



Standard Test Method for the Determination of Uranium or Gadolinium, or Both, in Gadolinium Oxide-Uranium Oxide Pellets or by X-Ray Fluorescence (XRF)¹

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1. Scope

1.1 This standard describes the steps necessary for the preparation and analysis by X-ray fluorescence (XRF) of gadolinium and/or uranium in gadolinium oxide-uranium oxide pellets or powders.

1.2 This method requires the use of appropriate internal standard(s). Care must be taken to ascertain that samples analyzed by this method do not contain the internal standard element(s) or that this contamination has been corrected for mathematically whenever present. Such corrections are not addressed in this standard.

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.* Specific precautions are given in Section 8 and various notes throughout the method.

2. Referenced Documents

2.1 ASTM Standards:

C 982 Guide for Selecting Components for Generic Energy Dispersive X-Ray Fluorescence (XRF) Systems²

C 1118 Guide for Selecting Components for Wavelength-Dispersive X-Ray Fluorescence (XRF) Systems²

D 1193 Specification for Reagent Water³

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials⁴

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, see Terminology E 135.

3.2 Symbol:

LiTB = lithium tetraborate (see 7.4).

4. Summary of Test Method

4.1 Solution or pellet standards containing the equivalent of

1–10 % gadolinium oxide and 90–99 % uranium oxide and appropriate internal standards are placed in the sample holder of a x-ray spectrometer and exposed to an x-ray beam capable of exciting the uranium and gadolinium L-α emission lines and the appropriate emission line for the internal standard. The intensities generated are measured by an appropriate detector. The intensity ratio values obtained from this data are used to calibrate the x-ray analyzer.

4.2 Samples are prepared in the same manner as the standards and analyzed using conditions and curves generated from those standards.

NOTE 1—Yttrium and strontium have been used successfully as internal standards for uranium and samarium for gadolinium. Scatter lines also have been used as internal standard lines (1).⁵ An explanation of internal standard method is found in several sources (2, 3).

5. Significance and Use

5.1 This guide is applicable to samples containing 2 to 10 % gadolinium oxide and 90 to 98 % uranium oxide on the “as received” basis. The method may be used to determine concentration of either uranium, gadolinium, or both.

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

6. Apparatus

6.1 *X-Ray Spectrometer*—See Guide C 982 or Guide C 1118 for the selection of the X-ray spectrometer. The method is valid for either energy-dispersive or wavelength-dispersive systems.

6.2 *Sample Cups/ HOLDERS*—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 between samples. Sample holders for fused pellets should keep any pellet chips from getting into the moving parts of the instrument.

6.3 *Window Film*—Polyester, polyethylene, and polypropylene films have been used successfully as the film window for

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² *Annual Book of ASTM Standards*, Vol 12.01.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 03.05.

⁵ The boldface numbers in parentheses refer to the list of references at the end of this standard.

cups or holders, or both. Tests should be performed to determine the serviceability of any film chosen before insertion into the instrument.

6.4 *Solution Dispenser (optional)*—The dispenser for the internal standard solution, if used, should be capable of reproducibility dispensing the internal standard solution to a level of 0.1 % relative standard deviation of the volume dispensed.

6.5 *Muffle Furnace*, 1100°C capacity.

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.⁶ 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 *Purity of Water*—Unless otherwise indicated, references to water shall mean reagent water conforming to Specification D 1193.

7.3 *Gadolinium Oxide, Gd₂O₃*—It is recommended that the standards be prepared using same batch as in pellets/powder.

7.4 *Lithium Tetraborate, Li₂B₄O₇*, fusion grade.

7.5 *Nitric Acid, HNO₃*, concentrated (70 %).

7.6 *Samarium Oxide, Sm₂O₃*, or other suitable internal standard for gadolinium (see Note 1).

7.7 *Uranium Oxide, U₃O₈*, NBL CRM-129 (or equivalent) (4).

NOTE 2—High purity UO₂ may be used if certification of uranium analysis is not required.

7.8 *Yttrium Oxide, Y₂O₃*, or other suitable internal standard for uranium (see Note 1).

8. Technical Precautions

8.1 XRF 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 modern XRF spectrometers are equipped with safety interlocks to prevent accidental penetration of the X-ray beam by the user. Do NOT override these interlocks without proper training. (See NBS Handbook 111.)

