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QUANTIFICATION OF RESIDUAL AMOUNTS OF CYCLIC VOLATILE METHYL SILOXANES IN SILICONE ELASTOMERS

1. PURPOSE

The purpose of this document is to provide a robust analytical method for quantification of low levels (~0.1%) of Cyclic Volatile Methyl Siloxanes (cVMS) in cured and uncured silicone elastomers. It is broadly applicable to one-part and two-part pastes, sealants, heat cured elastomers, liquid silicone rubbers and room temperature vulcanized silicones in their cured and uncured states. This method uses common laboratory reagents, solvents, and equipment and should be easy to install in a laboratory equipped with a Gas Chromatograph with a Flame Ionization Detector (FID).

Note: *Users of this method will need to validate the method in their own laboratory for their specific materials of interest prior to analysis of samples.*

2. SCOPE

2.1 Principle of the method

This method is applicable for the quantitation of cVMS in cured and uncured silicone elastomers (Table 1). The concept is to extract a sample with acetone containing a known amount of an internal standard. This is an effective method for isolating GC-elutable siloxanes from larger molecular weight siloxanes which are not amenable to GC analysis. With the use of suitable acetone to sample phase ratios, and demonstration of similar partition coefficients for the internal standard used and the analytes of interest, this method of analysis can provide accurate levels of cVMS in a material while reducing GC instrumentation fouling and contamination from large molecular weight and non-volatile substances in materials. This methodology can be applied in the analysis of other volatile siloxane species but would need to be validated prior to use.

TABLE 1 - CVMS COMPOUNDS COVERED BY METHODS

Chemical Name	Abbreviation
Octamethylcyclotetrasiloxane	D4
Decamethylcyclopentasiloxane	D5
Dodecamethylcyclohexasiloxane	D6

2.2 Field of application

This method has been employed for a variety of cured and uncured silicone elastomers. Based on experience with analysis of cVMS in these matrices, this method is expected to work over a range of concentrations between **0.01** to **0.5**%.

2.3 Limitations

As described above the method is aimed at the analysis of cVMS in silicone elastomers. It is not readily applicable to other products as the analysis of cVMS by GC is highly susceptible to matrix-induced errors. Within the analytical procedure, cVMS can be formed by induced degradation of silicone components present as ingredient of the sample itself or as integral part of the GC-system (e.g. column phase material). These processes are highly supported by substances like water, ionic substances, salts or catalysts, which might be present in solutions, mixtures and formulations, thus producing false high findings. For the reliable analysis of those products the use of additional matrix-specific pre-cleaning procedures (as e.g. described by Brothers et. al.[1]) is urgently advised.

[1] Brothers, H. M., Boehmer, T., Campbell, R. A., Dorn, S., Kerbleski, J. J., Lewis, S., Mund, C., Pero, D., Saito, K., Wieser, M. and Zoller, W. (2017), Determination of cyclic volatile methylsiloxanes in personal care products by gas chromatography. Int J Cosmet Sci, 39: 580-588. doi:10.1111/ics.12411

3. INTERFERENCES

As this method is a general procedure for the analysis of cVMS in various silicone elastomers, components of different matrices may interfere with the analytes of interest as well as the internal standards. GC/MS verification of the data should be considered in cases where interferences are suspected. The possibility of interference of the internal standard can be checked for each matrix using a preliminary GC analysis of the pure sample. The presence of multiple internal standards is intended to provide options should the peak for the primary internal standard be overlapped.

4. REAGENTS AND MATERIALS

REAGENTS	MATERIALS
n-Octane (Primary Internal Standard) – reagent grade or better obtained commercially	Disposable glass vials – 20 mL volume with a suitable screw-top closure
n-Nonane (Secondary Internal Standard) – reagent grade or better obtained commercially	Analytical balance – 4-decimal place accuracy
n-Decane (Secondary Internal Standard) – reagent grade or better obtained commercially[2]	Volumetric laboratory glassware
Pure (>99%) cVMS (D4, D5 and D6) - obtained commercially	Gas Chromatograph with FID detection and split injection capabilities
Acetone for extraction and dissolution - Fisher Optima grade or equivalent	HP-1 (or equivalent phase) GC column, 60 m × 0.25 mm × 0.25 µm
	Laboratory platform shaker

5. PROCEDURE

5.1 Internal Standard solution

Prepare an appropriate volume of internal standard solution in acetone for use in preparing stock standards, working standards, and for conducting sample extractions.

5.1.1 Stock Solution

Dissolve 0.5 g each of octane, nonane and decane in acetone to a total dilute volume of 50 mL (10 mg/mL solution).

