Designation: D8016 – 15

Standard Test Method for Silica, Precipitated, Hydrated—Sears Number[1]

This standard is issued under the fixed designation D8016; 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 is used to determine the number of silanol groups on the surface of silica by titration according to a method as developed by Sears. This test method is suitable for characterizing rubber-grade silicas.

1.2 *Units*—The values stated in SI units are to be regarded as the 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]

D6738 Test Method for Precipitated Silica—Volatile Content

3. Summary of Test Method

3.1 An ion exchange reaction in silica is possible based on the acidic character of the surface silanol groups. According to Sears,[3] it is possible to determine the surface area of colloidal silica on the basis of this ion exchange mechanism, after certain preliminary treatments, by titration with a basic solution. The initial preliminary treatment step consists of exposure of the silica to a sufficiently concentrated solution of sodium chloride (NaCl). After this the suspension of silica and NaCl is back-titrated with sodium hydroxide solution.

3.2 A 1.5 g sample of silica is weighed into a 250 cm^3 beaker containing 150 cm^3 NaCl solution adjusted to pH 3. The suspension is stirred for 3 min and brought to 25°C. The suspension is titrated first to pH 4 and then to pH 9 using a sodium hydroxide solution (c = 0.1 mol/dm^3). The volume of sodium hydroxide solution that is reacted between pH 4 and pH 9 is calculated and corrected with the volatile matter determined according to Test Method D6738. The consumption of sodium hydroxide solution minus the blank reading without silica is defined as the Sears Number given in cm^3/1.5 g. The specific consumption of sodium hydroxide solution in a silica suspension depends primarily on the silica surface area, the density of the silanol groups, and the degree of hydrophobicity.

4. Significance and Use

4.1 The rubber-filler interaction needed in silica technology for the rubber industry is based on the use of silane-coupling agents that react with the silanol groups on the surface of the silica during the processing step called silanization. Silane-coupling agents are multifunctional molecules able to create molecular bridges between the elastomer or rubber matrix and the silica surface.

5. Apparatus

5.1 *Precision Balance,* 0.01 g sensitivity.

5.2 *Automatic Titration Apparatus,* capable of performing a volumetric endpoint titration based on pH, as well as equipped with data storage and calculation modules.[4]

5.2.1 *Burette,* to titrate hydrochloric acid (c = 0.1 mol/dm^3), and

5.2.2 *Burette,* to titrate sodium hydroxide standard solution (c = 0.1 mol/dm^3).

5.3 *pH electrode.*

5.4 *Printer* (optional).

5.5 *Beakers,* glass, 250 cm^3.

5.6 *Laboratory Grinder,* for example, electro-mechanical.

5.7 *Wire Mesh Sieve,* 75 µm (200 mesh).

5.8 *Thermostated water bath.*

5.9 *Titration Beaker,* 150 cm^3 for determination of the actual concentration of the sodium hydroxide standard solution.

5.10 *Analytical Balance,* 0.1 mg sensitivity.

5.11 *Magnetic Stirrer with Stir Bar.*

[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.20 on Compounding Materials and Procedures.

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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] G. W. Sears, Anal. Chem., 1981-1983, 1956.

[4] Appropriate devices are commercially available.

5.12 *Graduated Cylinder,* 250 cm^3.

5.13 *Beaker,* glass, 2 dm^3.

5.14 *Volumetric Flask,* 2 dm^3.

6. Reagents and Materials

6.1 *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.[5] 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 *NaCl Solution*—Dissolve 400 g analytical grade NaCl in approximately 1.75 dm^3 deionized water in a 2 dm^3 beaker. Adjust the solution to pH 3 (±0.1) with hydrochloric acid, c = 1 mol/dm^3, and transfer the solution to a 2 dm^3 volumetric flask. When the temperature has reached 25°C, fill the volumetric flask to the calibration mark and mix well using the stirrer bar and the magnetic stirrer.

6.3 *Hydrochloric Acid (HCl),* 0.1 mol/dm^3.

6.4 *Sodium Hydroxide Standard Solution (NaOH),* 0.1 mol/dm^3.

6.5 *Deionized Water.*

6.6 *Buffer Solutions,* pH of 4, 7, and 9.

6.7 *Potassium Hydrogen Phthalate,* primary standard.

7. Procedure

7.1 Grind an appropriate quantity of silica sample in a laboratory grinder for 60 s. Approximately 6 to 8 g are recommended for a determination of the Sears Number in duplicate or in triplicate, respectively.

7.2 Pass ground sample (see 7.1) through a wire mesh sieve 75 µm (200 mesh). This can be accomplished manually or mechanically. Discard fraction retained on sieve. The fraction <75 µm (<200 mesh) is used for the determination of the Sears Number.

