



## Standard Test Method for Determination of Sulfur in Uranium Oxides and Uranyl Nitrate Solutions by X-Ray Fluorescence (XRF)<sup>1</sup>

This standard is issued under the fixed designation C 1296; 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 covers the sample preparation and analysis by X-ray fluorescence (XRF) of sulfur in uranium oxides and uranyl nitrate solutions.

1.2 This test method is valid for those solutions containing 100 to 500  $\mu\text{g}$  sulfur/mL. Higher concentrations may be measured by appropriate dilutions.

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.* See Section 9 and Note 1 for specific hazards statements.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

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

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

C 982 Guide for Selecting Components for Generic Energy-Dispersive X-Ray Fluorescence (XRF) Systems for Nuclear-Related Material, Analysis<sup>2</sup>

C 1118 Guide for Selecting Components for Wavelength-Dispersive X-Ray Fluorescence (XRF) Systems<sup>2</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

E 135 Terminology Relating to Analytical Atomic Spectroscopy<sup>4</sup>

#### 2.2 Other Documents:

NBS Handbook 111, *Radiation Safety for X-Ray Diffraction and X-Ray Fluorescence Analysis Equipment*<sup>5</sup>

### 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 Solution standards containing 0 (blank) to 500  $\mu\text{g}$  sulfur

per mL in a matrix of 0.08 g uranium per mL are placed in the liquid sample holder of an X-ray spectrometer and exposed to an X-ray beam capable of exciting the sulfur K-alpha emission line. The intensity values obtained from these standard solutions are used to calibrate the X-ray spectrometer.

4.2 Either wavelength-dispersive or energy-dispersive X-ray fluorescence systems may be used for this analysis.

### 5. Significance and Use

5.1 This test method is applicable to uranium solutions, uranium oxides, and other uranium compounds that are soluble in nitric acid and contain sulfur up to 5000  $\mu\text{g}/\text{g}$  sample. This test method can be used to determine conformance to specification for uranium ore concentrate (see Specification C 967), uranium trioxide ( $\text{UO}_3$ ), uranium dioxide ( $\text{UO}_2$ ), and uranyl nitrate (see Specification C 788). For uranium solutions, the uranium content should be between 0.07 g/mL and 0.10 g/mL.

### 6. Interferences

6.1 Sulfur X-rays (53.7 nm) are extremely soft (long wavelength) X-rays and are easily absorbed by uranium; therefore, it is important to match the uranium concentration in the standards and test samples to compensate for this absorption effect since no internal standard is used in this test method. Even if the sulfur content of the sample is in the correct range, errors can result if the uranium concentration is not matched.

6.2 As with all XRF methods, the choice of X-ray tube target is important. Because of the line overlap of molybdenum and sulfur, molybdenum target tubes are not recommended. Chromium, rhodium, and scandium target tubes have been found to be satisfactory.

6.3 The presence of impurities such as zirconium and cobalt also should be considered for their interfering effects. Such considerations are outside the scope of this test method.

### 7. Apparatus

7.1 *X-ray spectrometer*—See Specification C 982 or Guide C 1118 for the selection of the X-ray spectrometer. This test method is valid for either energy-dispersive or wavelength-dispersive systems. The system must be equipped with an inert gas flush system (normally helium). (See Section 11 on Preparation of Apparatus.)

7.2 *Sample cups*—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

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

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 03.05.

<sup>5</sup> Available from the U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899.

such analyses; such cups decrease the likelihood of contamination between samples.

7.2.1 Polypropylene film has been used successfully as the film window for such cups. Tests should be performed to determine the serviceability of any film chosen before insertion into the instrument. Care must be taken to ensure that the film chosen does not excessively or irreproducibly affect the net intensity of the sulfur X-rays.

## 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 of Analytical Reagents of the American Chemical Society where such specifications are available.<sup>6</sup> 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 mean reagent water conforming to Specification D 1193.

8.3 *Ammonium sulfate* ( $\text{NH}_4)_2\text{SO}_4$ .

8.4 *Hydrogen peroxide* ( $\text{H}_2\text{O}_2$ ), 30 %.

8.5 *Nitric Acid* ( $\text{HNO}_3$ ), concentrated (70 %).

8.6 *Nitric Acid*, 1 + 1—dilute equal volumes of nitric acid with water.

8.7 *Uranium oxide* ( $\text{U}_3\text{O}_8$ ), NBL CRM-129<sup>7</sup> or equivalent.

## 9. Hazards

9.1 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 (see NBS Handbook 111<sup>5</sup>).

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 equipment, or system, performance characteristics should be reviewed prior to use of this test method.

## 10. Preparation of Apparatus

10.1 *Chamber environment*:

10.1.1 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 atmo-

sphere (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.

NOTE 1—**Caution:** Take care to ensure that a vacuum environment is not chosen with liquid samples.

10.2 *X-ray power supply*:

10.2.1 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.

## 11. Calibration and Standardization

11.1 *Uranium Stock Solution, 0.20 g/mL*:

11.1.1 Weigh into a 600-mL beaker 118.01 g of uranium oxide (NBL CRM-129 or equivalent) that has been dried according to the instructions received with the material (each batch has the conditions under which its value was determined).

11.1.2 Dissolve each batch in 150 mL of 1 + 1 nitric acid and 5 mL of 30 % hydrogen peroxide. Heat on a hot plate, if necessary.

