Designation: D6844 – 10 (Reapproved 2015)

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

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

3. Terminology

3.1 *Definitions:*

3.1.1 S_x—Bis-(triethoxysilylpropyl)polysulfane or polysulfide, $(EtO)_3SiC_3H_6S_xC_3H_6Si(OEt)_3$

3.1.2 S_2—Bis-(triethoxysilylpropyl)disulfane or disulfide, $(EtO)_3SiC_3H_6S_2C_3H_6Si(OEt)_3$

3.1.3 S_3—Bis-(triethoxysilylpropyl)trisulfane or trisulfide, $(EtO)_3SiC_3H_6S_3C_3H_6Si(OEt)_3$

3.1.4 S_3—Bis-(triethoxysilylpropyl)tetrasulfane or tetrasulfide, $(EtO)_3SiC_3H_6S_4C_3H_6Si(OEt)_3$

3.1.5 S_3—Bis-(triethoxysilylpropyl)pentasulfane or pentasulfide, $(EtO)_3SiC_3H_6S_5C_3H_6Si(OEt)_3$

3.1.6 S_3—Bis-(triethoxysilylpropyl)hexasulfane or hexasulfide, $(EtO)_3SiC_3H_6S_6C_3H_6Si(OEt)_3$

3.1.7 S_3—Bis-(triethoxysilylpropyl)heptasulfane or heptasulfide, $(EtO)_3SiC_3H_6S_7C_3H_6Si(OEt)_3$

3.1.8 S_3—Bis-(triethoxysilylpropyl)octasulfane or octasulfide, $(EtO)_3SiC_3H_6S_8C_3H_6Si(OEt)_3$

3.1.9 S_3—Bis-(triethoxysilylpropyl)nonasulfane or nonasulfide, $(EtO)_3SiC_3H_6S_9C_3H_6Si(OEt)_3$

3.1.10 S_3—Bis-(triethoxysilylpropyl)decasulfane or decasulfide, $(EtO)_3SiC_3H_6S_{10}C_3H_6Si(OEt)_3$

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 mm^3 (µL) loop, integrator or data system.

[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.

6.2 *Column C18,* 5 µm, 4.6 × 250 mm.

6.3 *Column Oven.*

6.4 *Analytical Balance,* accuracy ±0.1 mg.

6.5 *Hamilton Syringe,* 100 mm^3 (µL).

6.6 *Volumetric Pipet,* 5 cm^3.

6.7 *Volumetric Flasks,* 50 and 2000 cm^3.

6.8 *Syringe,* 3 cm^3 or 5 cm^3.

6.9 *Glass Bottles,* 5 cm^3.

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 cm^3 of deionised water.

8.2 *Mobile Phase:*

8.2.1 *Mobile Phase for Method A (Isocratic)*—Transfer 180 cm^3 of tetrabutylammoniumbromide solution and 450 cm^3 ethanol into a 2000 cm^3 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 cm^3 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 cm^3 of this solution into a 50 cm^3 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 mm^3 (µL) of mesitylene may be added to the 50 cm^3 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 cm^3 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 cm^3 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 mm^3 (µL) of mesitylene may be added to the 50 cm^3 flask prior to making up with cyclohexane.

10.2 Purge the Hamilton syringe once with the solution before injecting 100 mm^3 (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 cm^3 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 cm^3 of the extract from 10.4 into a 3 cm^3- or 5 cm^3-syringe. Mount the PTFE filter on top of the syringe and transfer 1.5 cm^3 of the syringe contents into a waste bottle. The last 0.5 cm^3 are filtered into a small glass bottle from which 100 mm^3 (µL) are used to load the injection loop and analyzed as described in 10.2 and 10.3.

11. Calculation

11.1 *Sulfur Chain Distribution*—Calculations are performed utilizing the response factors for the individual silane (sulfur chain length) species contained in the following table:

