



Designation: E 402 – 02

Standard Test Method for Spectrographic Analysis of Uranium Oxide (U₃O₈) by Gallium Oxide-Carrier Technique¹

This standard is issued under the fixed designation E 402; 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 semiquantitative spectrographic analysis of high-purity U₃O₈ for the 32 elements in the ranges indicated in **Table 1**. (Quantitative analyses of boron, chromium, iron, magnesium, manganese, nickel, and other impurities can be performed using densitometric methods.)

1.2 The test method can be applied to those samples of uranium and uranium compounds, or both, which can be converted to the black oxide (U₃O₈) and which are of approximately 99.5 % purity or better.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis²

E 116 Practice for Photographic Photometry in Spectrochemical Analysis²

E 130 Practice for Designation of Shapes and Sizes of Graphite Electrodes²

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology **E 135**.

4. Summary of Test Method

4.1 The as-received sample is ignited to U₃O₈. It is important that the sample be in the same physical oxide form as are

the comparison standards. The sample is mixed with pure gallium sesquioxide (Ga₂O₃) in the ratio of 98 parts U₃O₈ to 2 parts Ga₂O₃. If densitometric determinations are desired, the Ga₂O₃ used in the mixture contains 1 % chromium or 1 % cobalt by weight. The chromium or cobalt is used as an internal standard element in the spectrochemical analysis. The U₃O₈-Ga₂O₃ mixture is placed in a special cupped electrode and excited in a d-c arc. Varying amounts of impurities either in vapor form or as solid particles are carried up into the arc stream, along with the vaporized Ga₂O₃, for excitation. The spectrum is recorded on a photographic plate and the selected lines are either visually compared with standard plates or photometrically measured and compared with synthetically prepared standards according to standard spectrochemical procedures.

5. Significance and Use

5.1 Impurities in the uranium used as fuel for nuclear reactors may affect the nuclear chain reaction. Their concentrations must be closely controlled. This method provides a technique for their determination.

6. Apparatus

6.1 *Sample Preparation Equipment:*

6.1.1 *Sample-Carrier Mixers*, either a highly polished agate mortar and pestle, or a clean plastic capsule with a plastic ball and a mechanical mixer.

6.2 *Balances*, torsion type, with capacities up to 1000 mg, capable of weighing ±0.1 mg accurately. When samples are hand ground it may be necessary to have a balance capacity of 2.500 g.

6.3 *Muffle Furnace*, capable of 1000° C.

6.4 *Excitation Source*, capable of providing a 14-A d-c arc (short-circuit).

6.5 *Excitation Stand*, conventional type with adjustable water cooled electrode holders.

6.6 *Spectrograph*, grating, providing preexposure and exposure timers, wavelength coverage from 2250 to 8650 Å, a reciprocal linear dispersion of at least 5 Å/mm and sufficient resolving power to separate cadmium 2288.02 Å from arsenic 2288.12 Å.

¹ This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.02 on Ores, Concentrates, and Related Metallurgical Materials.

Current edition approved October 10, 2002. Published June 2003. Originally approved in 1970. Last previous edition approved in 1995 as 402 – 95.

² *Annual Book of ASTM Standards*, Vol 03.05.

TABLE 1 Elements and Analytical Ranges^A

Element	Concentration Range, ppm	Element	Concentration Range, ppm	Element	Concentration Range, ppm
Antimony	1 to 200	Arsenic	10 to 200	Gold	1 to 100
Beryllium	1 to 200	Barium	10 to 200	Indium	1 to 100
Chromium	1 to 200	Cesium	10 to 200	Manganese	1 to 100
Cobalt	1 to 200	Phosphorus	10 to 200	Rubidium	1 to 100
Lead	1 to 200	Vanadium	10 to 200	Tin	1 to 100
Nickel	1 to 200	Zinc	10 to 200	Molybdenum	2 to 100
Potassium	1 to 200	Lithium	0.5 to 100	Thallium	5 to 100
Sodium	1 to 200	Magnesium	0.5 to 100	Silver	0.1 to 50
Aluminum	5 to 200	Copper	0.5 to 100	Cadmium	0.1 to 10
Iron	5 to 200	Bismuth	1 to 100	Boron	0.2 to 10
Silicon	5 to 200	Germanium	1 to 100		

^A ppm on uranium basis.

