INTERNATIONAL

Designation: C799 – 19

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 C799; 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:

A Discontinued July 2019.

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.* Specific precautionary statements are given in Section 6.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

C761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride

C788 Specification for Nuclear-Grade Uranyl Nitrate Solution or Crystals

C859 Terminology Relating to Nuclear Materials

C1219 Test Methods for Arsenic in Uranium Hexafluoride (Withdrawn 2015)[3]

C1233 Practice for Determining Equivalent Boron Contents of Nuclear Materials

C1254 Test Method for Determination of Uranium in Mineral Acids by X-Ray Fluorescence

C1267 Test Method for Uranium by Iron (II) Reduction in Phosphoric Acid Followed by Chromium (VI) Titration in the Presence of Vanadium

C1287 Test Method for Determination of Impurities in Nuclear Grade Uranium Compounds by Inductively

[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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

Coupled Plasma Mass Spectrometry
C1295 Test Method for Gamma Energy Emission from Fission and Decay Products in Uranium Hexafluoride and Uranyl Nitrate Solution
C1296 Test Method for Determination of Sulfur in Uranium Oxides and Uranyl Nitrate Solutions by X-Ray Fluorescence (XRF) (Withdrawn 2007)[3]
C1380 Test Method for the Determination of Uranium Content and Isotopic Composition by Isotope Dilution Mass Spectrometry (Withdrawn 2018)[3]
C1413 Test Method for Isotopic Analysis of Hydrolyzed Uranium Hexafluoride and Uranyl Nitrate Solutions by Thermal Ionization Mass Spectrometry
C1517 Test Method for Determination of Metallic Impurities in Uranium Metal or Compounds by DC-Arc Emission Spectroscopy
C1561 Guide for Determination of Plutonium and Neptunium in Uranium Hexafluoride and U-Rich Matrix by Alpha Spectrometry
C1871 Test Method for Determination of Uranium Isotopic Composition by the Double Spike Method Using a Thermal Ionization Mass Spectrometer
D1193 Specification for Reagent Water
E12 Terminology Relating to Density and Specific Gravity of Solids, Liquids, and Gases (Withdrawn 1996)[3]
E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
E115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis (Withdrawn 2002)[3]

2.2 *American Chemical Society Specification:*
Reagent Chemicals[4]

2.3 *Other Documents:*
ISO 7097 Determination of Uranium in Uranium Product Solutions and Solids with Cerium IV Oxidation Titrimetric Method[5]

3. Terminology

3.1 For definitions of terms used in this test method but not defined herein, refer to Terminology C859.

4. Significance and Use

4.1 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 C788.

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

4.1.2 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.

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

4.1.4 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).

5. Reagents

5.1 *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.[4] 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.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193.

5.3 Hydrofluoric acid (used in some of the procedures) is a highly corrosive acid that can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers. Unlike other acids that are rapidly neutralized, hydrofluoric acid reactions with tissue may continue for days if left untreated. Familiarization and compliance with the Safety Data Sheet is essential.

6. Safety Precautions

6.1 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.

6.2 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.

7. Sampling

7.1 Criteria for sampling this material are given in Specification C788.

DETERMINATION OF URANIUM

8. Scope

8.1 Uranium can be determined using iron (II) reduction and dichromate titration. Test Method C1267 can be used.

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

8.3 Uranium can also be determined by X-Ray Fluorescence using Test Method C1254.

[4] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[5] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

8.4 Previous sections have been deleted.

URANIUM BY IGNITION GRAVIMETRY

9. Scope

9.1 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.

10. Summary of Test Method

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

11. Interferences

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

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

12. Apparatus

12.1 *Heat Lamp,* infrared.

12.2 *Hot Plate.*

12.3 *Muffle Furnace.*

13. Procedure

13.1 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 %).

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

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

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

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

13.6 Weigh the dish; then repeat 13.4 – 13.6 until a constant weight is obtained.

14. Calculation

14.1 Calculate the uranium content as follows:

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

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).

