Designation: C1343 − 16

Standard Test Method for
Determination of Low Concentrations of Uranium in Oils and Organic Liquids by X-ray Fluorescence[1]

This standard is issued under the fixed designation C1343; 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 steps necessary for the preparation and analysis by X-ray fluorescence (XRF) of oils and organic solutions containing uranium. Two different preparation techniques are described.

1.2 The procedure is valid for those solutions containing 20 to 2000 µg uranium per mL as presented to the spectrometer for the solution technique and 200 to 50 000 µg uranium per g for the pellet technique.

1.3 This test method requires the use of an appropriate internal standard. Care must be taken to ascertain that samples analyzed by this test method do not contain the internal standard or that this contamination, whenever present, has been corrected for mathematically. Such corrections are not addressed in this procedure. Care must be taken that the internal standard and sample medium are compatible; that is, samples must be miscible with tri- *n*-butyl phosphate (TBP) and must not remove the internal standard from solution. Alternatively, a scatter line may be used as the internal standard.[2]

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

1.5 *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.* Specific precautionary statements are given in Section 9 and Note 2.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

C1110 Test Method for Determining Elements in Waste Streams by Inductively Coupled Plasma-Atomic Emission Spectroscopy (Withdrawn 2014)[4]

C1254 Test Method for Determination of Uranium in Mineral Acids by X-Ray Fluorescence

D1193 Specification for Reagent Water

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

2.2 *NIST Document:*

ANSI/HPS N43.2–2001 *Radiation Safety for X-ray Diffraction and X-ray Fluorescence Analysis Equipment*[5]

3. Terminology

3.1 *Definitions*—See definitions in Terminology E135.

4. Summary of Test Method

4.1 Solution standards containing 20 µg uranium per mL to 2000 µg uranium per mL or pellet standards containing 200 to 50 000 µg uranium per g and an internal standard are placed in a liquid sample holder of an X-ray spectrometer and exposed to an X-ray beam capable of exciting the uranium L-α emission line and the appropriate internal standard line. The intensities generated are measured by an appropriate detector. The intensity ratio values obtained from these data are used to calibrate the X-ray analyzer. Samples are prepared having a similar matrix to fit the calibration range and measured using the same analytical parameters.

NOTE 1—Yttrium, strontium, and bromine K-α and thorium L-α lines have been used successfully as internal standard lines. Explanation of the

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[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.

Current edition approved June 1, 2016. Published July 2016. Originally approved in 1996. Last previous edition approved in 2011 as C1343 – 11. DOI: 10.1520/C1343-16.

[2] Andermann, G., and Kemp, J. W., "Scattered X-rays as Internal Standards in X-ray Spectroscopy," *Analytical Chemistry*, Vol 20, No. 8, 1958.

[3] 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.

[4] The last approved version of this historical standard is referenced on www.astm.org.

[5] Available from U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899.

internal standard method of analysis is outside the scope of this test method and is found in several sources.[6,7]

5. Significance and Use

5.1 This test method is applicable to organic solutions containing 20 to 2000 µg uranium per mL of solution presented to the spectrometer for the solution techniques or 200 to 50 000 µg uranium per g using the fused pellet technique.

5.2 Either wavelength-dispersive or energy-dispersive XRF systems may be used, provided that the software accompanying the system is able to accommodate the use of internal standards.

6. Interferences

6.1 This test method requires the use of an internal standard. Care must be taken that the samples analyzed by this test method do not contain the internal standard or chemicals that would remove the internal standard from solution. The samples must also be miscible with TBP if using the solution technique.

7. Apparatus

7.1 *X-ray Spectrometer*—See manufacturers' literature for the selection of the X-ray spectrometer. The procedure is valid for either energy-dispersive or wavelength-dispersive systems.

7.2 *Sample Cups:*

7.2.1 Prepare liquid sample cups for the X-ray spectrometer as described by the manufacturer. Vented, disposable sample cups with snap-on caps are satisfactory for most such analyses; such cups decrease the likelihood of contamination of the samples.

7.2.2 Polyester, polyethylene, and polypropylene films have been used successfully as the film window for such cups. Tests should be performed to determine the serviceability of any film chosen before the insertion of samples into the instrument.

7.3 *Solution Dispenser (Optional)*—If used, the solution dispenser for the internal standard solution should be capable of dispensing the internal standard reproducibly to a level of 0.5 % relative standard deviation of the volume dispensed.

7.4 *Fusion Crucibles*—graphite or platinum are acceptable; platinum is recommended.

8. Reagents and Materials

8.1 *Purity of Reagents*—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 on Analytical Reagents of the American Chemical Society where such specifications are available.[8] 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water in conformance with Specification D1193.

