Designation: E 267 – 90 (Reapproved 2001)

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

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[1] This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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[2] The boldface numbers in parentheses refer to the list of references appended to this test method.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 11.02.

[5] *Annual Book of ASTM Standards*, Vol 05.03.

[6] *Annual Book of ASTM Standards*, Vol 12.02.

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the sample by environmental U. The level of U contamination 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 $\times 10^{-7}$ 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:

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

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

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

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,

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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.

place about 0.1 mL of ferrous solution and 1 mL of calibration 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:

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

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

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

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

$$S_{2/3} = S_2/S_3 \tag{5}$$

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 [$Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$] and 1 drop of 18 *M* H_2SO_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:

$$\begin{aligned}\mathrm{K}_{239} &= (\text{g Pu}/1000\text{ mL solution}) \times (\text{percent purity}/100)\\ &\times (6.022 \times 10^{23}\text{ atoms})/(\text{Pu molecular weight}) \times \mathrm{A}_9\end{aligned} \tag{6}$$

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_3O_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_3O_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_3O_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:

$$\begin{aligned}K_{238} &= (\text{g } U_3O_8/100\text{ mL solution}) \times (\text{percent purity}/100)\\ &\times (0.8480\ g\text{ U}/1\ g\ U_3O_8) \times (6.022 \times 10^{23}/238.03) \times A_8\end{aligned} \tag{7}$$

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:

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

where:

$\bar{R}_{i/j}$ = average measured atom ratio of isotope *i* to isotope *j*,

R_s = known value of the measured atom ratio. For the ratio of ^{235}U-to-^{238}U in natural U, $R_s = 0.007258$, and

c = Δ mass/mass. The values of c for various ratios and ion species include:

Ratio	U^+ or Pu^+	UO_2^+ or PuO_2^+
$^{235}U/^{238}U$	+ 3/238	+ 3/270
$^{236}U/^{235}U$	−1/235	−1/267
$^{233}U/^{238}U$	+ 5/238	+ 5/270
$^{234}U/^{235}U$	+ 1/235	+ 1/267
$^{242}Pu/^{239}Pu$	−3/239	−3/271
$^{240}Pu/^{239}Pu$	−1/239	−1/271
$^{241}Pu/^{239}Pu$	−2/239	−2/271

7.2 Correct every measured average ratio, $R_{i/j}$, for mass discrimination as follows:

$$R_{i/j} = \bar{R}_{i/j}/(1 + cB) \qquad (9)$$

where:

$R_{i/j}$ = the corrected average atom ratio of isotope *i* to isotope *j*.

8. Procedure

8.1 In mass-spectrometric isotope-dilution analysis it is imperative that (*1*) the sample be thoroughly mixed with the spike prior to any chemical operation, and (*2*) isotopic exchange between the ions of the sample and the ions of the spike be achieved prior to any chemical separation step. Thorough mixing can be accomplished in a number of ways.

8.2 Isotope exchange between the uranium ions in the sample and those in the spike is achieved by oxidation to the hexavalent state. Any of a number of oxidizing agents plus heat will accomplish this. In the perchloric acid fuming step of the following procedure, exchange is assured as soon as the fumes of perchloric acid appear.

8.3 Exchange between the plutonium ions in the sample and those in the spike is far more difficult to achieve. Polymerization of plutonium (IV) ions in the sample or spike, or both, often occurs and can inhibit, or even prevent, reduction or oxidation to a common oxidation state. Furthermore, even in the absence of plutonium (IV) polymers, complete oxidation (or reduction) requires a stringent set of conditions. In the following procedure, plutonium (IV) polymers are destroyed by the addition of a small amount of hydrofluoric acid. The plutonium ions are brought to a common oxidation state (hexavalent) by fuming the mixture of sample and spike strongly with perchloric acid. It is imperative that the fuming be brought to the point where the fumes are copious if the oxidation, and hence exchange, is to be satisfactorily made.

8.4 *Preparation of a Working Dilution of Dissolver Solution*:

8.4.1 Prepare a dilution of fuel dissolver solution with 8 *M* HNO_3—0.005 *M* HF to obtain a concentration of 100 to 1000 mg U/liter; mix well.