5.1.2 Working solution

Dilute 10 mL of the 10 mg/mL solution per liter final volume of acetone to a final internal standard solution concentration of 0.1 mg/mL.

5.2 Sample preparation

For uncured samples, weigh 0.5 g of sample (recorded to the nearest 0.1 mg) into a 20 mL glass vial, followed by the addition of 10 mL of internal standard working solution (0.1 mg/mL). Quickly cap the vial securely and extract for a minimum of 24 hours using gentle agitation. Multi-phase solutions may require time to separate or settle; however, the process may be accelerated, if necessary, by use of centrifugation. Fillers and pigments may need to be removed from the acetone phase even after settling and/or centrifugation. This can typically be achieved by filtration through a 0.45 µm GMF syringe filter, or similar. Place sample extracts in appropriate size autosampler vials for analysis.

Cured samples can be molded parts collected from a manufacturing process or cured sheets prepared expressly for the purpose of cVMS measurements. In either case, the samples should be cut into small pieces, no bigger than approximately 5 mm × 5 mm × 5 mm. For the most reproducible results, cured samples should be tested as soon as practical after they have been prepared. If the typical manufacturing processes include any post-curing treatment, such as post-baking, sterilization and so on, those processes should be followed prior to analyzing for cVMS. For the cured samples, weigh 1.0 g of sample cut into pieces (recorded to the nearest 0.1 mg) into a 20 mL glass vial, followed by the addition of 10 mL of internal standard working solution (0.1 mg/mL). Quickly cap the vial securely and extract for a minimum of 24 hours using gentle agitation. Place sample extracts in appropriate size autosampler vials for analysis.

[2] Other alkanes (e.g. dodecane) may be used as internal standard as well. In either case a detailed validation of the method for the given product has to be conducted.

5.3 GC Analysis

5.3.1 Recommended conditions

Injector temperature:	225 °C
Split:	50:1
Injection volume:	2 µL
Carrier gas:	Helium or nitrogen at 1.4 mL/min constant flow
Column:	HP-1 60 m x 0.25 mm x 0.25 µm film (or equivalent column)
Oven:	50 °C (5 min) to 250 °C at 10 °C/min, then to 315 °C for 10 min to elute higher boiling point species
Detector:	Flame Ionization (FID) at 350 °C (or 15 °C higher than the highest column temperature achieved during the analysis)

5.3.2 Method Notes

The analytical conditions listed above are recommended, because they have been proven to work; however chromatographic separation parameters should be adjusted as needed to avoid overlap of the internal standard and the analytes of interest with other components in the mixture. Alternate chromatographic columns may be required for specific sample matrices. Modified conditions should be validated prior to use.

With liquid injection, the entire matrix of the sample is injected onto the GC system. Non-volatile compounds like polymers are trapped in the injector. Thus, the use of filled injector liner (glass wool) is recommended. Based to the matrices analyzed, the injector liner may need to be exchanged on a regular basis. Semi-volatile substances may remain on the column, which may cause carry over effects disturbing subsequent analyses. Thus, the performance of cleaning runs and blank runs, on a regular basis are recommended.

6. CALIBRATION

6.1 Stock solution of cVMS

6.1.1 Stock solution A

Weigh 0.5 g each of D4, D5 and D6 into a 100 mL volumetric flask. The flask is filled up to the mark with the internal standard working solution prepared in 5.1.2. above.

6.1.2 Stock Solution B

Dilute 5 mL of Stock Standard Solution "A" to a final volume of 50 mL with the internal standard working solution prepared in 5.1.2. above.

6.2 Gas Chromatography Standards

Prepare the analytical standards in additional internal standard working solution according to Table 2. Transfer to appropriate size well-sealed glass vials or bottles and store in a cool location prior to use.

TABLE 2 – ANALYTICAL STANDARD PREPARATION

Standard Concentration (mg/mL)	Stock Standard Solution "B" Volume (mL)	Final Dilution Volume (mL)
0.005	1	100
0.010	1	50
0.025	5	100
0.050	5	50
0.100	10	50

***Note**: Mix each solution well prior to removing aliquots for instrument calibration. Place standard solutions in appropriate size autosampler vials for analysis.*

Standard curves should be linear over this range of concentrations (up to 0.5 mg/mL concentration) when following the parameters described in this method.

7. Calculation

This method uses internal standard calibration, and based on their corresponding peak areas, linear calibration functions of the form:

$$\frac{Area_{cVMS}}{Area_{internal\ standard}} = m * \frac{C_{cVMS}}{C_{internal\ standard}}$$

are established individually for each cVMS. By applying these calibration functions, the individual concentrations of each analyte are calculated and reported as % by weight.

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