Designation: C1432 − 15

Standard Test Method for
Determination of Impurities in Plutonium: Acid Dissolution, Ion Exchange Matrix Separation, and Inductively Coupled Plasma-Atomic Emission Spectroscopic (ICP/AES) Analysis[1]

This standard is issued under the fixed designation C1432; 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 25 elements in plutonium (Pu) materials. The Pu is dissolved in acid, the Pu matrix is separated from the target impurities by an ion exchange separation, and the concentrations of the impurities are determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

1.2 This test method is specific for the determination of impurities in 8 M HNO_3 solutions. Impurities in other plutonium materials, including plutonium oxide samples, may be determined if they are appropriately dissolved (see Practice C1168) and converted to 8 M HNO_3 solutions.

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions that are provided for information only and are not considered 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 and health practices and determine the applicability of regulatory limitations prior to use.*

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
C859 Terminology Relating to Nuclear Materials
C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis
D1193 Specification for Reagent Water

3. Terminology

3.1 Except as otherwise defined herein, definitions of terms are as given in Terminology C859.

4. Summary of Test Method

4.1 A sample of plutonium metal is dissolved in a small volume of 6 M hydrochloric acid (HCl). Then, 10 M (HNO_3)/0.03 M hydrofluoric acid (HF) is added to the dissolved plutonium to oxidize the plutonium to the Pu (IV) state. The sample solution is loaded onto a nitrate anion exchange resin and eluted with 8 M HNO_3/0.006 M HF. The rinses contain the target metallic impurities and less than 15 µg/mL Pu. The plutonium is stripped from the anion exchange resin with 0.1 M HCl. The rinses containing the metallic impurities are analyzed by ICP-AES.

5. Significance and Use

5.1 This test method can be used on plutonium matrices in nitrate solutions.

5.2 This test method has been validated for all elements listed in Test Methods C757 except sulfur (S) and tantalum (Ta).

5.3 This test method has been validated for all of the cation elements measured in Table 1. Phosphorus (P) requires a vacuum or an inert gas purged optical path instrument.

6. Interferences

6.1 Plutonium concentrations of less than 50 µg/mL in the final aqueous phase do not significantly affect the analytical results for most elements. Interference studies should be made to determine the degree of Pu and other elemental interferences on the target analytes; background and interelement corrections may be required.

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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] 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.

TABLE 1 Percent Recovery and Repeatability Standard Deviation for Sixteen Spiked Samples

Element	Wavelength/Order (nm)	Actual Conc (µg/mL)	Mean Conc (µg/mL)	Average (%R)	R.S.D. (%)
Aluminum	Al 396.152 {67}	2.5	2.4	95	6
Barium	Ba 455.403 {58}	2.5	2.4	95	5
Beryllium	Be 313.042 {84}	2.5	2.3	94	6
Boron	B 249.773 {106}	2.5	2.5	100	7
Cadmium	Cd 226.502 {116}	2.5	2.5	101	12
Calcium	Ca 396.847 {66}	2.5	2.6	104	20
Chromium	Cr 283.563 {93}	2.5	2.3	92	8
Cobalt	Co 228.616 {115}	2.5	2.5	101	6
Copper	Cu 324.754 {81}	2.5	2.4	97	6
Iron	Fe 259.940 {101}	2.5	2.5	101	12
Lead	Pb 220.353 {120}	2.5	3.1	122	12
Lithium	Li 670.784 {39}	2.5	2.2	87	6
Magnesium	Mg 280.270 {94}	2.5	2.4	95	6
Manganese	Mn 257.610 {102}	2.5	2.5	98	5
Molybdenum	Mo 202.030 {130}	2.5	2.6	103	10
Nickel	Ni 231.604 {114}	2.5	2.5	100	11
Silicon	Si 251.612 {104}	2.5	2.3	92	16
Sodium	Na 588.995 {45}	25.0	24.7	97	16
Strontium	Sr 421.552 {62}	2.5	2.4	95	5
Tin	Sn 189.989 {139}	2.5	2.7	109	19
Titanium	Ti 334.941 {79}	2.5	2.5	102	8
Tungsten	W 207.911 {127}	2.5	2.5	99	11
Vanadium	V 292.402 {90}	2.5	2.0	82	7
Zinc	Zn 213.856 {123}	2.5	2.5	100	8
Zirconium	Zr 339.198 {78}	2.5	2.5	101	10

7. Apparatus

7.1 An ICP-AES equipped with a Charge Injection Device (CID) detector or an ICP-AES with a spectral bandpass of 0.05 nm or less is required to provide the necessary spectral resolution. The spectrometer may be either a simultaneous multielement or a sequential spectrometer. The spectrometer may be either an inert gas-path or vacuum instrument; the appropriate spectral lines should be selected for each specific instrument. Either an analog or digital readout system may be used.

