Designation: C 1432 – 99

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 C 1432; 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). The elements determined are listed in Table 2.

1.2 This test method is specific for the determination of impurities in Pu in 8 M nitric acid (HNO_3) solutions. Impurities in other plutonium materials, including plutonium oxide samples, may be determined if they are appropriately dissolved (see Practices C 1168) and converted to 8 M HNO_3 solutions.

1.3 Plutonium bearing materials are radioactive and toxic. Adequate laboratory facilities, glove boxes, 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.

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 method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use of this standard.*

2. Referenced Documents

2.1 *ASTM Standards:*

C 697 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powers and Pellets[2]

C 757 Specification for Nuclear-Grade Plutonium Dioxide Powder, Sinterable[2]

C 758 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Metal[2]

C 759 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Plutonium Nitrate Solutions[2]

TABLE 1 ICP-AES Operating Conditions[A]

Parameter	Value
Forward rf power	1.4 kW
Reflected rf power	<10 W
Outer argon flow	15 L/min
Auxiliary argon flow	0.8 L/min
Carrier argon flow	0.7 L/min
Observation height	15 mm above load coil
Nebulizer	Cross flow type
Solution uptake rate	1.4 mL/min

[A] These conditions are typical for an ARL #3580.

TABLE 2 Repeatability Standard Deviation for Three Spike Recovery Experiments

Element	Wavelength (nm)	Actual Conc (µg/g)	Mean Conc (µg/g)	Experimental Determinations Avg % Recovery	RSD %
Aluminum	308.22	6.0	6.9	114	2.7
Barium	493.41	3.0	3.3	109	1.7
Beryllium	313.04	1.5	1.7	112	1.7
Cadmium	226.5	6.0	6.5	109	4.6
Calcium	393.37	3.0	3.3	109	1.8
Chromium	267.72	6.0	7.0	117	5.1
Cobalt	237.86	6.0	6.9	115	1.6
Copper	324.75	3.0	3.5	118	2.0
Hafnium	232.25	6.0	6.4	106	1.1
Iron	259.94	6.0	6.8	113	1.6
Lead	220.35	6.0	6.9	114	3.6
Lithium	670.78	3.0	3.4	112	1.8
Magnesium	279.55	3.0	3.5	116	1.8
Manganese	257.61	3.0	3.4	112	1.8
Molybdenum	202.03	6.0	4.5	75	22
Nickel	231.6	6.0	6.8	114	1.6
Niobium	316.34	6.0	5.9	98.9	2.2
Phosphorus	178.29	6.0	6.4	106	2.3
Potassium	766.49	30.0	33	110	1.8
Strontium	421.55	3.0	3.3	109	1.7
Titanium	368.52	3.0	3.3	111	1.1
Vanadium	292.4	6.0	6.8	113	1.9
Yttrium	371.03	3.0	3.3	109	1.7
Zinc	206.2	3.0	2.3	75.4	7.5
Zirconium	349.62	6.0	6.5	109	1.5

[1] This guide is under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.
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[2] *Annual Book of ASTM Standards*, Vol 12.01.

C 1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis[2]
D 1193 Specification for Reagent Water[3]

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, 1 mL of 10 M (HNO_3)/0.2 M hydrofluoric acid (HF) is added to the dissolved Pu to oxidize the Pu to the Pu (IV) state. The sample solution is loaded onto a nitrate anion exchange resin and eluted with 8 M HNO_3/0.2 M HF. The rinses contain the target metallic impurities and less than 15 µg/mL Pu. The Pu is stripped from the anion exchange resin with 0.1 M HCl. The rinses containing the metallic impurities are analyzed by ICP-AES.

4. Significance and Use

4.1 This test method measures all elements listed in Specification C 757, except sulfur (S) and tantalum (Ta).

4.2 This test method measures all of the cation elements measured in Test Methods C 697, except silver (Ag), gold (Au), and bismuth (Bi). Phosphorus (P) requires a vacuum instrument.

5. Interferences

5.1 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.

6. Apparatus

6.1 An ICP-AES with a spectral bandpass of 0.05 nm or less is required to provide the necessary spectral resolution.[4] 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.

6.2 The ICP-AES is interfaced to a glovebox. The torchbox is glovebox enclosed since Pu containing materials come in direct contact with the torch. The torchbox offers several safety features, such as a shielded window for observing the plasma, which allows the operator to view the plasma without risking damage to the eyes. The torchbox is equipped with an interlock that shuts off high voltage power to the torchbox when the torchbox door is open. The interlock prevents the operator from being exposed to high voltages during routine cleaning. This setup is described in ASTM STP 951.[5]

6.3 Vacuum manifold set at approximately 9 in. Hg (optional).[6] A gravity system is acceptable.

6.4 15-mL plastic disposable ion exchange columns.[7]

6.5 30-mL plastic vials.

