Designation: C 1287 – 03

Standard Test Method for Determination of Impurities in Nuclear Grade Uranium Compounds by Inductively Coupled Plasma Mass Spectrometry[1]

This standard is issued under the fixed designation C 1287; 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 67 elements in uranium dioxide samples and nuclear grade uranium compounds and solutions without matrix separation by inductively coupled plasma mass spectrometry (ICP-MS). The elements are listed in Table 1. These elements can also be determined in uranyl nitrate hexahydrate (UNH), uranium hexafluoride (UF_6), triuranium octoxide (U_3O_8) and uranium trioxide (UO_3) if these compounds are treated and converted to the same uranium concentration solution.

1.2 *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.* For a specific warning statement, see Note 1.

NOTE 1—**Warning:** The ICP-MS is a source of intense ultra-violet radiation from the radio frequency induced plasma. Protection from radio frequency radiation and UV radiation is provided by the instrument under normal operation.

1.3 The elements boron, sodium, silicon, phosphorus, potassium, calcium and iron can be determined using different techniques. The analyst's instrumentation will determine which procedure is chosen for the analysis.

1.4 The test method for technetium-99 is given in Annex A1.

2. Referenced Documents

2.1 *ASTM Standards:*

C 753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder[2]

C 776 Specification for Sintered Uranium Dioxide Pellets[2]

C 787 Specification for Uranium Hexafluoride for Enrichment[2]

C 788 Specification for Nuclear-Grade Uranyl Nitrate Solution[2]

C 967 Specification for Uranium Ore Concentrate[2]

C 996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ^{235}U[2]

C 1346 Practice for Dissolution of UF6 from P-10 Tubes[2]

D 1193 Specification for Reagent Water[3]

3. Summary of Test Method

3.1 The sample is dissolved in acid if it is not already a solution. A fixed quantity of internal standard is added to monitor and correct for signal instability. The level of impurities in the solution is measured by ICP-MS. Customized software calculates the concentration of each element.

3.2 Uranium-concentration-matched standard solutions are used to calibrate the ICP-MS instrument. The calibration is linear up to at least 0.2 µg/ml (100 µg/g U) for each analyte.[4,5]

4. Significance and Use

4.1 This test method is capable of measuring the elements listed in Table 1, some of which are required by Specifications C 753, C 776, C 787, C 788, C 967 and C 996.

5. Apparatus

5.1 *ICP-MS*, controlled by computer and fitted with the associated software and peripherals. May be fitted with cold plasma option.

5.2 *Autosampler*, with tube racks and disposable plastic sample tubes compatible with 5.1 (optional).

5.3 *Variable Micropipettes*:

5.3.1 10 µL to 100 µL capacity.

5.3.2 100 µL to 1000 µL capacity.

[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] *Annual Book of ASTM Standards*, Vol 12.01.

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

[4] "ICP-MS Versus Conventional Methods for the Analysis of Trace Impurities in Nuclear Fuel," by Allenby, P., Clarkson, A. S., Makinson, P. R., presented at 2nd Surrey Conference on Plasma Source Mass Spectrometry, Guildford, UK, July 1987.

[5] "Trace Metals in NBL Uranium Standard CRM 124 Using ICP-MS," by Aldridge, A. J., Clarkson, A. S., Makinson, P. R., Dawson, K. W., presented at 1st Durham International Conference on Plasma Source Mass Spectrometry, Durham, UK, September 1988.

TABLE 1 Reporting Limits of Impurity Elements

NOTE 1—The impurity elements were determined in 0.2 % uranium solutions, prepared following Section 8.

NOTE 2—Acquisition time = 10 s/isotope using peak jump mode.

NOTE 3—103 Rh was used as an internal standard. For the elements where the technique is identified as Perkin Elmer Elan 5000A P-E Elan 5000A scandium was used as internal standard.

NOTE 4—The LRL is based on the within run standard deviation (S_b) of 20 uranium-matched blank determinations for each analyte. This limit equals $4 \times S_b$, rounded up to a preferred value in the series 1, 1.5, 2, 3, 4, 6, multiplied or divided by the appropriate integer power of ten.

