

METHOD DEVELOPMENT FOR THE DETERMINATION OF SELECTED CYCLIC SILOXANES IN WASTEWATER AND SLUDGE AND STUDY OF THEIR HYDROLYSIS AT DIFFERENT TEMPERATURES

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ABSTRACT

An efficient and precise analytical method for the simultaneous determination of five cyclic siloxanes namely hexamethylcyclo-trisiloxane (D3), octamethylcyclo-tetrasiloxane (D4), decamethylcyclo-pentasiloxane (D5), dodecamethylcyclo-hexasiloxane (D6), dodecamethylcyclo-hexasilane (D6_silane) and the surrogate tetrakis(trimethylsiloxy)-silane (M4Q) in wastewater and sludge matrix was developed and fully validated. Gas chromatography-mass spectrometry (GC-MS) was used for the separation. Isolation of the target analytes was performed by liquid-liquid-extraction (LLE) and agitation for liquid and solid samples, respectively. Extraction procedures resulted in good repeatability and reproducibility with relative standard deviations (RSDs) less than 10% for all the tested compounds for both types of samples. Recoveries varied from 68% (D4) to 108% (D6_silane) and from 67% (D3) to 110% (D6_siloxane) for wastewater (RSDs \leq 13 %) and sludge (RSDs $<$ 11 %), respectively. D3 was the only compound for which low recoveries ($<$ 40 %) were obtained in the liquid phase. The achieved Limits of Detection (LODs) were adequate and low enough for environmental monitoring of the tested compounds in wastewater and sludge samples. Regarding abiotic degradation of the tested siloxanes, results indicated that all compounds undergo hydrolysis at different extend at temperatures of 4, 20, 35 and 55 °C. Among the five compounds, D3 found to be the most sensitive at all tested temperatures. Its removal ranged between 70% (4°C) and 90% (55 °C) after 15 h. The loss of other target compounds due to hydrolysis decreased with increase of their molecular weight. For the temperature of 20 °C, removal ranged from 70% (D4) to 40% (D6 silane) up to the end of the experiment (12 d). For all target compounds, the increase of temperature enhanced significantly hydrolysis, indicating that this mechanism could have a major role on their fate during sludge anaerobic digestion at mesophilic or thermophilic conditions.

Keywords: emerging contaminants; siloxanes; fate; analysis; abiotic degradation

1. Introduction

Siloxanes are polymeric organosilicon molecules that consist of a backbone of alternating silicon-oxygen [Si-O] units with organic side-chains attached to each silicon atom. The physicochemical properties of siloxanes vary, depending on their molecular weight. The very low electronegativity of Si (1.8) leads to a very polarized Si-O bond with large bond energy (108 kcal mol⁻¹). In general, siloxanes have low water solubility, while they are characterized by high stability, biocompatibility, surface activity, and lubricating properties.

Siloxanes are widely used in industrial applications as well as in personal care products and biomedical devices. As a result, they are usually detected in wastewater and sludge samples at concentrations ranging up to some $\mu\text{g L}^{-1}$ and mg Kg^{-1} , respectively. Regarding the abiotic degradation of these compounds and more specific their hydrolysis at neutral pH and mesophilic and thermophilic conditions which may be used during sludge treatment, so far data

in the open literature is scarce. Based on the above, the main objectives of this study were: a) to develop and fully validate a fast and efficient analytical method for the simultaneous determination of different cyclic siloxanes, (D3, D4, D5, D6, D6_silane) by LLE – GC-MS and b) to investigate the contribution of hydrolysis on the removal of these compounds. Hydrolysis experiments were conducted under different temperatures (4 °C, 20 °C, 35 °C and 55 °C) and at neutral pH.

2. Materials and methods

2.1. Chemicals and standards

High purity analytical standards of D3, D4, D5, D6, D6_silane and tetrakis(trimethylsiloxy)-silane (M4Q) (all >95% purity) were purchased from Sigma-Aldich (USA). M4Q was used as surrogate. Stock solutions of individual compounds were prepared both in pentane and methanol at 1000 mg L⁻¹ and kept at -18 °C. The stock solutions were used to regularly prepare working standard solutions for calibration and spiking experiments. HPLC grade water was prepared in the laboratory using a MilliQ/MilliRO Millipore system (USA). All organic solvents including ethyl acetate, methanol, pentane, dichloromethane and isooctane were supplied by Merck (Germany) and were of high purity (>95%). KH₂PO₄, Na₂HPO₄, CaCl₂ and MgSO₄·7H₂O were purchased by Fluka (USA).

