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Standard Test Methods for Silanes Used in Rubber Formulations (bis-(triethoxysilylpropyl)sulfanes): Sulfur Content[1]

This standard is issued under the fixed designation D6741; 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 These test methods cover the determination of the sulfur content of silanes, or of admixtures of silane and carbon black, of the type bis-(triethoxysilylpropyl)sulfane. The following test methods are included:

Test Method A: Combustion in an Oxygen Flask and Subsequent Titration of Sulfate
Test Method B: High-Temperature Combustion with Infrared Absorption Detection

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
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Significance and Use

3.1 The sulfur content can be used to characterize a silane or an admixture of silane and carbon black. It depends mainly on the average length of the sulfur chain.

Test Method A: Combustion in an Oxygen Flask and Subsequent Titration of Sulfate

4. Summary of Test Method

4.1 The weighed sample is burned in an oxygen atmosphere. The resulting sulfur dioxide and trioxide is absorbed in hydrogen peroxide solution, and the sulfate ions thus generated are titrated with barium perchlorate solution employing Thorin indicator. Taking into account the known concentration of the perchlorate solution, the volume consumed, and the sample mass, the sulfur content of the sample can be calculated.

5. Apparatus

5.1 *Analytical Balance,* accuracy ±0.1 mg.

5.2 *Combustion Apparatus,* according to Schoeniger, with 750 cm^3 flask.

5.3 *Ultrasonic Bath.*

5.4 *Automatic Titrator.*

5.5 *Photoelectrical Detector,* set at 550 nm.

5.6 *Volumetric Cylinder,* 100 cm^3.

5.7 *Volumetric Flask,* 100 cm^3.

5.8 *Volumetric Pipet,* 10 cm^3.

5.9 *Syringe,* 0.5 cm^3.

5.10 *Titration Beakers.*

5.11 *Magnetic Stirrer,* with stirring rod.

5.12 *Filter Paper,* for Schoeniger combustion (35 × 35 × 70 mm).

5.13 *Glass Tube,* attached to a rubber hose.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade 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

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[1] These test methods are under the jurisdiction of ASTM Committee D11 on Rubber and are 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.

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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193.

6.3 *2-propanol > 99 %.*

6.4 *Hydrogen Peroxide Solution,* (5 %) as absorbing liquid.

6.5 *Barium Perchlorate Solution,* 0.005 mol/dm^3 in 2-propanol/water.

6.6 *Thorin Solution,* 0.1 % in water (Thorin octahydrate).

6.7 *Sulfuric Acid,* as a standard solution (1.000 ± 0.002 g SO^{42-}).

6.8 *Deionized Water.*

6.9 *Oxygen.*

6.10 *Sulfanilic Acid,* (certified standard for elemental analysis).

7. Preparation of Apparatus

NOTE 1—The flask shall not contain any residues from solvents. Purge with compressed air if necessary.

NOTE 2—Check flask for damages. Do not use flasks having scratches or cracks.

NOTE 3—Ignite with safety shield lowered only.

NOTE 4—After combustion is finished, leave flask in the apparatus for 5 min cool-down.

7.1 Add 20 cm^3 of 5 % H_2O_2 solution into the combustion flask by means of a volumetric cylinder.

7.2 Add a magnetic stirring rod.

7.3 Purge the flask for 1 min with oxygen gas. Do this by directing a gentle stream from the glass tube towards the bottom of the flask.

8. Procedure

8.1 *Preparation of Liquid Samples (Silanes):*

8.1.1 Place a non-densified cotton wool swab between the platinum grids attached to the glass stopper. The spare place between the grids should be filled to ⅔ .

8.1.2 Attach the ignition strip in such way that it is in contact with the heating coil.

8.1.3 Transfer the stopper onto the balance, add approximately 60 mg of silane and record the mass to the nearest 0.1 mg.

8.2 *Preparation of Solid Samples (Admixtures of Carbon Black and Silane):*

8.2.1 Fold the special filter paper as to form a tunnel and transfer it onto the balance.

8.2.2 Add approximately 120 mg of the admixture and record the mass to the nearest 0.1 mg.

8.2.3 Fold the paper, roll it together and insert it between the platinum grids. Make sure the ignition strip is in contact with the heating coil.

8.3 *Combustion:*

8.3.1 Insert the stopper including the sample into the flask. Turn the flask upside down and fix it inside the combustion apparatus.

8.3.2 Lower the safety shield and start ignition by pushing the button.

8.3.3 After 5 min take the flask out of the apparatus and stir for 30 min with a magnetic stirrer.

8.3.4 Rinse the platinum grids with approximately 20 cm^3 of deionized water, while holding it above the combustion flask.

8.3.5 Transfer the liquid from the combustion flask to a 100 cm^3 volumetric flask, rinse, and make up to the mark with deionized water.

8.4 *Titration:*

8.4.1 Pipet 10 cm^3 from the volumetric flask into the titration beaker.

8.4.2 Add 40 cm^3 2-propanol and 0.1 cm^3 Thorin solution.

NOTE 5—It is important to respect the proportion of water/2-propanol (1:4).

8.4.3 Degas in the ultrasonic bath for 5 min.

8.4.4 Add barium perchlorate until the color changes from yellow to pale rose. Preferably use an automatic titrator equipped with photoelectrical detector.

8.5 *Standardization of the Barium Perchlorate Solution:*

8.5.1 Pipet 10 cm^3 of sulfuric acid standard solution into a titration beaker and proceed as described in 8.4. Result = V_0.