7.2 The ICP-AES is interfaced to an enclosure. The torch box is contained with an enclosure, since plutonium containing materials may come in direct contact with the torch despite the substantial removal by ion exchange in 10.3. A possible setup is described in ASTM STP 951.[3]

7.3 Vacuum manifold set at approximately 23 cm Hg (9 in. Hg) is optional. A gravity system is also acceptable.

7.4 15 mL plastic disposable ion exchange columns.

7.5 50 mL plastic vials.

7.6 Plastic micro and macro pipettes.

7.7 1000 mL plastic volumetric flasks.

8. Reagents and Materials

8.1 *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 (ACS), where such specifications are available.[4] Other grades could 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean laboratory accepted demineralized or deionized water as described by Type 1 of Specification D1193.

8.3 Ultra high purity acids shall be used for sample dissolution and calibration standards preparation unless otherwise noted.

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.

8.4 *Hydrochloric Acid* (HCl, 11.3 M), concentrated ultra high purity HCl.

8.5 *Hydrochloric Acid* (HCl, 6 M)—Add 531 mL of concentrated ultra high purity HCl (11.3 M) to less than 450 mL of water and dilute to 1 L with water.

8.6 *Hydrochloric Acid* (HCl, 0.1 M)—Add 8.8 mL of concentrated ultra high purity HCl (11.3 M) to water, while stirring, and dilute to 1 L with water. (Reagent grade HCl can be used in preparing this reagent.)

8.7 *Hydrofluoric Acid* (HF, 28.3 M), concentrated ultra high purity HF.

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[3] 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 STP 951*, ASTM, 1986.

[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.

8.8 *Nitric Acid* (HNO_3, 15.8 M), concentrated ultra high purity nitric acid.

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

8.10 *Nitric Acid-Hydrofluoric Acid Mixture,* 8 M HNO_3/0.006 M HF—Add 0.21 mL of concentrated ultra high purity HF (28.3 M) to water; using a plastic pipette, while stirring, add 506 mL of concentrated ultra high purity HNO_3 (15.8 M) and dilute to 1 L with water.

8.11 *Nitric Acid* (HNO_3, 4 M)—Add 253 mL of concentrated ultra high purity nitric acid (15.8 M) to water, while stirring, and dilute to 1 L with water.

8.12 *Anion Exchange Resin,* macroporous-1 (MP-1), 200-400 mesh, either nitrate form or chloride form, high purity.[5]

8.13 *Stock Solutions,* traceable to a national standard, of multielement spike solutions are available from a commercial vendor. The stock solutions of multielement spike solutions can also be prepared in-house.

8.13.1 *Spike Solution 1 (SS-1),* contains 500 µg/mL of Al, Ba, Be, Ca, Li, Mg, Sr, and Na in 0.8 M HNO_3.

8.13.2 *Spike Solution 2 (SS-2),* contains 500 µg/mL of B, Mo, Si, Sn, Ti, W, and Zr in 0.8 M HNO_3.

8.13.3 *Spike Solution 3 (SS-3),* contains 500 µg/mL of Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, V, and Zn in 0.8 M HNO_3.

8.14 *Stock Solutions,* traceable to a national standard, of multielement impurity standards are available from a commercial vendor. The stock solutions of multielement standards can also be prepared in-house.

8.14.1 *Calibration Stock Solution-2 (CSS-2),* contains 5000 µg/mL of Na in 0.8 M HNO_3.

8.14.2 *Calibration Stock Solution-3 (CSS-3),* contains 500 µg/mL of Mo, Si, Sn, Ti, W, and Zr in 0.3 M HNO_3/0.1 M HF.

8.14.3 *Calibration Stock Solution-5 (CSS-5),* contains 500 µg/mL of Al, Ba, and Sr in 0.8 M HNO_3.

8.14.4 *Calibration Stock Solution-6 (CSS-6),* contains 500 µg/mL of Be, B, Cd, Ca, Cr, Co, Cu, Fe, Li, Mg, Mn, Ni, Pb, V, and Zn in 0.8 M HNO_3.

8.15 Prepare the multielement impurity standards and blanks as described in 8.15.1 – 8.15.5. All calibration standard solutions are stored in PTFE containers.

8.15.1 *Calibration Standard One High (CAL 1 HI)*—Pipette 20 mL each, of stock solutions CSS-3, and CSS-5 into a 1 L volumetric flask. Dilute to 1 L with 8 M HNO_3/0.006 M HF. This standard solution contains the target analytes at a concentration of 10 µg/mL.