8.5 *U and Pu Separation*:

8.5.1 In a 10-mL beaker, place exactly 500 µL of spike solution, and exactly 500 µL of diluted sample solution containing about 50 to 500µ g U. Mix thoroughly, add 1 drop of 1 *M* HF and 10 drops concentrated $HClO_4$, and again mix. Place the beaker on a hot plate and heat to dense fumes of $HClO_4$, taking the sample to incipient dryness. Dissolve the residue in 250 µL of 8 *M* HNO_3; take care to ensure complete dissolution. Add about 100 µL of ferrous solution. In a second beaker, place about 100 µL of ferrous solution and 1 mL of sample without any spike solution. As a blank for each series of samples, place 500 µL of 8 *M* HNO_3, about 100 µL of ferrous solution, and 1 mL of spike solution in another beaker. Mix well and allow to stand for 5 min to reduce Pu (VI) to Pu (III) or Pu (IV) to promote isotopic exchange. Follow the remaining procedure on each solution.

8.5.2 Add 1 drop of nitrite solution to oxidize Pu to the tetravalent state and evaporate the solution to near dryness to reduce volume. Dissolve the residue in 250 µL of 8 *M* HNO_3; take care to ensure complete dissolution.

8.5.3 Prepare a 20-mm long anion exchange column (see 6.9) for operation at 50 to 60°C. Since the diameter of the column may vary from one laboratory to another, the quantity of resin and the quantity of liquid reagents used are specified in units of column length. Wash the column with 100 mm of 0.05 *M* HNO_3 followed by 100 mm of 8 *M* HNO_3.

8.5.4 Place a 5-mL beaker under the column to receive the unabsorbed fission product fraction and transfer the sample solution onto the column with a capillary pipet. Carefully wash the walls of the column with a few drops of 8 *M* HNO_3 to ensure that all the sample is absorbed on the column.

8.5.5 Complete the elution of unabsorbed fission products with 50 mm of 8 *M* HNO_3.

8.5.6 Elute the U into a second 5-mL beaker with 200 mm of 3 *M* HNO_3. Purify this U solution further by following the procedure given in 8.6.

8.5.7 Wash the column with 500 mm of 3 *M* HNO_3. Discard this wash. Elute Pu with 200 mm of 0.5 *M* HNO_3 into a third 5-mL beaker. Purify this Pu solution further by following the procedure given in 8.7.

8.6 *U Purification*:

8.6.1 Evaporate the U solution (see 8.5.6) to dryness. Add a few drops of concentrated HCl and again evaporate to dryness.

8.6.2 Prepare a 5-mm long anion exchange column (see 6.9) for operation at 50 to 60°C. Wash the column with 100 mm of 1 *M* HCl and 100 mm of 6 *M* HCl.

8.6.3 Redissolve U in 0.5 mL 6 *M* HCl and load it onto the column. Wash the column with 150 mm of 6 *M* HCl. Discard the washings.

8.6.4 Elute the U with 50 mm of 0.5 *M* HCl into a 5-mL centrifuge tube and evaporate to dryness in a boiling water bath with a gentle stream of filtered air. Dissolve the U in 1 drop of sucrose solution (see 6.13) and place a suitable portion (see 4.2) of it on a rhenium mass spectrometer filament. Evaporate it gently to dryness by passing a small electrical current (for example, less than 1.5 A at 6 V or less) through the filament. When dry, increase the current briefly (not over 2.5 A at 6 V) to char sucrose. The filament is now ready for insertion in the mass spectrometer (see 8.8).

8.7 *Pu Purification*:

8.7.1 To the Pu solution (see 8.5.7), add 1 mL of concentrated HNO_3 and evaporate to 100-µL volume. Do not evaporate to dryness, which might thermally decompose the nitrate to oxide; such oxides are difficult to redissolve.

8.7.2 Prepare a 5-mm long anion exchange column (see 6.9) for operation at 50 to 60°C. Wash the column with 100 mm of 0.05 *M* HNO_3 followed by 100 mm of 8 *M* HNO_3.

