Designation: C1637 − 13

Standard Test Method for the Determination of Impurities in Plutonium Metal: Acid Digestion and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) Analysis[1]

This standard is issued under the fixed designation C1637; 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 covers the determination of 58 trace elements in plutonium (Pu) metal. The Pu sample is dissolved in acid, and the concentration of the trace impurities are determined by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS).

1.2 This Test Method is specific for the determination of trace impurities in Pu metal. It may be applied to other types of Pu materials, such as Pu oxides, if the samples are dissolved and oxidized to the Pu(IV) state. However, it is the responsibility of the user to evaluate the performance of other matrices.

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 associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use of this standard.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C757 Specification for Nuclear-Grade Plutonium Dioxide Powder, Sinterable

C758 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Metal

C759 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Nitrate Solutions

C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis

C1432 Test Method for Determination of Impurities in Plutonium: Acid Dissolution, Ion Exchange Matrix Separation, and Inductively Coupled Plasma-Atomic Emission Spectroscopic (ICP/AES) Analysis

D1193 Specification for Reagent Water

3. Summary of Test Method

3.1 A sample of Pu metal is dissolved in a small volume of 6 M hydrochloric acid (HCl). Then, 10 M nitric acid (HNO_3)/ 0.03 M hydrofluoric acid (HF) is added to the dissolved Pu to oxidize the Pu to the Pu(IV) state. An aliquot of the original sample is taken and diluted with 1 % HNO_3 by volume to a prescribed volume. Aliquots from a second dilution of the original sample are used to prepare run batch dilutions that are analyzed for trace impurities by ICP-MS.[3]

4. Significance and Use

4.1 This test method may be run together with Test Method C1432 to analyze for trace impurities in Pu metal. Using the technique described in this test method and the technique described in Test Method C1432 will provide the analyst with a more thorough verification of the impurity concentrations contained in the Pu metal sample. In addition, Test Method C1432 can be used to determine impurity concentrations for analytes such as Ca, Fe, Na, and Si, which have not been determined using this test method.

4.2 This test method can be used on Pu matrices in nitrate solutions.

4.3 This test method has been validated for use on materials that meet the specifications described in Specification C757 and Test Methods C758 and C759.

4.4 This test method has been validated for all elements listed in Table 1.

---

[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.

Current edition approved Jan. 1, 2013. Published January 2013. Originally approved in 2006. Last previous edition approve in 2006 as D1637 – 06. DOI: 10.1520/C1637-13.

[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] "Inductively Coupled Plasma – Mass Spectrometry Using the VG Elemental Plasma Quad," *Actinide Analytical Chemistry Procedures*, Los Alamos National Laboratory, ANC102 R.1.2, LA-UR-05-7605, 2004.

TABLE 1 Impurity Elements, Mean Percent Recoveries and Percent Relative Standard Deviations

