Designation: E463 – 14a

Standard Test Method for Determination of Silica in Fluorspar by Silico-Molybdate Visible Spectrophotometry[1]

This standard is issued under the fixed designation E463; 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 determination of silica in fluorspar in concentrations from 0.5 % to 10 %.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

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

E276 Test Method for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Finer for Metal-Bearing Ores and Related Materials

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E135.

4. Summary of Test Method

4.1 The sample is fused with anhydrous sodium borate and the melt is dissolved in dilute HCl. Silica is determined photometrically after extraction of the silico-molybdate complex with normal butyl alcohol. Photometric measurement of the extract is made at 400 nm.

5. Significance and Use

5.1 This test method is intended as a referee method for compliance with compositional specifications for impurity content. It is assumed that all who use this procedure will be trained analysts capable of performing common laboratory practices skillfully and safely. It is expected that work will be performed in a properly equipped laboratory and that proper waste disposal procedures will be followed. Follow appropriate quality control practices such as those described in Guide E882.

6. Interferences

6.1 The elements ordinarily present in commercial fluorspars do not interfere in this test method.

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 on Analytical Reagents of the American Chemical Society where such specifications are available.[3] 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 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type I or II of Specification D1193. Type III or IV may be used if they effect no measurable change in the blank or sample.

7.3 *Ammonium Molybdate Solution* (100 g/L)—Dissolve 100 g of ammonium-heptamolybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in 500 mL of water, dilute to 1 L, and mix.

7.4 *Silica* (SiO_2)—Heat pure silicic acid in a platinum crucible to expel combined water by gradually increasing

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[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 Ores, Concentrates, and Related Metallurgical Materials.

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[2] 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.

[3] *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 the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

temperature to 1050 °C. Maintain at 1050 °C for at least 5 min. Cool to room temperature in a desiccator.

7.5 *Sodium Borate*($Na_2B_4O_7$)—Anhydrous powder, low-silica content.

NOTE 1—If low silica sodium borate is not available, prepare the reagent as follows: Transfer 247 g of boric acid to a large platinum dish. Expel water by gradually increasing the temperature to about 1000 °C. When effervescence ceases, gradually introduce 106 g of sodium carbonate into the molten mass. Maintain at a temperature of about 1000 °C until a clear melt is obtained.

8. Hazards

8.1 For precautions to be observed in this method, refer to Practices E50.

9. Sample Preparation

9.1 The analytical sample shall be pulverized, if necessary, to pass a 150-µm sieve (see Test Method E276). Dry at 105 °C to 110 °C for a minimum of 1 h.

10. Procedure

10.1 Transfer 7 g of $Na_2B_4O_7$ to each of six 25-mL platinum crucibles. Form a cavity in the center of the flux.

10.2 Into Crucibles 1 and 2, weigh 0.100 g to 1 g of the dry sample. Choose sample weights to provide from 5 mg to 10 mg of SiO_2.

10.3 Into Crucibles 3 and 4, weigh 10.0 mg of SiO_2 reagent.

10.4 Crucibles 5 and 6 serve as blanks.

10.5 Mix the contents of the crucibles with a platinum or polyethylene rod. Transfer adhering particles to the crucible.

10.6 Cover the crucible and heat gently until moisture is expelled. Increase the temperature until complete fusion results.

NOTE 2—A Meker burner or a muffle furnace maintained at 1000 °C may be used for this purpose.

10.7 Transfer the platinum crucible and cover to a 400-mL polyethylene or TFE-fluorocarbon beaker containing 150 mL water and 25 mL HCl (1 + 1). Cool the crucible for about 3 s, then pour the melt dropwise into the beaker so that most of the flux settles on the crucible cover (Note 3). Transfer the cooled crucible to the beaker. Cover the beaker with a polyethylene sheet and secure it to the beaker with a rubber band.

NOTE 3—Hold the crucible while cooling to avoid contamination problems. This prevents damage to the beaker.

10.8 Place the beaker on a steam bath and swirl occasionally until the melt is completely dissolved (Note 4). Cool, remove and rinse the platinum crucible and cover, and add the washings to the beaker. Transfer the solution to a 250-mL volumetric flask. Rinse the beaker and add the rinsings to the flask. Dilute to volume, mix, and examine the solution for any insoluble material (Note 4). Transfer the solution to a dry polyethylene bottle.