8.7.3 Dilute the Pu solution with 5 drops of 8 *M* HNO_3 and transfer it to the column. Rinse the beaker with 5 drops of 8 *M* HNO_3 and transfer the rinse to the column. Wash the column with 250 mm of 3 *M* HNO_3. Discard this wash. Elute the Pu with 50 mm of 1 *M* HCl into a 5-mL centrifuge tube.

8.7.4 Evaporate the solution to dryness in a boiling water bath with a gentle stream of filtered air. Dissolve Pu in 1 drop of 0.05 *M* HCl and place a suitable portion (see 4.2) of it on a rhenium mass-spectrometer filament. Evaporate the solution to dryness on the filament by passing a small electrical current (for example, less than 1.5 A at 6 V or less) through the filament. If it is desired to increase the ratio of Pu^+ ions to PuO^+ ions particularly on single filament mass spectrometers **(9)**, evaporate 1 drop of 0.002 *M* sucrose solution to dryness over the sample and increase the current briefly (not over 2.5 A at 6 V) to char sucrose. The filament is now ready for insertion in the mass spectrometer (see 8.8).

8.8 *Mass Analysis*:

8.8.1 Position the filament containing the sample in the source region. This may be accomplished by using a vacuum lock and rapid sample changing mechanism or by venting the instrument.

8.8.2 When a vacuum of less than 3×10^{-6} torr is reached in the source, heat the sample filament gently to a dull, red glow (500 to 700°C), for 5 to 30 min, to permit outgassing. When outgassing has ceased, increase the filament temperature to emit ions. Typical emitting temperatures are 1450 to 1650°C for Pu and 1650 to 1850°C for U.

8.8.3 For a single filament source, set accelerating voltage and magnet current to collect either U^+ or $UO_2{}^+$ ions and scan the region of interest. For a triple filament source, adjust the source controls to collect ions emitted from the center filament only; set accelerating voltage and magnet current to collect either U^+ or $UO_2{}^+$ ions, increase center filament temperature to working level, and increase the temperature of the sample filament slowly while scanning the mass region of interest. U ions are found by their emergence and growth from the background. A source pressure of 2 to 3×10^{-7} torr or better is desirable for good U^+ ion emission. A slightly higher pressure is satisfactory for $UO_2{}^+$ ion emission.

8.8.4 When the ion beam is found, focus the major isotope beam by adjusting the magnetic field, the accelerating voltage, and any electrical or mechanical controls available. The intensity of this beam may be recorded on a fast-response (1 s or better) strip-chart recorder. Adjustment of the filament current (a-c or d-c) will determine the intensity of the ion beam.

8.8.4.1 This intensity is selected to provide a good statistical measurement of the ion abundance and permit its comparison with another isotope of lesser abundance with good precision. The intensity of the major beam is adjusted until stable emission of the desired intensity is achieved. The emission rate should be constant or at least increase or decrease slowly and evenly.

8.8.5 When acceptable ion emission is reached, measure the relative intensities of the ion peaks of interest by scanning alternately up mass and down mass either magnetically or by changing the accelerating voltage. Sequential measurement of isotope pairs may be made to provide good statistical precision.

8.8.5.1 Adjustments are made in beam focus or filament current before a spectrum sweep or an isotope ratio measurement. If a strip-chart recorder is used, the read-out sensitivity may be switched to obtain comparable displacements for masses of widely varying abundances. If the beam intensity is changing slowly, an extrapolation in time will be necessary to correct for this change **(2).** Usually, a linear rate of change is assumed for short periods (less than 1 min).

Note 4—Comparison of isotopes is often made by measuring intensities of peaks observed when increasing or decreasing either the magnetic field or the accelerating voltage. An empirical correction must be made to remove the effect of any change in source transmission and the gain of an electron multiplier detector. This correction should be determined by measuring the isotopic abundance of a well-known sample, such as a National Institute for Standards and Technology Natural Uranium Oxide Standard Sample 950. The same sensitivity levels should be used in the measuring system for standards and samples whenever practical to avoid correction for any inherent nonlinearity in the amplification factor.