8.15.2 *Calibration Standard One Low (CAL 1 LO)*—Pipette 10 mL each, of stock solutions CSS-3, and CSS-5 into a 1 L volumetric flask. Dilute to 1 L with 8 M HNO_3/0.006 M HF. This standard solution contains the target analytes at a concentration of 5 µg/mL.

8.15.3 *Calibration Standard Two High (CAL 2 HI)*—Pipette 20 mL each, of stock solutions CCS-2, and CSS-6 into a 1 L volumetric flask. Dilute to 1 L with 8 M HNO_3/0.006 M HF. This standard solution contains the target analytes at a concentration of 10 µg/mL, except Na. Na is 100 µg/mL.

8.15.4 *Calibration Standard Two Low (CAL 2 LO)*—Pipette 10 mL each, of stock solutions CCS-2, and CCS-6 into a 1 L volumetric flask. Dilute to 1 L with 8 M HNO_3/0.006 M HF. This standard solution contains the target analytes at a concentration of 5 µg/mL, except Na. Na is 50 µg/mL.

8.15.5 *Calibration Standard Blank (CAL BL)*—This blank is an 8 M HNO_3/0.006 M HF solution.

9. Hazards

9.1 Plutonium bearing materials are radioactive and toxic. Adequate laboratory facilities, gloveboxes and fume hoods 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.

9.2 Hydrofluoric acid 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.

10. Procedure

10.1 *Preparation of Anion Exchange Resin Slurry:*

10.1.1 If the anion exchange resin was purchased in the nitrate form, prepare a 1:1 (volume:volume) slurry of the resin in 4 M HNO_3 and proceed to 10.2.

10.1.2 If the anion resin was purchased in the chloride form, convert it to the nitrate form using 4 M HNO_3 as necessary to be sure that chloride has been completely exchanged.

10.2 *Sample Dissolution and Preparation:*

10.2.1 Obtain an aliquot of plutonium metal of approximately 0.5 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 analytical batch of samples.

10.2.1.1 Leach all sample dissolution vials, sample collection vials, and ion exchange columns with 10 M HNO_3/0.03 M HF for 48 h (use reagent grade acids to prepare the leaching acid). Rinse thoroughly with water and allow the vials to air dry before proceeding with sample dissolution.

NOTE 3—Pu samples of 0.25 g can be analyzed using this test method. The amount of acids and resin used for the 0.5 g sample should be decreased by one half for the preparation of the 0.25 g Pu sample.

10.2.2 Label (using the sample identification) a clean plastic vial for each sample to be analyzed. Label three additional vials as follows: (*1*) spiked sample (include the identification of

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[5] The sole source of supply of the resin known to the committee at this time is AG MP-1 anion exchange resin, Bio-Rad, Hercules, CA. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

the Pu sample that will be used), (*2*) blank, and (*3*) spike. These vials will be used as *dissolution vials*. Weigh and record the weight of each of the plutonium metal aliquots to ±0.0001 g. Place the weighed plutonium metal aliquot into the appropriately labeled plastic vial.

10.2.3 Pipette 0.1 mL each of the SS-1, SS-2, and SS-3 into the vials labeled *Spike* and *Spiked Sample*.

10.2.4 Pipette 2 mL of 6 M HCl into the *Blank* and *Spike* vials.

10.2.5 Add 2 mL of 6 M HCl to the vial labeled *spiked sample* and all vials containing samples.

10.2.5.1 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 vial; if the reaction becomes to vigorous the solution may bubble out of the plastic vial. Do not cap and do not vigorously shake the vials containing samples.

10.2.6 Add 4 mL of 10 M HNO_3/0.03 M HF to each vial.

10.3 *Ion Exchange:*

10.3.1 Label 15 mL plastic disposable ion exchange columns for each vial.

10.3.2 Fill the ion exchange columns with ~ 15 mL of the resin slurry, MP-1, 200-400 mesh, wet resin, in the nitrate form. Compress the resin to ~ 8 mL with the PTFE frit. Pour off the 4 M HNO_3 solution, and rinse above the frit with water so that no resin remains. Step 10.3.2 may be performed in a fume hood; the columns can be introduced into a containment box after they are rinsed with water.

10.3.3 Place each resin column on the manifold. Place vials under each column.

10.3.4 Immediately prior to sample separation, condition each column with 7 to 8 mL of 10 M HNO_3/0.03 M HF. Adjust the vacuum, if used, to the appropriate setting.

10.3.5 Turn off the vacuum, remove the conditioning vials, and discard the conditioning solutions to the appropriate waste containers. These vials may be reused for subsequent column conditioning steps and Pu recovery steps but should not be used to collect the samples.