8.3 *Nitric Acid,* HNO_3, concentrated (70 %).

8.4 *1,3,5-Tribromobenzene,* technical grade (or substitute for internal standard).

8.5 *Tri-n-Butyl Phosphate* (TBP), technical grade.

8.6 *Uranium Oxide,* U_3O_8, NBL CRM 129-A,[9] or equivalent.

8.7 *Lithium Tetraborate,* $Li_2B_4O_7$ or LiTB, technical grade, fused and ground (or other fusion flux material).

8.8 *Yttrium Oxide,* Y_2O_3, spectrographically pure (or suitable internal standard substitute).

9. Technical Precautions

9.1 X-ray fluorescence equipment analyzes by the interaction of ionizing radiation with the sample. Applicable safety regulations and standard operating procedures must be reviewed prior to the use of such equipment. All current XRF spectrometers are equipped with safety interlock to prevent accidental penetration of the X-ray beam by the user. Do *not* override these interlocks (see ANSI/HPS N43.2–2001).

9.2 Instrument performance may be influenced by environmental factors such as heat, vibration, humidity, dust, stray electronic noise, and line voltage stability. These factors and performance characteristics should be reviewed prior to the use of this test method.

10. Preparation of Apparatus

10.1 *Chamber Environment*—The standards and samples used in this test method are corrosive liquids. Some fumes will be emitted from the sample cups. These fumes may be detrimental to the spectrometer chamber. It is desirable to flush this chamber with an inert gas (usually helium) before and during analysis. Some X-ray spectrometers control the change of sample chamber environment (air, vacuum, and helium) automatically through the software; in others, it must be done manually. Follow the instrument manufacturer's recommendations to achieve the inert gas environment.

NOTE 2—**Caution:** Allow sufficient stabilization time before analysis. Care must be taken to ensure that a vacuum environment is not chosen with liquid samples. Standards and samples must be counted in same environment.

10.2 *X-ray Power Supply*—If the power to the X-ray tube is not controlled by the instrument software, set the proper combination of voltage and current for the instrument in use. These settings must be ascertained by the user for his instrument and choice of X-ray tube. Rhodium, gold, tungsten, and

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[6] Bertin, E. P., *Introduction to X-ray Spectrometric Analysis*, Plenum Press, New York and London, 1978.

[7] Tertian, R., and Claisse, F., *Principles of Quantitative X-ray Fluorescence Analysis*, Heyden & Son, London, Philadelphia, and Rheine, 1982.

[8] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[9] Available from U.S. Department of Energy, New Brunswick Laboratory, D350, 9800 South Cass Avenue, Argonne, IL 60439, Attn: Reference Material Sales.

molybdenum target X-ray tubes have been used successfully for this analysis. Allow sufficient stabilization time prior to analysis.

11. Calibration and Standardization

11.1 Solution Technique

11.1.1 *Internal Standard Solution:*

11.1.1.1 Weigh 65.64 g of *1,3,5*-tribromobenzene to the nearest 0.1 mg. Transfer the material to a 400-mL beaker; add 200 mL of TBP.

11.1.1.2 Dissolve the material in TBP; heat on a hot plate, if necessary.

11.1.1.3 Transfer the dissolved material to a 1000-mL volumetric flask, and dilute to volume with TBP. (Storage of the solution in an opaque container with a screw cap is recommended.)

11.1.2 *"Master" Standards:*

NOTE 3—Because of the difficulty of accurately weighing the small amounts of uranium oxide necessary for low-concentration standards, calibration standards are made by dilution from "master" standards. The total volume of the standard prepared may be adjusted to meet the user's analytical throughput if the weights are adjusted appropriately.

11.1.2.1 Prepare the standards at each desired concentration level by weighing the quantities of uranium oxide given in Table 1 into 400-mL beakers.

TABLE 1 "Master" Standards for Uranium in Organic Liquids

Uranium Oxide, g[A]	Concentration, µg U/mL
2.9490	5000
0.5898	1000

[A] The weight of uranium oxide is based on the value of NBL CRM 129. Weights will need to be adjusted for the purity of the uranium reference material used. Follow instructions on the certificate accompanying the material for drying and purity correction, where applicable.

11.1.2.2 Dissolve the oxide in 50 mL of water and 10 mL of concentrated nitric acid. Evaporate the solution to near dryness or to a syrupy solution.

11.1.2.3 Add enough TBP to bring the uranium back into solution. (Keep the volume below 200 mL.)

11.1.2.4 Transfer the solution to a 500-mL volumetric flask using TBP. When cool, add 1 mL of concentrated nitric acid while diluting to volume with TBP; cap and mix thoroughly.

