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.

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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] *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 µg/mL of aluminum in 1 % nitric acid. This solution must be used within one week of preparation.

7.3 Mixed standard solution E is prepared from stock solutions of each element from analyte group E. 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.

7.4 Rhodium internal standard solution is prepared from the stock solution. Transfer 1000 µL of the stock solution (1000 µg/mL Rh) into a 100 mL polypropylene volumetric flask and add 1000 µL of concentrated nitric acid. Dilute to 100 mL with water and mix. This internal standard solution contains 10 µg/mL Rh in a 1 % nitric acid solution. Other internal standards such as scandium (used with B, Na, Si, P, K and Ca) may be used. With high mass elements the analyst may choose internal standards such as iridium or terbium. Other elements may be applicable as well but it is up to the analyst to conduct the appropriate testwork.

7.5 Diluent solution is prepared from rhodium stock standard solution. Transfer 1000 µL of the stock solution (1000 µg/mL Rh) into a 1 L volumetric flask and add 10.00 mL of concentrated nitric acid. Dilute to 1 L with water and mix. This diluent solution contains 1 µg/mL Rh in 1 % nitric acid solution. Other internal standard diluent solutions may be used.

NOTE 3—Throughout this standard, references to Rh internal standard solution will include all other internal standard elements that may be used.

8. Procedure

NOTE 4—A uranium-free reagent blank is used to eliminate bias due to the analyte concentrations in the uranium standard base solution. A uranium-matched reagent blank is necessary to provide a constant acid concentration in the nebulized solution.

8.1 *Sample Preparation for the Determination of All Elements Except Boron, Silicon, Potassium, and Calcium*:

8.1.1 Weigh a portion of uranium oxide containing between 2.45 and 2.55 g of uranium into a platinum dish. Record the weight to the nearest 0.001 g. For uranyl fluoride solutions prepared using Practice C 1346 and uranyl nitrate solutions, aliquot between 2.45 and 2.55 g of uranium into a platinum dish. Use a variable volume plastic pipet for the transfer of uranyl fluoride solutions. Record the weight to the nearest 0.001 g.

8.1.2 Add 10 mL of water and 12.5 mL of concentrated nitric acid. Heat on a hotplate to assist dissolution.

8.1.3 Add 2.5 mL of hydrofluoric acid (40 g/100 g) and warm at about 80°C for 5 min.

8.1.4 Allow the solution to cool and transfer quantitatively to a 50 mL polypropylene volumetric flask. Dilute to 50 mL with water and mix. This solution contains 50 g of uranium per litre in 25 % nitric acid/5 % hydrofluoric acid.

8.1.5 Transfer 4.00 mL of the solution in 8.1.4 and 1.00 mL of the rhodium internal standard solution (see 7.4) into a 100 mL polypropylene volumetric flask. Dilute to 100 mL with water and mix. This solution contains 2 g of uranium per litre and 0.1 µg/mL Rh in 1 % nitric acid/0.2 % hydrofluoric acid.

8.1.6 A uranium-free reagent blank (see 8.3.1) and a control or recovery sample must be prepared with every run of samples.

8.1.7 Analyze these solutions as in 8.4 using the calibration solutions prepared in 8.3. The solutions must be analyzed within 8 h of preparation to minimize the effects of analyte precipitation.

8.2 *Sample Preparation for the Determination of Boron and Silicon Potassium and Calcium*:

8.2.1 Weigh a portion of uranium dioxide, uranium octoxide or uranium trioxide containing between 0.095 and 0.105 g of uranium into a graduated 50 mL polypropylene tube (or alternative).The accuracy of the graduations on the tube must be verified. Record the weight to the nearest 0.001 g. For uranyl fluoride solutions prepared using Practice C 1346 and uranyl nitrate solutions, aliquot between 0.095 and 0.105 g of uranium using variable volume plastic pipets. Record the weight to the nearest 0.001 g.

