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Comment on "Volatile methylsiloxanes in personal care products – Using QuEChERS as a "green" analytical approach" by Daniela Capela, Vera Homem, Arminda Alves, Lúcia Santos

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ABSTRACT

In this recent paper, Capela et al. (2016) [1] describe an analytical method for determination of volatile methylsiloxanes (VMS) in a variety of personal care products (PCPs) using QuEChERS methodology (Lehotay et al., 2010) [2]. Subsequently, this method was then used by the authors to measure VMS levels in a cross-section of PCPs to estimate average daily dermal exposure, average daily inhalation exposure, and down the drain emissions of VMS components to the environment (Capela et al., 2016) [3]. The authors are commended for selecting a broad range of sample types for the investigation and for thoroughly describing the approaches used to validate the method. However, a careful analysis of the reported cyclic volatile methylsiloxane (cVMS) concentrations raises concerns that artifacts of cVMS analysis were not adequately controlled for in the method used to determine the cVMS concentrations in PCPs. The comments presented here apply beyond this particular article and serve as an opportunity to inform other researchers about the potential pitfalls and difficulties associated with cyclosiloxane analyses, even with what might appear to be a successfully validated method, while providing examples of the concerns and precautions that must be taken into consideration whenever analyzing for cVMS in complex matrices such as PCPs.

1. Siloxane chemistry considerations

It is well known that siloxane polymers can decompose through a thermal degradation mechanism known as back biting resulting in the formation of cyclic siloxanes. Siloxane back biting is the common cause of column bleed on gas chromatography columns that use polydimethylsiloxane (PDMS) as a stationary phase [4]. When analyzing for cVMS analytes using GC, it is important to control for potential side-reactions in the heated injection port of the gas chromatograph which can generate cyclic siloxanes from the thermal degradation of higher molecular weight silicone polymers present in the samples. This is especially true for OH terminated PDMS polymers where the silanol group at the end of the polymer chain can reach back on itself a few repeat units and break an Si–O bond resulting in the liberation of a cyclic species as seen in Fig. 1. This back biting can be a primary thermal degradation mechanism for OH-ended silicones and can also occur in the interior of a siloxane chain, especially when catalyzed by the presence of other components in the sample (*e.g.*, acids, bases, salts, water, *etc.*). Additionally, with *in situ* generation of cyclic siloxanes in the GC injection port, even the specificity of mass spectrometric detection will not eliminate such artifacts as the instrument cannot distinguish between the levels of cyclics present in the sample *vs*. the contribution from the formation of cyclics in the GC injection port.

The potential for degradation of siloxanes to form cyclic siloxanes during the course of GC analysis without proper sample pretreatment has been studied and demonstrated in silicone-containing emulsions, a complex matrix similar to personal care products [5]. To minimize the formation of cVMS, it is a common practice to derivatize the end-groups on OH-ended siloxanes with a silylation reagent to abate this known decomposition mechanism [6].

While QuEChERS has been successfully used to reduce matrix effects in the determination of pesticide residues in fruits and vegetables [2], the use of this methodology is questionable when applied to analysis of cyclic siloxanes, especially in materials containing siloxane polymers. Cyclic and linear siloxanes are known to undergo hydrolysis at acidic and basic pH [7,8] and can potentially undergo the same backbiting reaction as seen in thermal degradation. For the extract cleanup, the first QuEChERS step used sodium acetate to maintain a pH of 5–5.5 during sample extraction followed by the second QuEChERS step which uses a primary and secondary amine (PSA) exchange material (pKa > 10) to further cleanup the hexane extract. However, it does not appear that the authors have evaluated the possibility for hydrolysis of siloxanes to occur when using these sample preparation conditions. In addition, the effectiveness of QuEChERS in reducing co-extracted matrix is dependent on the solvents used. In this case it is doubtful that the C18 sorbent used to clean up the hexane extract was very effective in removing non-polar co-extracted matrix as there is no driving force to partition to the C18 from the hexane. The high recovery of the non-polar siloxanes support this assertion. It is regrettable that the authors did not provide a figure of a typical chromatogram (full scan and selected ion) of sample extracts with and without cleanup to permit evaluation of the effectiveness of the QuEChERS in reducing co-extracted matrix. In addition, the visual examination of peak shapes can sometimes be used as an indication of cyclics formation during the analysis. An asymmetrical tailing peak can be an indication that cyclics are being introduced, through decomposition of the sample in the hot inlet of the GC, over a longer period of time than the normal injection and vaporization process.

A strong indication that the formation of cyclics is occurring during analysis in this study is the frequent presence of the cyclic siloxane D3 observed in the sampled PCPs, "Highest mean concentrations were obtained for D5 in body moisturizers (356 μg g^{-1}), followed by D3 in shampoo

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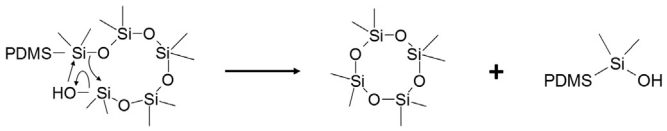

Fig. 1. Schematic of siloxane backbiting mechanism showing the formation of D4; however, other cyclic species (*e.g.* D3 D5, D6...) can also be formed.

(296 μg g^{-1})... For all the analyzed compounds, only D3 and D6 were detected simultaneously in all samples." (Capela et al. [1], p. 99). The presence of D3 in shampoos samples is surprising as it is not a prominent cyclic siloxane found in silicone emulsions which are a common ingredient used in formulation of personal care products, and D3 itself is not used as an additive in the formulation of PCPs. However, D3 is a prominent thermal degradation decomposition product of siloxanes, so one possible explanation for higher frequency and concentrations of D3 than expected is that the QuEChERS method used for sample clean-up may not be appropriate for analysis of cVMS as the method utilized high concentrations of salt and an amine functionalized solid phase adsorbent which are potential catalysts for the thermal decomposition process.

2. Background contamination

As described by Warner et al., contamination and analytical variation can cause issues in the trace analysis of cVMS, potentially resulting in the reporting of false positives at concentrations approaching detection limits [9]. Even though the authors describe efforts to correct for background signal, they did not report actual concentrations and variation of the procedural blanks used for background correction. Laboratory air can be a significant source of background signal which can be impacted by the number of people in the building or by tasks such as weighing out analytical standards in the laboratory. This background and variation can be reduced by use of closed systems, cleanrooms, and clean cabinets [10,11] and system background can be reduced by using Merlin Microseal septa [12]; however it does not appear that the authors utilized these systems to reduce background.

3. Summary

In summary, these comments serve as a reminder of the importance of understanding the chemistry of components within the sample (*e.g.,* in this case higher molecular weight siloxanes) and the possibility of the components to interfere with the analysis through potential reactions or degradation during the course of analysis. It is also important to understand how background contamination can interfere with analysis, especially when performing low level VMS analyses as described in this paper. Overall, these factors can have a profound impact regarding proper interpretation of analytical findings and subsequent calculation of the quantities of cVMS released to the environment [3].

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