Designation: E 402 – 02

Standard Test Method for Spectrographic Analysis of Uranium Oxide (U_3O_8) by Gallium Oxide-Carrier Technique[1]

1. Scope

1.1 This test method covers the semiquantitative spectrographic analysis of high-purity U_3O_8 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 (U_3O_8) 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 Analysis[2]

E 116 Practice for Photographic Photometry in Spectrochemical Analysis[2]

E 130 Practice for Designation of Shapes and Sizes of Graphite Electrodes[2]

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[2]

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 U_3O_8. 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 (Ga_2O_3) in the ratio of 98 parts U_3O_8 to 2 parts Ga_2O_3. If densitometric determinations are desired, the Ga_2O_3 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 U_3O_8-Ga_2O_3 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 Ga_2O_3, 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 Cu, Pb, Zn, Cd, Sn, Be, their Alloys and Related Metals.

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 ±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 Ga_2O_3.

7.1.2 For densitometric analysis except for chromium, use a mixture containing 98.54 parts of Ga_2O_3 and 1.46 parts of chromium sesquioxide (Cr_2O_3). This is equivalent to 1 % chromium in this mix or to 200 ppm chromium in the final U_3O_8-Ga_2O_3 mixture.

7.1.3 For densitometric analysis except for cobalt, use a mixture of 98.53 parts of Ga_2O_3 and 1.47 parts of cobalt oxide (Co_2O_3). This is equivalent to 1 % cobalt in this mix or to 200 ppm cobalt in the final U_3O_8-Ga_2O_3 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/cm^3 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 U_3O_8 and homogenizing. Impurities in a solid or powder form, preferably as oxides, may be blended with 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, 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 U_3O_8 should be as nearly identical as possible. Similar element responses should be obtained with U_3O_8 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 U_3O_8 standards should be of the highest purity. Refer to **(1, 2,** and **3)**[3] for sources of such materials.

8.3 If U_3O_8 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 U_3O_8 sample and 20 mg of the proper Ga_2O_3 carrier by thoroughly grinding with an agate mortar and pestle. Weigh quadruplicate 100-mg U_3O_8-Ga_2O_3 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

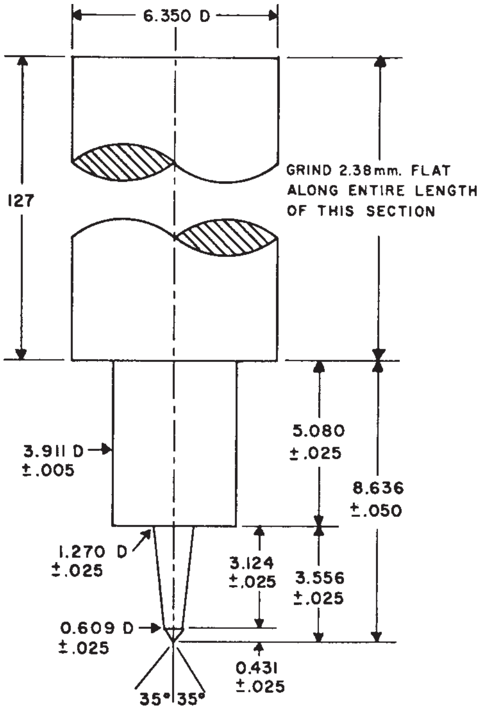
10.1 *Electrode System*—Insert a ⅛-in. counter electrode in the upper holder. Mount a ⅛-in. pedestal electrode so as to extend ½ in. above the lower electrode holder. Insert the anode electrode, with its charge, firmly on the pedestal. Adjust to an analytical gap of 4 mm, with its center aligned with 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.



NOTE 1—All dimensions are in millimetres.

FIG. 1 Venting Tool

Voltage	250 V
Current	14 A (short circuit)

10.2.2 *Exposure Conditions*:

10.2.2.1 *General Procedure for 26 Elements (Ag, Al, As, Au, B, Be, Bi, Cd, Co, Cr, Cu, Fe, Ge, In, Mg, Mn, Mo, Ni, P, Pb, Sb, Si, Sn, Tl, V, Zn):*

Spectral region, Å	2250 to 3500
Slit width, µm	20
Preburn period, s	5
Exposure period, s	35
Step sector may be used to increase concentrational ranges covered by spectral lines.	
Photographic emulsion, Eastman Kodak Type SA-1	

10.2.2.2 *Ba, Li and Na*:

Spectral region, Å	4300 to 6800
Slit width, µm	20
Preburn period, s	0
Exposure period, s	40
Photographic emulsion, Eastman Kodak Type II-F Filter	Corning No. 3850

10.2.2.3 *Cs, K and Rb:*

Spectral region, Å	7400 to 8650
Slit width, µm	20
Preburn period, s	0
Exposure period, s	40
Photographic emulsion, Eastman Kodak Type I-N Filter	Corning 3480

10.2.3 *Replicate Exposures*—Make duplicate or quadruplicate exposures of each sample.