8.8.6 When sufficient data are collected to obtain the desired precision, turn off the filament current and discontinue the analysis. If the $UO_2{}^+$ ion is measured, the natural abundance of oxygen isotopes must be considered for their contribution to the various mass positions **(2).**

8.8.7 Record and correct (see Section 7) the isotopic ratios, $R_{i/j}$, of the *i*th to the *j*th species in the unspiked sample, as required in the calculations (see Section 9). Similarly, record and correct the isotopic ratios for the spike, $S_{i/j}$ and for the sample-plus-spike mixture, $M_{i/j}$. The symbols for the isotopes ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu are abbreviated to 3, 4, 5, 6, 8, 9, 0, 1, and 2, respectively (see Section 9). In this nomenclature, the observed ratios of ^{238}U to ^{233}U in the sample, the spike, and the sample-plus-spike mixture ($R_{i/j}$, $S_{i/j}$, and $M_{i/j}$) become $R_{8/3}$, $S_{8/3}$, and $M_{8/3}$, respectively.

9. Calculation

9.1 Calculate atom fraction ^{235}U, A_5, on the unspiked U as follows:

$$A_5 = R_{5/8}/(R_{4/8} + R_{5/8} + R_{6/8} + R_{8/8}) \tag{10}$$

where $R_{8/8}$ (which equals 1) is retained for clarity. Next, calculate atom fraction ^{238}U, A_8, as follows:

$$A_8 = R_{8/8}/(R_{4/8} + R_{5/8} + R_{6/8} + R_{8/8}) \tag{11}$$

In these equations, ^{238}U is assumed to be the principal isotope. For highly enriched U where ^{235}U is the principal isotope, obtain the ratio of each isotope to ^{235}U instead of to ^{238}U by using $R_{4/5}$, $R_{5/5}$, $R_{6/5}$, $R_{8/5}$ in place of $R_{4/8}$, $R_{5/8}$, $R_{6/8}$, and $R_{8/8}$. Finally, calculate N_5 and N_8 as follows:

$$N_5 = 100A_5 \tag{12}$$

$$N_8 = 100A_8 \tag{13}$$

If desired, calculate N_4 and N_6 similarly by dividing the corresponding atom ratio by the same sum of four ratios as shown in Eq 10 and Eq 11 and by multiplying the resultant atom fraction by 100 to obtain percent as shown in Eq 12 and Eq 13.

9.2 Calculate the corresponding atom fraction ^{239}Pu, A_9, and atom percent ^{239}Pu, N_9, on the unspiked Pu fraction as follows:

$$A_9 = R_{9/9} / (R_{9/9} + R_{0/9} + R_{1/9} + R_{2/9}) \tag{14}$$

$$N_9 = 100A_9 \tag{15}$$

where $R_{9/9}$ (which equals 1) is retained for clarity. If desired, calculate N_0, N_1, and N_2 similarly by dividing the corresponding atom ratio by the same sum of four ratios shown in Eq 14 and by multiplying by 100 to obtain percent as shown in Eq 15.

9.3 As required for Test Method E 219, calculate the U atoms per milliliter. U, for low- and high-^{235}U-enrichment samples as follows::

$$U = (\text{mL spike/mL sample}) \times (S_3/A_8)\{(M_{8/3} - S_{8/3})/[1 - (M_{8/3}/R_{8/3})]\} \tag{16}$$

$$U = (\text{mL spike/mL sample}) \times (S_3/A_5)\{(M_{5/3} - S_{5/3})/[1 - (M_{5/3}/R_{5/3})]\} \tag{17}$$

Calculate Pu atoms per milliliter, Pu, as follows:

$$Pu = (\text{mL spike/mL sample}) \times (S_2/A_9)\{(M_{9/2} - S_{9/2})/[1 - (M_{9/2}/R_{9/2})]\} \tag{18}$$