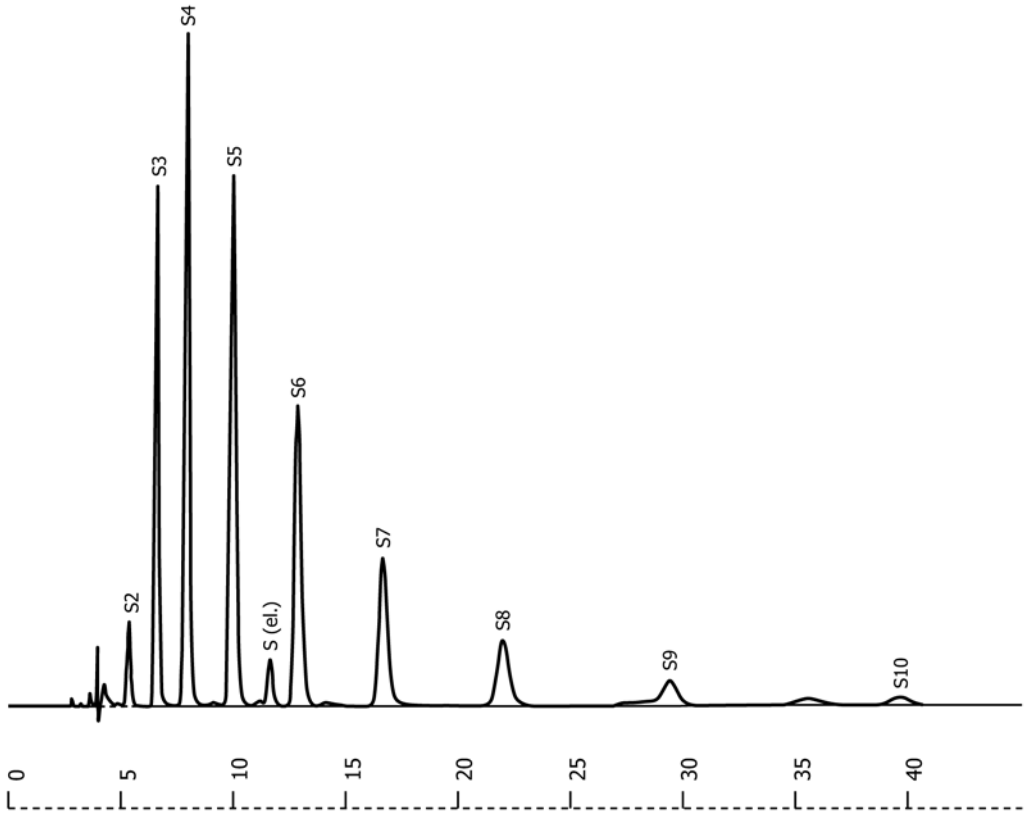

FIG. 1 Typical Chromatogram for Method A (Isocratic)

Sulfur Chain Length	Molecular Mass g mol^{-1}	Response Factor *R*
S_2	474.8	31.3
S_3	506.9	8.87
S_4	539.0	4.88
S_5	571.0	3.24
S_6	603.1	2.36
S_7	635.2	1.82
S_8	667.2	1.46
S_9	699.3	1.19
S_{10}	731.4	1.00

$$S_i = \frac{A_i \cdot R_i}{\sum_{i=2}^{10} A_i \cdot R_i} \cdot 100 \quad (2)$$

where:

S_i = relative amount of silane species with i sulfur atoms in %,
A_i = peak area of silane species with i sulfur atoms, and
R_i = response factor of silane species with i sulfur atoms.

NOTE 5—Short-chain silanes may exhibit additional peaks at retention times higher than the one of the S_7 species. These peaks, due to oligomers, are not taken into consideration when calculating the sulfur chain distribution and the average chain length.

11.2 *Average Chain Length:*

$$\bar{S} = \frac{\sum_{i=2}^{10} i \cdot A_i \cdot R_i / M_i}{\sum_{i=2}^{10} A_i \cdot R_i / M_i} \quad (3)$$

where:

$\bar{S}$ = average sulfur chain length,
i = number of sulfur atoms in the silane species, and
M_i = molecular mass of silane species with i sulfur atoms.

11.2.1 Example for calculation:

Species	M_i	Rel RF R_i	Result A_i	Corrected Area	% S_x
S_2	474	31.3	1 407 938	44 068 459	16.8
S_3	506	8.87	8 607 037	763 444 189	29.1
S_4	538	4.88	12 988 212	63 382 475	24.2
S_5	570	3.24	13 083 349	42 390 051	16.2
S_6	602	2.36	8 534 198	20 140 707	7.7
S_7	634	1.82	5 149 428	9 371 959	3.6
S_8	666	1.46	2 815 133	4 110 094	1.6
S_9	698	1.19	1 375 780	1 637 178	0.6
S_{10}	730	1.00	768 474	768 474	0.3
Average Sulfur Chain Length (S-bar)					3.78

11.3 *Elemental Sulfur:*

$$S = \frac{A_s \cdot R_s}{m} \quad (4)$$

where:

S = elemental sulfur content in %,
A_s = peak area of elemental sulfur,
R_s = response factor for sulfur, and
m = mass of silane or admixture in mg in 50 cm^3 cyclohexane.