Element	N	Mean R, %	RSD, %
Lithium	22	93.65	7.26
Beryllium	22	96.46	8.14
Boron	22	98.48	6.97
Magnesium	22	98.30	7.58
Aluminium	22	99.66	8.62
Phosphorus	22	99.43	8.96
Titanium	22	99.25	2.44
Vanadium	22	94.44	7.38
Chromium	22	97.29	3.90
Manganese	22	95.48	3.46
Cobalt	22	95.92	4.35
Nickel	22	96.78	3.98
Zinc	22	94.24	4.12
Copper	22	96.66	3.70
Germanium	22	98.16	4.54
Arsenic	22	101.38	8.67
Selenium	22	101.15	8.00
Rubidium	22	100.24	5.36
Strontium	22	98.89	4.16
Yttrium	22	98.07	3.81
Zirconium	22	98.10	3.41
Niobium	22	96.92	3.65
Molybdenum	22	97.82	3.81
Molybdenum[A]	*21*	*98.36*	*2.90*
Ruthenium	22	98.32	2.14
Palladium	22	97.69	2.49
Silver	22	105.14	7.88
Silver[A]	*21*	*106.56*	*4.26*
Cadmium	22	96.03	3.72
Indium	22	98.01	3.57
Tin	22	97.25	3.94
Antimony	22	95.05	6.21
Tellurium	22	100.10	6.86
Caesium	22	101.81	6.93
Barium	22	97.99	3.68
Lanthanum	22	98.31	3.84
Cerium	22	97.57	3.72
Praeseodymium	22	97.32	3.00
Neodymium	22	97.22	3.56
Samarium	22	98.39	3.34
Europium	22	97.43	3.02
Gadolinium	22	100.04	2.78
Terbium	22	97.62	2.72
Dysprosium	22	98.18	2.20
Holmium	22	98.61	2.21
Erbium	22	98.05	2.29
Ytterbium	22	99.59	2.43
Lutetium	22	97.06	5.00
Lutetium[A]	*21*	*97.79*	*3.72*
Hafnium	22	100.32	3.95
Tantalum	22	93.42	3.21
Tantalum[A]	*21*	*93.89*	*2.43*
Tungsten	22	96.29	3.54
Rhenium	22	99.75	3.28
Iridium	22	99.88	3.70
Platinum	22	100.57	3.93
Gold	22	101.20	5.35
Gold[A]	*21*	*100.41*	*3.96*
Thallium	22	100.09	5.02
Lead	22	101.58	5.54
Bismuth	22	100.70	5.43
Thorium	22	103.30	6.89
Uranium	22	104.14	9.11

[A] Without Outlying Value

5. Interferences

5.1 Ions from doubly charged (2+) species are formed in the ICP-MS. The actinide related spectral interferences are from actinide 2+ and actinide-oxide 2+. The spectral interferences are observed at 120.5 and 127.5 atomic mass unit (amu), when analyzing plutonium-239.

5.2 Spectral interferences from the argon plasma and the acid used to transport the sample to the plasma. These spectral interferences occur between 12 and 80 amu.

5.3 Ions from plutonium cause a matrix related signal suppression. Signal suppression increases as the Pu concentration increases. In order to minimize signal suppression effects from Pu, samples are diluted so that the concentration of Pu in the analyzed aliquot is less than 500 µg/mL. Three internal standards are added to samples to correct for matrix related signal suppression and signal drift. Scandium, rhodium and thulium are used as internal standards. Analytes at the low end of the mass range (below 75 amu) are referenced to scandium. Rhodium is a reference for analytes at the middle of the mass range (76-138) and all analytes at the high end of the mass range are referenced to thulium (139-238 amu).

6. Apparatus

6.1 An ICP-MS instrument with a quadrupole mass spectrometer and a electron multiplier that operates at 1 amu resolution is used for this determination. The instrument can also be a magnetic sector instrument or a time of flight instrument.

6.2 The ICP-MS is interfaced to a glovebox. The torch box, and the analyzer region of the mass spectrometer are glovebox enclosed, since Pu containing materials come in direct contact with these sections of the instrument. Methods for enclosing plasma spectroscopic sources so that hazardous materials can be analyzed safely are described in ASTM STP 951.[4]

6.3 Graduated 14 mL disposable plastic round bottom tubes and caps or similar.

6.4 Electronic pipettes.

7. Reagents and Materials

7.1 Ultra high purity acids shall be used for sample dissolution and calibration standards preparation unless otherwise noted.[5]

7.2 *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 (ACS), where such specification are available.[6]

---

[4] Edellson, M. C., and Daniel, J. Leland, "Plasma Spectroscopy of the Analysis of Hazardous Materials: Design and Application of Enclosed Plasma Sources," *Conference Proceedings, ASTM 951*, ASTM, 1986.

[5] "The ULTREX II (J. T. Baker) and INSTRUMENT QUALITY (Seastar Chemicals) lines of ultra high purity acids have been found satisfactory for this purpose."

[6] *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.

7.3 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean laboratory accepted demineralized or deionized water as described by Type I of Specification D1193.

NOTE 1—The molarity of ultra high purity acids may vary from standard ACS specifications for concentrated acids.

