



Standard Test Method for Determination of Uranium in Mineral Acids by X-Ray Fluorescence¹

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1. Scope

1.1 This test method covers the steps necessary for the preparation and analysis by X-ray fluorescence (XRF) of mineral acid solutions containing uranium.

1.2 This test method is valid for those solutions containing 0.05 to 20 g uranium/L as presented to the spectrometer. Higher concentrations may be covered by appropriate dilutions.

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 element or that this contamination has been corrected for mathematically whenever present. Such corrections are not addressed in this test method. Care must also be taken that the choice of internal standard and sample medium are compatible; that is, do not use yttrium with solutions containing HF or strontium with those having H₂SO₄. Alternatively a scatter line may be used as internal standard.²

1.4 The values stated in SI units are to be regarded as the standard.

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 8 and Note 1.

2. Referenced Documents

2.1 ASTM Standards:

C 982 Guide for Selecting Components for Energy Dispersive X-Ray Fluorescence (XRF) Systems³

C 1118 Guide for Selecting Components for Wavelength-Dispersive X-Ray Fluorescence (XRF) Systems³

D 1193 Specification for Reagent Water⁴

E 135 Terminology Relating to Analytical Chemistry for

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² Andermann, George, and Kemp, J. W., "Scattered X-Rays as Internal Standards in X-ray Spectroscopy," *Analytical Chemistry*, Vol 20(8), 1958.

³ *Annual Book of ASTM Standards*, Vol 12.01.

⁴ *Annual Book of ASTM Standards*, Vol 11.01.

Metals, Ores, and Related Materials⁵

2.2 Other Document:

NBS Handbook 111, *Radiation Safety for X-Ray Diffraction and X-Ray Fluorescence Analysis Equipment*⁶

3. Terminology

3.1 Definitions:

3.1.1 See Terminology E 135 for definitions of terms applicable to this test method.

4. Summary of Test Method

4.1 Solution standards containing 0.025 g/L uranium to 20 g/L uranium and an appropriate internal standard (usually either yttrium or strontium) 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-alpha emission line and the appropriate emission line for the internal standard (usually the K-alpha line). 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.

5. Significance and Use

5.1 This test method is applicable to aqueous solutions of uranium containing 0.05 to 20 g uranium per litre of solution presented to the spectrometer.

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. This test method is valid for either energy-dispersive or wavelength-dispersive systems.

6.2 Sample Cups:

6.2.1 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 between samples.

⁵ *Annual Book of ASTM Standards*, Vol 03.05.

⁶ Available as a photocopy from the U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899.

6.2.2 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 insertion into the instrument.

6.3 *Solution Dispenser*—The dispenser for the internal standard solution should be capable of reproducibly dispensing the internal standard to a level of 0.5 % relative standard deviation of the volume dispensed.

7. Reagents and Materials

7.1 *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.⁷ 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 *Ferric Nitrate*, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

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

7.5 *Strontium Carbonate*, SrCO_3 .

7.6 *Uranium Oxide*, U_3O_8 , NBL CRM-129⁸ (or equivalent).

7.7 *Yttrium Oxide*, Y_2O_3 .

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, or a second knowledgeable person present during such operation. (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 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 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.

NOTE 1—**Caution:** Allow sufficient stabilization time before analysis. Care must be taken to ensure that a vacuum environment is not chosen with liquid samples.

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* (25.0 g/L):

10.1.1 Weigh 25 g of the chosen internal standard compound into an 800-mL beaker. Cover with water. Add concentrated nitric acid slowly. For yttrium oxide the reaction will be slow and may require heating. For strontium carbonate, the reaction will be vigorous.

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 *Impurity Stock Solution (Optional):*

10.2.1 Weigh 50 g of reagent grade ferric nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, into a 600-mL beaker.

10.2.2 Dissolve the crystals in 200 mL of water and 50 mL of concentrated nitric acid.

10.2.3 When cool, transfer the solution to a 1000-mL volumetric flask and dilute to volume with water.

10.3 *Uranium Calibration Standards:*

10.3.1 Prepare a uranium standard for each concentration level by weighing into a 150-mL beaker the amounts of uranium oxide given in Table 1.

10.3.2 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.

10.3.3 When cool, transfer each solution to a properly labeled 100-mL volumetric flask. Add the amount of internal standard solution and impurity solution (if desired) indicated in Table 1 to each volumetric flask.

NOTE 2—The internal standard solution may be added using a dispensing pipet if desired. However, care must be taken to ensure that no adjustment to the dispenser is made between use for standards and use for samples.

10.3.4 Dilute to volume with water and mix thoroughly.

10.4 *Instrument Calibration:*

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

10.4.2 Exercise care 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.

10.4.3 Calculate the uranium/internal standard ratios from

⁷ *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.

⁸ Available from the U.S. Department of Energy, New Brunswick Laboratory, D350, 9800 South Cass Avenue, Argonne, IL 60439, Attn: Reference Material Sales.