11. Photographic Processing

11.1 Process the emulsions in accordance with Practices E 115.

12. Photometry

12.1 *Visual Comparative Analyses*:

12.1.1 Visually compare the density of the sample impurity spectral line with the corresponding line on a standard reference plate. Estimate the impurity concentration using the lines listed in Table 2.

12.1.2 It is highly improbable that many of the 32 impurities will appear simultaneously in any one sample in the 100 to 200 ppm concentration range. However, in most cases, the initial or alternate spectral lines designated will be free of spectral interference even when the other elements are near the maximum concentration indicated in Table 1. A notable exception is the cadmium 2288.02-Å line which is subject to interference from arsenic above the 30-ppm level. Unusually high concentration of one or more elements in a sample requires a cautious checking for unexpected spectral interferences.

12.2 *Densitometric Analyses*—Chromium and cobalt have been used beneficially as internal standards to determine four commonly encountered impurities. For best precision the analytical line pairs shown in Table 3 should be measured with a microphotometer. An internal standard is not used for boron, but its reliability is improved by using the measured transmittances of the line shown in Table 3.

13. Calibration

13.1 *Densitometric Method*:

TABLE 2 Visual Spectral Lines, Å

Ag	3280.68	Cd	2288.02	Li	6707.84	Rb	7800.23
Ag^{A}	3382.89	Co	3453.51	Mg	2802.70	Sb	2598.06
Al	3092.71	Co^{A}	2424.93	Mg^{A}	2795.53	Sb^{A}	2877.92
Al^{A}	3082.16	Cr	2835.63	Mn	2798.27	Si	2506.90
As	2349.84	Cr^{A}	2843.35	Mn^{A}	2794.82	Si^{A}	2881.58
As^{A}	2780.22	Cs	8521.10	Mo	3132.59	Sn	3175.02
Au	2675.95	Cu	3247.54	Mo^{A}	3170.35	Sn^{A}	3262.33
Au^{A}	2427.95	Cu^{A}	3273.96	Na	5889.95	Tl	2767.87
B	2497.73	Fe	2599.40	Na^{A}	3302.32	V	3185.40
B^{A}	2496.78	Fe^{A}	2788.10	Ni	3050.82	V^{A}	3183.98
Ba	4934.08	Ge	2651.18	Ni^{A}	3002.49	Zn	3345.02
Be	2348.61	Ge^{A}	2651.58	P	2553.28	Zn^{A}	3282.33
Be^{A}	3130.42	In	3256.09	P^{A}	2554.93		
Bi	3067.72	In^{A}	3039.36	Pb	2833.07		
Bi^{A}	2897.98	K	7664.91	Pb^{A}	2802.00		

TABLE 3 Analytical Lines Used for Densitometry, Å

Element and Wavelength	Internal Standard Element and Wavelength		
B 2497.73	none		none
Cr 2835.63	Co 3044.00		
Fe 2599.40	Co 3044.00	or	Cr 2762.59
Mg 2802.70	Co 3044.00	or	Cr 2762.59
Mn 2798.27	Co 3044.00	or	Cr 2762.59
Ni 3050.82	Co 3044.00	or	Cr 2762.59

13.1.1 *Emulsion Calibration*—Calibrate the emulsion in accordance with Practice E 116.

13.1.2 *Preparation of Analytical Curves*—Make quadruplicate exposures of at least four standards. Convert the percent transmittances of the analytical lines and the internal standard lines to log intensity ratios using the emulsion calibration curve. Prepare analytical curves by plotting the log intensity ratio versus the log concentration for each element.

13.2 *Preparation of Visual Standard Plate*—Make a single exposure of each standard so that each exposure is adjacent to the preceding one, producing a gradating pattern of element concentrations. Tag the spectral lines indicated in Table 2. Using ink, write the ppm concentrations of each element of the respective standards next to the chosen spectral lines.