NOTE 2—All reagents are prepared and stored in polytetrafluoroethylene (PTFE) containers.

7.4 *Hydrochloric Acid* (HCl, 11.3 M), concentrated HCl.

7.5 *Hydrochloric Acid* (HCl, 6 M), Add 531 mL of concentrated HCl (11.3 M) to less than 450 mL of water and dilute to 1 liter with water.

7.6 *Nitric Acid* (HNO_3, 15.8 M)— concentrated nitric acid.

7.7 *Nitric Acid,* 1 % by volume— One volume of concentrated nitric acid (HNO_3, 15.8 M) brought to one hundred volumes with water.

7.8 *Hydrofluoric Acid* (HF, 28.3 M), concentrated HF.

7.9 *Nitric Acid-Hydrofluoric Acid Mixture,* 10 M HNO_3 / 0.03 M HF— Add 1 mL of concentrated HF (28.3 M) to water; using a plastic pipette, while stirring, add 633 mL concentrated HNO_3 (15.8 M) and dilute to 1 L with water.

7.10 Stock solutions, traceable to a national standards organization, of multielement spike solutions are available from commercial vendors. The stock solutions of mulielement spike solutions can also be prepared in-house.

7.10.1 *Spike Solution 1 (SS-1)*—contains 500 µg/mL of Al, As, Ba, Be, Bi, Cs, In, Li, Mg, Rb, Se and Sr in 0.8 M HNO_3.[7]

7.10.2 *Spike Solution 2 (SS-2)*—contains 500 µg/mL of B, Ge, Hf, Mo, Nb, P, Re, Sb, Sn, Ta, Ti, W and Zr in 0.8 M HNO_3.[7]

7.10.3 *Spike Solution 3 (SS-3)*—contains 500 µg/mL of Ag, Cd, Cr, Co, Cu, Mn, Ni, Pb, Tl, V and Zn in 0.8 M HNO_3.[7]

7.10.4 *Spike Solution 4 (SS-4)*—contains 500 µg/mL of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Th, U, Yb and Y in 0.8 M HNO_3.[7]

7.10.5 *Spike Solution 5 (SS-5)*—contains 500 µg/mL of Au, Ir, Pd, Pt, Ru and Te in 0.8 M HNO_3.[7]

7.11 Stock solutions, traceable to a national standards organization, of multielement impurity standards are available from commercial vendors. The stock solutions of multielement standards can also be prepared in-house.

7.11.1 *Inductively Coupled Plasma Calibration Standard-One (ICPCS-1)* contains 10 µg/mL of Ag, Al, As, Be, B, Cr, Co, Cu, Ge, Li, Mg, Mn, Ni, P, Pr, Rb, Se, Ti, V, and Zn in 10 % HNO_3 by volume and < 0.5 % HF by volume.[8]

7.11.2 *Inductively Coupled Plasma Calibration Standard-Two (ICPCS-2)* contains 10 µg/mL of Ba, Bi, Cd, Cs, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pb, Re, Sm, Sr, Tb, Tl, Th, U, Yb, and Y in 10 % HNO_3 by volume.[8]

7.11.3 *Inductively Coupled Plasma Calibration Standard-Three (ICPCS-3)* contains 10 µg/mL of Au, Hf, In, Ir, Mo, Nb, Pd, Pt, Ru, Ta, Te, Sb, Sn, W, and Zr in 10 % HCl by volume, 2 % HF by volume and < 0.5 % HNO_3 by volume.[8]

7.12 Stock solutions, traceable to a national standards organization, of single element internal standard are available from commercial vendors.

7.12.1 *Internal Standard-One (IS-1),* contains 10 µg/mL of Sc in 2 % HNO_3 by volume.

7.12.2 *Internal Standard-Two (IS-2),* contains 10 µg/mL of Rh in 2 % HCl by volume.

7.12.3 *Internal Standard-Three (IS-3),* contains 10 µg/mL of Tm in 2 % HNO_3 by volume.