6.7 *Photographic Processing Equipment*, to provide developing, fixing, washing, and drying operations, and conforming to the requirements of Practices **E 115**.

6.8 *Comparator-Microphotometer*, as a comparator to provide sufficient magnification and facility to compare spectral line densities of the sample and a reference standard plate or film; as a microphotometer having a precision of $\pm 1.0\%$ or better for transmittance values between 5 and 90%.

6.9 *Calculating Equipment*, capable of transposing percent transmission values into intensity or density values.

7. Reagents and Materials

7.1 Carrier:

7.1.1 For visual comparison analysis, use a 99.99% pure Ga₂O₃.

7.1.2 For densitometric analysis except for chromium, use a mixture containing 98.54 parts of Ga₂O₃ and 1.46 parts of chromium sesquioxide (Cr₂O₃). This is equivalent to 1% chromium in this mix or to 200 ppm chromium in the final U₃O₈-Ga₂O₃ mixture.

7.1.3 For densitometric analysis except for cobalt, use a mixture of 98.53 parts of Ga₂O₃ and 1.47 parts of cobalt oxide (Co₂O₃). This is equivalent to 1% cobalt in this mix or to 200 ppm cobalt in the final U₃O₈-Ga₂O₃ mixture.

7.2 *Electrodes*—The anode, pedestal and the counter electrodes should be respectively of the S-1, S-2 and C-1 types as given in Practice **E 130**. The graphite should be a high-purity type with an average density near 1.85 g/cm³ and a specific electrical resistance near 4.5×10^{-4} Ω-in.

7.3 *Photographic Emulsion*, Eastman Kodak, Type SA No. 1, II-F and I-N plates or film, or equivalent.

NOTE 1—Type II-F plates are not available. Comparable results may be obtained for Ba on SA No. 1 and Li and Na on I-N plates.

7.4 *Photographic Processing Solutions*, Formulas for processing solutions are given in Practices **E 115**.

8. Standards

8.1 Standards can be synthesized by adding the impurity elements to purified U₃O₈ and homogenizing. Impurities in a solid or powder form, preferably as oxides, may be blended with U₃O₈; impurities in solution may be added to U₃O₈, and the mixture dried, blended, and reignited; or the impurities and uranium may be combined in solution and reconverted to U₃O₈. The individual elements should grade in such a ratio as

to facilitate visual comparisons, such a ratio as 10–5–2–1 covering the desired analytical range for each. No single standard should have a total concentration of impurities exceeding 2000 ppm. The bulk densities of the standards and the sample U₃O₈ should be as nearly identical as possible. Similar element responses should be obtained with U₃O₈ standards with similar bulk densities, regardless of the method used to make the standards. The sample and comparison standards should have the same physical oxide form and oxide preparation, if possible. Wherever possible an independent analytical method should be used to verify the established concentrations in the standards.

8.2 The elements or compounds used to synthesize U₃O₈ standards should be of the highest purity. Refer to **(1, 2, and 3)**³ for sources of such materials.

8.3 If U₃O₈ of suitable purity is not available for the base material of the standards, the uranium may be purified by following qualitatively steps 1 through 10 of Section F, Method A of Ref **(4)**.

9. Preparation of Samples

9.1 Ignite sample as received in a muffle furnace at 950°C for 30 min.

9.2 Combine 980 mg of the U₃O₈ sample and 20 mg of the proper Ga₂O₃ carrier by thoroughly grinding with an agate mortar and pestle. Weigh quadruplicate 100-mg U₃O₈-Ga₂O₃ charges into anode electrodes held in a plastic electrode board. Gently tap the electrode board to settle the electrode charges. Compress the charges and introduce center vent hole in the charge with a venting tool similar to the one shown in **Fig. 1**.

10. Preparation of Apparatus

10.1 *Electrode System*—Insert a 1/8-in. counter electrode in the upper holder. Mount a 1/8-in. pedestal electrode so as to extend 1/2 in. above the lower electrode holder. Insert the anode electrode, with its charge, firmly on the pedestal. Adjust to an analytical gap of 4 mm, with its center aligned with the optical axis of the spectrograph. The sample is electrically positive.

10.2 *Excitation and Exposure*—Produce and record the spectra in accordance with the following conditions:

10.2.1 Electrical Parameters:

³ The boldface numbers in parentheses refer to the list of references at the end of this method.