11.1.3 *"Secondary Master" Standards:*

11.1.3.1 Prepare a 500 µg/mL standard by pipetting 25 mL of the 5000 µg/mL "master" standard into a 250-mL volumetric flask. Dilute to volume with TBP, and mix thoroughly.

11.1.3.2 Prepare a 100 µg/mL standard by pipetting 25 mL of the 1000 µg/mL "master" standard into a 250-mL volumetric flask. Dilute to volume with TBP, and mix thoroughly.

11.1.4 *Calibration Standards:*

11.1.4.1 Prepare the calibration standards by pipetting into labeled 50-mL volumetric flasks the amounts of each "master" standard given in Table 2.

11.1.4.2 Add 2 mL of the internal standard to each flask. Dilute to volume with TBP, and mix thoroughly.

NOTE 4—The internal standard solution may be added using an automatic dispenser or dispensing pipette. However, care must be taken to ensure that no adjustment to the dispenser is made between use for standards and use for samples.

TABLE 2 Calibration Standards for Uranium in Organic Liquids

"Master" Standard Used, µg U/mL	"Master" Standard Pipetted, mL	Calibration Standard Concentration, µg U/mL
5000	20	2000
5000	15	1500
5000	10	1000
1000	25	500
500	25	250
500	10	100
100	25	50
100	10	20

11.2 Pellet Technique

11.2.1 *Internal Standard Solution (25.0 g/L):*

11.2.1.1 Prepare the internal standard solution as described in the Calibration & standardization section of Test method C1254. Alternately, the internal standard may be weighed directly as powder and added to each crucible prior to fusion.

11.2.2 *Calibration Standards:*

11.2.2.1 Prepare a standard at each desired level by adding 15.00 ± 0.03 g of LiTB into a labeled crucible.

11.2.2.2 Add to each crucible the amount of uranium oxide shown in Table 3.

11.2.2.3 Mix the LiTB and uranium oxide in the crucible carefully to avoid loss of material.

11.2.2.4 Add the equivalent of 0.0500 g of internal standard to each crucible.

11.2.2.5 Fuse each standard. Description of fusion techniques are outside the scope of this method and may be found in the literature[6,7] or as described in Practice C1110. Automatic fusion devices or air-gas burners may be used in place of muffles. Adjustment of fusion time may be required depending on the equipment used. This time must be determined by the operator. Swirling or mixing during the fusion process results in more complete fusion.

11.2.2.6 When fusion is complete (pellet should have no visible particles), remove from heat source and allow to cool.

NOTE 5—No two crucibles are identical nor are fusion devices; heating rates and cooling rates may vary and cause cracking or poor crystallization of melt. Remelting in same crucible does not invalidate the analysis.

TABLE 3 Standards for Pellet Technique

Standard Value (µg U/g)	Uranium Oxide (g)[A]
250	0.00029
500	0.00059
1000	0.00118
1750	0.00206
2500	0.00295
5000	0.00590
7500	0.00885
10 000	0.01180
15 000	0.01769
20 000	0.02359
25 000	0.02949
30 000	0.03539
35 000	0.04129
40 000	0.04719
50 000	0.05898

[A] Based on value of NBL CRM-129. Follow instructions on certificate with material for drying or isotopic correction, or both.

11.3 *Instrument Calibration:*

NOTE 6—The frequency of calibration, use of blanks, spikes and duplicates, labeling, and length of storage of solutions shall be in accordance with the user's quality assurance/quality control plan and requirements.

11.3.1 Follow the manufacturer's instructions for the instrument in use to obtain intensity data for the uranium L-α and the internal standard line for each standard.

11.3.2 Care must be exercised that the analytical conditions determined appropriate for the instrument in use are documented, or recorded, in sufficient detail that these may be reproduced in subsequent runs and when analyzing the samples.

11.3.3 Calculate the uranium/internal standard ratios from the data obtained in 11.3.1. Calculate a calibration curve using these ratios. The curve should be at least a second order polynomial (quadratic) or should have a term to correct for uranium self-absorption. Both have been found acceptable. Currently available instrument software would contain one or the other, or perhaps both. (A complete discussion of the mathematical derivation of the following equations is outside the scope of this test method. Explanations of correction models and interelement effects are found in several sources.[6,7]) The quadratic equation will have the form

$$Y = CX^2 + BX + A \quad (1)$$

where:

Y = concentration of uranium,
X = uranium/internal standard intensity ratio, and
A,B,C = coefficients of quadratic equation.

11.3.4 For self-absorption, the equation will have the form

$$Y = (MX + B)(1 + \alpha X/100) \quad (2)$$

where:

Y = concentration of uranium,
X = uranium/internal standard intensity ratio,
M = slope of straight line,
B = intercept of straight line, and
α = self-absorption coefficient.