8.2.2 Add 1 mL of water and 1.25 mL of concentrated nitric acid. Cap. Heat in a hot water bath at about 80°C to assist dissolution.

8.2.3 Cool to room temperature Add 0.1 mL of hydrofluoric acid (40 g/100 g) and cap. Heat in a hot water bath at about 80°C for 5 min.

8.2.4 Allow the solution to cool. Add 0.5 mL of scandium internal standard solution (see 7.4). Dilute to 50 mL with water and mix. This solution contains 2 g of uranium per litre and 0.1 µg/mL Sc in 2.5 % nitric acid/0.2 % hydrofluoric acid.

8.2.5 A uranium-free reagent blank and a control or recovery sample must be prepared with every run of samples.

8.2.6 Analyze these solutions as in 8.4 using the calibration solutions prepared in 8.3. The solutions must be analyzed within 8 h of preparation to minimize the effects of analyte precipitation.

8.3 *Preparation of Blanks and Calibration Standard Solutions*:

8.3.1 *For the Determination of All Elements Except Boron Silicon Potassium and Calcium*:

8.3.1.1 *Uranium-free Reagent Blank*—Transfer 12.5 mL of concentrated nitric acid and 2.5 mL of hydrofluoric acid (40 g/100 g) into a 50 mL polypropylene volumetric flask. Continue as instructed from 8.1.5 onwards.

8.3.1.2 *Uranium-matched Calibration Blank*—Transfer 2.00 mL of the uranium standard base solution (see 6.1.6; this is equivalent to 0.20 g of uranium) into a 100 mL polypropylene volumetric flask. Add 1000 µL of concentrated nitric acid, 200 µL of hydrofluoric acid (40 g/100 g) and 1000 µL of rhodium internal standard solution (see 7.4). Dilute to 100 mL with water and mix. This solution contains 2 g of uranium per litre and 0.1 µg/mL Rh in 1 % nitric acid/0.2 % hydrofluoric acid.

8.3.1.3 *Uranium-matched Calibration Standard*—Transfer 2.00 mL of the uranium standard base solution (see 6.1.6; this is equivalent to 0.20 g of uranium) into a 100 mL polypropylene volumetric flask. Add 1000 µL of concentrated nitric acid, 200 µL of hydrofluoric acid (40 g/100 g), 1000 µL of each mixed standard solution (see 7.1.1, 7.1.2 and 7.1.3) and 1000 µL of rhodium internal standard solution (see 7.4). Dilute to

100 mL with water and mix. This solution contains 2 g of uranium per litre, 0.2 µg/mL of each analyte (equivalent to 100 µg/g U) and 0.1 µg/mL Rh in 1 % nitric acid/0.2 % hydrofluoric acid.

8.3.2 *For the Determination of Boron, Silicon, Potassium and Calcium (mass 44)*:

8.3.2.1 *Uranium-matched Reagent/Calibration Blank*—Transfer 2.00 mL of the uranium standard base solution (see 6.1.6; this is equivalent to 0.20 g of uranium) into a 100 mL polypropylene volumetric flask. Add 2.5 mL of concentrated nitric acid, 200 µL of hydrofluoric acid (40 g/100 g), and 1000 µL of scandium internal standard solution (see 7.4). Dilute to 100 mL with water and mix. This solution contains 2 g of uranium per litre and 0.1 µg/mL Sc in 1 % nitric acid/0.2 % hydrofluoric acid.

8.3.2.2 *Uranium-matched Calibration Standard*—Transfer 2.00 mL of the uranium standard base solution (see 6.1.7; this is equivalent to 0.20 g of uranium) into a 100 mL polypropylene volumetric flask. Add 2.5 mL of concentrated nitric acid, 200 µL of hydrofluoric acid (40 g/100 g), 1000 µL of mixed standard solution (see 7.1 and 7.3), and 1000 µL of scandium internal standard solution (see 7.4). Dilute to 100 mL with water and mix. This solution contains 2 g of uranium per litre, 0.2 µg/mL of each analyte (equivalent to 100 µ/g U) and 0.1 µg/mL Sc in 1 % nitric acid/0.2 % hydrofluoric acid.

