



Standard Test Method for Determination of Impurities in Uranium Dioxide by Inductively Coupled Plasma Mass Spectrometry¹

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 61 elements in uranium dioxide samples by inductively coupled plasma mass spectrometry (ICP-MS). The elements are listed in Table 1 along with their lower reporting limits.

1.2 Similar levels of these elements in other uranic compounds can also be determined if they are treated and converted to the same uranium concentration solution.

1.3 *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.

1.4 The test method for the additional elements boron, sodium, silicon, phosphorus, potassium, and calcium is given in Appendix X1.

1.5 The test method for technetium-99 is given in Appendix X2.

2. Referenced Documents

2.1 ASTM Standards:

- C 753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder²
- C 776 Specification for Sintered Uranium Dioxide Pellets²
- C 787 Specification for Uranium Hexafluoride for Enrichment²
- C 788 Specification for Nuclear-Grade Uranyl Nitrate Solution²
- C 967 Specification for Uranium Ore Concentrate²
- C 996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ²³⁵U²

¹ This test method 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.

D 1193 Specification for Reagent Water³

3. Summary of Test Method

3.1 The sample is dissolved in acid. 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 $\mu\text{g/ml}$ (100 $\mu\text{g/g}$ U) for each analyte.^{4,5}

4. Significance and Use

4.1 This test method is capable of measuring the elements 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.

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.
- 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.

6. Reagents

6.1 The sensitivity of the ICP-MS technique requires the use

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 in Uranium Dioxide

NOTE 1—Acquisition time = 10 s/isotope using peak jump mode.

NOTE 2—103 Rh was used as an internal standard.

NOTE 3—The LRL is based on the within run standard deviation (S_p) of 20 uranium-matched blank determinations for each analyte. This limit equals $4 \times S_p$, 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 4—The upper reporting limit can be increased by extending the calibration to 10 $\mu\text{g/mL}$ (5000 $\mu\text{g/g U}$) if the ICP-MS used has an extended dynamic range (EDR) accessory.

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

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 $\mu\text{g/mL}$ for all the elements in Table 1.

6.1.2 *Hydrofluoric acid* (40 g/100 g).

6.1.3 *Nitric acid* (specific gravity 1.42)—Concentrated nitric acid (HNO_3).

6.1.4 *Orthophosphoric acid* (specific gravity 1.70).

6.1.5 *Rhodium Stock Solution* (1000 $\mu\text{g/mL Rh}$)—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.

6.1.6 *Sulfuric acid* (specific gravity 1.84)—Concentrated sulfuric acid (H_2SO_4).

6.1.7 *Uranium Standard Base Solution*—Uranyl nitrate solution to Specification C 788, of known uranium (100 g/L) and aluminum content ($\leq 2 \mu\text{g/g U}$). The total metallic impurity (TMI) content must not exceed 50 $\mu\text{g/g U}$ and no individual analyte must exceed 10 $\mu\text{g/g U}$.

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

7. Standards

7.1 Three separate mixed standard solutions (A, B and C) 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 , and analyte group C contains the rare earth element stock solutions. 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 $\mu\text{g/mL}$) 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 $\mu\text{g/mL}$ 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 $\mu\text{g/mL}$) 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 2 $\mu\text{g/mL}$ 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 $\mu\text{g/mL}$) 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 mL 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 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 may be used.

7.4 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 0.1 µg/mL Rh in 1 % nitric acid solution. Other internal standard diluent solutions may be used.

8. Procedure

NOTE 3—A uranium-free reagent blank is used to eliminate bias due to the analyte concentrations in the uranium standard base solution. However, a uranium-free reagent blank for the determination of aluminum cannot be prepared. Small variations in the concentration of the orthophosphoric acid/sulfuric acid mixture cause large variations in aluminum and rhodium signals. This leads to large errors in the reagent blank correction. 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 Aluminum:*

8.1.1 Weigh a portion of uranium dioxide containing between 2.45 and 2.55 g of uranium into a platinum dish. 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 7.3) 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 8.3.1. 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 Aluminum:*

8.2.1 Weigh a portion of uranium dioxide powder or pellet sample equivalent to 1.00 ± 0.05 g of uranium into a silica beaker. Record the weight to the nearest 0.001 g.