8. Hazards

8.1 Plutonium bearing materials are radioactive and toxic. Adequate laboratory facilities, gloveboxes and fumehoods along with safe techniques, must be used in handling samples containing these materials. A detailed discussion of all the precautions necessary is beyond the scope of this test method; however, personnel who handle these materials should be familiar with such safe handling practices.

8.2 Extreme care should be exercised in using concentrated acids.

8.3 **Warning—** Hydrofluoric acid is a highly corrosive acid that can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid. 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 unattended. Due to the serious consequences of hydrofluoric acid burns, prevention of exposure or injury of personnel is the primary goal. Utilization of appropriate laboratory controls (hoods) and wearing adequate personal protective equipment to protect from skin and eye contact is essential. Acute exposure to HF can cause painful and severe burns upon skin contact that require special medical attention. Chronic or prolonged exposure to low levels on the skin may cause fluorosis.

9. Procedure

9.1 Sample Dissolution

9.1.1 Obtain an aliquot of Pu metal of approximately 0.25 g for every sample that will be analyzed. For one of the samples that will be analyzed obtain a second aliquot to be analyzed as a "spiked sample." A "spiked sample" should be analyzed with each batch of samples.

9.1.2 Label (using the sample identification) a clean 14 mL plastic tube for each sample to be analyzed. Label two additional tubes as follows: 1) "spiked sample" (include the identification of the Pu sample that will be used) and 2) "blank". These tubes will be used as "dissolution tubes". Weigh and record the weight of each of the Pu metal aliquots to ±0.0001 g. Place the weighed Pu metal aliquot into the appropriately labeled plastic tube.

9.1.3 Pipette 0.1 mL each of the SS-1, SS-2, SS-3, SS-4 and SS-5 into the tube labeled "SPIKED SAMPLE".

---

[7] Multielement spike solutions, Inorganic Ventures, NJ, has been found to be acceptable.

[8] Multielement impurity standards, High Purity Standards, Charleston, SC, has been found to be acceptable.

9.1.4 Pipette 1 mL of 6 M HCl into each of the "dissolution tubes", including the one labeled "blank" (see Practice C1168).

NOTE 3—Addition of the dissolution acid (6 M HCl) to the samples should be performed by slowly adding a few drops at a time and swirling the sample tube; if the reaction becomes too vigorous the solution may bubble out of the plastic tube. Do not cap and do not vigorously shake the tubes containing samples.

9.1.5 Add enough 10 M HNO_3 / 0.03 M HF so that the final volume is 3.0 mL and mix thoroughly.

9.1.6 Label another set of tubes as in 9.1.2.

9.1.7 Pipette 0.3 mL from each of the *dissolution tubes* into each of the identically labeled tubes in step 9.1.6.

9.1.8 Dilute to 5 mL with 1 % HNO_3 by volume and mix thoroughly (the samples will be analyzed from further dilutions of this second dilution).

NOTE 4—The remainder of the sample in the dissolution tubes may be used for analysis using Test Method C1432 or can be disposed of using the appropriate laboratory protocol.

9.2 Internal Standard and Calibration Standard Preparation

NOTE 5—Steps 9.2.1-9.2.7 may be performed in a fumehood; the tubes can be introduced into a glovebox after the *internal standard mixture* is added to each tube in the analytical run and the calibration standards are prepared.

9.2.1 Pipette equal volumes of IS-1, IS-2 and IS-3 into a clean 14 mL plastic tube. The concentration of the *internal standard mixture* will be 3.333 µg/mL.

9.2.2 Label another set of 14 mL tubes as in 9.1.2.

9.2.3 Label 14 mL plastic tubes for calibration standards.

9.2.4 Add ~ 5 mL of 1 % HNO_3 by volume to each of the tubes in 9.2.2 and 9.2.3.

9.2.5 Pipette 0.3 mL of the *internal standard mixture* into each of the tubes in 9.2.4.

9.2.6 Prepare calibration standards using ICPCS-1, ICPCS-2 and ICPCS-3.

9.2.7 Dilute the calibration standards to 10 mL with 1 % HNO_3 by volume.

9.3 Sample Preparation

9.3.1 Pipette 0.5 mL from each of the 14 mL plastic tubes in 9.1.8 into the corresponding 14 mL plastic tube in 9.2.2, which contain the *internal standard mixture* (9.2.5).