8.4 *Measurement of Elements by ICP-MS*:

8.4.1 To avoid contamination problems when nebulizing the samples, which contain hydrofluoric acid, the nebulizer system (that is, spray chamber and nebulizer) must be made from fluorinated plastic materials (for example, TFE-fluorocarbon or polychlorotrifluoroethylene).

NOTE 5—For the analysis of boron and silicon, the alumina injector for the Perkin Elmer Elan 5000 was fitted with a TFE-fluorocarbon inner sleeve.

8.4.1.1 Set up the ICP-MS for the analysis using the parameters given in the manufacturer's operating manual. Nebulize the uranium-matched reagent/calibration blank solution to optimize conditions using the 103 Rh internal standard.

Instrument Operating Conditions

Solution Pumping Rate	Sample solution IN: 1.25 mL/min
ICP Incident Power	1400 watts
ICP Reflected Power	<10 watts
Plasma Argon Coolant	14 L/min at 70 psig
Plasma Argon Auxiliary	0.7 L/min at 70 psig
Plasma Argon Nebulizer	0.93 L/min at 40 psig
Integration Method	Valley Int.
Integration Area	0.80000 daltons (Atomic Mass Units—AMU)
Background Counts	10.0000 counts/s
Dead Time	100.000 µs
Safe Resting Mass	129.253 daltons (AMU)

Perkin Elmer Elan 5000A Instrument Operating Conditions for Boron, Sodium, Silicon, Phosphorus, Potassium, Calcium-44

Solution pumping rate	1.1 mL/min
ICP incident power	1000 W
Plasma argon coolant	15 L/min
Plasma argon auxiliary	0.87 L/min
Plasma argon nebulizer	1.1 L/min
Acquisition method	Peak jump
Number of points across mass peak	1
Dead time	35 nanoseconds
Dwell time/mass	50 ms
Sweeps/reading	12
Readings/replicate	3
Sample cone	platinum
Skimmer cone	platinum

8.4.1.2 Acquire the data for all blank, calibration standard, control/recovery and sample solutions using the ICP-MS for the analytes required using the masses specified by the element menu and given in Table 1. The element menu must also contain the mass for the internal standard (normally 103 Rh). Uranium-matched calibration solutions are run at the start and end of each run. Recalibration during the run may be necessary.

9. Calculation

9.1 The use of a uranium-free reagent blank allows the analyte concentrations in the uranium-matched blank to be ignored. For boron, silicon, potassium, calcium (mass-44), however, a uranium-matched reagent/calibration blank must be used. The concentration of boron, silicon, potassium, calcium (mass-44) in the uranium standard base solution (Z) must be added to the sample concentration to avoid reporting biased results (that is, if the boron content of the uranium standard base solution is 2 µg/g U, the uranium-matched reagent/calibration blank contains 2 µg/g U and the uranium-matched calibration standard contains 102 µg/g U. The calculation software sets these values at zero and 100 µg/g U, respectively.)

NOTE 6—Analyte counts are normalized using the internal standard count ratio (ISCR).

$$ISCR = \frac{\text{103 Rh counts for first solution nebulized}}{\text{103 Rh counts for each subsequent solution}} \quad (1)$$

The first solution nebulized is usually the uranium-matched reagent/calibration blank solution. The normalization and calculation of analyte concentrations is performed by the ICP-MS software.

9.2 The element concentration, M (expressed as µg/g U), for the elements in 8.1 and 8.2 is calculated from:

$$M = \frac{(A_s - A_b)}{(A_c - A_u)} \times C_c \times 500 \quad (2)$$

for elements in 8.1, and

$$M = \left[\frac{(A_s - A_u)}{(A_c - A_u)} \times C_c \times 500\right] + Z \quad (3)$$

for boron, silicon, potassium and calcium (mass 44) in 8.2 and 8.3.