TABLE 1 Uranium Calibration Standards

Concentration, (g/L)	Weight U ₃ O ₈ (CRM-129) ^A	Internal Standard, (mL)	Impurity Solution, (mL) ^A	Final Volume, (mL)
0.025	0.00295	4	5	100
0.050	0.00590	4		100
0.100	0.01180	4	5	100
0.500	0.05898	4		100
1.000	0.11796	4	5	100
1.250	0.14745	4		100
1.500	0.17694	4	5	100
1.750	0.20644	4		100
2.00	0.23593	4	5	100
4.00	0.47185	4		100
6.00	0.70778	4	5	100
8.00	0.94370	4		100
10.00	1.17963	4	10	100
12.00	1.41556	4		100
14.00	1.65148	4	10	100
16.00	1.88741	4		100
18.00	2.12333	4	10	100
20.00	2.35926	4		100

^A Weights will need to be adjusted for the purity of the uranium reference material used. See the certification accompanying the material. Weights indicated are for NBL CRM-129 (no longer available; use NBL CRM-129 or equivalent). Use of the impurity solution is optional.

the data obtained in 10.4.1. 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. A third-order equation may be used if the software allows. All 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 procedure. Explanations of correction models and inter-element effects are found in several sources.^{9,10}) The quadratic equation will have the form:

$$Y = DX^3 + CX^2 + BX + A \quad (1)$$

where:

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

10.4.4 For self-absorption the equation will have the form:

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

where:

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

NOTE 3—Units used for Y in Eq 1 and Eq 2 may be changed as appropriate for the software used.

11. Procedure

11.1 Sample Preparation:

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

NOTE 4—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 standard.

11.1.2 Obtain the gross weight of the sample and flask. (If an answer on a weight basis is not desired, this may be omitted.)

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

11.2 Counting the Sample:

11.2.1 Set the X-ray spectrometer to the conditions noted in 10.4.1. If the analytical conditions are controlled by computer, start the computer according to manufacturer's instructions for the software in use.

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

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

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

NOTE 5—Additional factors, such as volume, weight, isotopic correction, secondary dilutions, may be included with the listed equations to obtain results on the proper basis for the user's application.

12. Precision and Bias

12.1 There is no readily available certified material (uranium dissolved in mineral acid) for this test method. However, two solutions of NBL CRM-114¹¹ (U₃O₈) were prepared.

12.1.1 The first solution, with a theoretical value of 0.03916 g uranium per g solution (g U/g solution), corresponding to ~42.4 g U/L, was prepared by dissolving ~50 g (weighed to the nearest 0.1 mg) as outlined in 10.3.4 and transferring to a tared 1000-mL volumetric flask. This solution was diluted to volume with water, mixed thoroughly and weighed. Aliquots of this solution were prepared by five different technicians and analyzed on two different X-ray spectrometers over a four-month period. The average of 30 determinations (see Table 2 for data) was 0.03923 g U/g solution, a relative difference of 0.27 % from the theoretical value, with a relative standard deviation of 0.53 %

12.1.2 The second solution, with a theoretical value of 0.000984 g uranium per gram solution, corresponding to ~0.1 g U/L, was prepared by dissolving ~0.59 g (weighed to the nearest 0.1 mg) as outlined in 10.3.4 and transferring to a tared 500-mL volumetric flask. This solution was diluted to volume with water, mixed thoroughly and weighed. Aliquots of this solution were prepared by nine different technicians and analyzed on two different X-ray spectrometers over a seven-month period. The average of 30 determinations (see Table 3 for data) was 0.000987 g U/g solution, a relative difference of 0.35% from the theoretical value, with a relative standard deviation of 1.79%.

12.1.3 The t-test for bias as described by Youden¹¹ was

⁹ Bertin, Eugene P., *Introduction to X-Ray Spectrometric Analysis*, Plenum Press, New York and London, 1978.

¹⁰ Tertian, R., and Claisse, F., *Principles of Quantitative X-Ray Fluorescence Analysis*, Heyden and Son, London, Philadelphia, and Rheine, 1982.

¹¹ No longer available; see Table 1, Footnote A.

applied to each set of data. It indicated no significant bias in either set.

TABLE 2 Data for Solution #1

NOTE 1—Uranium in Mineral Acid by XRF
Theoretical value 0.03916 g U/g solution.

0.039178
0.039669
0.039574
0.039480
0.038924
0.039356
0.038952
0.038976
0.039405
0.038952
0.039313
0.038925
0.039126
0.039138
0.039213
0.039356
0.039331
0.039418
0.039241
0.039190
0.039640
0.039210
0.038910
0.039133
0.039320
0.039198
0.039291
0.039100
0.039143
0.039123
$\bar{X} = 0.039226$
$s = 0.000208$

TABLE 3 Data for Solution #2

NOTE 1—Uranium in Mineral Acid by XRF
Theoretical value 0.000984 g U/g solution.

0.0010027
0.001019
0.001006
0.00995
0.000959
0.00998
0.000987
0.000994
0.000989
0.000977
0.000988
0.000965
0.000985
0.000983
0.000982
0.000948
0.000984
0.000962
0.000974
0.001017
0.000996
0.000994
0.000994
0.000968
0.000979
0.001002
0.000976
0.001002
0.000989
0.000984
$\bar{X} = 0.000987$
$s = 0.000018$

13. Keywords

13.1 mineral acid; uranium; X-ray fluorescence (XRF)

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