6.6 Plastic micro and macro pipettes.

6.7 A 500-mL fritted column.

7. Reagents and Materials

7.1 *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.[8] Other grades should 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean laboratory accepted demineralized or deionized water as describe by Type 1 of Specification D 1193.

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

NOTE 1—All reagents are prepared and stored in polytetrafluoroethylene (PTFE) containers.

7.4 *Hydrochloric Acid* ((HCl) (sp gr 1.18)), concentrated ultra high purity[9] HCl.

7.5 *Hydrochloric Acid* (HCl, 6 M)—Add 500 mL of concentrated ultra high purity HCl (sp gr 1.18) to less than 500 mL of water and dilute to 1 L with water.

7.6 *Hydrochloric Acid* (HCl, 0.1 M)—Add 8.3 mL of concentrated ultra high purity HCl (sp gr 1.18) to water, while stirring, and dilute to 1 L with water. (Reagent grade HCl can be used in preparing this reagent.)

7.7 *Hydrofluoric Acid* ((HF) (sp gr 1.15)), concentrated ultra high purity[9] HF.

7.8 Nitric Acid ((HNO_3) (sp gr 1.42)), concentrated ultra high purity[9] HNO_3.

7.9 *Nitric Acid-Hydrofluoric Acid Mixture*, 10 M HNO_3/0.2 M HF—Add 7.2 mL of concentrated ultra high purity HF (sp gr 1.15) to water, using a plastic pipet, while stirring; add 637-mL concentrated ultra high purity HNO_3 (sp gr 1.42); and dilute to 1 L with water.

7.10 *Nitric Acid-Hydrofluoric Acid Mixture*, 8 M HNO_3/0.2 M HF—Add 7.2 mL of concentrated ultra high purity HF (sp gr 1.15) to water, using a plastic pipet, while stirring; add 510 mL of concentrated ultra high purity HNO_3 (sp gr 1.42); and

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

[4] An Applied Research Laboratories 3580 ICP-AES instrument (Fisons Instruments, Dearborn, MI) has been found to be acceptable. The ARL 3580 is a combination Pashen-Runge type spectrometer containing a 58 channel simultaneous spectrometer and a sequential spectrometer, both with a 1-m focal length and capable of operating in the 165 to 800-nm range.

[5] Edelson, 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.

[6] Speed Mate 10 Vacuum Extraction System, Applied Separations, Bethlehem, PA, has been found to be acceptable.

[7] Ion exchange columns from either Applied Separation or Bio-Rad Inc. have been found to be acceptable.

[8] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D.C. 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.

[9] The Ultrex (J. T. Baker, Inc.) and Seastar brands of ultra high purity acids have been found to be acceptable.

dilute to 1 L with water.

7.11 *Nitric Acid* (HNO_3, 4 M)—Add 255 mL of concentrated ultra high purity HNO_3 (sp gr 1.42) to water, while stirring, and dilute to 1 L with water.

7.12 *Nitric Acid* (HNO_3, 8 M)—Add 510 mL of concentrated ultra high purity HNO_3 (sp gr 1.42) to water, while stirring, and dilute to 1 L with water.

7.13 *Anion Exchange Resin*, Bio-Rad® AG MP-1, 200-400 mesh, either nitrate form or chloride form, high purity.[10]

8. ICP-AES Standards

NOTE 2—Stock solutions of the multielement impurity standards are prepared and stored in PTFE. These solutions are prepared in-house and have been found to be stable for one year.

8.1 Prepare the multielement impurity standards and blanks as described in 8.1.1-8.1.8.

8.1.1 *Common Impurity High (COMHI)*—This standard is prepared from stock solutions and contains 15 µg/mL of beryllium (Be), 30µg/mL of strontium (Sr), barium (Ba), zinc (Zn), copper (Cu), lithium (Li), titanium (Ti), yttrium (Y), calcium (Ca), magnesium (Mg), and manganese (Mn), 60 µg/mL of iron (Fe), aluminum (Al), lead (Pb), cobalt (Co), chromium (Cr), nickel (Ni), vanadium (V), cadmium (Cd), and molybdenum (Mo), 300 µg/mL of potassium (K) in 8 M HNO_3.

8.1.2 *Common Impurity Middle (COMMI)*—This standard is prepared from stock solutions and contains 10 µg/mL of Be, 20 µg/mL of Sr, Ba, Zn, Cu, Li, Ti, Y, Ca, Mg, and Mn, 40 µg/mL of Fe, Al, Pb, Co, Cr, Ni, V, Cd, and Mo, 200 µg/mL of K in 8 M HNO_3.

