



Standard Test Method for Determination of Metallic Impurities in Uranium Metal or Compounds by DC-Arc Emission Spectroscopy¹

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1. Scope

1.1 This test method describes the steps necessary for the preparation and determination of impurity metals in uranium metal and uranium compounds by DC arc emission spectroscopy.

1.2 The method is valid for those materials that can be dissolved in acid and/or converted to an oxide in a muffle furnace (see Practice C1347).

1.3 This method uses the carrier distillation technique to selectively carry the impurities into the arc, leaving the uranium oxide in the electrode. If it is necessary to determine the carrier metal (usually a silver or strontium, or gallium compound) as an impurity, another technique must be chosen for that element.

1.4 *Units*—The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.5 *This standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

C753 Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder

C761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride

C776 Specification for Sintered Uranium Dioxide Pellets

C788 Specification for Nuclear-Grade Uranyl Nitrate Solution or Crystals

C859 Terminology Relating to Nuclear Materials

C967 Specification for Uranium Ore Concentrate

C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis

E130 Practice for Designation of Shapes and Sizes of Graphite Electrodes

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

3. Terminology

3.1 See definitions and terms in Terminologies C859 and E135.

4. Summary of Test Method

4.1 Uranium metal, solutions and compounds are converted to uranium oxide (U_3O_8) in a muffle furnace. A weighed amount of the oxide is mixed with an appropriate spectrographic carrier and loaded into a graphite electrode. The electrode is excited in a DC arc and the light is dispersed by a spectrograph or spectrometer. The resulting spectrum is measured electronically using a CCD, CID or CMOS camera or photographed on photographic plates or film sensitive to the proper regions. The line intensities are compared directly to standard plates or to calibration curves derived from the arced standards.

5. Significance and Use

5.1 This test method is applicable to uranium metal, uranium oxides and compounds soluble in nitric or sulfuric acid, and uranium solutions which can be converted to uranium oxide (U_3O_8) in a muffle furnace. It may be used to determine the impurities in uranium compounds as listed in Specifications C753, C776, C788, and C967.

6. Apparatus

6.1 *Spectrograph or Spectrometer*—A spectrograph with sufficient resolving power and linear dispersion to separate the analytical lines from other lines in the spectrum of the sample in the spectral region of 230.0 to 855.0 nm is required.

¹ This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Instruments with a reciprocal linear dispersion in the first order of 0.5 nm/mm or less are satisfactory. A direct-reading spectrometer of comparable quality may be substituted for equipment listed, in which case the directions given by the manufacturer should be substituted for those in this procedure.

6.2 Excitation Source—Use an arc power source capable of providing a dc arc of up to 14-A dc, depending on the carrier used and electrode design.

6.3 Excitation Stand—Conventional type with adjustable water-cooled electrode holders (may be fitted with automatic sample changers if desired).

6.4 Photographic Processing Equipment—Use developing, fixing, washing and drying equipment.

6.5 Microphotometer, having a precision of at least $\pm 1\%$ for transmittances.

6.6 Mixer, for dry materials.

6.7 Platinum Crucible.

6.8 Venting Tool, (see Fig. 8, Test Methods C761).

6.9 Muffle Furnace, 1000°C capability.

7. Reagents and Materials

7.1 Purity of Materials—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society where such specifications are available. Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Electrodes—The anode and counter electrodes should be of the S-2, S 16 and C-1 types as given in Practice E130 (or equivalent).

NOTE 1—Exact shapes and dimensions of the electrodes are not as critical as given in Practice E130; however, dimensions of the electrodes used should be consistent and it is essential that the same dimension electrodes be used for standards and samples.

7.3 Photographic Processing Solutions—Prepare solutions as noted in available literature (1,2).

7.4 Photographic Film/Plates—Use photo emulsion SA-1 and 1-N or equivalent.

7.5 Powder Paper.

7.6 Nitric Acid (HNO_3)—concentrated (70 %), electronic grade, or equivalent.

7.7 Sulfuric Acid (H_2SO_4)—concentrated, electronic grade, or equivalent.

7.8 Spectrographic Carrier—The following spectrographic carriers have been used successfully for DC Arc analysis:

7.8.1 Silver Chloride-Lithium Fluoride, 11:1 w/w ratio.

7.8.2 Silver Chloride-Silver Fluoride, 4:1 w/w ratio.

7.8.3 Gallium Oxide, 99.99 % or better.

7.8.4 Silver Chloride-Strontium Fluoride, 16.4 mol % SrF_2 in AgCl .

7.8.5 Gallium Oxide-Lithium Fluoride, 11:1 w/w ratio.

TABLE 1 Carrier—Sample Combinations

Carrier Material	Carrier Wt, (mg)	Oxide Wt, (mg)	Electrode Charge, (mg)	Mixing Time, (s)
AgCl/AgF (4:1)	50	250	50	180
AgCl/LiF (11:1)	30	270	100	60
AgCl/SrF_2 (~6:1)	50	450	100	30
$\text{Ga}_2\text{O}_3/\text{LiF}$ (11:1)	20	380	100	25
Ga_2O_3^A	7	343	100	60

^A For the determination of Ag and Li only.