TABLE 3 NBL CRM 124 Series (U_3O_8) Results Comparison—CRM 124-2[A,B,C,D,E]

Analyte	Prepared Value (µg/g U)	NBL Mean (µg/g U)	BNFL1 Mean (µg/g U)	BNFL1 Standard Deviation (1s)	BNFL2 Mean (µg/g U)	BNFL2 Standard Deviation (1s)	Cameco Mean (µg/g U)	Cameco Standard Deviation (1s)
Beryllium	12.5	12.3 (11.6 ± 0.2)	11	1.6	11.6	0.83		
Boron	2.6	2.8					2.9	0.3
Sodium	200	232					206	10
Magnesium	51	60 (51.0 ± 4.0)	...	...	52	3.7		
Aluminum	105	99 (103 ± 10)	...	...	95	2.3		
Silicon	102	97					115	19
Calcium (mass 44)	100	107					104	8
Titanium	25	19 (32.0 ± 1.2)	26	3.8	28	1.1		
Vanadium	25	25 (24.0 ± 3.1)	23	3.8	30	1.0		
Chromium	52	58 (52.2 ± 4.3)	54	9.2	59	1.7		
Manganese	26	28 (25.3 ± 1.5)	27	3.6	26	0.9		
Cobalt	12.5	12.6 (12.5)	12.9	1.6	12.7	0.49		
Nickel	102	112 (103 ± 3)	106	15	104	4.4		
Copper	25	25 (24.5 ± 1.7)	27	4.4	29	1.2		
Zinc	102	98 (113 ± 2)	119	16	101	3.5		
Zirconium	100	87 (130 ± 8)	119	21	139	2.9		
Molybdenum	50	45 (50.0 ± 0.3)	49	5.9	51	0.7		
Cadmium	2.7	2.7 (2.8 ± 0.1)	2.4	0.4	2.4	0.04		
Tin	26	21 (26.8 ± 1.1)	23	3.3	17	0.6		
Tungsten	100	91 (92 ± 2)	67	14	98	2.2		
Lead	26	23 (26.4 ± 2.0)	23	1.4	25	0.6		
Bismuth	25	29 (25)	19	2.5	25	0.7		

[A] BNFL1 results were obtained on VG Elemental PlasmaQuad PQ1[6] in 1988 using mass scan for data acquisition (120-s scan—approximately 0.5 s/isotope). Precision data is based on within-run analysis of ten portions of sample. (0.2 g U dissolved in HNO_3 and diluted to 100 mL using 193 Ir as internal standard.) Uranium-matched blanks and standard solutions used for instrument calibration.

[B] BNFL2 results were obtained on VG Elemental PlasmaQuad PQ2 + Turbo[9] in 1993 using peak jump for data acquisition (120-s acquisition—approximately 10 s/isotope). Precision data is based on within-run analysis of five portions of sample. (0.2 g U dissolved in HNO_3/HF and diluted to 100 mL using 103 Rh as internal standard.) Uranium-matched blanks and standard solutions used for instrument calibration.

[C] CRM 124-2 and 124-6 were obtained from New Brunswick Laboratory, D350, 9800 South Cass Ave., Argonne, IL 60439, USA.

[D] Results in parentheses are NBL revised provisional certified values (October 1993).

