Issue date: September 2018
Revised version: January 2019

QUANTIFICATION OF RESIDUAL AMOUNTS OF CYCLIC VOLATILE METHYL SILOXANES IN FULLY-FORMULATED PERSONAL CARE PRODUCTS

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 fully-formulated wash-off personal care products such as shampoos and conditioners. 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). Further details on this method and its development can be found in the work of Brothers et al.[1]

***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 fully-formulated wash-off personal care products (Table 1). The concept involves three steps. First the sample is dissolved in an acetonitrile/dimethylacetamide mix. Hexane is added to separate the cVMS into an organic phase leaving behind the polar phase. Finally, the hexane phase is treated with N-methyl-N-trimethylsilyl trifluoroacetamide (MSTFA). The MSTFA treatment has three aims; to derivatize silanol end-groups to prevent generation of cVMS by back biting, to silylate reactive species that might facilitate the generation of cVMS by back biting and to derivatize co-extracted species that might interfere with the chromatographic analysis. This is an effective method for isolating GC-elutable siloxanes from complex formulations which are not amenable to GC analysis whilst minimizing the generation of cVMS during the sample preparation and testing process. This method of analysis can provide accurate levels of cVMS in a material while reducing GC instrumentation fouling and contamination from non-volatile substances in the formulations. 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 variety of fully-formulated wash-off personal care products. 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 fully-formulated wash-off personal care products. It is not readily applicable to other products such as silicone fluids and elastomers. Methods for these types of materials can be found on CES website or upon request to CES or your supplier.

[1] Brothers, H.M., et al. (2017). International Journal of Cosmetic Science, **39**, 580-588.

3. INTERFERENCES

As this method is a general procedure for the analysis of cVMS in wash-off personal care products, components of different matrices may interfere with the analytes of interest as well as 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%) cVMS (D4, D5 and D6) - obtained commercially	Analytical balance – 4-decimal place accuracy
Hexane for extraction and dissolution (> 95 %)	Volumetric laboratory glassware
N,N-dimethylacetamide for extraction and dissolution (> 99 %)	Microliter syringes
N-methyl-N-trimethylsilyl trifluoroacetamide (MSTFA) for derivatization	Gas Chromatograph with FID detection and split injection capabilities
	HP-1 (or equivalent phase) GC column, 30 m × 0.32 mm × 0.25 µm
	Vortex mixer
	Heating block capable of 80 °C

5. PROCEDURE

5.1 Internal Standard solution

Weigh 400 mg of n-dodecane into a 200 mL volumetric flask. Add 50 mL dimethylacetamide and then dilute to the mark with acetonitrile.

5.2 Sample preparation

Weigh 400 mg of the sample to the nearest 0.1 mg into a screw-capped vial. Add 2 mL of the acetonitrile/dimethylacetamide internal standard solution and shake gently to disperse. Add 8 mL of hexane and shake vigorously using a vortex mixer for 1 minute. Allow the mixture to phase separate and then remove 1 mL of the upper hexane phase into a GC autosampler vial. Add 100 µL of MSTFA and incubate at 80 °C for 30 minutes. The sample is now ready for injection into the GC.

5.3 GC Analysis

5.3.1 Recommended conditions

Injector temperature:	225 °C
Split:	50:1
Injection volume:	1 µL
Carrier gas:	Helium at 2 mL/min constant flow
Column:	HP-1 30 m x 0.32 mm x 0.25 µm film (or equivalent column)
Oven:	60 to 150 °C at 8 °C/min then 25 °C/min to 300 °C with a 5 min hold
Detector:	Flame Ionization (FID) at 350 °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. 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 100 mg each of D4, D5 and D6 into a 10 mL volumetric flask. Fill the flask to the mark with hexane.

6.1.2 Stock Solution B

Dilute 1 mL of Stock Standard Solution "A" to a final volume of 10 mL with hexane.

6.1.2 Stock Solution B

Weigh 80 mg of n-dodecane into a 100 mL volumetric flask. Fill the flask to the mark with hexane.

6.2 Gas Chromatography Standards

Prepare the analytical standards in additional internal standard working solution according to Table 3. All standards are prepared in 10 mL volumetric flasks. Transfer to appropriate size well-sealed glass vials or bottles and store in a cool location prior to use. Refrigerated solutions have been shown to be stable over a period of at least 2 weeks.

TABLE 3 – ANALYTICAL STANDARD PREPARATION

Concentration (mg/mL)	Internal standard solution (mL)	Stock Standard Solution "B" Volume (µl)	Stock Standard Solution "A" Volume (µl)
0.0025	5	25	-
0.0050	5	50	-
0.0100	5	100	-
0.0150	5	150	-
0.0200	5	200	-
0.0500	5	-	50
0.1000	5	-	100
0.2000	5	-	200
0.5000	5	-	500
1.0000	5	-	1000

***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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