8.1.3 *Common Impurity Low (COMLO)*—This standard is prepared from stock solutions and contains 5 µg/mL of Be, 10 µg/mL of Sr, Ba, Zn, Cu, Li, Ti, Y, Ca, Mg, and Mn, 20 µg/mL of Fe, Al, Pb, Co, Cr, Ni, V, Cd, and Mo, 100 µg/mL of K in 8 M HNO_3.

8.1.4 *Refractory High (REFHI)*—This standard is prepared from stock solutions and contains 60 µg/mL of hafnium (Hf), niobium (Nb), zirconium (Zr), and P in 8 M HNO_3/0.2 M HF.

8.1.5 *Refractory Middle (REFMI)*—This standard is prepared from stock solutions and contains 40 µg/mL of Hf, Nb, Zr, and P in 8 M HNO_3/0.2 M HF.

8.1.6 *Refractory Low (REFLO)*—This standard is prepared from stock solutions and contains 20 µg/mL of Hf, Nb, Zr, and P in 8 M HNO_3/0.2 M HF.

8.1.7 *COMBL*—This blank standard is an 8 M HNO_3 solution.

8.1.8 *REFBL*—This blank standard is an 8 M HNO_3/0.2 M HF solution.

9. Procedure

9.1 *Preparation of Anion Exchange Resin Slurry*:

9.1.1 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 9.2.

9.1.2 If the anion resin was purchased in the chloride form, convert it to the nitrate form.

9.2 *Sample Dissolution and Preparation*:

9.2.1 Obtain an aliquot of Pu 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.

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

9.2.2 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 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 Pu metal aliquots to ±0.0001 g. Place the weighed Pu metal aliquot into the appropriately labeled plastic vial.

9.2.3 Pipette 1.0 mL each of the COMHI and REFHI solutions into the vials labeled *Spike* and *Spiked Sample*.

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

NOTE 4—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.

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

9.2.6 Add 1 mL of 10 M HNO_3/0.2 M HF to each vial.

9.3 *Ion Exchange*:

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

9.3.2 Fill the ion exchange columns with ~15 mL of the resin slurry of Bio Rad®, AG 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 plugs with water so that no resin remains. Step 9.3.2 may be performed in a fume hood; the columns can be introduced into a containment box after they are rinsed with water.

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

9.3.4 Immediately prior to sample separation, condition each column with 7 to 8 mL of 10 M HNO_3/0.2 M HF. Adjust the vacuum, if used, to the appropriate setting.

9.3.5 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.

9.3.6 Label another set of vials as in 9.2.2 (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.

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

9.3.8 Rinse each dissolution vial with 2 mL of 10 M HNO_3/0.2 M HF, and transfer these solutions to the appropriate

[10] AG MP-1 anion exchange resin, Bio-Rad, Richmond, CA, has been found to be acceptable.

anion exchange columns when <5 % of the Pu solution remains above the column. Repeat with an additional 2 mL of 10 M HNO_3/0.2 M HF before proceeding to 9.3.9.

9.3.9 Rinse the columns with an additional 15 mL of 8 M HNO_3/0.2 M HF.

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

9.3.11 Dilute the samples to 25.0 mL with 8 M HNO_3/0.2 M HF.

9.4 *Plutonium Recovery*—Elute the Pu on 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.

9.5 *Instrumental Analysis*:

9.5.1 Calibrate the ICP-AES instrument in accordance with standard instrumental procedures, using the COMHI, COMMI, COMLO, COMBL, REFHI, REFMI, REFLO, and REFBL solutions.

9.5.2 Analyze the sample solutions obtained in 9.3.11 in accordance with standard instrumental procedures. If the results exceed the calibration range, dilute the samples and rerun them. Typical operating parameters for an ARL 3580 are given in Table 1. Typical wavelengths are given in Table 2.

10. Calculation

10.1 Calculate the impurity element concentration in the Pu sample in µg/g as follows:

$$I_C = \frac{M \times F_V}{S_W} \quad (1)$$

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:

$$M = S - L \quad (2)$$

where:

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

10.2 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:

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

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.

11. Precision and Bias

11.1 *Precision*—The repeatability standard deviation for three spike recovery experiments are given in Table 2 for 25 common impurities found in Pu samples. Three integrations of the signals were performed for each spike recovery experiment. The reproducibility of this test method is being determined and will be available on or before January 1, 2004.

11.2 *Bias*—No information can be presented on the bias of the procedure in Test Method C 1432 for measuring 25 common impurity elements in a Pu sample because no material having an accepted reference value is available.

12. Keywords

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