9.4 As required for Test Method E 244, calculate $R_{9/8}$, $R_{0/8}$, $R_{1/8}$, $R_{2/8}$, $R_{5/8}$, $R_{6/8}$, and $R_{6/5}$ as follows:

$$R_{9/8} = S_{2/3}\frac{\{(M_{9/2} - S_{9/2}) / [1 - (M_{9/2} / R_{9/2})]\}}{\{(M_{8/3} - S_{8/3}) / [1 - (M_{8/3} / R_{8/3})]\}} \tag{19}$$

$$R_{0/8} = S_{2/3}\frac{\{(M_{0/2} - S_{0/2}) / [1 - (M_{0/2} / R_{0/2})]\}}{\{(M_{8/3} - S_{8/3}) / [1 - (M_{8/3} / R_{8/3})]\}} \tag{20}$$

$$R_{1/8} = S_{2/3}\frac{\{(M_{1/2} - S_{1/2}) / [1 - (M_{1/2} / R_{1/2})]\}}{\{(M_{8/3} - S_{8/3}) / [1 - (M_{8/3} / R_{8/3})]\}} \tag{21}$$

$$R_{2/8} = R_{9/8} \times R_{2/9} \tag{22}$$

$$R_{5/8} = N_5 / N_8 \tag{23}$$

$$R_{6/8} = N_6 / N_8 \tag{24}$$

$$R_{6/5} = N_6 / N_5 \tag{25}$$

9.5 Isotopic abundances have been expressed in atom percent and concentrations used for obtaining atom percent fission have been expressed in atoms per milliliter (see 9.1, 9.2, and 9.3). For accountability, it may be necessary to report isotopic abundances in weight percent and concentrations in milligrams per milliliter. Calculate weight percent ^{235}U and ^{239}Pu as follows:

$$\text{Weight percent } ^{235}\text{U} = (W_5 \times 100)/(W_4 + W_5 + W_6 + W_8) \tag{26}$$

where:
W_4 = $A_4 \times 234.04$,
W_5 = $A_5 \times 235.04$,
W_6 = $A_6 \times 236.05$, and
W_8 = $A_8 \times 238.05$.

$$\text{Weight percent } ^{239}\text{Pu} = (W_9 \times 100)/(W_9 + W_0 + W_1 + W_2) \tag{27}$$

where:
W_9 = $A_9 \times 239.05$,
W_0 = $A_0 \times 240.05$,
W_1 = $A_1 \times 241.06$, and
W_2 = $A_2 \times 242.06$.

9.5.1 If desired, calculate the weight percent ^{234}U, ^{236}U, and ^{238}U similarly by dividing W_4, W_6, and W_8 in turn by ($W_4 + W_5 + W_6 + W_8$) and by multiplying the resultant weight fraction by 100 to obtain percent. The weight percent ^{240}Pu, ^{241}Pu, and ^{242}Pu can be found similarly by dividing W_0, W_1, and W_2 by ($W_9 + W_0 + W_1 + W_2$) and by multiplying the resulting weight fraction by 100 to obtain percent. Calculate the weight concentration of U by multiplying the atoms U/mL, U, by the millimolecular weight of the U under test (that is, $W_4 + W_5 + W_6 + W_8$) and dividing by the number of atoms in a millimole as follows:

$$\text{mg U/mL} = U\ \frac{\text{millimolecular weight of U}}{6.022 \times 10^{20}\text{atoms/millimole}} \tag{28}$$

Similarly for Pu,

$$\text{mg Pu/mL} = Pu\ \frac{\text{millimolecular weight of Pu}}{6.022 \times 10^{20}\text{atoms/millimole}} \tag{29}$$

10. Report

10.1 Report the following information:

10.1.1 U and Pu concentrations in atoms or milligrams per milliliter to four significant figures.

10.1.2 The atom or weight percent abundance of each isotope to the nearest 0.01 % absolute for abundance levels between 6 and 100 % to the nearest 0.001 % at lower levels.

11. Precision and Bias

11.1 *Precision of Uranium and Plutonium Concentration Results*—No significant difference has been observed in the precision with which the uranium and plutonium concentrations are determined by this test method. In an interlaboratory comparison, the estimated precision of the average of duplicate results of a single laboratory was 0.6 % relative standard deviation. The relative standard deviation is the estimated standard deviation of a single laboratory multiplied by 100 and divided by the average of all laboratories. The corresponding precision between laboratories is 0.7 % relative standard deviation for the participating laboratories. These values were obtained by analyzing five selected samples for U and two selected samples for Pu. A total of seven laboratories measured U and five measured Pu.