NOTE 1—The above listed combinations of carrier, uranium oxide and electrode charge have been successfully used for the determination of impurities in uranium oxide. Other combinations may be available or suitable. However, the user must demonstrate comparable precision and bias.

7.9 Mixing Vial, plastic, 12.7 mm (1/2 in.) by 25.4 mm (1 in.) with cap and 10 mm (3/8 in.) plastic mixing bead.

7.10 Standard Uranium Oxide (U_3O_8) Diluent—Use NBL CRM 129⁴ (or its replacement or equivalent) of known impurity level as a diluent.

8. Precautions

8.1 Consult manufacturer's Material Safety Data Sheets (MSDS) for chemical incompatibilities, specific hazards, or spill cleanup for any hazardous materials used in this method.

8.2 All mixing and weighing operations involving uranium oxides should be carried out in properly functioning hoods or exhaust boxes.

9. Standardization and Calibration

9.1 Standards:

9.1.1 Standards may be synthesized by adding the impurity elements to purified U_3O_8 (NBL CRM 129³, or equivalent) and homogenizing. Impurities in powder form, preferably as oxides, may be blended in U_3O_8 ; impurities in solution may be added to U_3O_8 and the mixture dried, blended and reignited, or the impurities and uranium may be combined in solution and reconverted to U_3O_8 . The individual elements should grade in such a ratio as to facilitate visual comparisons covering the desired analytical range for each.

9.1.2 The compounds used to make U_3O_8 impurity standards should be of the highest purity available.

9.1.3 Alternatively, commercially available uranium impurity standards, such as NBL CRM 123³ and 124³ series standards, may be used. (Other standards may be available; the user should determine quality and/or applicability prior to use.) These may be supplemented by synthetic standards to extend calibration ranges, if necessary.

9.1.4 For each standard used, prepare in the same ratio of uranium oxide to carrier as for samples (see Table 1 for further details).

³ Available from the US Department of Energy, New Brunswick Laboratory, D350, 9800 South Cass Avenue, Argonne, IL 60439, ATTN: Reference Material Sales. <http://www.nbl.doe.gov/>

9.1.5 Charge the electrode and arc at the same conditions as determined to be optimum for the instrument in use.

9.2 Calibration Curves:

9.2.1 If a microphotometer is used, determine emulsion calibration curves and analytical curves as described in available literature (1,2).

9.2.2 If a direct reading spectrometer is used, calibrate according to manufacturer's instruction.

9.2.3 For visual comparison, the darkness/width of each standard and impurity element line will establish the individual analyte concentrations.

10. Procedure

10.1 Sample Preparation

10.1.1 Liquid Samples:

10.1.1.1 Transfer into a platinum crucible a sufficient amount of liquid to yield not more than 2 g uranium oxide.

10.1.1.2 Place the crucible on a hot plate and evaporate to dryness. Do not allow to boil.

NOTE 2—The addition of H_2SO_4 may be necessary for solutions of uranyl chloride to effect complete conversion to oxide.

10.1.1.3 Continue the preparation at 10.1.2.2.

10.1.2 Miscellaneous Uranium Oxides, Solids or Compounds:

10.1.2.1 Transfer not more than 2 g of the uranium compound to a platinum crucible.

10.1.2.2 Place in a cool muffle and set the muffle to $900 \pm 50^\circ C$.

NOTE 3—Some impurities (for example, Mo, W, Cr) may be lost at high temperatures. Do NOT place samples directly in hot muffle. Lower temperatures may be used if it is determined that complete oxide conversion is achieved.

10.1.2.3 Leave the crucibles and samples in the muffle until conversion to U_3O_8 is complete.

NOTE 4—Times will vary depending on amount and type of sample; the user must determine optimum time experimentally for his sample types.

10.2 Addition of Carrier:

10.2.1 Weigh an appropriate amount of uranium oxide into a mixing vial and add the amount of carrier chosen (see Table 1).

10.2.2 Mix on a mixer for at least 1 min.

NOTE 5—Exact time will depend on efficiency of mixing action of the mixer chosen, the amount of sample and carrier used. The user must determine this experimentally for his sample type (see Table 1).

10.3 Charge each electrode with the amount of uranium oxide and carrier determined to be optimum. For each sample charge duplicate electrodes.

10.4 Grip each electrode with forceps and pack the charge by tapping on a solid surface.

10.5 Further compress and vent the charge with the venting tool shortly before arcing the samples. Wipe the venting tool with tissue between different samples.