9.3.2 Dilute the tubes to 10 mL with 1 % HNO_3 by volume.

9.4 Instrumental Analysis

9.4.1 Consult the instrument manufacturer's operating manual for typical operating parameters. Following plasma initiation, allow sufficient time for the instrument's electronics to equilibrate.

9.4.2 Calibrate the ICP-MS instrument according to standard instrument procedures using the calibration standards that were prepared in 9.2.7.

9.4.3 Analyze the sample solutions obtained in 9.3.2 according to standard instrumental procedures. If the results exceed the calibration range, dilute the samples and rerun them.

10. Calculation

10.1 The impurity element concentration in the Pu sample in µg/g is calculated as follows:

$$I_c = \left[M \times \left(\frac{F_v \times I_d}{S_w} \right) \right] \times A \qquad (1)$$

where:

I_c = impurity concentration, µg/g
M = measured concentration, ng/mL,
F_v = final volume, mL,
S_w = weight of sample, g
I_d = dilution factor of the analyzed sample solution (instrument dilution) and
A = 0.001, is a conversion factor that converts ng to µg, 1000ng = 1 µg

The ICP-MS instrumental software can be preset to perform a blank subtraction automatically before output of the concentration value. If blank subtraction is not performed automatically, the measured concentration can be corrected for background contributions as follows:

$$M_b = S - B \qquad (2)$$

where:

M_b = blank corrected measured concentration, ng/mL,
S = instrumentally determined sample concentration, ng/mL,
B = instrumentally determined blank concentration, ng/mL.

10.2 The spike recovery for each analyte is used to determine if a result is quantitative. Spike recoveries from 75 to 125 % are considered quantitative. The spike recovery is calculated as follows:

$$\%R = \frac{(M_s - M_a)}{A_c} \times 100 \qquad (3)$$

where:

$\%R$ = percent spike recovery,
M_s = blank corrected measured concentration of the spiked sample solution, µg/g,
M_a = blank corrected measured concentration of the sample solution, µg/g,
A_c = actual concentration of the spike solution, µg/g.

11. Precision and Bias

11.1 A high-purity plutonium sample was spiked with a National Institute of Standards and Technology (NIST) traceable standard. Twenty-two analytical batches were prepared and analyzed for 58 impurities commonly found in plutonium samples. The analyses were done at a single laboratory, by two operators over a sixteen-month period using a VG Elemental PlasmaQuad2 (PQ2) mass spectrometer under normal operating conditions.[9] Three integrations of the signals were performed for each *spiked sample*. The results for the analyses are contained in Table 1. For five of the impurities' data sets, a gross outlier was detected in the set. For these five impurities, results are given both with and without their outlying values.

11.1.1 *Precision*—The within-laboratory reproducibility percent relative standard deviation (RSD, %) of the twenty-two

---

[9] A VG Elemental PlasmaQuad2 (PQ2) mass spectrometer (Thermo Electron, Waltham, MA), has been found to be acceptable.

spiked samples range from 2 to 9 % depending on the impurity. These values reflect uncertainties in both the sample preparation and the analysis.

11.1.2 *Bias*—Since there is no standard plutonium matrix material having accepted reference values for these impurities, no definitive information can be presented on the biases of the test method.

11.1.3 The analyses presented in Table 1 can provide some indication of biases possible when using the test method. The percent recovery (Mean R, %) data suggest that there may be biases up to about ±7 % (±6 % without the outlying values) depending on the impurity. Facility results may vary depending on the actual matrix being analyzed.

12. Keywords

12.1 Dissolution; Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS); impurities in plutonium; plutonium.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the ASTM website (www.astm.org/COPYRIGHT/).