10.3.6 Label another set of vials as in 10.2.2 (these vials will be used to collect the rinses). Place the clean plastic vials labeled with the appropriate sample identification in the manifold system below the corresponding column.

10.3.7 Carefully pour the contents of each dissolution vial into the appropriate ion exchange column. Adjust the vacuum, if used, to the appropriate setting.

10.3.8 Rinse each dissolution vial with 2 mL of 10 M HNO_3/0.03 M HF, and transfer these solutions to the appropriate anion exchange columns when < 5 % of the Pu solution remains above the column. Repeat with an additional 2 mL of 10 M HNO_3/0.03 M HF before proceeding to 10.3.9.

10.3.9 Rinse the columns with an additional 14 mL of 8 M HNO_3/0.006 M HF.

10.3.10 When all columns have drained, carefully remove the collection vials containing the rinses.

10.3.11 Dilute the samples to 25.0 mL with 8 M HNO_3/0.006 M HF. Cap the vials until they are analyzed.

10.4 *Plutonium Recovery:*

10.4.1 Elute the Pu from the anion exchange columns with 0.1 M HCl until the column effluent is colorless. This will require ~ 30 mL of 0.1 M HCl. Follow laboratory protocol regarding disposal of the eluted Pu samples.

10.5 *Instrumental Analysis:*

10.5.1 Consult the instrument manufacturer's operating manual for typical operating parameters. Following plasma initiation, allow 45 min for the system to equilibrate.

10.5.2 Calibrate the ICP-AES instrument according to standard instrumental procedures using the CAL 1 HI, CAL 1 LO, CAL 2 HI, CAL 2 LO, and CAL BL solutions.

10.5.3 Analyze the sample solutions obtained in 10.3.11 according to standard instrumental procedures. If the results exceed the calibration range, dilute the samples and rerun them. Typical wavelengths are given in Table 1.

11. Calculation

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

$$I_C = \frac{M \times F_V}{S_W} \tag{1}$$

where:

I_C = impurity concentration, µg/g,
M = measured concentration, µg/mL,
F_V = final volume of rinses, mL, and
S_W = weight of sample, g.

The ICP-AES instrumental software will usually perform a blank subtraction before output of a concentration value. If this is not performed automatically, correct the measured concentration for background contributions as follows:

$$M = S - L \tag{2}$$

where:

M = blank corrected measured concentration, µg/mL,
S = instrumentally determined sample concentration, µg/mL, and
L = instrumentally determined blank concentration, µg/mL.

11.2 The spike recovery is used to determine whether a result is quantitative or semi-quantitative. Spike recovery from 75 to 125 % are considered quantitative. The spike recovery is calculated as follows:

$$\% R = \frac{(M_A - M_B) \times 100}{A_C} \tag{3}$$

where:

$\% R$ = percent spike recovery,
M_A = measured concentration of the spiked sample solution, µg/mL,
M_B = measured concentration of the sample solution, µg/mL, and
A_C = actual concentration of the spike solution, µg/mL.

12. Precision and Bias

12.1 Within the different stages of the nuclear fuel cycle, many challenges lead to the inability to perform interlaboratory studies for precision and bias. These challenges may include variability of matrices of material tested, lack of suitable reference or calibration materials, limited laboratories performing testing, shipment of materials to be tested, and regulatory constraints. Because of these challenges, each laboratory utilizing these test methods should develop their own precision and bias as part of their quality assurance program.

12.2 A high-purity plutonium sample was spiked with a National Institute of Standards and Technology (NIST) traceable standard. Sixteen analytical batches were prepared and analyzed for 25 impurities commonly found in plutonium samples. The analyses were done at a single laboratory, by three operators over a twelve-month period using a Thermo Jarrell Ash PolyScan Iris spectrometer under normal operating conditions. Three integrations of the signals were performed for each *spiked sample*. The results of the analyses are contained in Table 1.

12.2.1 *Precision*—The within-laboratory reproducibility percent relative standard deviation (% RSD) of the sixteen *spiked samples* range from 5 to 20 % depending on the impurity. These values reflect uncertainties in both the sample preparation and the analysis.

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

12.2.3 The analyses presented in Table 1 can provide some indication of biases possible when using the test method. The percent recovery (% R) data suggest that there may be biases up to about ± 20 % depending on the impurity. Facility results may vary depending on the actual matrix being analyzed.

13. Keywords

13.1 dissolution; inductively coupled plasma-atomic emission spectroscopy (ICP-AES); impurities in plutonium; ion exchange separation; plutonium