11.2 *Precision of Isotopic Abundances*—The single laboratory and multilaboratory precisions vary with abundance, as shown in Fig. 1 and Fig. 2, expressed as relative standard deviation for the average of duplicate analyses. Each plotted point was obtained for the average of duplicate analyses by one analyst in each laboratory (seven for U and five for Pu) on two separate days for each isotopic abundance level. To avoid confusion, the points for multilaboratory precision are not shown, but they show a comparable amount of scatter about the plotted multilaboratory line.

11.3 *Bias (Systematic Error)*—In mass spectrometry, the presence of a bias is possible, but mass spectrometers can be calibrated so that bias is eliminated. Isotopic abundances shall

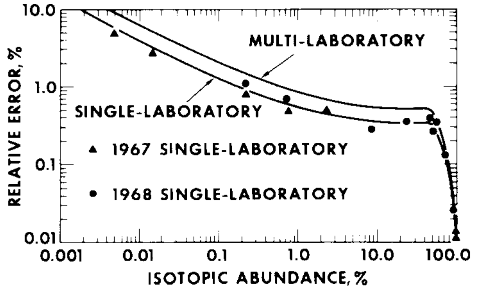

FIG. 1 Variation of Relative Error With Uranium Isotopic Abundance

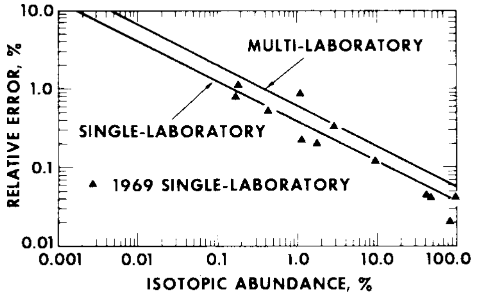

FIG. 2 Variation of Relative Error With Plutonium Isotopic Abundance

be bias corrected in accordance with Section 7 and concentrations shall be obtained from spikes calibrated against accurately known concentrations of New Brunswick Laboratory Reference Samples. It is expected that the test method so calibrated will be free of bias and that the bias can be taken to be equal to the precision (see 11.1 and 11.2).

12. Keywords

12.1 concentrations; isotopic abundance; nuclear fuel; uranium and plutonium; uranium and plutonium fuel

REFERENCES

(**1**) Rodden, C. J., "Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle," TID-7029 (2nd Ed.), National Technical Information Service, U.S. Department of Commerce, Springfield, VA 22151 (1972), p. 310.

(**2**) Jones, R. J., "Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle," *United States Atomic Energy Commission Doc., TID-7029,* 1963, pp. 207–305.

(**3**) Webster, R. K., et al. "The Determination of Plutonium by Mass Spectrometry Using a (242)-Plutonium Tracer," *Analytica Chimica Acta,* Vol 24, April 1961, pp. 370–380.

(**4**) Maeck, W. J., et al, "Simultaneously Determining Pu and U in Dissolver Samples," *Nucleonics,* Vol 20, No. 5, May 1962, pp. 80–84.

(**5**) Goris, P., Duffy, W. E., and Tingey, F. H., "Uranium Determination by Isotope Dilution Technique," *Analytical Chemistry,* Vol 30, 1958, p. 1902.

(**6**) Rider, B. F., et al., "Determination of Uranium and Plutonium Concentrations and Isotopic Abundances," *General Electric Company Report, APED-4527,* May 1, 1964.

(**7**) Wilson, H. W., and Daly, N. R., "Mass Spectrometry of Solids," *Journal of Scientific Instruments*, Vol 40, 1963, p. 273.

(**8**) Steyermark, A. L., et al, "Report on Recommended Specification for Microchemical Apparatus," *Analytical Chemistry,* Vol 30, 1958, p. 1702.

(**9**) Studier, M. H., Sloth, E. H., and Moore, C. P., "The Chemistry of Uranium in Surface Ionization Sources," *Journal of Physical Chemistry,* Vol 66, No. 1, 1962, p. 133.

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