7.3 *Determination of the Actual Concentration of the NaOH Standard Solution:*

7.3.1 If the method is used regularly, the concentration of the NaOH standard solution is determined at least every month or as needed with three replicate determinations. Otherwise, it is recommended that the concentration of the NaOH solution should be validated before use regardless of the storage time.

7.3.2 To determine the concentration of the NaOH solution, weigh between 0.1 and 0.2 g potassium hydrogen phthalate accurately to 0.1 mg into a 150 cm^3 titration beaker. Dissolve the potassium hydrogen phthalate in approximately 75 cm^3 of deionized water. Bring the solution to 25°C in a water bath. Titrate potentiometrically to endpoint with the NaOH standard solution. The endpoint is indicated by steepest slope between pH 7 and pH 9.

7.3.3 Calculate the actual concentration of the NaOH standard solution:

$$C_{ACTUAL} = \frac{m_{KHP}}{M_{KHP} \times V_{NaOH}} \quad (1)$$

where:

c_{ACTUAL} = actual concentration of sodium hydroxide solution in mol/dm^3,
m_{KHP} = mass of potassium hydrogen phthalate in mg,
M_{KHP} = molar weight of potassium hydrogen phthalate; 204.22 g/mol, and
V_{NaOH} = volume of sodium hydroxide solution consumed in cm^3, 1000 cm^3 correspond to 1 dm^3.

7.4 *Determination of the Blank Reading of the NaCl Solution (pH 3):*

7.4.1 Before measuring the silica sample, carry out a double determination of the blank reading of the NaCl solution, that is, performing the titration without silica.

7.4.1.1 Use a graduated cylinder to transfer 150 cm^3 of the NaCl solution (pH 3) into a 250 cm^3 titration beaker.

7.4.1.2 Stir the solution for approximately 1 min and bring the temperature to 25.0 ± 0.5°C.

7.4.2 Calibrate the pH electrode using the buffer solutions pH 4, 7, and 9.

7.4.3 Place a stirring bar in the solution and place the titration beaker on the titrator.

7.4.4 Start the corresponding method for the blank reading on the automated titrator. The following settings are recommended: endpoint 1 at pH 4: control range pH: 0.6, minimum rate: 10 µL/min, and maximum rate: 100 µL/min and endpoint 2 at pH 9: control range pH: 2, minimum rate: 10 µL/min, and maximum rate: 200 µL/min.

7.4.5 The consumption of sodium hydroxide solution to raise the pH from 4.0 to 9.0 is noted as blank reading V_{BR}.

7.5 *Determination of the Sears Number (Tested in Duplicate):*

7.5.1 Weigh 1.50 ± 0.01 g of the silica sample into a 250 cm^3 titration beaker on a precision or analysis balance.

7.5.2 Add 150 cm^3 NaCl solution (pH 3) using a graduated cylinder and then place a stirring bar in the vessel.

7.5.3 Stir the suspension with a magnetic stirrer for about 2 min and then bring it up to a temperature of 25.0 ± 0.5°C in a water bath.

7.5.4 Place the titration beaker on the automated titrator and check the pH. If the initial pH is above pH 4 titrate with the HCl solution, c = 0.1 mol/dm^3 to pH of 3.95 before proceeding.

7.5.5 Start the Sears Number titration. The following settings are recommended: endpoint 1 at pH 4: control range pH: 0.2, minimum rate: 50 µL/min, and maximum rate: 500 µL/min and endpoint 2 at pH 9: control range pH: 0.2, minimum rate: 15 µL/min, and maximum rate: 2000 µL/min, switch-off delay: 3s.

[5] *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 *Annual 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.

8. Calculation of Results

8.1 When titration is finished, the titration curve and the following results are displayed by the titrator.

8.2 If the calculation function of the titrator is not used, all relevant data (actual concentration of NaOH standard solution, NaOH consumption between pH 4 and 9, blank reading, volatile matter, and initial pH) are to be considered for the calculation of the Sears Number, SN:

$$SN = (V_{pH4-9} - V_{BR})\left(\frac{C_{ACTUAL}}{C_{NOMINAL}}\right)\left(\frac{100}{100 - VM}\right) \quad (2)$$

where:

$V_{pH\ 4–9}$ = volume of NaOH solution consumed to raise the pH from 4.0 to 9.0 in cm^3,

V_{BR} = volume of NaOH solution consumed for the blank in cm^3,

$C_{NOMINAL}$ = nominal concentration (=0.1000 mol/dm^3) of NaOH standard solution,

C_{ACTUAL} = actual concentration of NaOH standard solution in mol/dm^3, and

VM = volatile matter according to Test Method D6738 in percent.

9. Report

9.1 Identification of the silica sample.

9.2 Sears Number in cm^3/1.5 g (reporting: one decimal place).

10. Precision and Bias

10.1 Precision and bias statements have not been generated but will be available within five years of publication of the test method.

11. Keywords

11.1 Sears Number; silane; silanol groups; silica