NOTE 5—The upper reporting limit can be increased by extending the calibration to 10 µg/mL (5000 µg/g U) if the ICP-MS used has an extended dynamic range (EDR) accessory.

NOTE 6—For the elements where the technique is listed as P-E Elan 5000A, the instrumentation may be specific to those elements. Alternatively cold plasma technique may be used and it is up to the analyst to perform testwork using spikes and reference materials and to determine the lower reporting levels.

NOTE 7—Some of the elements are not included in the material specifications and have been included only as a research record for the reader's interest.

Analyte	Mass Used	Analyte Group	Lower Reporting Limit (LRL), µg/g U	Upper Reporting Limit (URL), µg/g U	Technique
Lithium	7	A	0.01	100	normal plasma
Beryllium	9	A	0.04	100	normal plasma
Boron	11	E	0.3	100	P-E Elan5000A
Sodium	23	E	0.3	100	P-E Elan5000A
Magnesium	24	A	4	100	normal plasma
Aluminum	27	D	2	1000	normal plasma
Silicon	28	E	1.5	100	P-E Elan5000A
Phosphorus	31	E	1.5	100	P-E Elan5000A
Potassium	39	E	2	100	P-E Elan5000A
Calcium	44	E	6	100	P-E Elan5000A
Scandium	45	A	4	100	normal plasma
Titanium	48	B	0.2	100	normal plasma
Vanadium	51	B	0.04	100	normal plasma
Chromium	52	B	0.1	100	normal plasma
Manganese	55	A	0.1	100	normal plasma
Iron	56	A	15	100	normal plasma
Cobalt	59	A	0.02	100	normal plasma
Nickel	60	A	0.4	100	normal plasma
Copper	65	A	0.2	100	normal plasma
Zinc	66	A	0.3	100	normal plasma
Gallium	69	A	0.04	100	normal plasma
Germanium	74	A	0.2	100	normal plasma
Arsenic	75	A	0.2	100	normal plasma
Selenium	82	A	3	100	normal plasma
Rubidium	85	A	0.06	100	normal plasma
Strontium	88	A	0.06	100	normal plasma
Yttrium	89	A	0.04	100	normal plasma
Zirconium	90	B	0.02	100	normal plasma
Niobium	93	B	0.01	100	normal plasma
Molybdenum	95	B	0.04	100	normal plasma
Ruthenium	102	B	0.02	100	normal plasma
Palladium	106	B	0.2	100	normal plasma
Silver	107	A	0.1	100	normal plasma
Cadmium	111	A	0.03	100	normal plasma
Indium	115	A	0.04	100	normal plasma
Tin	116	B	0.04	100	normal plasma
Antimony	121	B	0.02	100	normal plasma
Tellurium	130	B	0.4	100	normal plasma
Caesium	133	A	0.06	100	normal plasma
Barium	138	A	0.02	100	normal plasma
Lanthanum	139	C	0.1	100	normal plasma
Cerium	140	C	0.01	100	normal plasma
Praseodymium	141	C	0.01	100	normal plasma
Neodymium	146	C	0.01	100	normal plasma
Samarium	149	C	0.01	100	normal plasma
Europium	151	C	0.01	100	normal plasma
Gadolinium	158	C	0.01	100	normal plasma
Terbium	159	C	0.01	100	normal plasma
Dysprosium	163	C	0.01	100	normal plasma
Holmium	165	C	0.01	100	normal plasma
Erbium	166	C	0.01	100	normal plasma
Thulium	169	C	0.01	100	normal plasma
Ytterbium	174	C	0.01	100	normal plasma
Lutetium	175	C	0.01	100	normal plasma
Hafnium	178	B	0.01	100	normal plasma
Tantalum	181	B	0.01	100	normal plasma
Tungsten	184	B	0.01	100	normal plasma
Rhenium	187	A	0.02	100	normal plasma
Osmium	190	B	0.2	100	normal plasma
Iridium	193	B	0.2	100	normal plasma
Platinum	195	B	0.2	100	normal plasma
Gold	197	B	0.06	100	normal plasma
Mercury	202	A	0.4	100	normal plasma
Thallium	205	A	0.02	100	normal plasma
Lead	208	A	0.02	100	normal plasma
Bismuth	209	A	0.03	100	normal plasma
Thorium	232	B	0.01	100	normal plasma

5.3.3 1000 µL to 10.00 mL capacity.