15. Precision

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

SPECIFIC GRAVITY BY PYCNOMETRY

16. Scope

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

17. Summary of Test Method

17.1 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 E12).

18. Apparatus

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

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

19. Procedure

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

19.2 Fill the volumetric flask with the uranyl nitrate solution to a point close to the volume mark, using a thin-stemmed funnel and a glass dropper.

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

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

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

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

19.7 Repeat 19.2 – 19.6 using boiled and cooled distilled water instead of the uranyl nitrate solution.

20. Calculation

20.1 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.

21. Precision

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

FREE ACID BY OXALATE COMPLEXATION

22. Scope

22.1 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.

23. Summary of Test Method

23.1 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)**.

24. Apparatus

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

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

25. Reagents

25.1 *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 25.4).

25.2 *Potassium Oxalate* ($K_2C_2O_4 \cdot H_2O$), crystals.

25.3 *Potassium Hydrogen Phthalate* ($C_8H_5KO_4$), acidimetric standard grade.

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

26. Procedure

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

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

26.3 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.

26.4 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.

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

26.6 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 $\Delta^2 pH/\Delta vol^2$ is zero at the point where the slope $\Delta pH/\Delta vol$ is a maximum.

27. Calculation

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

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

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.

28. Precision

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

DETERMINATION OF THORIUM

29. Scope

29.1 The determination of thorium by the arsenazo (III) (photometric) method has been discontinued, (see C799-93).

29.2 As an alternative, thorium can be determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). See Test Method C1287.

29.3 Previous sections have been deleted.

DETERMINATION OF CHROMIUM

30. Scope

30.1 The determination of chromium by the diphenyl carbazide method has been discontinued, (see C799-93).

30.2 As an alternative, chromium can be determined using inductively coupled plasma atomic emission spectrometry (ICP-AES). Test Method C761 can be used providing a transformation to U_3O_8 so described hereafter in Sections 72 – 75. A direct conversion to the amonium fluoride plus nitric acid solution can also be used, (see C761).

30.3 As an alternative, chromium can be determined using atomic absorption spectroscopy. Test Method C761 can be used.

30.4 As an alternative, chromium can be determined using ICP-MS. Test Method C1287 can be used.

30.5 Previous sections have been deleted.

DETERMINATION OF MOLYBDENUM

31. Scope

31.1 The determination of molybdenum by the thiocyanate (photometric) method has been discontinued, (See C799-93).

31.2 As an alternative, molybdenum can be determined using ICP-MS. Test Method C1287 can be used.

31.3 As an alternative, molybdenum can be determined using ICP-AES. Test Method C761, Sections 251 to 271 can be used providing a tranformation to U_3O_8 as described hereafter in Sections 72 – 75. A direct conversion to the amonium fluoride plus nitric acid solution can also be used, (see C761, Section 251).

31.4 Previous sections have been deleted.

HALOGENS SEPARATION BY STEAM DISTILLATION

32. Scope

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

33. Summary of Test Method

33.1 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.

34. Apparatus

34.1 *Steam Distillation Apparatus* (see Fig. 1).
34.1.1 *Distilling Flask,* 200-mL with thermometer well.
34.1.2 *Condenser.*
34.1.3 *Heating Mantle.*
34.1.4 *Steam Boiler,* 500-mL flask.

35. Reagents

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

35.2 *Acid Mixture*—Mix 0.2 *M* ferrous ammonium sulfate-0.5 *M* sulfamic acid (see 35.3), phosphoric acid (85 %), and sulfuric acid (sp gr 1.84) in the ratio of 1 + 2 + 5.

35.3 *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).

