QUANTIFICATION OF RESIDUAL AMOUNTS OF LINEAR VOLATILE METHYL SILOXANES IN SILICONE PRODUCTS

1 PURPOSE

The purpose of this document is to provide a robust analytical method for quantification of low levels (~0.1%) of Linear Volatile Methyl Siloxanes (VMS) 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 linear VMS 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. Using suitable acetone to sample ratios and having demonstrated that partition coefficients of internal standard and analytes are similar, the method developed can determine accurate levels of linear VMS in a variety of silicone materials. Fouling and contamination of the GC-equipment from higher molecular weight and non-volatile substances present in the materials analysed, can be avoided for the most part. This methodology can be applied in the analysis of other volatile siloxane species but would need to be validated prior to use.

TABLE 1. Linear VMS Compounds Covered By Method

Chemical Name	Abbreviation
Hexamethyldisiloxane	L2 (or MM)
Octamethyltrisiloxane	L3 (or MDM)
Decamethyltetrasiloxane	L4 (or MD2M)
Dodecamethylpentasiloxane	L5 (or MD3M)
Tetradecamethylhexasiloxane	L6 (or MD4M)
1,1,1,3,5,5,5-Heptamethyltrisiloxane	H-L3 (or MD'M)
1,1,1,3,5,5,5-Heptamethyl-3-[(trimethylsilyl)oxy] trisiloxane	M3T

2.2 Field of Application

This method has been employed for a wide variety of silicone-based sample matrices including polydimethylsiloxane (PDMS) fluids, amino-functional siloxanes, silicone polyether and vinyl-functional siloxanes. This method might not be conducive for samples with high silanol content due to cyclics formation during the analysis (this can be minimized by conducting all sample prep steps in

HDPE vials). Sample with high content of quaternary ammonium may not be applicable for this method. Based on experience with analysis of volatile siloxanes in the matrices mentioned, 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 aims to analyse linear VMS in silicone-based products. It is not readily applicable to other products as the analysis of linear VMS by GC is highly susceptible to matrix induced errors. Within the analytical procedure linear VMS 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 advised.

i. 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.

ii. REAGENTS AND MATERIALS

REAGENTS	MATERIALS
n-Dodecane (Primary Internal Standard) – reagent grade or better obtained commercially[2]	Disposable glass vials – 20 mL volume with a suitable screw-top closure
Toluene (Primary Internal Standard) – reagent grade or better obtained commercially	Analytical balance – 4-decimal place accuracy
Pure (>98%) linear VMS (L2, L3, L4, L5, L6, H-L3, and M3T) – obtained commercially	Volumetric laboratory glassware
Acetone for extraction and dissolution – Fisher Optima grade or equivalent	Laboratory platform shaker
	Gas Chromatograph with FID detection and split injection capabilities
	HP-1 (or equivalent phase) GC column, 60 m × 0.25 mm × 0.25 µm

3 Procedure

3.1 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.

3.1.1 Stock Solution

Dissolve 0.5 g each of toluene and dodecane in acetone to a total dilute volume of 50 mL (10 mg/mL solution).

3.1.2 Working Solution

Dilute 5 mL of the 10 mg/mL solution per litre final volume of acetone to a final internal standard solution concentration of 0.05 mg/mL.

3.2 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 overnight (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. 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.*

4 GC Analysis

4.1 Recommended Conditions

Injector temperature:	250 °C
Split:	50:1
Injection volume:	2 µL
Carrier gas:	Helium
Column:	HP-1 60 m × 0.25 mm I.D. × 0.25 µm film (or equivalent column)
Oven:	50 °C (5 min) to 250 °C at 6 °C/min and hold for 5 min, then to 340 °C at 15 °C/min and hold for 10 min to elute species with higher boiling points
Detector:	Flame Ionization (FID) at 325 °C (or 15 °C higher than the highest column temperature achieved during the analysis)

4.2 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 analysed, 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.

5 Calibration

5.1 Stock Solution of Linear VMS

5.1.1 Stock Solution A

Weigh approximately 0.5 g each of L2, L3, L4, L5, L6, H-L3, and M3T, weighed to the nearest 0.1 mg, 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 (5 mg/mL solution).

5.1.2 Stock Solution B

Dilute 5 mL of Stock Solution "A" to a final volume of 50 mL with the internal standard working solution prepared in 5.1.2. above (0.5 mg/mL solution).

5.2 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	10
0.050	5	50
0.100	10	50
0.250	5	10

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

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

6 Calculation

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

$$\frac{Area(lVMS)}{Area(internal\ standard)} = m^* \frac{C(lVMS)}{C(internal\ standard)}$$

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

REFERENCE

[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

[2] Other alkanes (e.g. octane, nonane, decane, etc.) may be used as internal standard as well. In either case a detailed validation of the method for the given product must be conducted.

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