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Standard Test Method for
Uranium and Plutonium Concentrations and Isotopic Abundances[1]

This standard is issued under the fixed designation E 267; 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 is applicable to the determination of uranium (U) and plutonium (Pu) concentrations and their isotopic abundances (Note 1) in solutions which result from the dissolution of nuclear reactor fuels either before or after irradiation. A minimum sample size of 50 μg of irradiated U will contain sufficient Pu for measurement and will minimize the effects of cross contamination by environment U.

NOTE 1—The isotopic abundance of ^{238}Pu can be determined by this test method; however, interference from ^{238}U may be encountered. This interference may be due to (*1*) inadequate chemical separation of uranium and plutonium, (*2*) uranium contamination within the mass spectrometer, and (*3*) uranium contamination in the filament. One indication of uranium contamination is a changing 238/239 ratio during the mass spectrometer run, in which case, a meaningful ^{238}Pu analysis cannot be obtained on that run. If inadequate separation is the problem, a second pass through the separation may remove the uranium. If contamination in the mass spectrometer or on the filaments is the problem, use of a larger sample, for example, 1 μg, on the filament may ease the problem. A recommended alternative method of determining ^{238}Pu isotopic abundance without ^{238}U interference is alpha spectroscopy using Practice D 3084. The ^{238}Pu abundance should be obtained by determining the ratio of alpha particle activity of ^{238}Pu to the sum of the activities of ^{239}Pu and ^{240}Pu. (**1**)[2] The contribution of ^{239}Pu and ^{240}Pu to the alpha activity differs from their isotopic abundances due to different specific activities.

1.2 The procedure is applicable to dissolver solutions of uranium fuels containing plutonium, aluminum, stainless steel, or zirconium. Interference from other alloying constituents has not been investigated and no provision has been made in the test method for fuels used in the ^{232}Th-^{233}U fuel cycle.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[3]
D 3084 Practice for Alpha-Particle Spectrometry of Water[4]
E 137 Practice for Evaluation of Mass Spectrometers for Quantitative Analysis from a Batch Inlet[5]
E 219 Test Method for Atom Percent Fission in Uranium Fuel (Radiochemical Method)[6]
E 244 Test Method for Atom Percent Fission in Uranium and Plutonium Fuel (Mass Spectrometric Method)[6]

3. Summary of Test Method

3.1 An aliquot of solution to be analyzed is spiked with known amounts of ^{233}U and ^{242}Pu (**2–6**). U and Pu are separated by ion exchange and analyzed mass spectrometrically.

4. Significance and Use

4.1 This test method is specified for obtaining the atom ratios and U atom percent abundances required by Test Method E 244 and the U concentration required by Test Method E 219.

NOTE 2—The isotopic abundance of ^{238}Pu normally is not required for burnup analysis of conventional light-water reactor fuel.

4.2 The separated heavy element fractions placed on mass spectrometric filaments must be very pure. The quantity required depends upon the sensitivity of the instrument detection system. If a scintillator (**7**) or an electron multiplier detector is used, only a few nanograms are required. If a Faraday cup is used, a few micrograms are needed. Chemical purity of the sample becomes more important as the sample size decreases, because the ion emission of the sample is repressed by impurities.

4.3 Operation at elevated temperature (for example, 50 to 60°C) (Note 3) will greatly improve the separation efficiency of ion exchange columns. Such high-temperature operation yields an iron-free U fraction and U-free Pu fraction, each of which has desirable emission characteristics.

NOTE 3—A simple glass tube column can be heated by an infrared lamp until it is warm to the touch.

4.4 Extreme care must be taken to avoid contamination of the sample by environmental U. The level of U contamination

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should be measured by analyzing an aliquot of 8 *M* nitric acid (HNO$_3$) reagent as a blank and computing the amount of U it contains.

4.4.1 The U blank is normally 0.2 ng of total U. Blanks larger than 0.5 ng are undesirable, because as much as 5 ng of natural U contamination in a 50 µg sample of fully enriched U will change its ^{235}U-to-^{238}U ratio from 93.3-to-5.60 to 93.3-to-5.61 (that is, 16.661 to 16.631) or 0.18 %.

