



# Standard Test Method for Determination of Metallic Impurities in Uranium Metal or Compounds by DC-Arc Emission Spectroscopy<sup>1</sup>

This standard is issued under the fixed designation C 1517; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 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 C 1347).

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 *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:

C 753 Specification for Nuclear Grade, Sinterable Uranium Dioxide Pellets<sup>2</sup>

C 761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride<sup>2</sup>

C 776 Specification for Sintered Uranium Dioxide Pellets<sup>2</sup>

C 788 Specification for Nuclear Grade Uranyl Nitrate Solutions<sup>2</sup>

C 859 Terminology Relating to Nuclear Materials<sup>2</sup>

C 967 Specification for Uranium Ore Concentrate<sup>2</sup>

C 1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis<sup>2</sup>

E 115 Practice for Photographic Processing in Optical

Emission Spectrographic Analysis<sup>3</sup>

E 116 Practice for Photographic Photometry in Spectrochemical Analysis<sup>3</sup>

E 130 Practice for Designation of Shapes and Sizes of Graphite Electrode<sup>3</sup>

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores and Related Materials<sup>3</sup>

E 402 Test Method for Spectrographic Analysis of Uranium Oxide ( $U_3O_8$ ) by Gallium Oxide Carrier Technique<sup>4</sup>

## 3. Terminology

3.1 See definitions and terms in Terminologies C 859 and E 135.

## 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 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 C 753, C 776, C 788, and C 967.

## 6. Apparatus

6.1 *Spectrograph*—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. Instruments with a reciprocal linear dispersion in the first order of 0.5 nm/mm or

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 12.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 03.05.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 03.06.

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 conforming to Practice E 115.

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. 1, Test Method E 402 or Fig. 8, Test Methods C 761).

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 E 130 (or equivalent).

NOTE 1—Exact shapes and dimensions of the electrodes are not as critical as given in Practice E 130; 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 Practice E 115.

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

7.5 *Powder Paper*.

7.6 *Nitric Acid (HNO<sub>3</sub>)*—concentrated (70 %), electronic grade, or equivalent.

7.7 *Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>)*—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<sub>2</sub> in AgCl.

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

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<sub>3</sub>O<sub>8</sub>) Diluent*—Use NBL CRM 129<sup>4</sup> (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<sub>3</sub>O<sub>8</sub> (NBL CRM 129<sup>5</sup>, or equivalent) and homogenizing. Impurities in powder form, preferably as oxides, may be blended in U<sub>3</sub>O<sub>8</sub>; impurities in solution may be added to U<sub>3</sub>O<sub>8</sub> and the mixture dried, blended and reignited, or the impurities and uranium may be combined in solution and reconverted to U<sub>3</sub>O<sub>8</sub>. 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<sub>3</sub>O<sub>8</sub> impurity standards should be of the highest purity available.

9.1.3 Alternatively, commercially available uranium impurity standards, such as NBL CRM 123<sup>5</sup> and 124<sup>5</sup> 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).

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 Practice E 116.

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

<sup>5</sup> Available from the US Department of Energy, New Brunswick Laboratory, D 350, 9800 South Cass Avenue, Argonne, IL 60439, ATTN: Reference Material Sales.

**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 <sub>2</sub> (~6:1)	50	450	100	30
Ga <sub>2</sub> O <sub>3</sub> /LiF (11:1)	20	380	100	25
Ga <sub>2</sub> O <sub>3</sub> <sup>A</sup>	7	343	100	60

<sup>A</sup> For the determination of Ag and Li only.

NOTE—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.

**TABLE 2 Typical Wavelengths and Limits of Detection**

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

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<sub>2</sub>SO<sub>4</sub> 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 ± 50°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<sub>3</sub>O<sub>8</sub> 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 1 to 3 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.

10.7 If photographic film or plates are used, process as directed in Practice E 115. 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 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. For different elements the relative standard deviation was found to be between 9 % and

**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 (U<sub>3</sub>O<sub>8</sub> 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

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. Relative standard deviations are calculated relative to average value. For other elements not in these standards, the precision is normally -50 % to +100 % of the determined value (Test Method E 402). 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

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