NOTE 6—Ion chromatography can be used as an alternative method for sulfate determination.

9. Calibration

9.1 Use sulfanilic acid as a standard for calibration. Carry out the test as described in Sections 7 and 8. The theoretical sulfur content of sulfanilic acid is 18.5 %. If this value is not obtained within ±0.2 % (absolute), check reagents and apparatus, glassware, and calculation.

10. Calculation

10.1 Calculate the sulfur content in percentage, according to the following equation:

$$S = \frac{V \cdot F \cdot 0.1603 \cdot V_{total}}{m \cdot V_{aliquot}} \cdot 100 \qquad (1)$$

where:

V = volume of barium perchlorate solution,

F = factor of barium perchlorate solution $F = {}^{10.41}\!/\!{}_{V_0}$ (determined using sulfuric acid standard solution),

0.1603 = conversion factor from cm^3 0.005 m barium perchlorate solution to mg S,

V_{total} = total volume of sulfate-containing solution (here: 100 cm^3),

$V_{aliquot}$ = aliquot part used for titration, cm^3, and

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[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 *Analar 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.

TABLE 1 Sulfur Content (wt %)

Material	Average[A]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	22.57	1.68	0.21	1.70	0.58	4.78

[A] The average of the laboratories calculated averages.

m = original sample mass, mg.

Test Method B: High-Temperature Combustion with Infrared Absorption Detection

11. Summary of Test Method

11.1 The specimen is burned in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen to oxidize the sulfur. Moisture and particulates are removed from the gas by traps filled with anhydrous magnesium perchlorate. The gas stream is passed through a cell in which sulfur dioxide is measured by an infrared (IR) absorption detector. Sulfur dioxide absorbs IR energy at a precise wavelength within the IR spectrum. Energy is absorbed as the gas passes through the cell body in which the IR energy is being transmitted. Thus, at the detector, less energy is received. All other IR energy is eliminated from reaching the detector by a precise wavelength filter. Thus, the absorption of IR energy can be attributed only to sulfur dioxide whose concentration is proportional to the change in energy at the detector. One cell is used as both a reference and a measurement chamber. Total sulfur as sulfur dioxide is detected on a continuous basis. This test method is empirical. Therefore, the apparatus shall be calibrated by the use of a standard reference material.

11.2 This test method is for use with commercially available sulfur analyzers equipped to carry out the preceding operations automatically and shall be calibrated using a standard reference material (sulfanilic acid) containing sulfur in the same order of magnitude as the samples to be analyzed.

12. Apparatus

12.1 *Measurement Apparatus,* equipped to automatically combust the specimen.

12.2 *Combustion Tube,* made of mullite, porcelain, or zircon, approximately 40 to 45 mm inside diameter with a 3-mm thick wall, at least 450 mm long with provisions for routing the gases produced by combustion through the infrared cell.

12.3 *Boat Puller,* rod of a heat-resistant material with a bent or disk end to insert and remove boats from the combustion tube.

13. Reagents

13.1 *Purity of Reagents*—see 6.1.

13.2 *Magnesium Perchlorate.*

14. Preparation of Apparatus

14.1 Assemble the apparatus according to the manufacturer's instructions. Make a minimum of two determinations to condition the system prior to calibrating the system.

15. Calibration

15.1 Carry out four tests with different amounts of sulfanilic acid. Choose the sample mass such that it includes the expected amount of sulfur present in the silane sample.

15.2 Follow the instructions of the manufacturer.

16. Procedure

16.1 Stabilize and calibrate the analyzer (see 15.1 and 15.2).

16.2 Raise the furnace temperature as recommended by the manufacturer to at least 1350°C. Weigh the specimen to the nearest 0.1 mg into a combustion boat and use a boat puller to position the specimen in the hot zone of the furnace for at least 2 min, or until completely combusted.

NOTE 7—The analytical cycle should begin automatically as soon as sulfur is detected.

16.3 When the analysis is complete, the instrument should indicate the sulfur value. Refer to the manufacturer's recommended procedure.

17. Report

17.1 Proper identification of the sample.

17.2 Sulfur content to the nearest 0.1 mass %.

18. Precision and Bias[4]

18.1 The precision of this test method is based on an interlaboratory study conducted in 2008. Six laboratories participated in this study. Each of the labs reported up to four replicate test results for a single material. Every "test result" reported represents an individual determination. Except for the use of only a single material, Practice E691 was followed for the design and analysis of the data.

18.1.1 *Repeatability limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

18.1.1.1 Repeatability limits are listed in Table 1.

18.1.2 *Reproducibility limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D11-1101.

18.1.2.1 Reproducibility limits are listed in Table 1.

18.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

18.1.4 Any judgment in accordance with statement 18.1.1 or 18.1.2 would have an approximate 95 % probability of being correct, however the precision statistics obtained in this ILS must not be treated as exact mathematical quantities which are applicable to all circumstances and uses. The limited number of laboratories reporting results guarantees that there will be times when differences greater than predicted by the ILS results will arise, sometimes with considerably greater or smaller frequency than the 95 % probability limit would imply. As all laboratories did not report the same number of replicates, consider the repeatability limit as a general guide, and the associated probability of 95 % as only a rough indicator of what can be expected.

18.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

18.3 The precision statement was determined through statistical examination of 22 results, from six laboratories, on one material. Due to the small number of participating labs, no outliers were removed. This material was described as follows: Material A is a commercially available bis-(triethoxysilylpropyl)tetrasulfane.

19. Keywords

19.1 organosilanes; silanes; sulfur

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