Designation: D6843 – 10 (Reapproved 2019)

Standard Test Method for Silanes Used in Rubber Formulations (bis-(triethoxysilylpropyl)sulfanes): Characterization by Gas Chromatography (GC)[1]

This standard is issued under the fixed designation D6843; 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 of the type bis-(triethoxysilylpropyl)sulfanes by gas chromatography.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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]

D4626 Practice for Calculation of Gas Chromatographic Response Factors
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E355 Practice for Gas 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 *PTES*—Propyltriethoxysilane $CH_3CH_2CH_2Si(OEt)_3$

3.1.2 *Cl-PTES*—Chloropropyltriethoxysilane $Cl\text{-}CH_2CH_2CH_2Si(OEt)_3$

4. Summary of Test Method

4.1 In this test method, a sample of the silane is analyzed by gas chromatography in order to determine the amount of volatile components. From the peak areas in the chromatogram, the percents by weight of volatiles are totaled and designated as the total volatile impurities or volatile by-products.

5. Significance and Use

5.1 The amount of volatile components reflects the impurity level in the product, and as a consequence, its behavior in a rubber mixture.

6. Apparatus

6.1 *Gas Chromatograph,* equipped with:

6.1.1 *Flame Ionization Detector (FID).*

6.1.2 *Capillary Column,* typical is 30 m length, 0.25 to 0.53 mm internal diameter, fused silica, 0.1 to 1.0 µm film thickness.

6.1.3 *Carrier Gas Flow Control,* with splitter.

6.1.4 *Temperature Controls,* for injector, detector and column.

6.2 *Syringe,* 1 mm^3 (µL).

6.3 *Analytical Balance,* accuracy ±0.1 mg.

6.4 *Automatic Pipets,* 0.2 to 1.0 cm^3, 5 cm^3.

6.5 *Sample Vials,* approximately 15 cm^3.

7. Reagents

7.1 *Methanol,* analytical grade (for cleaning syringe).

7.2 *Undecane,*[3]analytical grade (used as internal standard).

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[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] Similar hydrocarbons like decane, analytical grade, can be used in place of undecane, as long as they do not interfere with peaks from the sample.

TABLE 1 Volatile Components

Components	Retention Time [min]	Peak Area [µV*s]	Response Factor	Initial Weight [g]	Concentration [wt %]
Ethanol	1.46	5774	2.52		0.42
PTES	12.99	6660	2.28		0.44
Unknown	16.79	859	2.70		0.07
Cl-PTES	18.35	27 557	2.70		2.15
Total volatiles					3.01
Sample mass				5.2529	
Undecane (internal std.)	14.79	483 627	1.00	0.7335	

7.3 *Optional: Cyclohexane,* analytical grade (used to dilute the sample).

7.4 *Helium,* minimum 99.99 % purity, suitable for chromatographic use, dried (carrier gas).

7.5 *Hydrogen Gas,* minimum 99.99 % purity, total hydrocarbons ≤1 ppm (for detector).

7.6 *Air,* suitable for chromatographic use, total hydrocarbons ≤2 ppm, moisture ≤3 ppm (for detector).

8. Procedure

8.1 Set up the gas chromatograph using the following example parameters as a guide:

Carrier gas	He, linear velocity 20 to 50 cm/s
Split ratio	1:4 to 1:10
Injector temperature	250°C
Oven temperature	Temperature program: for example, 50°C / 2 min 6.5 °C / min 260°C / 15 min NOTE 1—The above parameters can be adjusted as appropriate to match the column characteristics. For example, a more narrow column can use a faster program (such as 50°C for 1 min. hold/15°C/min. ramp/300°C for 15 min hold).
Detector temperature	320°C
Combustion gasses	H_2, air as needed for FID

8.2 Tare a sample vial (W_1).

8.3 Weigh 5 cm^3 of Bis-(triethoxysilylpropyl)sulfanes into the tared sample vial (W_2).

8.4 Add 1 cm^3 undecane[3] (internal standard) and weigh again (W_3).

8.5 Homogenize the solution by shaking gently.

NOTE 1—Before injection, the sample may be diluted 1:5 with cyclohexane.

8.6 Inject 0.5 mm^3 (µL) of the neat sample or 1.0 mm^3 (µL) of the diluted sample into the gas chromatograph and start the measurement process.

8.7 Clean the syringe immediately with methanol and dry.

8.8 The measurement is finished when the base line is reached after a broad peak (indicative of the trisulfane species). Typically, a run takes less than 30 min.

8.9 Allow the oven to cool down to the start temperature. The next measurement may be started as soon as the GC indicates a ready condition.

9. Calculation

9.1 The amount of each volatile component is calculated as follows:

$$I = \frac{A_i}{A_{std}} \cdot \frac{(W_3 - W_2)}{(W_2 - W_1)} \cdot RR_i \cdot 100\,[\%] \qquad (1)$$

where:

I = weight per cent of component i in the test sample,
A_i = peak area of component i,
A_{std} = peak area of undecane[3] (internal standard),
RR_i = response factor of component i,
$(W_3 - W_2)$ = weight in g of undecane[3] (internal standard), and
$(W_2 - W_1)$ = weight in g of silane sample.

9.2 All components with a retention time smaller or equal to Cl-PTES are considered to be "volatile impurities" or "volatile by-products." If the identity of a volatile component is not known, the response factor of Cl-PTES will be applied.

9.3 See Table 1.

10. Report

10.1 Report the following information:

10.1.1 Identification of the sample, and

10.1.2 Volatile impurities to the nearest 0.1 weight %.

11. Precision and Bias[4]

11.1 The precision of this test method is based on an interlaboratory study conducted in 2008. Nine laboratories participated in this study. Each of the labs reported four replicate test results for the sum of volatile components 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.

11.1.1 *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

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D11-1103.