8.2 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 use of this standard.

9. Preparation of Apparatus

9.1 *Chamber Environment*—The liquid standards and samples used in this method are corrosive. 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 atmosphere (air, vacuum, helium) automatically through the software; in others, it must be done manually. Follow the instrument manufacturer's recommendations to achieve the inert gas environment. Allow sufficient stabilization time before analysis. Fused pellet standards and samples may be analyzed using either a vacuum or helium environment. Line intensities will be slightly higher using a vacuum environment.

NOTE 3—**Caution:** Care must be taken to assure that a vacuum environment is not chosen with liquid samples. Analyze standards and samples under the same environment.

9.2 *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 determined by the user for his instrument and choice of x-ray tube. Allow sufficient stabilization time prior to analysis.

10. Calibration and Standardization

10.1 Internal Standard Solution:

10.1.1 Weigh 45 g of the internal standard compound chosen for uranium and 5 g of the internal standard compound chosen for gadolinium into a beaker. Cover with a minimum amount of water. Add concentrated nitric acid slowly.

NOTE 4—For yttrium oxide and samarium oxide, the reaction will be slow and may require heating. If strontium carbonate is used for uranium, the reaction will be vigorous. The strength of the internal standard solution may be changed to achieve optimum excitation with the equipment being used. The exact concentration of the internal standard solution is not critical; however, it is critical that the internal standard solution added to standards and samples be the same.

10.1.2 Heat on a hot plate if necessary to complete the dissolution.

10.1.3 Cool the solution to room temperature, and transfer to a 1000-mL volumetric flask. Filter the solution if necessary. Dilute to volume with water and mix thoroughly.

10.2 Calibration Standards:

10.2.1 Liquid Standards:

10.2.1.1 Prepare a calibration standard for each concentration level by weighing into a beaker the amounts of uranium oxide and gadolinium oxide, which have been ignited according to directions on analysis certificate, given in Table 1.

10.2.1.2 Dissolve the oxide in 25 mL of water and 25-mL concentrated nitric acid. Heat on a hot plate, if necessary to complete the dissolution. Reduce volume to ≈15 mL.

10.2.1.3 When cool, transfer each solution to a properly labeled 25-mL volumetric flask containing the amount of internal standard solution indicated in Table 1.

NOTE 5—The internal standard solution may be added using a dispensing pipet if desired; however, care must be taken to assure that no adjustment to the dispenser is made between use for standards and use for samples.

10.2.1.4 Dilute to volume with water and mix thoroughly.

10.2.2 Pellet Standards:

⁶ *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.

TABLE 1 Uranium Oxide-Gadolinium Oxide Standards

% U ₃ O ₈ ^A	Wt. U ₃ O ₈ (g)	% Gd ₂ O ₃	Wt. Gd ₂ O ₃ (g)	Internal Std (mL)
90	0.9000	10	0.1000	5
91	0.9100	9	0.0900	5
92	0.9200	8	0.0800	5
93	0.9300	7	0.0700	5
94	0.9400	6	0.0600	5
95	0.9500	5	0.0500	5
96	0.9600	4	0.0400	5
97	0.9700	3	0.0300	5
98	0.9800	2	0.0200	5
99	0.9900	1	0.0100	5

^AUse of NBL CRM-129, or the equivalent, is recommended if uranium determination is used for accountability purposes.

10.2.2.1 For each standard, weigh 15 g lithium tetraborate into a labeled crucible suitable for the fusion technique.

NOTE 6—Explanation of the fusion technique is beyond the scope of this guide. Description of the technique may be found in several sources (2,3). Platinum, platinum-gold or graphite crucibles have been found acceptable.

10.2.2.2 Add the amounts of uranium oxide and gadolinium oxide indicated in Table 1.

10.2.2.3 Add the amount of internal standard solution (see 10.1) indicated in Table 1.

NOTE 7—The dry-weight equivalent amount of internal standard compounds may be weighed directly into each crucible in place of internal standard solution. If the solution is used with graphite crucibles, pipette into the center of the crucible. Do not allow the solution to touch the sides of crucible.

10.2.2.4 Fuse in a muffle furnace set at 1000–1100°C until all materials are in solution. The pellet will be clear and without streaks. Mixing while melting is recommended.