[E] Cameco results were obtained with a Perkin Elmer Elan 5000A[7] using peak jump mode for data acquisition with 2 s/isotope dwell time. Precision data are based on 9 determinations over 6 months by 2 analysts.

where:

C_c = the concentration of the element in the uranium-matched calibration standard solution (µg/mL),
A_s = the normalized peak signal of each element in the sample,
A_b = the normalized peak signal of each element in the uranium-free reagent blank solution,
A_c = the normalized peak signal of each element in the uranium-matched calibration standard solution,
A_u = the normalized peak signal of each element in the uranium-matched reagent/calibration blank solution, and
Z = the boron, silicon, potassium, calcium (mass-44) content of the uranium standard base solution (µg/g U),

9.3 Corrections for isobaric effects are not needed when impurities are at or below the upper reporting limit. The isotopes listed in Table 1 can be measured without significant isobaric interference except 48-titanium which suffers an interference from 48-calcium. Four hundred µg Ca/g U is equivalent to about 1 µg Ti/g U. Other titanium isotopes (mass 47 or mass 49) can be used but the lower reporting limit is increased to 1.5 and 2 µg/g U, respectively.

9.4 There is a correction for the molecular interference of $ArCl^+$ on arsenic at mass 75. This can be corrected by monitoring $ArCl^+$ at mass 77 and correcting by direct proportion the contribution of $ArCl^+$ at mass 75 from theknown ratio of $ArCl^+$ 77:75. This correction is only required if concentrations of chloride are greater than 10 µg/mL in the nebulized solutions.

9.5 There is a significant interference on Ca at mass 44 from Sr^{++} at mass 88. One mg/L Sr is equivalent to 0.26 mg/L Ca in 1 % nitric acid solutions.

TABLE 4 NBL CRM 124 Series (U_3O_8) Results Comparison—CRM 124-6[A,B,C,D,E]

Analyte	Prepared Value (µg/g U)	NBL Mean (µg/g U)	BNFL1 Mean (µg/g U)	BNFL1 Standard Deviation (1s)	BNFL2 Mean (µg/g U)	BNFL2 Standard Deviation (1s)	Cameco Mean (µg/g U)	Cameco Standard Deviation (1s)
Beryllium	0.5	0.4 (0.51 ± 0.01)	0.38	0.15	0.31	0.036		
Boron	0.3	0.21					0.3	0.2
Sodium	10	7.5					13	3
Magnesium	3.0	2.5 (2.4 ± 0.8)	...	...	3.6	0.39		
Aluminum	10	8.3 (6.7 ± 2.3)	...	...	6.9	0.58		
Silicon	7.3	7.5					22	18
Calcium (mass 44)	5.8	9.0					9	2
Titanium	1.3	1.2 (8.4 ± 1.0)	1.1	0.2	1.3	0.06		
Vanadium	1.0	1.1 (1.2 ± 0.1)	0.93	0.16	1.1	0.045		
Chromium	4.3	7.8 (4.6 ± 0.8)	4.6	0.7	9.0	0.70		
Manganese	1.7	2.6 (1.4 ± 0.1)	1.5	0.2	1.6	0.12		
Cobalt	0.6	1.0 (0.5)	0.57	0.09	0.50	0.020		
Nickel	7.0	6.8 (6.0 ± 0.9)	6.4	1.2	6.4	0.52		
Copper	1.4	1.2 (1.6 ± 0.5)	1.2	0.5	2.0	0.19		
Zinc	6.6	7.1 (2.5 ± 0.2)	7.4	1.0	5.7	0.53		
Zirconium	5	<20 (<6)	6.3	1.3	6.9	0.22		
Molybdenum	2.0	2.0 (2.0 ± 0.1)	2.1	0.4	3.0	0.48		
Cadmium	0.3	≤0.3 (0.12 ± 0.01)	<0.5	...	0.08	0.008		
Tin	1.6	1.5 (1.6 ± 0.1)	1.1	0.35	0.71	0.020		
Tungsten	5	<25 (<10)	4.3	0.2	4.6	0.13		
Lead	1.8	1.4 (1.0 ± 0.1)	1.3	0.2	1.3	0.03		
Bismuth	1.0	0.9 (1.0)	0.35	0.24	1.0	0.01		

[A] BNFL1 results were obtained on VG Elemental PlasmaQuad PQ1[6] in 1988 using mass scan for data acquisition (120-s scan—approximately 0.5 s/isotope). Precision data is based on within-run analysis of ten portions of sample. (0.2 g U dissolved in HNO_3 and diluted to 100 mL using 193 Ir as internal standard.) Uranium-matched blanks and standard solutions used for instrument calibration.