NOTE 6—Venting is dependent on the carrier used and may not be required. A combination tamping/venting tool is permissible.

10.6 Arc the electrodes at the conditions determined optimum for the instrument in use.

TABLE 2 Typical Wavelengths and Limits of Detection

Element	Wavelength (nm)	LOD using AgCl/AgF (ppm)	LOD using AgCl/LiF (ppm)	LOD using Ga_2O_3/LiF (ppm)
Al	308.21 236.70	1	5	1
As	234.98	10	...	
Au	267.59	1	...	
B	249.77	0.1	0.4	0.5
Ba	455.40 493.41	2	1	
Be	234.86 249.45	0.1	1	1
Bi	306.77	1	...	
Ca	396.84 422.64	10	25	
Cd	228.80	0.1	0.3	0.5
Co	240.72 340.51	1	5	
Cr	284.33 425.44 427.48	2	10	3
Cs	852.11	10	...	
Cu	324.75 327.40	1	2	1
Fe	248.33 252.28 302.06	10	20	2
Ga	294.36	1	...	
Ge	265.12	1	...	
K	769.89	10	...	
Li	670.78	0.2		
Mg	279.55 280.27	2	10	1
Mn	279.48 279.83	1	10	1
Mo	313.21	10		
Na	588.99 589.59	1	10	
Nb	316.34	10	...	
Ni	300.25 341.48	1	5	2
P	255.33 213.62	100	25	
Pb	283.31	4	3	1
Pd	340.46	1	...	
Rb	780.02	20	...	
Sb	259.81	2	10	
Si	250.69 251.61 288.16	10	10	1
Sn	283.99 317.50	10	2	
Sr	407.77	20	...	
Ta	265.33		35	
Ti	334.90 337.28	4	5	
V	292.40 318.34	1	5	
W	294.70	100	...	
Zn	330.25 213.86	10		30

10.7 If photographic film or plates are used, process as directed in available literature (1,2). If a direct reading spectrograph is used, the impurity values will be reported as each electrode is arced.

10.8 Determine each impurity by comparing the lines for each element using the calibration curves established in 9.2.

11. Precision and Bias

11.1 There are not certified materials for the determination of all elements that may be analyzed by this method. Nor

TABLE 3 Typical Data Using AgCl/AgF Carrier for NBL CRM 124-2 (Data from Lab A)

Element	# Points	Value (ppm)	Average (ppm)	Absolute Difference (Avg-Value)	% Relative Difference	Std. Dev	% Rel Std. Dev
Al	30	105	103	-2	2	15	15
Cr	30	52	61	9	17	12	20
Cu	30	25	27	2	8	6	22
Fe	30	110	116	6	5	27	23
Mo	30	50	53	3	6	11	21
Ni	30	102	113	11	11	18	16
Si	30	102	83	-19	19	13	16

TABLE 4 Typical Data Using AgCl/LiF Carrier Synthetic Standards (U₃O₈ Spiked with Traceable Impurities) (Data from Lab B)

Element	# Points	Value (ppm)	Average (ppm)	Absolute Difference (Avg-Value)	% Relative Difference	Std. Dev	% Rel Std. Dev
Al	143	140	138	-2	1	12	9
Ca	139	60	60	0	0	10	16
Cr	142	60	58	-2	3	10	17
Fe	135	220	239	19	9	39	16
Ni	130	120	119	-1	1	14	12
Si	110	100	91	-9	9	9	10

would all the elements be expected in these materials. However, there are standards available from the New Brunswick Laboratory certified for many of the elements of interest. Data using these standards and other available standards are listed in [Tables 3 and 4](#). Each user must determine the proper quality control and assurance measures for his application and the carrier/sample combination used. Relative standard deviations are calculated relative to average value. For different elements the relative standard deviation was found to be between 9 % and 23 %. These sigma are an indication of precision. The relative difference from the certified values vary from 0 % to 20 %. These numbers are an indication of the potential bias. This data was collected over a 12-month period in two different

laboratories by several different technicians and is typical of data for these techniques. For other elements not in these standards, the precision is normally –50 % to +100 % of the determined value. The user can expect precision and bias values for some elements (those with weak emission lines or highly refractory elements) to be greater than the values listed in [Tables 3 and 4](#). Those values must be determined by the user.

12. Keywords

12.1 carrier distillation; dc-arc; emission spectroscopy; impurities in uranium

REFERENCES

- (1) Anderson, J. W. and Lincoln, A. J., “General Mathematical Approach to Emulsion Calibration in Optical Emission Spectroscopy,” *Applied Spectroscopy*, Vol 22, 1968, p. 753.
- (2) Woodyard, J. R., Piper, B. C., and Stever, K. R., “The Functional Form of the Emulsion Calibration Curve,” *Applied Spectroscopy*, Vol. 33, 1979, p. 25.

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