Designation: D6843 – 10 (Reapproved 2015)

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

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).

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).

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[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] 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.

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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	

7.6 *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 results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

11.1.1.1 Repeatability limits are listed in Table 1 and Table 2.

11.1.2 *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

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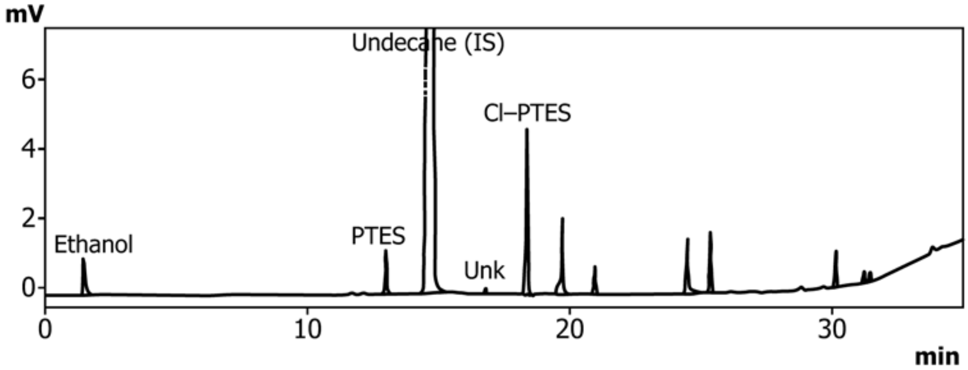
[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D11-1103.



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***   Peak Report   ***
PKNO     TIME        AREA      HEIGHT     CONC [W %]      NAME
   1    1.465        5744         962         0.4057    Ethanol
   2   12.989        6660        1247         0.4698    PTES
   3   14.777      483627       38160                   Undecane (IS)
   4   16.787         859         181         0.0670    Unk
   5   18.354       27557        4570         2.1479    Cl–PTES
   6   18.916        1037          51
   7   19.704       14764        1939
   8   20.962        4043         688
   9   24.473       10662        1451
  10   25.368        9519        1597
  11   30.153        5409         986
  12   31.218        1658         333
  13   31.469        1295         221
-------------------------------------------------------------------
                   572834       52386         3.0904
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FIG. 1 Peak Report

TABLE 2 Volatile Impurities (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	1.12	0.09	0.04	0.10	0.11	0.27

[A] The average of the laboratories calculated averages.

difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

11.1.2.1 Reproducibility limits are listed in Table 1 and Table 2.

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

11.1.4 Any judgment in accordance with statement 11.1.1 or 11.1.2 would have an approximate 95 % probability of being correct.

11.2 *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.

11.3 The precision statement was determined through statistical examination of 36 results, from nine 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)tetra sulfane.

12. Keywords

12.1 organisilanes; silanes; volatile components

ANNEX

(Mandatory Information)

A1. DETERMINATION OF RESPONSE FACTORS

A1.1 Scope

A1.1.1 Mass (weight) relative response factors convert measured peak areas into weight % of a component. Response factors should be determined for Ethanol, Propyltriethoxysilane (PTES) and Chloropropyltriethoxysilane (Cl-PTES).

A1.2 Standard Components

A1.2.1 *Ethanol,* absolute.

A1.2.2 *Propyltriethoxysilane (PTES),* purity >99 %

A1.2.3 *Chloropropyltriethoxysilane (Cl-PTES),* purity >99 %.

A1.2.4 *Cyclohexane,* analytical grade.

A1.2.5 *Undecane,*[3](internal standard, this will have a defined response factor R_{std} = 1.00).

A1.3 Procedure

A1.3.1 Weigh 0.1 to 0.2 cm^3 of each component to be determined to the nearest 0.1 mg into one 15 cm^3 weighing bottle.

A1.3.2 Add approximately 5 cm^3 cyclohexane to the mixture.

A1.3.3 Reweigh the bottle to the nearest 0.1 mg; the net weight of the mixture represents the sample mass, m.

A1.3.4 Add approximately 1 cm^3 undecane, the internal standard, to the mixture.

A1.3.5 Reweigh the bottle to the nearest 0.1 mg.

A1.3.6 Homogenize the contents of the bottle by shaking gently.

A1.3.7 Inject 0.3 mm^3 (µL) of the final mixture into the gas chromatograph.

A1.4 Calculation

A1.4.1 The mass relative response factors are individually calculated as follows:

$$RR_{mi} = \frac{W_i \cdot A_{std}}{A_i \cdot W_{std}} \tag{A1.1}$$

where:

RR_{mi} = mass relative response factor of component *i*,
W_i = weight of component *i*,
A_i = peak area of component *i*,
W_{std} = weight of standard (undecane),
A_{std} = peak area standard, and
i = analyte component.

A1.4.2 See Table A1.1.

TABLE A1.1 Mass Relative Response Factors

Components	Retention Time [min]	Peak Area [from integrator]	Component Weight [g]	Total Sample Weight [g]	Calculated Relative Response Factor [RR_i]	Concentration [wt %]
Ethanol	1.44	32 928	0.1358		2.52	2.484
PTES	13.05	46 550	0.1741		2.28	3.184
Cl-PTES	18.39	41 886	0.1850		2.70	3.383
Cyclohexane			4.9729			
Sample weight				5.4678		
Undecane (internal std.)	14.79	446 926	0.7321		1.00	

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