4.4.2 Where a 10 % decrease in ^{235}U-to-^{238}U ratio from neutron irradiation of a fuel is being measured, such contamination introduces a 1.8 % error in the difference measurement. It is clear that larger blanks or smaller samples cannot be tolerated. In the analysis of small samples, environmental U contamination can introduce the largest single source of error.

5. Apparatus

5.1 *Shielding*—To work with highly irradiated fuel, shielding is required for protection of personnel during preparation of the primary dilution of dissolver solution. The choice of shielding is dependent upon the type and level of the radioactivity of the samples being handled.

5.2 *Glassware*—To avoid cross contamination, use only new glassware (beakers, pipets, and columns) from which surface U has been removed by boiling in HNO$_3$(1 + 1) for 1 to 2 h. Glassware is removed from the leaching solution, rinsed in redistilled water, oven-dried, and covered until used to avoid recontamination with U from atmospheric dust. Wrapping clean glassware in aluminum foil or plastic film will protect it against dust.

5.2.1 For accurate delivery of 500-µL volumes specified in this procedure for spike and sample, a Kirk-type micropipet (**8**) (also known as a "lambda" transfer pipet) is required. Such a pipet is calibrated to contain 500 µL with ±0.2 % accuracy and is designed to be rinsed out with dilute acid to recover its contents. Volumetric, measuring, and other type pipets are not sufficiently accurate for measuring spike and sample volumes.

5.3 *Mass Spectrometer*—The suitability of mass spectrometers for use with this test method of analysis shall be evaluated by means of performance tests described in this test method and in Practice E 137. The mass spectrometer used should possess the following characteristics:

5.3.1 A thermal-ionization source with single or multiple filaments of rhenium (Re),

5.3.2 An analyzer radius sufficient to resolve adjacent masses in the mass-to-charge range being studied, that is, m/e = 233 to 238 for U$^+$ or m/e = 265 to 270 for UO$_2^+$ ions. Resolution must be great enough to measure one part of ^{236}U in 250 parts of ^{235}U,

5.3.3 A minimum of one stage of magnetic deflection. Since the resolution is not affected, the angle of deflection may vary with the instrument design,

5.3.4 A mechanism for changing samples,

5.3.5 A direct-current, electron multiplier, scintillation or semi-conductor detector (**7**) followed by a current-measuring device, such as a vibrating-reed electrometer or a fast counting system for counting individual ions,

5.3.6 A pumping system to attain a vacuum of 2 or 3 × 10^{-7} torr in the source, the analyzer, and the detector regions, and

5.3.7 A mechanism to scan masses of interest by varying the magnetic field or the accelerating voltage.

6. Reagents and Materials

6.1 *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.[7] 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.

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

6.3 *Anion Exchange Resin*.[8]

6.4 *Blended ^{239}Pu and ^{238}U Calibration Standard*—Prepare a solution containing about 0.25 mg ^{239}Pu/liter and 25 mg ^{238}U/liter in 8 *M* HNO$_3$, as follows. With a new, calibrated, clean Kirk-type micropipet, add 0.500 mL of ^{239}Pu known solution (see 6.12) to a calibrated 1-L volumetric flask. Rinse the micropipet into the flask three times with 8 *M* HNO$_3$. In a similar manner, add 0.100 mL of ^{238}U known solution (see 6.14). Dilute exactly to the 1-L mark with 8 *M* HNO$_3$ and mix thoroughly. From the value K_{239}(see 6.12), calculate the atoms of ^{239}Pu/mL of calibration standard, C_{239}, as follows:

$$C_{239} = (\text{mL } ^{239}\text{Pu solution/1000 mL calibration standard}) \times K_{239} \tag{1}$$

From the value K_{238}(see 6.14), calculate the atoms of ^{238}U/mL of calibration standard, C_{238}, as follows:

$$C_{238} = (\text{mL } ^{238}\text{U solution/1000 mL calibration standard}) \times K_{238} \tag{2}$$

Flame-seal 3 to 5-mL portions in glass ampoules to prevent evaporation after preparation until time of use. For use, break off the tip of an ampoule, pipet promptly the amount required, and discard any unused solution. If more convenient, the calibration standard can be flame-sealed in premeasured portions for quantitative transfer when needed.