5.4 *Volumetric Flasks*:

5.4.1 50 mL capacity—polypropylene.

5.4.2 100 mL capacity—polypropylene.

5.4.3 1 L capacity—glass.

5.5 *Platinum Dish*—100 mL capacity.

5.6 *Silica Beaker*—250 mL capacity.

5.7 *Watch Glasses*—75 mm diameter.

5.8 *Polypropylene Tubes*—50 mL, with graduation marks and with caps.

6. Reagents

6.1 The sensitivity of the ICP-MS technique requires the use of ultra high purity reagents in order to be able to obtain the low levels of detection. All the reagents below are ultra high purity grade unless otherwise stated:

6.1.1 Element stock standards at 1000 µg/mL for all the elements in Table 1.

6.1.2 *Hydrofluoric acid (HF)*, (40 g/100 g), 23 molar.

6.1.3 *Nitric acid*—Concentrated nitric acid (HNO_3), 15 molar.

6.1.4 *Rhodium Stock Solution* (1000 µg/mL Rh)—Commercially available solution (see Note 2).

NOTE 2—Rhodium stock solution is commercially available supplied with a certificate of analysis for the element and a full range of trace impurities. The solutions are prepared by the manufacturer using a variety of media designed to keep each element in solution for a minimum of one year.

6.1.5 *Sulfuric acid* —Concentrated sulfuric acid (H_2SO_4), 18 molar.

6.1.6 *Uranium Standard Base Solution*—Uranyl nitrate solution to Specification C 788, of known uranium (100 g/L) and aluminum content (≤ 2 µg/g U). The total metallic impurity (TMI) content must not exceed 50 µg/g U and no individual analyte must exceed 10 µg/g U.

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

TABLE 2 Precision Data Derived from PCS and CRM Samples

NOTE 1—Acquisition time = 10 s/isotope using peak jump mode. Acquisition time is 2 s / isotope for B, Na, Si, P, K, Ca (mass 44).

NOTE 2—Table 2 is a list of "between-run" standard deviations for a single determination based on the analysis of in-house primary control samples (PCS series), NBL Certified Reference Material CRM 124-2 and CRM 98-2.

NOTE 3—103 rhodium was used as the internal standard for all elements except 45 scandium was used as the internal standard for B, Na, Si, P, K and Ca (mass 44).

NOTE 4—Some of the elements are not included in the material specifications and have been included only as a research record for the reader's interest.

