



## Standard Test Method for Silica in Cellulose<sup>1</sup>

This standard is issued under the fixed designation D 2438; 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 determination of silica in cellulose and is applicable to all pulps. It is designed to measure up to 200  $\mu\text{g}$  of silica ( $\text{SiO}_2$ ) in 50 mL of solution.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems 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 Document

2.1 *ASTM Standard:*  
D 1348 Test Methods for Moisture in Cellulose<sup>2</sup>

### 3. Summary of Test Method

3.1 The cellulose is ashed and hydrochloric acid (HCl)-soluble compounds are extracted. The ash is then fused with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) to form soluble silicates. The salt is dissolved, acidified, and converted to a yellow-colored complex of silicomolybdic acid. The complex is reduced to silicomolybdenum blue by treatment with aminonaphthol sulfonic acid plus sodium sulfite ( $\text{Na}_2\text{SO}_3$ ). The concentration of silica is determined spectrophotometrically. When compared with gravimetric procedures for silica, the spectrophotometric method has better specificity, sensitivity, and precision.

### 4. Significance and Use

4.1 Low-silica specifications are required by viscose rayon processors. The general claims are that (1) silica may affect the filterability of viscose by forming insoluble silicates, (2) silica and the formation of insoluble silicates can contribute to spinneret crater formation during spinning (deposits which build up around spinneret holes to deform yarn cross section and ultimately block the holes; these deposits occur on the acid-wet face), and (3) particulate silica can blind spinneret holes or pass through and cause partial or complete discontinuity in yarn.

### 5. Apparatus

5.1 *Dish*, platinum.

5.2 *Stirring Rod*, plastic.

5.3 *Spectrophotometer*, for measuring absorbance at 700 nm.

### 6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>3</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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean distilled water.

6.3 In some cases, it may be necessary to select specific lots of chemicals to avoid high blank corrections. Minimize the use of glassware; particularly avoid holding alkaline solutions in glassware. Store all reagents in plastic bottles.

6.4 *1-Amino-2-Naphthol-4-Sulfonic Acid Solution*—Dissolve 7 g of anhydrous sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) in 100 mL of water. Add 1.5 g of 1-amino-2-naphthol-4-sulfonic acid. Dissolve 90 g of sodium bisulfite ( $\text{NaHSO}_3$ ) in 800 mL of water. Blend the two solutions and filter through a double thickness of an acid-washed general purpose filter paper into a 1000-mL volumetric flask. Dilute to volume.

NOTE 1—Some batches of commercial aminonaphtholsulfonic acid are incompletely soluble or produce dark-colored solutions. These are not satisfactory for silica analysis. The reagent solution should always be discarded if a dark color appears with age. Stability of the solution is improved by refrigeration and protection from light.

6.5 *Ammonium Molybdate Solution*—Dissolve 100 g of ammonium heptamolybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{23}\cdot 4\text{H}_2\text{O}$ ) in approximately 800 mL of water. Adjust to a pH of 8 by adding sodium hydroxide (NaOH). Dilute to 1000 mL.

NOTE 2—If necessary, filter the ammonium molybdate solution. With the pH adjusted to 8, the reagent is stable indefinitely. If the pH adjustment is not made, a precipitate will form on standing and the solution must be discarded. The added NaOH can be a significant source of  $\text{SiO}_2$  contamination. Use a 50 % NaOH solution that has not been in glassware. About 35 mL of this solution are required for 1000 mL of molybdate solution.

6.6 *Hydrochloric Acid Solution A*—Dilute 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of water. Determine the volume of this acid that is required to adjust the pH of a solution of 1 g of sodium

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 15.04.

<sup>3</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY and the "United States Pharmacopeia."

carbonate ( $\text{Na}_2\text{CO}_3$ ) in 15 mL of water of 4.

6.7 *Hydrochloric Acid, Solution B*—Dilute 150 mL of concentrated HCl to 1000 mL with water. Determine the volume of this acid that is required to adjust the pH of a solution of 1 g of  $\text{Na}_2\text{CO}_3$  in 15 mL of water to 4.

6.8 *Oxalic Acid Solution* (100 g/L)—Dissolve 10 g of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) in water and dilute to 100 mL.

6.9 *Silica, Standard Solution*—The standard solution may be prepared from  $\text{SiO}_2$  or silicic acid ( $\text{H}_2\text{SiO}_3$ ). In either case, add about 0.5 g of material to a platinum crucible and dehydrate by heating in a muffle furnace at 1050 to 1100°C, for 1 h. Cool in a desiccator and, without delay, weigh 0.1000 g of the dry sample into a platinum crucible. Add 1.00 g of  $\text{Na}_2\text{CO}_3$  to the dish, and fuse in a muffle furnace at 850 to 900°C. Hold in the melted state for at least 5 min and swirl occasionally to ensure complete mixing of the silica and the fused carbonate. Allow to cool, add water to dissolve the melt, and transfer quantitatively to a 1000-mL volumetric flask. Dilute to volume, and transfer to a plastic bottle for storage. Discard after 7 days. The standard solution contains the equivalent of 100  $\mu\text{g}$  of  $\text{SiO}_2/\text{mL}$ .