6.5 *Blended ^{242}Pu[9] and ^{233}U Spike Solution*—Prepare a solution containing about 0.25 mg ^{242}Pu/liter and 5 mg ^{233}U/liter in 8 *M* HNO$_3$.[10] Standardize the spike solution as follows:

6.5.1 In a 5-mL beaker, place about 0.1 mL of ferrous solution, exactly 500 µL of calibration standard (see 6.4), and exactly 500µ L of spike solution (see 6.5). In a second beaker, place about 0.1 mL of ferrous solution and 1 mL of calibration

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[7] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY and the "United States Pharmacopeia."

[8] Dowex-1-type resins (either AG 1-X2 or AG 1-X4, 200 to 400 mesh) obtained from Bio-Rad Laboratories 32nd St. and Griffin Ave., Richmond, CA, have been found satisfactory.

[9] When ^{244}Pu becomes available, it can be substituted for ^{242}Pu with the advantage that it does not appear in the sample as a normal constituent.

[10] These isotopes in greater than 99 % isotopic purity are obtained through the Division of Research of the Atomic Energy Commission from the Isotopes Distribution Office of Oak Ridge National Laboratory.

standard without any spike. In a third beaker, place 0.1 mL of ferrous solution and 1 mL of spike without standard. Mix well and allow to stand for 5 min to reduce Pu to Pu (III) or Pu (IV) to promote Pu isotopic exchange.

6.5.2 Follow the procedure described in 8.5.2-8.8.6. On the Pu fraction, record the isotopic ratios of ^{242}Pu to ^{239}Pu in the calibration standard, $C_{2/9}$; in the spike solution, $S_{2/9}$; and in the standard-plus-spike mixture, $M_{2/9}$. On the U fraction, record the corresponding ^{233}U-to-^{238}U ratios, $C_{3/8}$, $S_{3/8}$, and $M_{3/8}$. Correct all ratios for mass discrimination bias (see Section 7).

6.5.3 Calculate the number of atoms of ^{242}Pu/mL of spike, S_2, as follows:

$$S_2 = C_{239} \{(M_{2/9} - C_{2/9})/[1 - (M_{2/9}/S_{2/9})]\} \quad (3)$$

6.5.4 Calculate the number of atoms of ^{233}U/mL of spike, S_3, as follows:

$$S_3 = C_{238} \{(M_{3/8} - C_{3/8})/[1 - (M_{3/8}/S_{3/8})]\} \quad (4)$$

6.5.5 Calculate the ratio of ^{242}Pu atoms to ^{233}U atoms in the spike, $S_{2/3}$, as follows:

$$S_{2/3} = S_2/S_3 \quad (5)$$

6.5.6 Store in the same manner as the calibration standard (see 6.4), that is, flame-seal 3 to 5-mL portions in glass ampoules. For use, break off the tip of an ampoule, pipet promptly the amount required, and discard any unused solution. If more convenient, spike solution can be flame-sealed in premeasured portions for quantitative transfer to individual samples.

6.6 *Ferrous Solution (0.001 M)*—Add 40 mg of reagent grade ferrous ammonium sulfate [Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O] and 1 drop of 18 M H$_2$SO$_4$ to 5 mL of redistilled water. Dilute to 100 mL with redistilled water, and mix. This solution does not keep well. Prepare fresh daily.

6.7 *Hydrochloric Acid*—Prepare reagent low in U and dissolved solids by distilling 6 M HCl or by saturating redistilled water in a polyethylene container with HCl gas which has passed through a quartz-wool filter. Dilute to 6 M, 1 M, 0.5 M, and 0.05 M HCl with redistilled water. Store each solution in a polyethylene container. One drop of acid, when evaporated on a clean microscope slide cover glass, must leave no visible residue. Test monthly. Commercial HCl (CP grade) in glass containers has been found to contain excessive residue (dissolved glass) which inhibits ion emission.

6.8 *Hydrofluoric Acid*—Reagent grade concentrated HF (28 M).