NOTE 7—Units used for Y in Eq 1 and Eq 2 may be changed, as appropriate, for the software in use.

12. Procedure

NOTE 8—Some estimate of the approximate g U/L will be necessary to determine the appropriate dilution. This may be obtained by gamma counting of the incoming sample, prior knowledge of the origin of the sample, or some other scheme devised by the user. Such schemes are outside the scope of this test method.

12.1 *Sample Preparation:*

12.1.1 *Solution Technique*

12.1.1.1 Shake the sample and pipet an appropriate amount into a tared 50-mL volumetric flask.

12.1.1.2 Obtain the gross weight of the sample and flask. (This may be omitted if an answer on a weight basis is not desired.)

12.1.1.3 Add 2 mL of the internal standard solution; dilute to volume with TBP and mix thoroughly.

12.1.2 *Pellet Technique*

12.1.2.1 Weigh 15.00 ± 0.03 g LiTB into a labeled crucible for each test sample desired.

12.1.2.2 Shake the sample to homogenize contents. For extremely thick or viscous samples, stirring with a glass rod may be the best option for mixing.

12.1.2.3 Add an appropriate amount of sample to be within standard range (see Note 8).

12.1.2.4 Add the equivalent of 0.0500 g of internal standard to each crucible.

12.1.2.5 Fuse using same time, temperature, mixing, and cooling as was used to prepare standards in Section 11.

12.2 *Counting the Sample:*

12.2.1 Set the X-ray spectrometer to the conditions noted in 11.3.2 above. If the analytical conditions are controlled by computer, start the computer in accordance with the manufacturer's instructions for the software in use.

12.2.2 Shake each flask to mix thoroughly. Fill the liquid sample cup with the recommended amount of liquid for the instrument in use.

12.2.3 Following the manufacturer's instrumental instructions, obtain intensities for the uranium L-α line and the internal standard line.

12.2.4 Calculate the uranium concentration in the flask using the appropriate equation.

NOTE 9—Additional factors, such as volume, weight, isotopic correction, and secondary dilutions, may be added to the listed equations to obtain results on the proper basis for the user's application.

13. Precision and Bias

13.1 There is no readily available certified material (uranium in organic liquids) for this test method. However, a solution of NBL CRM 129-A (U_3O_8) was prepared by dissolving approximately 5.9 g (weighed to the nearest 0.1 mg) as outlined in 11.2. Thirty test samples of 5 mL each were prepared and analyzed by seven different technicians over an eight-month period (Bromine was used as the internal standard.) (See Table 4). The average of the 30 determinations was 0.010169 g uranium/g solution, with a relative standard deviation of 0.8 %. The theoretical value for the solution was 0.010141 g U/g. Using the t-test for bias as described by Youden,[10] there is no significant bias shown for these data. For the pellet technique, a solution was prepared as described in Section 10.3 of Test Method C1254 by weighing ~1.65 gm of NBL CRM 129-A (weighed to nearest mg), diluting to 500 mL in a tared flask and obtaining the gross weight. Sixteen determinations over a 23-month period gave an average result of 0.002792 gU/g solution (prepared value 0.002798 gU/g) with a relative standard deviation of 0.5 % and an absolute bias of -0.000006 gU/g (see Table 5).

14. Keywords

14.1 organic solutions; uranium; X-ray fluorescence; XRF

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[10] Youden, W. J., *Statistical Methods for Chemists*, John Wiley & Sons, Inc., New York, NY, 1951.

TABLE 4 Uranium in Tri-*n*-Butyl Phosphate Solution (Theoretical Value 0.01014 g U/g Solution)

Observed X_i
0.010219
0.010220
0.010160
0.010210
0.010168
0.010250
0.010300
0.010301
0.010151
0.010136
0.010050
0.010120
0.010110
0.010040
0.010060
0.010190
0.010080
0.010275
0.010334
0.010221
0.010054
0.010121
0.010088
0.010260
0.010144
0.010160
0.010212
0.010181
0.010140
0.010111
$\bar{X} = 0.010169$, $s = 0.000080$

TABLE 5 Uranium by Pellet Technique (Theoretical Value 0.002798 g U/g Solution)

Observed Values ($\bar{x}$)	
0.0027882	0.0027735
0.0027761	0.0027841
0.0027852	0.0027796
0.0028195	0.0028018
0.0027811	0.0028004
0.0027790	0.0027856
0.0028054	0.0027918
0.0027998	0.0028145
$\bar{X} = 0.0027916$, $s = 0.000013$	

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