NOTE 4—Complete dissolution of the melt requires about 2 h. In cases of incomplete dissolution, a new sample must be taken.

10.9 Transfer 50-mL aliquots of the blank and sample solutions to 200-mL polyethylene or TFE-fluorocarbon beakers.

10.10 Transfer (10.0, 20.0, 30.0, 40.0, and 50.0)-mL aliquots of the standard solutions to 200-mL polyethylene or TFE-fluorocarbon beakers. Dilute, if necessary, to a 50-mL volume with the remaining blank solution.

NOTE 5—Since commercially available $Na_2B_4O_7$ frequently contains appreciable amounts of silica, each standard and sample solution must contain the same amounts of this reagent. The dilution of the aliquots to a 50-mL volume should, therefore, be carried out using a buret.

10.11 Determine the pH of the blank, standard, and sample solutions using a pH meter. If the pH of the solutions lies between 0.5 and 0.9 and within 0.1 units of each other, proceed to 10.12. If the pH lies outside these parameters, adjust the pH with HCl (1 + 1).

NOTE 6—Accurate pH adjustments are essential for maximum color development and color stability.

10.12 Add, while stirring, 10 mL of ammonium molybdate solution. Allow 10 min for color development, then dilute to 100 mL. Transfer the solution to a 250-mL separatory funnel and add 25 mL of cool H_2SO_4 (1 + 1).

10.13 Add 75 mL of normal butyl alcohol and shake vigorously for 1 min. Allow the phases to separate and discard the acid (lower) layer. Add 20 mL of H_2SO_4 (1 + 99) to the

TABLE 1 Precision Data

Average Concentration,[A] %	Standard Deviation, %	Relative Standard Deviation,[B] %	Number of Participating Laboratories
0.71	0.03	4.2	6
2.16	0.11	5.1	7
6.94	0.10	1.4	6

[A] Each concentration represents a different grade of fluorspar.

[B] Relative Standard Deviation (RSD), in this test method is calculated as follows:

$$\text{RSD} = \left(100/\bar{X}\right)\sqrt{\sum d^2/(n-1)} \quad (2)$$

where:

$\bar{X}$ = average concentration, %,
d = difference of the determination from the mean, and
n = number of determinations.

separatory funnel, shake for 30 s, allow the phases to separate, and discard the acid layer. Repeat the washing twice more.

10.14 Transfer the butyl alcohol phase to a dry 100-mL volumetric flask. Wash the separatory funnel twice with 1-mL or 2-mL portions of butyl alcohol, and add the washings to the volumetric flask. Add 1 mL of ethyl alcohol, dilute to volume with butyl alcohol, and mix.

11. Photometry

11.1 *Concentration Range:*

11.1.1 The recommended concentration range is from 0.2 mg to 2.0 mg of silica per 100 mL of solution, using a 1-cm cell.

NOTE 7—Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagent used.

11.2 Adjust the photometer to the initial setting using water as the reference solution. While maintaining this setting, take photometric readings of the blank, standard, and sample solutions using a light band centered at approximately 400 nm.

11.3 *Stability of Color:*

11.3.1 After the addition of the ammonium molybdate, color is fully developed within 10 min and is stable after extraction with butyl alcohol

12. Preparation of Calibration Curve

12.1 Subtract the average absorbance of the blank solution from the average absorbance of each standard solution and plot the net absorbances against milligrams of silica per 100 mL of solution.

13. Calculation

13.1 Subtract the average absorbance of the blank solutions from absorbances of the sample solutions. Convert the net absorbance of the sample solution to milligrams of SiO_2 by means of the calibration curve. Calculate the percentage of SiO_2 as follows:

$$\text{Silica, \%} = A/(B \times 10) \quad (1)$$

A = silica found in the aliquot used, mg, and
B = sample represented by the aliquot, g.

14. Precision and Bias

14.1 *Precision*—Table 1 indicates the precision of the test method between laboratories.

14.2 *Bias*—No information on the accuracy of this test method is known. The accuracy of this test method may be judged by comparison of accepted values for standard reference materials with the mean determined through interlaboratory testing.

15. Keywords

15.1 fluorspar; photometric; silica; silico-molybdate magnesium