11.4 *Examples for Chromatograms:*

11.4.1 See Fig. 1.

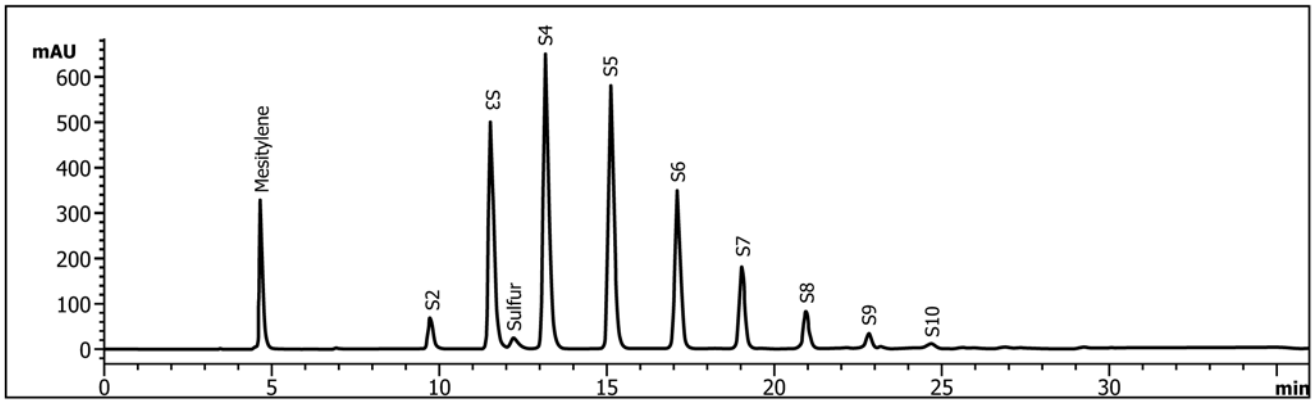

FIG. 2 Typical Chromatogram for Method B (With Gradient)

11.4.2 See Fig. 2.

12. Report

12.1 Report the following information:

12.1.1 Identification of the silane sample,

12.1.2 Average chain length to the nearest 0.01,

12.1.3 Sulfur content to the nearest 0.1 weight %, and

12.1.4 Relative amount of silane species with *i* sulfur atoms in % (optional).

13. Precision and Bias[3]

13.1 The precision of this test method is based on an interlaboratory study conducted in 2008. Up to ten laboratories participated in this study. Each of the labs reported four replicate test results for a variety of analytical parameters, on 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.

13.1.1 *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.

13.1.1.1 Repeatability limits are listed in Tables 1-11.

13.1.2 *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.

13.1.2.1 Reproducibility limits are listed in Tables 1-11.

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

13.1.4 Any judgment in accordance with statement 13.1.1 or 13.1.2 would have an approximate 95 % probability of being correct.

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

13.3 The precision statement was determined through statistical examination of the reported results from ten laboratories, on one material. Due to the small number of participating labs, usually no outliers were removed. However in one case, i.e. for elemental sulfur testing one lab was an extreme outlier and had to be removed from the precision calculation. This material was described as follows: Material A is a commercially available bis-(triethoxysilylpropyl)tetra sulfane.

14. Keywords

14.1 chain length; chain length distribution; elemental sulfur; organosilane; silane

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D11-1104.

TABLE 1 Elemental Sulfur (%)[A]

Material	Average[B]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	0.32	0.02	0.02	0.02	0.04	0.06

[A] Eight labs reported (one outlier lab excluded from calculations).
[B] The average of the laboratories calculated averages.

TABLE 2 Average Chain Length[A]

Material	Average[B]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	3.625	0.017	0.007	0.018	0.018	0.051

[A] Ten labs reported.
[B] The average of the laboratories calculated averages.

TABLE 3 S2 (relative %)[A]

Material	Average[B]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	19.7	0.5	0.2	0.5	0.5	1.4

[A] Ten labs reported.
[B] The average of the laboratories calculated averages.

TABLE 4 S3 (relative %)[A]

Material	Average[B]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	31.0	0.8	0.1	0.8	0.3	2.1

[A] Ten labs reported.
[B] The average of the laboratories calculated averages.

TABLE 5 S4 (relative %)[A]

Material	Average[B]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	23.5	0.3	0.09	0.3	0.2	1.0

[A] Ten labs reported.
[B] The average of the laboratories calculated averages.

TABLE 6 S5 (relative %)[A]

Material	Average[B]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	14.5	0.2	0.04	0.2	0.1	0.6

[A] Ten labs reported.
[B] The average of the laboratories calculated averages.

TABLE 7 S6 (relative %)[A]

Material	Average[B]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	6.6	0.2	0.1	0.2	0.2	0.5

[A] Ten labs reported.
[B] The average of the laboratories calculated averages.

TABLE 8 S7 (relative %)[A]

Material	Average[B]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	2.9	0.1	0.04	0.1	0.1	0.3

[A] Ten labs reported.
[B] The average of the laboratories calculated averages.

TABLE 9 S8 (relative %)[A]

Material	Average[B]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	1.2	0.1	0.02	0.1	0.05	0.2

[A] Ten labs reported.
[B] The average of the laboratories calculated averages.

TABLE 10 S9 (relative %)[A]

Material	Average[B]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	0.5	0.1	0.02	0.1	0.1	0.3

[A] Ten labs reported.
[B] The average of the laboratories calculated averages.

TABLE 11 S10 (relative %)[A]

Material	Average[B]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	0.2	0.1	0.02	0.1	0.1	0.2

[A] Ten labs reported.
[B] The average of the laboratories calculated averages.