



Designation: D6844 – 10 (Reapproved 2023)

Standard Test Method for Silanes Used in Rubber Formulations (bis-(triethoxysilylpropyl)sulfanes): Characterization by High Performance Liquid Chromatography (HPLC)¹

This standard is issued under the fixed designation D6844; 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 characterization of silanes, or of admixtures of silane and carbon black (see 10.4), of the type bis-(triethoxysilylpropyl)sulfane by high performance liquid chromatography.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

D5297 Test Methods for Rubber Chemical Accelerator—Purity by High Performance Liquid Chromatography

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E682 Practice for Liquid Chromatography Terms and Relationships

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

¹ This test method is under the jurisdiction of ASTM Committee D11 on Rubber and Rubber-like Materials 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. Terminology

3.1 *Definitions:*

3.1.1 S_x —Bis-(triethoxysilylpropyl)polysulfane or polysulfide, $(\text{EtO})_3\text{SiC}_3\text{H}_6\text{S}_x\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3$

3.1.2 S_2 —Bis-(triethoxysilylpropyl)disulfane or disulfide, $(\text{EtO})_3\text{SiC}_3\text{H}_6\text{S}_2\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3$

3.1.3 S_3 —Bis-(triethoxysilylpropyl)trisulfane or trisulfide, $(\text{EtO})_3\text{SiC}_3\text{H}_6\text{S}_3\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3$

3.1.4 S_3 —Bis-(triethoxysilylpropyl)tetrasulfane or tetrasulfide, $(\text{EtO})_3\text{SiC}_3\text{H}_6\text{S}_4\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3$

3.1.5 S_3 —Bis-(triethoxysilylpropyl)pentasulfane or pentasulfide, $(\text{EtO})_3\text{SiC}_3\text{H}_6\text{S}_5\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3$

3.1.6 S_3 —Bis-(triethoxysilylpropyl)hexasulfane or hexasulfide, $(\text{EtO})_3\text{SiC}_3\text{H}_6\text{S}_6\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3$

3.1.7 S_3 —Bis-(triethoxysilylpropyl)heptasulfane or heptasulfide, $(\text{EtO})_3\text{SiC}_3\text{H}_6\text{S}_7\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3$

3.1.8 S_3 —Bis-(triethoxysilylpropyl)octasulfane or octasulfide, $(\text{EtO})_3\text{SiC}_3\text{H}_6\text{S}_8\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3$

3.1.9 S_3 —Bis-(triethoxysilylpropyl)nonasulfane or nonasulfide, $(\text{EtO})_3\text{SiC}_3\text{H}_6\text{S}_9\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3$

3.1.10 S_3 —Bis-(triethoxysilylpropyl)decasulfane or decasulfide, $(\text{EtO})_3\text{SiC}_3\text{H}_6\text{S}_{10}\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3$

3.1.11 *average sulfur chain length*—the weighted average of the sulfur bridge in the polysulfide mixture. Includes S_2 to S_{10} species.

4. Summary of Test Method

4.1 A sample of the silane is analyzed by high performance liquid chromatography to determine amounts of each component, the average chain length and the amount of dissolved elemental sulfur.

4.2 Two methods are described: Method A with a constant composition of the mobile phase (isocratic), and Method B using a gradient. Both methods will give similar chromatograms.

5. Significance and Use

5.1 The average sulfur chain length is an important parameter in determining the behavior of the silane in a rubber mixture.

6. Apparatus

6.1 *HPLC with UV Detector*, operating at 254 nm, Inlet Valve with 5 mm³ (μL) loop, integrator or data system.

6.2 *Column C18*, 5 μm, 4.6 mm × 250 mm.

6.3 *Column Oven*.

6.4 *Analytical Balance*, accuracy ±0.1 mg.

6.5 *Hamilton Syringe*, 100 mm³ (μL).

6.6 *Volumetric Pipet*, 5 cm³.

6.7 *Volumetric Flasks*, 50 cm³ and 2000 cm³.

6.8 *Syringe*, 3 cm³ or 5 cm³.

6.9 *Glass Bottles*, 5 cm³.

6.10 *Disposable PTFE Filters*, 0.20 μm, d = 25 mm.

6.11 *Mechanical Flask Shaker*.