NOTE 8—Automatic fusers are available and may be substituted, if desired. Follow the manufacturer's operating instruction. Fusion in platinum crucibles also may be done over an air-gas burner. If the pellet cracks or recrystallizes while cooling, remelting in the same crucible will not invalidate analysis.

10.3 Instrument Calibration:

10.3.1 Follow the manufacturer's instructions for the instrument in use to obtain intensity data for the uranium L- α , gadolinium L- α and the internal standard lines for each standard.

10.3.2 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.

10.3.3 Calculate the analyte/internal standard ratios from the data obtained in 10.3.1. Calculate a calibration curve using these ratios. The calibration curve will normally be a straight line of form:

$$Y = mX + b \quad (1)$$

where:

Y = concentration of analyte (U or Gd),

X = analyte/internal standard ratio,

m = slope of line, and

b = intercept of straight line.

11. Procedure

11.1 Sample Preparation (Liquid):

11.1.1 Mix the powder or grind pellet to ensure homogeneity. Weigh, to the nearest 0.1 mg, a 1.00-g portion of the sample into a beaker or flask. Duplicate aliquots may be required to meet site or customer quality assurance requirements.

11.1.2 Dissolve in 1+1 (volume/volume) HNO₃. Heat on hot plate, if necessary, to achieve complete dissolution.

11.1.3 Cool and transfer into a 25-mL volumetric flask containing the internal standard solution.

11.1.4 Dilute to volume with water and mix thoroughly.

11.2 Sample Preparation (Fusion):

11.2.1 Mix the powder or grind pellet to ensure homogeneity.

11.2.2 Weigh, to the nearest 0.1 mg, a 1.00-g portion of the sample into fusion crucible containing 15 g LiTB. Duplicate aliquots may be required to meet site or customer quality assurance requirements.

11.2.3 Add the internal standard(s) for the analytes (see Note 6).

11.2.4 Place the crucibles in a muffle furnace set at 1100°C and fuse until all materials are in solution (see Note 7).

11.2.5 When cool, label the pellets or place in labeled boxes for identification.

11.3 Counting the Sample:

11.3.1 Set the x-ray spectrometer to the conditions noted in 10.3.2. If the analytical conditions are controlled by computer, start the computer according to manufacturer's instructions for the software in use.

11.3.2 For liquid samples, shake each flask to mix thoroughly. Fill the liquid sample cup with the recommended amount of liquid for the instrument in use.

11.3.3 Following manufacturer's instrumental instructions, obtain intensities for the analyte and the internal standard lines.

11.3.4 Calculate the analyte concentration using the calibration curves generated in 10.3. Weight corrections must be added if the sample weight is not 1.0000 g.

12. Precision and Bias

12.1 There is no readily available certified material (uranium oxide-gadolinium oxide powder/pellet) for this guide; however, control samples of 93 % uranium oxide (U₃O₈) and gadolinium oxide were prepared by weighing 0.9300 g U₃O₈ and 0.0700 g Gd₂O₃ and dissolving, or fusing, or both, as described in Section 11. Twelve determinations of uranium oxide and gadolinium oxide over a three-month period gave an average of 93.16 % U₃O₈ and 7.00 % Gd₂O₃ by the fusion process with a relative standard deviation of 0.27 % and 0.64 %, respectively. The same number prepared as liquid gave an average of 92.98 % U₃O₈ and 6.99 % Gd₂O₃ with a relative standard deviation of 0.37 % and 0.68 %, respectively.

12.2 The t-test for bias showed no statistically significant bias in the data.

13. Keywords

13.1 gadolinium oxide; uranium oxide; x-ray fluorescence; XRF

REFERENCES

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- (3) Tertian, R. and Claisse, F., *Principles of Quantitative X-Ray Fluorescence Analysis*, Heyden and Son, London, Philadelphia and Rheine, 1982.
- (4) Available from the U.S. Department of Energy, New Brunswick Laboratory, D 350, 9800 South Cass Avenue, Argonne, IL 60439, ATTN: Reference Material Sales.
- (5) NBS Handbook 111, *Radiation Safety for X-Ray Diffraction and X-ray Fluorescence Analysis Equipment* U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899.

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