8.2.2 Add 50 mL of concentrated nitric acid and heat the mixture on a hotplate to assist dissolution.

8.2.3 Add further 10 mL portions of concentrated nitric acid until dissolution is complete.

8.2.4 Evaporate the solution until fumes of nitric acid are no longer evolved.

8.2.5 Add 5 mL of concentrated sulfuric acid and 1 mL of orthophosphoric acid (specific gravity 1.70) and evaporate the mixture until fumes are no longer evolved. This acid mixture aids the dissolution of alumina which has been heated above 1000°C.

8.2.6 Add 5 mL of concentrated nitric acid and evaporate the mixture until fumes are no longer evolved.

8.2.7 Add 20 mL of water and heat gently to assist dissolution. Allow the solution to cool and quantitatively transfer it into a 50 mL volumetric flask. Dilute to 50 mL with water and mix.

8.2.8 Dispense 1.00 mL of the solution in 8.2.7 and mix with 9.00 mL of the diluent solution (see 7.4). This solution contains 2 g of uranium per litre and 0.09 µg/mL Rh.

8.2.9 A uranium-matched reagent blank (see 8.3.2) and a control or recovery sample must be prepared with every run of samples.

8.2.10 Analyze these solutions as in 8.4 using the calibration solutions prepared in 8.3.2. 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 Aluminum:*

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 6.1.8; 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 7.3). 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 6.1.8; 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 7.3). 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 Aluminum:

8.3.2.1 Uranium-matched Reagent/Calibration Blank—Transfer 10.00 mL of the uranium standard base solution (see 6.1.8; this is equivalent to 1.0 g of uranium) into a silica beaker. Continue as instructed from 8.2.2 onwards. The final solution contains 2 g of uranium per litre and 0.09 µg/mL Rh.

8.3.2.2 Uranium-matched Calibration Standard—Transfer 10.00 mL of the uranium standard base solution (see 6.1.8; this is equivalent to 1.0 g of uranium) into a silica beaker. Add 100 µL of aluminum standard solution (see 7.2) and continue as instructed from 8.2.2 onwards. The final solution contains 2 g of uranium per litre, 0.2 µg/mL Al (equivalent to 100 µg/g U) and 0.09 µg/mL Rh.

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).

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)

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.

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 aluminum, however, a uranium-matched reagent/calibration blank must be used. The aluminum concentration of the uranium standard base solution (Z) must be added to the sample concentration to avoid reporting biased results (that is, if the aluminum 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 4—Analyte counts are normalized using the internal standard count ratio (ISCR).

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

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 aluminum in 8.2.

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 aluminum 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 the known ratio of ArCl^+ 77:75. This correction is only required if concentrations of chloride are greater than 10 µg/mL in the nebulized solutions.

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

TABLE 2 Precision Data Derived from PCS and CRM Samples

NOTE 1—Acquisition time = 10 s/isotope using peak jump mode.
 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) and NBL Certified Reference Material CRM 124-2.

Analyte	Isotope	Concentration, µg/g U	Standard Deviation, µg/g U	Number of Determinations
Lithium	7	A	A	...
Beryllium	9	10	1.5	10
Magnesium ^B	24	52	3.7	5
Aluminum	27	21.5	2.5	50
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 ^C
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 N/A = Data not available; still being obtained.