6.10 *Sodium Carbonate*—Granular solid anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Select a lot that does not contain more than 20 ppm of  $\text{SiO}_2$  by this test method.

## 7. Test Specimen

7.1 Select a specimen weight, on the basis of the anticipated silica level in the pulp, to provide 500  $\mu\text{g}$ , or more, of  $\text{SiO}_2$ . Weigh out a second specimen for determination of moisture in accordance with Test Methods D 1348.

## 8. Procedure

8.1 Weigh the specimen into a platinum dish. Ash in a muffle furnace at  $575 \pm 25^\circ\text{C}$ . Cool the ash, add 10 mL of HCl Solution A, and simmer on a hot plate (under a hood). Continue heating until all of the acid has evaporated and the dry residue has been baked for at least 10 min. Add a small volume of water to dissolve the soluble chlorides. Heat, and stir with a rubber-tipped or plastic stirring rod. Filter through an ashless, medium-speed filter paper and discard the filtrate. Place the filter paper in the original platinum dish, and ignite in the muffle furnace at  $575^\circ\text{C}$ .

8.2 Cool the dish, add 1.00 g of solid  $\text{Na}_2\text{CO}_3$ , and melt in a muffle furnace at 850 to 900°C. Swirl gently to wet all the ash with the melt. Hold in the melted state for 5 to 6 min. Remove the melt from the furnace, allow to cool, and add approximately 15 mL of water. Stir with a plastic rod until solution is complete, transfer quantitatively, without filtration, to a 50-mL flask, and dilute to volume. There may be a small amount of insoluble carbonate which will settle rapidly. Without delay, transfer an aliquot that is expected to contain not more than 200  $\mu\text{g}$  of  $\text{SiO}_2$  to a 50-mL volumetric flask. The volume of this aliquot must not exceed 25 mL. Immediately add 5 mL of HCl Solution B plus the calculated volume of HCl Solution A or B that would be required to adjust the amount of carbonate contained in the test aliquot to pH 4. The total volume at this stage must not exceed 35 mL. When small specimen aliquots are used, add water to bring the volume to 25 to 35 mL.

8.3 A reagent blank is required. Prepare for the blank by adding 5 mL of HCl Solution B to approximately 25 mL of

water in a 50-mL volumetric flask.

8.4 For each series of analyses, prepare a color standard equivalent to 200  $\mu\text{g}$  of  $\text{SiO}_2$ . Prepare for the standard by adding 2 mL of the standard silica solution to a 50-mL volumetric flask. Dilute to approximately 25 mL and add 5 mL of HCl Solution B.

8.5 A correction for silica in  $\text{Na}_2\text{CO}_3$  is also required. Fuse 1 g of  $\text{Na}_2\text{CO}_3$  as though it were a specimen. After cooling, dissolve in a small volume of water and transfer to a 50-mL volumetric flask. Immediately add HCl Solution A to adjust to pH 4, then add 5 mL of HCl Solution B. Do not dilute beyond 35 mL. Develop color in this flask as described in 8.6.

8.6 Develop color in the blank,  $\text{Na}_2\text{CO}_3$ , standard, and test solutions as follows:

8.6.1 Add 5 mL of ammonium molybdate solution and allow to stand at room temperature for 20 min.

NOTE 3—A yellow-colored complex of silicomolybdic acid forms at this stage. If this color does not occur in the presence of silica, the pH control is not correct. Solutions must be at a pH of 0.9 to 1 before addition of the ammonium molybdate reagent and a pH of 1.1 to 1.3 following addition of this reagent.

8.6.2 Add 2 mL of oxalic acid solution, followed by 5 mL of amino naphthol reagent, dilute to volume with water, and mix well.

8.6.3 Allow to stand at room temperature for 20 min.

8.7 Within 1 h after color development, read the absorbance of all solutions against the reagent blank with a spectrophotometer at 700 nm.

8.8 Prepare a standard curve of absorbance versus concentration by drawing a straight line through the origin and the observed value of the 200- $\mu\text{g}$  standard. Convert all absorbance values for test solutions to  $\text{SiO}_2$  weight units by reference to this curve.

## 9. Calculation

9.1 Calculate the parts per million of  $\text{SiO}_2$  in the pulp as follows:

$$\text{SiO}_2, \text{ ppm} = [(50A/B) - C]/W$$

where:

$A$  =  $\text{SiO}_2$  in the aliquot,  $\mu\text{g}$ ,

$B$  = aliquot, mL,

$C$  =  $\text{SiO}_2$  in the  $\text{Na}_2\text{CO}_3$ , ppm, and

$W$  = dry specimen, g.

## 10. Report

10.1 Report the result to the nearest part per million. Random replicate determinations should not differ by more than 10 % of the observed value.

## 11. Precision and Bias

11.1 A precision of less than 10 % relative is found by replicate runs by a single analyst.

11.2 No statement of bias can be made as no suitable reference material exists for determining bias.

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