Analyte	Isotope	Concentration, µg/g U	Standard Deviation, µg/g U	Number of Determinations
Lithium	7	[A]	[A]	...
Beryllium	9	10	1.5	10
Boron[B]	11	2.9	0.3	8
Sodium[B]	23	206	10	8
Magnesium[B]	24	52	3.7	5
Aluminum	27	21.5	2.5	50
Silicon[B]	28	115	19	8
Phosphorus[C]	31	204	19	9
Potassium[C]	39	288	20	9
Calcium[B]	44	104	8	8
Scandium	45	[A]	[A]	...
Titanium	48	2.0	0.21	29
Vanadium	51	2.0	0.19	27
Chromium	52	5.0	0.51	27
Manganese	55	5.0	0.80	10
Iron	56	[A]	[A]	...
Cobalt[B]	59	12.7	0.49	5
Nickel	60	22	3.2	7
Copper	65	25	4.6	6
Zinc[B]	66	101	3.5	5
Gallium	69	[A]	[A]	...
Germanium	74	[A]	[A]	...
Arsenic	75	1.0	0.14	10
Selenium	82	[A]	[A]	...
Rubidium	85	[A]	[A]	...
Strontium	88	N/A[D]	...	...
Yttrium	89	[A]	[A]	...
Zirconium	90	1.00	0.090	27
Niobium	93	1.00	0.095	15
Molybdenum	95	2.00	0.091	20
Ruthenium	102	2.00	0.141	17
Palladium	106	[A]	[A]	...
Silver	107	N/A	...	...
Cadmium	111	5.0	0.29	10
Indium	115	5.0	0.21	10
Tin	116	5.0	0.16	9
Antimony	121	1.0	0.10	27
Tellurium	130	[A]	[A]	...
Caesium	133	[A]	[A]	...
Barium	138	10	1.5	10
Lanthanum	139	[A]	[A]	...
Cerium	140	[A]	[A]	...
Praseodymium	141	[A]	[A]	...
Neodymium	146	[A]	[A]	...
Samarium	149	N/A	...	...
Europium	151	N/A	...	...
Gadolinium	158	N/A	...	...
Terbium	159	[A]	[A]	...
Dysprosium	163	N/A	...	...
Holmium	165	[A]	[A]	...
Erbium	166	[A]	[A]	...
Thulium	169	[A]	[A]	...
Ytterbium	174	[A]	[A]	...
Lutetium	175	[A]	[A]	...
Hafnium	178	1.00	0.093	35
Tantalum	181	1.00	0.100	27
Tungsten	184	1.00	0.060	27
Rhenium	187	[A]	[A]	...
Osmium	190	[A]	[A]	...
Iridium	193	[A]	[A]	...
Platinum	195	[A]	[A]	...
Gold	197	[A]	[A]	...
Mercury	202	[A]	[A]	...
Thallium	205	5.0	0.16	10
Lead	208	5.0	0.25	10
Bismuth	209	5.0	0.60	10
Thorium	232	5.00	0.020	22

[A] The elements are not determined on a routine basis. Insufficient precision data are available but are expected to be similar to those of the analytes where data are available.
[B] Data obtained from CRM 124-2 analytes.
[C] Data obtained from CRM 98-2 analytes.
[D] N/A = Data not available; still being obtained.

7. Standards

7.1 Four separate mixed standard solutions (A, B, C, and E) are prepared to prevent the precipitation of some elements (as insoluble chlorides, fluorides etc; see Table 1 for details of the analyte groups). Analyte group A contains element stock solutions prepared in HNO_3 or HNO_3/HF, analyte group B contains element stock solutions prepared in HCl or HCl/HF, analyte group C contains the rare earth element stock solutions, and analyte group E contains boron sodium silicon, phosphorus, potassium and calcium. The mixed standard solutions should be prepared to contain only the analytes of interest. Other combinations of mixed standard solutions may be prepared to minimize the precipitation of the analytes.

7.1.1 Mixed standard solution A is prepared from stock solutions of each element from analyte group A. Transfer 1000 µL of the stock solution (1000 µg/mL) of each element into a 50 mL polypropylene volumetric flask and add 500 µL of concentrated nitric acid. Dilute to 50 mL with water and mix. This multi-element standard contains 20 µg/mL of each analyte in 1 % nitric acid. This solution must be used on the day of preparation.

7.1.2 Mixed standard solution B is prepared from stock solutions of each element from analyte group B. Transfer 1000 µL of the stock solution (1000 µg/mL) of each element into a 50 mL polypropylene volumetric flask and add 500 µL of concentrated nitric acid. Dilute to 50 mL with water and mix. This multi-element standard contains 20 µg/mL of each analyte in 1 % nitric acid. This solution must be used within one week of preparation.

7.1.3 Mixed standard solution C is prepared from stock solutions of each element from analyte group C. Transfer 1000 µL of the stock solution (1000 µg/mL) of each element into a 50 mL polypropylene volumetric flask and add 500 µL of concentrated nitric acid. Dilute to 50 mL with water and mix. This multi-element standard contains 20 µg/mL of each analyte in 1 % nitric acid. This solution must be used within one week of preparation.

7.2 Standard solution D is prepared from the stock solution of aluminum from analyte group D. Transfer 1000 µL of the stock solution (1000 µg/mL Al) into a 50 mL polypropylene volumetric flask and add 500 µL of concentrated nitric acid. Dilute to 50 µL with water and mix. This standard contains 20