[B] BNFL2 results were obtained on VG Elemental PlasmaQuad PQ2 + Turbo[7] in 1993 using peak jump for data acquisition (120-s acquisition—approximately 10 s/isotope). Precision data is based on within-run analysis of five portions of sample. (0.2 g U dissolved in HNO_3/HF and diluted to 100 mL using 103 Rh as internal standard.) Uranium-matched blanks and standard solutions used for instrument calibration.

[C] CRM 124-2 and 124-6 were obtained from New Brunswick Laboratory, D350, 9800 South Cass Ave., Argonne, IL 60439, USA.

[D] Results in parentheses are NBL revised provisional certified values (October 1993).

[E] Cameco results were obtained with a Perkin Elmer Elan 5000A using peak jump mode for data acquisition with 2 s/isotope dwell time. Precision data are based on 9 determinations over 6 months by 2 analysts.

TABLE 5 NBL CRM 98 Series Results Comparison

NOTE 1—Results were obtained using a Perkin-Elmer Sciex Elan 5000A[7] Sciex using peak hop mode and 2 s/isotope for data acquisition. Precision data are based on 9 determinations analyses over 6 months by 2 analysts. The calibration procedure is described in sections 8.3 and 9.

Analyte	Standard	Prepared Value (µg/g U)	NBL Mean (µg/g U)	Analyzed Mean (µg/g U)	Standard Deviation (1s)
Phosphorus[A]	98-6	...	12.9	14	3.0
	98-4	...	51.3	54	5.5
	98-2	...	198	204	19
Potassium[A]	98-6	...	10.9	14	2.5
	98-4	...	61.0	72	4
	98-2	...	264	287	20

[A] CRM 124-2 and 124-6 were obtained from New Brunswick Laboratory, D350, 9800 South Cass Ave., Argonne, IL 60439, USA.

10. Precision and Bias

10.1 *Precision*:

10.1.1 The primary control samples (PCS) used were prepared in-house. They were prepared by adding a known amount of each analyte, as a solution, to characterized, high purity UO_3 hydrate (UOH). The UOH was then dried, blended, and ignited to the octoxide (U_3O_8). The U_3O_8 was then thoroughly blended and checked for homogeneity by replicate analysis. To aid the validation of results, the standard solutions used to prepare the PCS materials were obtained from a different supplier than those used in this procedure.

10.1.2 The precision data obtained from the routine analysis of a PCS and CRM 124-2 is given in Table 2. The precision data was collected over a period of 18 months from the work of four analysts using one instrument.[6] The precision data for the elements B, Na, Si, P, K and Ca (mass 44) was obtained from the analysis of CRM 124-2 and CRM 98-2. The data was collected over a period of 6 months from the work of 2 analysts using one instrument.[7]

10.2 *Bias*—Data to assess bias is given in Table 3, Table 4, Table 5. The data comes from the analysis of NBL CRM series U_3O_8. The second and third columns, labelled "Prepared Value" and "NBL Mean" provide estimates of the true amount of impurities in the standards.

10.2.1 The "Prepared Value" represents the expected calculated analyte level from the preparation process. The "NBL Mean" is the arithmetic mean of an interlaboratory measurement program designed by NBL for analytes measured. The data was published in 1984. The numbers in parentheses in the third column are explained in footnote D of Table 3 and Table 4. Because of the lack of agreement about the amount of impurities actually in the standards, a statement of bias is impossible to make. The data is provided to allow interested and knowledgeable readers to make their own assessment of the applicability of the test method to their circumstances.

11. Keywords

11.1 impurities; inductively coupled plasma—mass spectrometry; uranium; uranium dioxide; uranium hexafluoride; uranyl nitrate solutions; uranium oxide; uranium trioxide

[6] A VG PlasmaQuad PQ1, available from Fisons Instruments, Inc., 55 Cherry Hill Drive, Beverley, MA 01915, was used for this purpose.

