232}U daughters can be used by counting the dishes and tubes of the samples and the natural uranium standards and recounting them in the same manner 87 h later. The half-life of ^{224}Ra (a ^{232}U daughter) which determines the decay rate of the ^{232}U daughters is 87 h.

103. Calculation

103.1 Calculate the ^{232}U correction factor (beta, *B*), from the spiked standard as follows:

$$B = A_1/C_1 \tag{14}$$

where:

A_1 = beta activity obtained on the beta counter, Bq,
C_1 = gamma activity of ^{208}Tl peak obtained on the pulse-height analyzer, Bq, and

103.2 Determine the fission product, *F*, beta activity of the sample as follows:

$$F_{(\text{beta})} = \frac{A_2 - (C_2 \times B)}{A_3} \times 100 \tag{15}$$

A_2 = beta activity of sample, Bq,
A_{32} = beta activity of natural uranium standard, Bq,
C_2 = gamma activity of ^{208}Tl peak of sample, Bq,

103.3 Determine the fission product, *F*, beta and gamma activity of the sample by the alternative method as follows:

$$F_{(\text{beta})} = \frac{A_2}{A_3} - 2\left(\frac{A_2}{A_3} - \frac{A_2'}{A_3'}\right) \times 100 \tag{16}$$

A_2 = beta activity of sample, Bq,
A_2' = beta activity of sample after 87 h, Bq,
A_3 = beta activity of natural uranium standard, Bq,
A_3' = beta activity of natural uranium standard after 87 h, Bq,

104. Precision

104.1 The limit of error at the 95 % confidence level for a single beta determination of a sample containing 4 % fission product beta activity is ±20 %.

ENTRAINED ORGANIC MATTER BY INFRARED SPECTROPHOTOMETRY

105. Scope

105.1 The determination of entrained organic matter by infrared spectrophotometry method has been discontinued, (see C 799-93).

FISSION PRODUCT ACTIVITY BY GAMMA COUNTING

106. Scope

106.1 The determination of gamma emiters fission products can be done with Test Method C 1295.

DETERMINATION OF ARSENIC

107. Scope

107.1 The determination of arsenic can be done with atomic absorption. Test Method C 1219 can be used.

107.2 As an alternative, arsenic can be determined using ICP-MS. Test Method C 1287 can be used.

DETERMINATION OF IMPURITIES FOR THE EBC CALCULATION

108. Scope

108.1 The determination of impurities for the Equivalent Boron Content can be done with ICP-MS. Test Method C 1287 can be used. The EBC table described in C 1233 can be used.

DETERMINATION OF TECHNETIUM 99

109. Scope

109.1 The determination of Technetium 99 can be done using ICP-MS. Test Method C 1287 can be used.

109.2 As an alternative, Technetium can be determined after solvent extraction by beta counting. Test Method C 761 can be used.

DETERMINATION OF PLUTONIUM AND NEPTUNIUM

110. Scope

110.1 Plutonium can be determined by alpha counting after ion exchange. Test Method C 761 can be used.

110.2 As an alternative, plutonium can be determined by alpha counting after solvent extraction. Test Method C 761 can be used.

110.3 Neptunium can be determined by alpha counting after solvent extraction. Test Method C 761 can be used.

110.4 Previous sections have been deleted.

111. Keywords

111.1 impurity content; isotopic composition; stoichiometry; uranium content; uranyl nitrate

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