11.1.3 Cool the solution and transfer to a 500-mL volumetric flask. Dilute to volume with water and mix thoroughly.

11.2 *Sulfur Stock Solutions*:

11.2.1 Weigh into 400-mL beakers the amounts of ammonium sulfate shown in Table 1 for each of the sulfur stock solutions.

11.2.2 Dissolve in water and dilute to the volume shown in Table 1. Mix thoroughly.

11.2.3 Store in appropriately labeled glass bottles.

11.3 *Sulfur Calibration Standards*:

11.3.1 Label a 100-mL volumetric flask for each standard desired (see Table 2).

11.3.2 Pipette the amount of uranium stock solution and the amount of appropriate sulfur stock solution into each volumetric flask as shown in Table 2.

11.3.3 Dilute to volume with water and mix thoroughly.

11.4 *Instrument Calibration*:

11.4.1 Follow manufacturer's instructions for the instrument in use to obtain net intensity data for the sulfur K-alpha line for each standard.

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

11.4.3 Calculate a curve (concentration versus net intensity) using those standards analyzed in 11.4.1. The curve will have the form

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

TABLE 1 Sulfur Stock Solutions

Stock value ( $\mu\text{g/mL}$ )	Ammonium sulfate (g)	Final volume (mL)
100	0.2061	500
500	2.0606	1000
1000	2.0606	500

<sup>6</sup> *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

<sup>7</sup> Available from the U.S. Department of Energy, New Brunswick Laboratory, D350, 9800 South Cass Avenue, Argonne, IL 60439, ATTN: Reference Material Sales.

**TABLE 2 Sulfur Calibration Standards**

Standard value ( $\mu\text{g/mL}$ )	mL pipetted	S stock used ( $\mu\text{g/mL}$ )	U stock (mL)
Blank	0	0	40
10	10	100	40
20	20	100	40
25	25	100	40
50	10	500	40
75	15	500	40
100	20	500	40
200	20	1000	40
250	25	1000	40
400	40	1000	40
500	50	1000	40

where:

- $Y$  =  $\mu\text{g S}$ , per mL,  
 $m$  = slope of calibration curve,  
 $I$  = net intensity of sulfur peak, and  
 $b$  = intercept of calibration curve.

## 12. Procedure

### 12.1 Sample Preparation:

#### 12.1.1 Uranium Oxides:

12.1.1.1 Weigh, to the nearest 0.1 mg, duplicate aliquots of the samples into 250-mL beakers. An aliquot weight of 5.00 g is satisfactory.

12.1.1.2 Dissolve in  $\sim 20$  mL 1 + 1 nitric acid; heat (if necessary) to complete the dissolution.

12.1.1.3 Transfer to an appropriately labeled 50-mL volumetric flask.

12.1.1.4 Cool to room temperature, dilute to volume with water and mix thoroughly.

#### 12.1.2 Uranium Solutions:

12.1.2.1 Label duplicate 50-mL volumetric flasks for each sample. (Measure the tare weight of each flask if answers are desired on a weight basis.)

12.1.2.2 Pipette into each flask the amount of sample necessary to matrix match the uranium content of sample and standards. (Measure the gross weight of sample and flask if answers are desired on a weight basis.)

12.1.2.3 Dilute to volume with water and mix thoroughly.

#### 12.2 Counting the Sample:

12.2.1 Set the X-ray spectrometer to the conditions noted in 11.4.2. If the analytical conditions are controlled by computer, start the computer according to the manufacturer's instructions for the software in use.

12.2.2 Shake the contents of 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 manufacturer's instrumental instructions, obtain the net intensity for the sulfur K-alpha line.

12.2.4 Calculate the sulfur concentration of the solutions in the flask.

## 13. Calculation of Results

13.1 Sample calculation may be carried out by the computer software with the instrument or may be done manually. The equation will have the form:

$$Y = [(mI + b) \times 50]/W \quad (2)$$

where:

- $Y$  =  $\mu\text{g S}$ , per g (or mL if on volume basis) sample,  
 $m$  = slope of calibration curve (see 11.4.3),  
 $I$  = net intensity of sulfur peak (see 12.2.3),  
 $b$  = intercept of calibration curve (see 11.4.3),  
 $W$  = weight (mL if on volume basis) of sample used, and  
 $50$  = dilution volume.

## 14. Precision and Bias

14.1 There is no certified reference material (sulfur in uranium solutions) for this test method. However, a solution of ammonium sulfate (see 8.3) and uranium oxide (NBL CRM-129, see 8.6) was prepared. Aliquots of this solution were prepared by eight different technicians and analyzed over a 30-month period. The average of 16 determinations was 296  $\mu\text{g S/g}$  solution (theoretical value 300  $\mu\text{g S/g}$  solution) with a relative standard deviation of 3.9 % (see Table 3 for data). No significant bias was found.

## 15. Keywords

15.1 sulfur; uranium oxides; uranium solutions; X-ray fluorescence (XRF)

**TABLE 3 Sulfur in Uranium Solutions<sup>A</sup>**

Observed Values <sup>B</sup> ( $\mu\text{g S/g}$ )
307
294
298
310
288
299
287
318
286
297
276
286
307
304
298
281
$X = 296.00$
$s = 11.48$

<sup>A</sup>Theoretical 300  $\mu\text{g S/g}$  solution.

<sup>B</sup>Data obtained by eight different technicians over a 30-month period.

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