[7] The Perkin-Elmer Sciex Elan 5000A is available from Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859-0012.

ANNEX

(Mandatory Information)

A1. DETERMINATION OF TECHNETIUM-99 IN URANIUM DIOXIDE POWDER AND PURE URANIUM SOLUTIONS

A1.1 This test method can be used to determine technetium-99 in uranium oxide powders (not sintered pellets), and pure uranium solutions (for example, hydrolyzed UF6 and UNL) using a "cold" dissolution procedure necessary to prevent volatilization of technetium, (A1.2 and A1.3) and data acquisition parameters (Table A1.1).[8] The procedure cannot be used to analyze sintered UO_2 pellets as the dissolution conditions are too mild to dissolve the material. The instrument operating conditions described in 8.4.1 are used. The instrumentation was a Fisons Instruments PlasmaQuad PQ2 + Turbo.[9]The reporting limits and precision data are listed in Table A1.2. The determination may be possible using other manufacturer's instruments that have similar background, sensitivity, and stability characteristics.

NOTE A1.1—For sintered UO_2 pellets closed vessel microwave digestion may be used for dissolution. It is the responsibility of the analyst to determine the dissolution conditions and perform testwork using spikes to validate the closed vessel microwave dissoution.

A1.2 Weigh 0.226 ± 0.002 g of uranium dioxide (that is, 0.200 g U) into a 100-mL glass beaker. Add 10.00 mL of water and 2.00 mL of concentrated nitric acid and allow the mixture to stand for about 10 min until dissolution is complete. Transfer the solution into a 100-mL volumetric flask and add 100 µL of rhodium internal standard solution (10 µg Rh mL^{-1}). Dilute the solution to 100 mL with water. This solution contains 2 g U L^{-1} and 10 ng Rh mL^{-1} in HNO_3 (1 + 49).

A1.3 For pure uranium solutions, transfer an aliquot of the solution containing 0.200 ± 0.002 g U into a 100-mL volumetric flask. Using a micropipette, add 100 µL of rhodium standard solution (10 µg Rh mL^{-1}) and 2.00 mL of concentrated nitric acid. Dilute the solution to 100 mL with water.

TABLE A1.1 Data Acquisition Parameters

Acquisition mode	Peak jump
Masses monitored	99Tc, 100Mo, 101Ru, 102Ru, 103Rh
Number of sweeps	59
Channels per mass	25
Dwell time per channel	20.48 ms
Total acquisition time	120 s (30 s per mass)
Detector mode	Pulse count

TABLE A1.2 Reporting Limits and Precision

	Lower Reporting Limit	Upper Reporting Limit	Control Sample Value	Precision (s)	Number of Determinations
	ng Tc g^{-1} U				
Technetium	0.6	10 000	10.2	0.39	15 (3 operators)

[8] "The Comparison of Sample Preparation Techniques for the Determination of Technetium-99 in Pure Uranium Compounds and Subsequent Analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)" by Peter R. Makinson, presented at the Symposium On Applications of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to Radionuclide Determinations, Gatlinburg, TN, October 1994.

[9] A VG Plasma Quad PQ2, available from Fisons Instruments, Inc., 55 Cherry Hill Drive, Beverley, MA 01915, was used for this purpose.

TABLE A1.3 Calibration Solution Preparation

Standard	Vol of UF6 Base (10 g UF6/100 g)	Vol of Concentrated HNO3	Vol of Rh Int. Std. (10 µg mL^{-1})	Vol of Tc Standard (7.70 µg mL^{-1})	Vol of Tc Standard (100 ng mL^{-1})	Final Volume
Blank	2.68 mL	2.00 mL	100 µL	Nil	Nil	100 mL
100 ng Tc/g U	2.68 mL	2.00 mL	100 µL	Nil	200 µL	100 mL
10 000 ng Tc/g U	2.68 mL	2.00 mL	100 µL	260 µL	Nil	100 mL

A1.4 Prepare a range of uranium-matched calibration solutions as shown in Table A1.3. Technetium standard solution is available from Isotope Products Inc.[10] or Amersham International[11].