7. Reagents, AR Grade or Equivalent

7.1 Reagents for Method A (without gradient):

7.1.1 *Ethanol*, absolute.

7.1.2 *Methanol*.

7.1.3 *Tetrabutylammoniumbromide*.

7.1.4 *Cyclohexane*.

7.1.5 *Sulfur*.

7.1.6 *Deionised Water*.

7.2 Reagents for Method B (with gradient):

7.2.1 *2-Propanol (IPA)*.

7.2.2 *Acetonitrile (AcCN)*.

7.2.3 *Tetrabutylammoniumbromide*.

7.2.4 *Hexane*.

7.2.5 *Sulfur*.

7.2.6 *Mesitylene*.

7.2.7 *Deionised Water*.

8. Preparation of Solutions

8.1 *Tetrabutylammoniumbromide Solution*—Dissolve 400 mg of tetrabutylammoniumbromide in 1000 cm³ of deionised water.

8.2 *Mobile Phase*:

8.2.1 *Mobile Phase for Method A (Isocratic)*—Transfer 180 cm³ of tetrabutylammoniumbromide solution and 450 cm³ ethanol into a 2000 cm³ volumetric flask. Make up to the mark with methanol and mix well.

NOTE 1—Separation between peaks of the silane species and elemental sulfur can be optimized by carefully varying the amount of water in the mobile phase. In general, higher water content extends retention time, with the silane species being more affected than the elemental sulfur.

8.2.2 *Mobile Phase for Method B (With Gradient)*—The composition of the mobile phase is variable:

Time (min.)	IPA (%)	AcCN (%)	TBAB (0.04 %)
0	20	60	20
20	50	40	10
25	50	40	10
28	80	15	5
30	80	15	5
32	20	60	20

NOTE 2—The combination of solvents will affect the retention times and peak separation efficiency. The above recommendation is one of many possibilities. The specific solvents and ratios used can be determined by the technician to fit the needs of the lab. It is important to maintain the separation of the peaks so they can be unambiguously identified and quantified.

8.3 *Sulfur Standard*—Weigh approximately 20 mg of sulfur to the nearest 0.1 mg into a 20 cm³ volumetric flask and make up to the mark with cyclohexane. Stopper the flask and agitate until the solution looks homogeneous. Using a volumetric pipet, transfer 5 cm³ of this solution into a 50 cm³ volumetric flask, make up to the mark with cyclohexane and mix well.

NOTE 3—If the test shall be run with an internal standard, 100 mm³ (μL) of mesitylene may be added to the 50 cm³ flask prior to making up with cyclohexane.

9. Calibration

9.1 *Elemental Sulfur*—The response factor R_s for converting peak area to weight % sulfur is determined by injecting the sulfur standard into the HPLC unit and making the following calculation:

$$R_s = m_s / A_s \cdot 100 \quad (1)$$

where:

m_s = mass of sulfur made up to 50 cm³ with cyclohexane, and

A_s = area of sulfur peak.

10. Procedure

10.1 Weigh approximately 160 mg of the silane sample to be analyzed, to the nearest 0.1 mg, into a 50 cm³ volumetric flask. Fill the flask to the mark with cyclohexane, stopper and agitate thoroughly to completely dissolve the sample.

NOTE 4—If the test shall be run with an internal standard, 100 mm³ (μL) of mesitylene may be added to the 50 cm³ flask prior to making up with cyclohexane.

10.2 Purge the Hamilton syringe once with the solution before injecting 100 mm³ (μL) into the inlet loop. Take care that no air bubbles are injected.

10.3 Turn the inlet loop into the injection position and start the integrator (or data system) immediately. After 40 min, terminate the run and print the chromatogram, including a peak list.

10.4 When analyzing admixtures of silane and carbon black, weigh approximately 320 mg of the sample to the nearest 0.1 mg into a 50 cm³ volumetric flask. Make up to the mark with cyclohexane, stopper the flask and shake for 20 min to extract the silane from the black.

10.5 Load 2 cm³ of the extract from 10.4 into a 3 cm³- or 5 cm³-syringe. Mount the PTFE filter on top of the syringe and transfer 1.5 cm³ of the syringe contents into a waste bottle. The last 0.5 cm³ are filtered into a small glass bottle from which