TABLE 3 NBL CRM 124 Series (U₃O₈) Results Comparison—CRM 124-2^{A,B,C,D}

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)
Beryllium	12.5	12.3 (11.6 ± 0.2)	11	1.6	11.6	0.83
Magnesium	51	60 (51.0 ± 4.0)	52	3.7
Aluminum	105	99 (103 ± 10)	95	2.3
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 PQ1⁶ 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 HNO₃ 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 + Turbo⁷ 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 HNO₃/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).

of four analysts using one instrument.⁶

10.2 *Bias*—Data to assess bias is given in Table 3 and Table 4. The data comes from the analysis of NBL CRM series U₃O₈. 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

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

**TABLE 4 NBL CRM 124 Series (U₃O₈) Results Comparison—
CRM 124-6^{A,B,C,D}**

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)
Beryllium	0.5	0.4 (0.51 ± 0.01)	0.38	0.15	0.31	0.036
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
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 PQ1⁶ 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 HNO₃ 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 + Turbo⁷ 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 HNO₃/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).

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 oxides

measured. The data was published in 1984. The numbers in parentheses in the third column are explained in Note 4 of

APPENDIXES

(Nonmandatory Information)

X1. DETERMINATION OF ADDITIONAL IMPURITIES

X1.1 This test method can be used to determine the additional elements boron, sodium, silicon, phosphorus, potassium, and calcium. The isotopic mass and the reporting limits are listed in Table X1.1. The instrumentation was the Perkin-Elmer Sciex Elan 5000A.⁷ The determination may be possible with other manufacturer's instrumentation, provided the background ion count rate is sufficiently low to achieve the required detection limits.

X1.2 To prevent corrosion and contamination of the samples from the sample introduction system due to hydrofluoric acid, the spray chamber and nebulizer must be made from HF inert material. Platinum skimmer and sampling cones are recommended. The alumina injector is fitted with a TFE-fluorocarbon inner sleeve.

X1.3 To determine silicon, the loss of volatile SiF₄ after digestion with HF must be minimized. Graduated polypropylene tubes with caps are used as sealed low pressure digestion vessels in place of the platinum dishes (see 8.1.1). Other plastic vessels may be equivalent. The reagent volume and sample weight are reduced to eliminate the dilution step (see 8.1.4). The polypropylene tubes were leached in acid before use.

X1.3.1 The tubes are capped immediately after addition of HF (see 8.1.3) to prevent the loss of volatile SiF₄.

X1.4 The water is polished by deionization in order to remove traces of boron, silicon, and sodium. The quartz distilled water contains traces of the impurities.

X1.5 Data are acquired by ICP-MS using the conditions shown in Table X1.2.

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

TABLE X1.1 Reporting Limits of Additional Elements in Uranium Dioxide

NOTE 1—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 using the series 1, 1.5, 2, 3, 4, 6.

NOTE 2—No internal standard was used for the LRL calculations. Neither scandium nor rhodium matched the behavior of the impurity elements during long-term signal drift.

NOTE 3—Acquisition time = 0.6 s/isotope using peak hop mode.

NOTE 4—The URL can be increased by utilizing range-extending features and accessories provided by the instrument manufacturers.

Analyte	Mass Used	Lower Reporting Limit (LRL) $\mu\text{g/g U}$	Upper Reporting Limit (URL) $\mu\text{g/g U}$
Boron	11	0.3	200
Sodium	23	0.3	200
Silicon	28	1.5	200
Phosphorus	31	1.5	200
Potassium	39	2	200
Calcium	44	6	200

TABLE X1.2 Instrument Operating Conditions

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 hop
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

X1.6 The precision data obtained from the analysis of the NBL CRM 124 series is given in Table X1.3. 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.

TABLE X1.3 NBL CRM 124 Series and 98 Series Results Comparison

NOTE 1—Results were obtained using a Perkin-Elmer Sciex Elan 5000A⁸ using peak hop and 0.6 s/isotope for data acquisition. Precision data is based on 6 analyses over a three-week period. The calibration procedure is described in 8.3 and Section 9.

NOTE 2—The calibration standards were run after every two samples.