A1.5 Nebulize the calibration blank, standard, and sample solutions in accordance with the conditions described in 8.4.1 and Table A1.1.

A1.6 Technetium-99 suffers from an isobaric interference with ruthenium-99 and a molecular interference due to ^{98}MoH, which can cause biased results. These are corrected by monitoring molybdenum-100 and mass 101 in the samples and calculating the ^{100}MoH-to-^{100}Mo ratio found by nebulizing a molybdenum solution (10 µg Mo mL^{-1} in HNO3 (1 + 49)).

A1.6.1 The materials covered in this test method (see Section 2) should not give rise to any significant amount of MoH + ions, and any ruthenium present should be of natural isotopic composition. Visual examination of the mass spectrum shows whether the 102Ru-to-101Ru ratio is natural (that is, about 2:1) or arises from the presence of reprocessed uranium (that is, about 1:1).

A1.6.2 If the natural ratio is found, the following expressions then are used to correct for the interferences after the counts for each mass have been normalized using the rhodium internal standard counts:

$$^{100}MoH = {}^{100}Mo \times 0.000013 \quad \text{(A1.1)}$$

$$^{98}MoH = {}^{100}MoH \times 2.542 \quad \text{(A1.2)}$$

$$^{101}Ru = Mass101 - {}^{100}MoH \quad \text{(A1.3)}$$

$$^{99}Ru = {}^{101}Ru \times 0.7427 \quad \text{(A1.4)}$$

$$^{99}Tc = Mass99 - ({}^{99}Ru + {}^{98}MoH) \quad \text{(A1.5)}$$

where:

^{100}MoH	=	calculated normalized count for MoH$^+$ at Mass 101,
^{98}MoH	=	calculated normalized count for MoH$^+$ at Mass 99,
2.542	=	^{98}Mo-to-^{100}Mo isotope ratio,[12]
^{100}Mo	=	normalized count for molybdenum-100,
0.000013	=	^{100}MoH-to-^{100}Mo ratio,[12]
^{101}Ru	=	normalized count for ruthenium-101,
Mass101	=	total normalized count for Mass 101,
^{99}Ru	=	normalized count for ruthenium-99,
0.7427	=	^{99}Ru-to-^{101}Ru ratio,[12]
^{99}Tc	=	calculated normalized count for technetium-99, and
Mass99	=	total normalized count for Mass 99.

A1.6.3 If the "reprocessed" ratio is found, then no simple correction can be applied, and technetium results that have a high bias will be obtained. However, the technetium level is likely to be some orders of magnitude above the specification limit for the materials covered in this test method.

A1.6.4 The MoH-to-Mo ratio must be determined for individual instruments and checked when the instrument conditions or the nebulizer system is changed.

A1.6.5 These expressions are incorporated into the ICP-MS software (Fisons Instruments ′PQ Vision') and are automatically used as part of the calculation procedure.

A1.6.6 Any ruthenium-99 present in the reagents and rhodium internal standard solution is corrected by blank subtraction.

[10] Technetium standard solution is available from Isotope Products Laboratories, 1800 North Keystone Street, Burbank, CA 91504.

[11] Technetium standard solution also can be obtained from Amersham International plc, Amersham Place, Little Chalfont, Amersham, Bucks, HP7 9NA, UK.

[12] The isotope abundances used to calculate the ^{100}MoH-to-^{100}Mo and ^{99}Ru-to-^{101}Ru ratios were obtained from The International Journal of Mass Spectrometry and Ion Processes, 1985, Vol 65, p. 211 to 230 and The Handbook of Chemistry and Physics, 73rd Edition, p. 11–28 to 11–132.