13.3 *Standardization*:

13.3.1 *Densitometric Method*—With each group of samples, analyze two standard samples in quadruplicate. If the averages of control values indicate a curve shift of 20 % or more, make one half of the correction needed.

13.3.2 *Visual Analysis*—With each group of samples, analyze two control samples in quadruplicate. If the averages of control values exceed their established values by 25 %, correct all sample values proportionately.

14. Calculation

14.1 *Densitometric Method*—Calculate the log intensity ratio for each analytical line pair from the emulsion calibration curve. Refer this ratio to the previously prepared analytical curve to obtain the percent concentration.

15. Precision and Bias

15.1 *Precision*:

15.1.1 *Densitometric Method*—The average relative standard deviation is 14.5 for boron, chromium, iron, magnesium, manganese, and nickel in the range of concentrations stated in Table 1.

15.1.2 *Visual Method*—Normally a +100 percent −50 % indication of precision is assigned to visual analytical results. For certain elements with sharply differing gradations in spectral responses for adjacent standards, a standard deviation of ±30 % can be obtained.

15.2 *Bias*—The bias of the test method can approach the precision stated in 15.1, provided that appropriate standards are used.

15.3 This test method has been studied in a cooperative test. Summaries of test data from five laboratories reporting data are presented in Table 4 and Table 5. A complete set of cooperative data is on file at ASTM Headquarters.

16. Keywords

16.1 D-C arc; gallium oxide carrier; optical emission; spectrographic; uranium oxide

TABLE 4 Summary of Cooperative Test Results for the Spectrochemical Analysis of U_3O_8 for Impurities Determined by the Gallium Oxide Carrier D-C Arc Technique—Densitometric Analyses

	U-1		U-2		U-3	
	Average Value[A]	RSD[B]	Average Value[A]	RSD[B]	Average Value[A]	RSD[B]
Boron	0.87	12.7	0.38	8.7	0.57	7.5
Chromium	31	16.3	7	23.1	47	18.7
Iron	18	20.7	119	9.4	190	11
Magnesium	49	21.8	6	28.9	...	...
Manganese	29	8.9	8	13	38	10.1
Nickel	...	...	97	8.7	120	12.3

[A] Each value represents the average (ppm/U basis) from five laboratories, each laboratory making four determinations on each of 10 days.

[B] RSD = Relative Standard Deviation

$$RSD\ X = (100/\bar{X}\sqrt{\Sigma\ d^2/(n-1)}$$

where:

$\bar{X}$ = average concentration in ppm,

d = difference of the determinations from the mean, and

n = number of determinations.

TABLE 5 Summary of Cooperative Test Results for the Spectrochemical Analysis of U_3O_8 for Impurities Determined by the Gallium Oxide Carrier D-C Arc Technique—Visual Comparative Analyses

	U-1		U-2		U-3	
	Average Value[A]	RSD[B]	Average Value[A]	RSD[B]	Average Value[A]	RSD[B]
Aluminum	62	11.6	8	21.1	...	...
Bismuth	35	17.6	5	19.3	...	...
Copper	2	12.2	46	8.5	50	5.4
Molybdenum	35	19.4	6	18.3	...	...
Phosphorus	203	13.8	...	...	...	...
Silicon	...	...	193	9.0	267	6.7
Tin	27	19.9	2	33.8	...	...
Vanadium	70	14.6	20	16.1	...	...
Zinc	...	...	133	13.6	...	...

[A] Each value represents the average (ppm/U basis) from three laboratories, each laboratory making four determinations on each of 10 days.

[B] RSD = Relative Standard Deviation

$$RSD\ X = (100/\bar{X})\sqrt{\Sigma\ d^2/(n-1)}$$

where:

$\bar{X}$ = average concentration, ppm,

d = difference of the determinations from the mean, and

n = number of determinations.

REFERENCES

(**1**) *Report on Available Standard Samples and Related Materials for Spectrochemical Analysis, ASTM DS2,* 1960.

(**2**) Covey, E. H., *Availability and Sources of the Ninety-Six Elements in High Purity Form, USAEC Report AECU-222*, March 1, 1969.

(**3**) Standard Materials Issued by the National Institute of Standards and Technology, *National Bureau of Standards* (*U.S.*) *Circular*, No. 552, 3rd Ed., 1959.

(**4**) Jones, R. J., Ed., “Selected Measurements Methods for Plutonium and Uranium in the Nuclear Fuel Cycle,” *USAEC Report TID-7029*, pp. 385–6, 1963.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).