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

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 a variety of silicone products. 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 prior to analysis of unknown samples.*

2. SCOPE

2.1 Principle of the method

This method is applicable for the quantitation of cVMS in a variety of silicone products classes (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 cVMSin a material while reducing GC instrumentation fouling and contamination from large molecular weight and nonvolatile 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 METHOD

Chemical Name	Abbreviation
Octamethylcyclotetrasiloxane	D4
Decamethylcyclopentasiloxane	D5
Dodecamethylcyclohexasiloxane	D6

2.2 Field of application

This method has been employed for a wide variety of silicone based sample matrices including hydroxyl-functional siloxanes, polydimethylsiloxane (PDMS) fluids, amino-functional siloxanes, silicone polyethers and vinyl-functional siloxanes. Based on experience with analysis of volatile siloxanes 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 based products. 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 like emulsions (e.g. as parts of commercial personal care products), 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 volatile siloxanes in various classes of siloxanes, components of different matrices may interfere with the analytes of interest as well as that of the internal standard. 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.

4. REAGENTS AND MATERIALS

REAGENTS	MATERIALS
Dodecane (Internal Standard) – reagent grade or better obtained commercially[2]	Disposable glass vials – 20 mL volume with a suitable screw-top closure
Pure (>99%) Volatile Siloxanes - obtained commercially	Analytical balance – 4-decimal place accuracy
Acetone for extraction and dissolution - Fisher Optima grade or equivalent	Volumetric laboratory glassware
	Gas Chromatograph with FID detection and split injection capabilities

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 of dodecane 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

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 over night (or minimum of 12 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. Place sample extracts in appropriate size autosampler vials for analysis.

Note: *shorter extraction times may be used for some matrices, however this would need to be validated by the testing laboratory for each matrix.*

5.3 GC Analysis

5.3.1 Recommended conditions

Injector temperature:	250 °C
Split:	50:1
Injection volume:	1 µL
Carrier gas:	Helium 1.5 mL/min constant flow
Column:	DB-5 30 m x 0.25 mm x 0.1 µm film (or equivalent column)
Oven:	50 °C (5 min) to 200 °C at 15 °C/min then to 315 °C for 20 min to elute higher boiling point species
Detector:	Flame Ionization (FID) at 325 °C (or 15 °C higher than the highest column temperature achieved during the 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.

5.3.2 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. Specifically, functionalized siloxane products may contain a variety of volatile species that may interfere with each other (e.g., L4 and monovinylheptamethyl-cyclotetrasiloxane or ViD4 and ViD2D3 in vinyl-functional silicone polymers). 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 can 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

Approximately 50 mg of cVMS are weighed to the nearest 0.1 mg into a 10 mL volumetric flask. The flask is filled up to the mark with the internal standard working solution.

6.1.2 Stock Solution B

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

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
0.025	5	100
0.050	5	50
0.250	25	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 quite 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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