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

36. Procedure

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

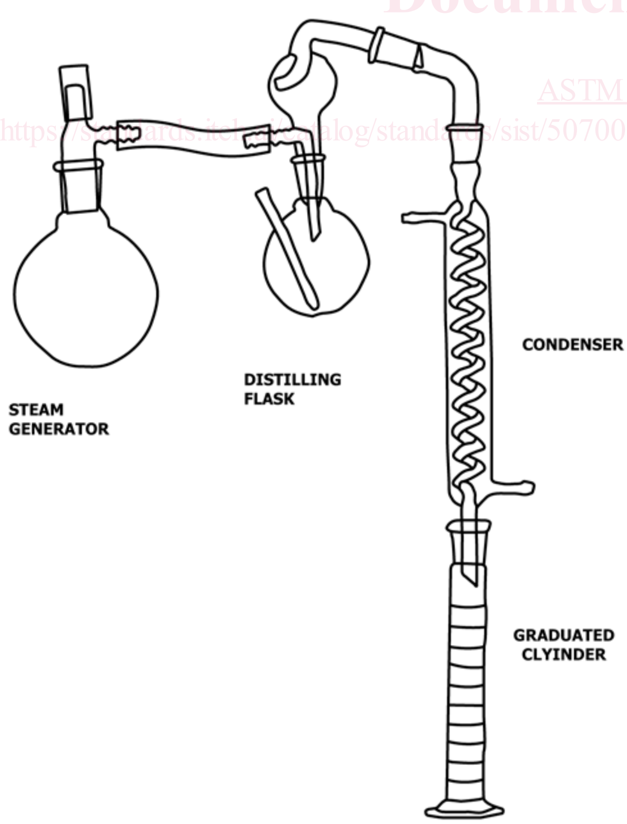

FIG. 1 Halogen Distillation Apparatus

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

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

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

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

36.6 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.

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

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

FLUORIDE BY SPECIFIC ION ELECTRODE

37. Scope

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

38. Summary of Test Method

38.1 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**).

39. Apparatus

39.1 *pH Meter,* expanded scale.

39.2 *Ion-Selective Electrode,* fluoride.

39.3 *Reference Electrode,* single-junction.

40. Reagents

40.1 *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.

40.2 *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.

40.3 *Fluoride Standard Solution B (1 mL = 5 µg F)*—Dilute 5 mL of the fluoride standard Solution A (see 40.2) to 1 L with water.

41. Procedure

41.1 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.

41.2 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.

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

42. Calculation

42.1 Calculate the F^- content as follows:

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

where:

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

43. Precision

43.1 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

44. Scope

44.1 The determination of chloride, bromide and iodide by microtitrimetric method has been discontinued, (see C799-93).

44.2 Previous sections have been deleted.

DETERMINATION OF CHLORIDE AND BROMIDE

45. Scope

45.1 Determination of bromide by the fluorescein (photometric) method has been discontinued, (see C799-93).

45.2 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.

45.3 Previous sections have been deleted.

DETERMINATION OF SULFUR BY X-RAY FLUORESCENCE

46. Scope

46.1 Sulfur can be determined using X-Ray Fluorescence. See Test Method C1296.

SULFATE SULFUR BY (PHOTOMETRIC) TURBIDIMETRY

47. Scope

47.1 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.

48. Summary of Test Method

48.1 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**).

49. Interferences

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

49.2 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.

50. Apparatus

50.1 *Spectrophotometer*—See Practice E60.

51. Reagents

51.1 *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.

51.2 *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.

51.3 *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.

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

52. Procedure

52.1 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.

52.2 Add 10 mL of TBP solution (see 51.4) and equilibrate the solutions.

52.3 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.

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

52.5 Add 0.50 g of $BaCl_2$ (see 51.1), stopper the flask, and invert the solution 20 times to dissolve the $BaCl_2$. This step must be performed in the same manner for standards and for samples.

52.6 Allow the solution to stand 60 ± 5 min. This step must be performed in the same manner for standards and for samples.

52.7 Measure the absorbance at 450 nm in 5-cm cells with a blank containing all of the reagents except sample as the reference.

52.8 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 52.2 – 52.6.