NOTE 3—Neither scandium nor rhodium matched the behavior of the impurity elements over a long time period and were not used as an internal standard to compensate for instrument drift.

Analyte	Standard	Prepared Value (µg/g U)	NBL Mean (µg/g U)	Analyzed Mean Without IS (µg/g U)	Standard Deviation (1σ) Without IS (µg/g U)
Boron	124-6	0.2	0.21	0.18	0.10
	124-3	1.1	1.1	0.97	0.22
	124-2	2.6	2.8	2.39	0.11
Sodium	124-6	10	7.5	14	3.5
	124-3	100	130	100	4.8
	124-2	200	232	200	9.3
Silicon	124-6	7.3	7.5	9	3.6
	124-3	52	56	50	2.8
	124-2	102	97	99	4.8
Phosphorus	98-6	...	12.9	10	0.9
	98-4	...	51.3	50	1.4
	98-2	...	198	200	7.6
Potassium	98-6	...	10.9	16	3.6
	98-4	...	61.0	74	3.4
	98-2	...	264	282	11.6
Calcium	124-6	5.8	9.0	11	4.1
	124-3	51	55	54	5.2
	124-2	100	107	106	6.1

X2. DETERMINATION OF TECHNETIUM-99 IN URANIUM DIOXIDE POWDER

X2.1 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, (X2.2 and X2.3) and data acquisition parameters (Table X2.1).⁸ The procedure cannot be used to analyze sintered UO₂ 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 X2.2. The determination may be possible using other manufacturer’s instruments that have similar background, sensitivity, and stability characteristics.

TABLE X2.1 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

X2.2 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

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, Beverly, MA 01915, was used for this purpose.

TABLE X2.2 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)

and 2.00 mL of concentrated nitric acid (sp gr 1.42) 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 HNO₃ (1 + 49).

X2.3 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.

X2.4 Prepare a range of uranium-matched calibration solutions as shown in Table X2.3. Technetium standard

TABLE X2.3 Calibration Solution Preparation

Standard	Vol of UF ₆ Base (10 g UF ₆ /100 g)	Vol of Concentrated HNO ₃	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

solution is available from Isotope Products Inc.¹⁰ or Amersham International¹¹.

X2.5 Nebulize the calibration blank, standard, and sample solutions in accordance with the conditions described in 8.4.1 and Table X2.1.

X2.6 Technetium-99 suffers from an isobaric interference with ruthenium-99 and a molecular interference due to ⁹⁸MoH, which can cause biased results. These are corrected by monitoring molybdenum-100 and mass 101 in the samples and calculating the ¹⁰⁰MoH-to-¹⁰⁰Mo ratio found by nebulizing a molybdenum solution (10 µg Mo mL⁻¹ in HNO₃ (1 + 49)).

X2.6.1 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).

X2.6.2 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:

$$^{100}\text{MoH} = ^{100}\text{Mo} \times 0.000013 \quad (\text{X2.1})$$

$$^{98}\text{MoH} = ^{100}\text{MoH} \times 2.542 \quad (\text{X2.2})$$

$$^{101}\text{Ru} = \text{Mass101} - ^{100}\text{MoH} \quad (\text{X2.3})$$

$$^{99}\text{Ru} = ^{101}\text{Ru} \times 0.7427 \quad (\text{X2.4})$$

$$^{99}\text{Tc} = \text{Mass99} - (^{99}\text{Ru} + ^{98}\text{MoH}) \quad (\text{X2.5})$$

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.

X2.6.3 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.

X2.6.4 The MoH-to-Mo ratio must be determined for individual instruments and checked when the instrument conditions or the nebulizer system is changed.

X2.6.5 These expressions are incorporated into the ICP-MS software (Fisons Instruments ‘PQ Vision’) and are automatically used as part of the calculation procedure.

X2.6.6 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 ¹⁰⁰MoH-to-¹⁰⁰Mo and ⁹⁹Ru-to-¹⁰¹Ru 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.

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