6.9 *Ion Exchange Column*—One method of preparing such a column is to draw out the end of a (150-mm) (6-in.) length of 4-mm inside diameter glass tubing and force a glass wool plug into the tip tightly enough to restrict the linear flow rate of the finished column to less than 10 mm/min. By means of a capillary pipet add resin (see 6.3) suspended in water to the required bed length. Since the diameter of glass tubing may vary from piece to piece, the quantities of resin and of liquid reagents used are specified in millimeters of column length. To simplify use, mark the tubing above the resin bed in millimeters with a marking pen or back with a strip of millimeter graph paper. Dispense liquid reagents into the column from a polyethylene wash bottle to the length specified in the procedure. Thus 500 mm of wash solution can be added by filling to the 100-mm mark five times.

6.10 *Nitric Acid (sp gr 1.42)*—Distill to obtain a 16 M reagent low in U and dissolved solids. Dilute further with redistilled water to 8 M, 3 M, 0.5 M, and 0.05 M concentrations.

6.11 *Nitrite Solution (0.1 M)*—Add 0.69 g of sodium nitrite (NaNO$_2$) and 0.2 g of NaOH to 50 mL of redistilled water, dilute to 100 mL with redistilled water, and mix.

6.12 ^{239}*Pu Known Solution*—Add 10 mL of 6 M HCL to a clean calibrated 1-L flask. Cool the flask in an ice water bath. Allow time for the acid to reach approximately 0°C and place in a glove box. Displace the air in the flask with inert gas (A, He, or N$_2$). Within the glove box, open the U.S. New Brunswick Laboratory Plutonium Metal Standard Sample 126, containing about 0.5 g Pu (actual weight individually certified) and add the metal to the cooled HCl. After dissolution of the metal is complete, add 10 drops of concentrated HF and 400 mL of 8 M HNO$_3$ and swirl. Place the flask in a stainless-steel beaker for protection and invert a 50-mL beaker over the top and let it stand for at least 8 days to allow any gaseous oxidation products to escape. Dilute to the mark with 8 M HNO$_3$ and mix thoroughly. By using the individual weight of Pu in grams, the purity, and the molecular weight of the Pu given on the NBL certificate, with atom fraction ^{239}Pu, A_9, determined as in Eq 14, (see 9.2), calculate the atoms of ^{239}Pu/mL of ^{239}Pu known solution, K_{239}, as follows:

$$K_{239} = (\text{g Pu}/1000 \text{ mL solution}) \times (\text{percent purity}/100)$$
$$\times (6.022 \times 10^{23} \text{ atoms})/(\text{Pu molecular weight}) \times A_9 \quad (6)$$

6.13 *Sucrose Solution (0.002 M)*—Dissolve 0.07 g of reagent grade sucrose in 100 mL of redistilled water. Store in polyethylene to prevent alkali contamination. Prepare fresh weekly to avoid fermentation.

6.14 ^{238}*U Known Solution*—Heat triuranium octoxide (U$_3$O$_8$) from the New Brunswick Laboratory Natural Uranium Oxide Standard Sample 129 in an open crucible at 900°C for 1 h and cool in a desiccator in accordance with the certificate accompanying the standard sample. Weigh about 6.0 g U$_3$O$_8$ accurately to 0.1 mg and place it in a calibrated 100-mL volumetric flask. Dissolve the oxide in 8 M HNO$_3$ and dilute to the 100-mL mark with 8 M HNO$_3$ and mix thoroughly. By using the measured weight of U$_3$O$_8$ in grams, the purity given on the NBL certificate, and the atom fraction ^{238}U, A_8, determined as in Eq 11, (see 9.1), calculate the atoms of ^{238}U/mL of ^{238}U known solution, K_{238}, as follows:

$$K_{238} = (\text{g U}_3\text{O}_8/100 \text{ mL solution}) \times (\text{percent purity}/100)$$
$$\times (0.8480 \text{ g U}/1 \text{ g U}_3\text{O}_8) \times (6.022 \times 10^{23}/238.03) \times A_8 \quad (7)$$

7. Instrument Calibration

7.1 In the calibration of the mass spectrometer for the analysis of U and Pu, the measurement and correction of mass discrimination bias is an important factor in obtaining accurate and consistent results. The mass discrimination bias can be measured on natural U where the ^{235}U-to-^{238}U ratio spans almost a 1.3 % spread in mass. Calculate the mass discrimination bias factor, B, as follows:

$$B = (1/c) [(\bar{R}_{i/f}/R_s) - 1] \quad (8)$$