2.2. Extraction of wastewater and sludge

Isolation of target compounds from both liquid and solid samples was based on previously developed method (Bletsou *et al.*, 2013) but with many modifications. For wastewater, 10 mL of sample were transferred into a 40 mL Eppendorf centrifuge tube and 300 ng of M4Q (prepared in methanol) were added. After 20 min of equilibration, target analytes were extracted for 1 min by LLE with 10 mL of pentane. The sample was extracted two more times with 2.5 mL mixture of pentane: dichloromethane (1:1) and 2.5 mL of mixture pentane: ethyl acetate (1:1). Each LLE step lasted 1 min. The combined organic layers were evaporated to a final volume of 500 µL under a gentle stream of N₂. Finally, the extracts were transferred into a vial containing 0.5 mL of pentane and subjected to GC-MS analysis.

Regarding sewage sludge, 85 mg of dry sludge were spiked with 300 ng of M4Q and allowed to equilibrate for 20 min in the freezer. Then, 5 mL of pentane and 1 mL of isooctane were added to the sample, shaken for 24 hours and centrifuged for 10 minutes at 5000 rpm. The organic layer was transferred into an Eppendorf centrifuge tube and the extraction was repeated three more times. First with 5 mL of pentane for 1 h, second with 2.5 mL of pentane: dichloromethane (1:1) for 1h and third with 2.5 mL of pentane: ethyl acetate (1:1) for 1h. All extracts were combined and a procedure similar to that reported above for wastewater samples was followed. The gas chromatographic vial caps were free of silicon to minimize background levels of siloxanes. The analysts refrained from using hand lotions and other personal care products that contained siloxanes. The procedural blank was analyzed with every 10 samples and background levels of siloxanes were taken into account during interpretation of the results. Prior to instrumental analysis, pentane was injected into GC-MS, until the background levels of siloxanes became stable. In addition, standard solution and spiked sample were injected after every 10 sample injection to evaluate the drift in instrumental sensitivity. Pentane was injected after every 10 samples as a check for background contamination and carry-over.

2.3. Instrumental analysis

Analysis was performed on an Agilent 7890A GC interfaced with an Agilent 5975C MS. Separation was achieved by a DB5MS capillary column (60 m) with a film thickness of 0.25 µm and internal diameter of 0.32 mm (Agilent Technologies, USA). Two µL of extract were injected using a 768313 Agilent autosampler (Agilent Technologies, USA) in a splitless mode at 200 °C and helium was used as a carrier gas at a flow rate of 1.0 mL min⁻¹. The oven temperature was programmed from 40 °C (held for 1 min); it was then increased to 220 °C at a rate of 20 °C min⁻¹ and from 220 to 280 °C at a rate of 25 °C min⁻¹, with a postrun time of 5 min at 300 °C.

The MS was operated in an electron-impact ionization mode (EI) at 70 eV, and the data were acquired by selected ion monitoring (SIM).

2.4. Validation of the analytical methods

Calibration of the GC-MS system was performed using eight different concentrations in the range of 10-1000 $\mu\text{g L}^{-1}$ for each compound, with three replicates per concentration. Matrix matched calibrations were also performed using fortified samples in the range of 10-1000 ng for both types of samples. For the determination of the analytical LOD, 10 mL of surface water were spiked with 7 ng of the target siloxanes, whereas 85 mg of dry sludge spiked with 10 ng. The LOD of each compound was calculated as three times the standard deviation of nine independent replicate analyses. Precision was assessed performing repeatability (intra-day precision) and reproducibility (inter-day precision) experiments. Intra-day precision data was obtained by analyzing six samples ($n = 6$) spiked at a level of 30 $\mu\text{g L}^{-1}$ of each compound. Inter-day precision data was obtained by analyzing six samples ($n = 6$), spiked at a level of 30 $\mu\text{g L}^{-1}$ of each compound, at three different days ($k = 3$). Sludge samples were spiked with 300 ng of siloxanes during precision experiments. Recovery studies were performed at three fortification levels of the substances in wastewater (10, 30 and 80 $\mu\text{g L}^{-1}$) and two in sludge (100, 300 and 800 ng) in order to evaluate the trueness of the method.

2.5. Hydrolysis experiments

For the hydrolysis experiments buffer solution at pH=7 prepared in MilliQ water, according to OECD protocol 111(OECD 2004) was used. This solution was also enriched with small amounts of CaCl_2 (0.03 g L^{-1}) and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.02 g L^{-1}). A volume (43 mL) of buffer solution was placed in amber glass vial and spiked with a mixture of the target siloxanes (100 $\mu\text{g L}^{-1}$). Spiking was performed under surface taking special care so as to avoid headspace in the vials. Experiments were performed in the dark at four different temperatures: 4, 20, 35 and 55 $^\circ\text{C}$. For each temperature, there were three replicates and one blank solution. The total duration of experiments was 12 d and samples were taken at $t=0$ and in regular intervals (3 h, 6 h, 15 h, 24 h, 3 d, 7 d and 12 d) for GC-MS analysis.

3. Results and discussion

3.1. Instrumental analysis

According to the results, the best chromatographic separation of the six siloxanes was obtained in almost 15 min (Fig. 1) using pentane as the carrier solvent.

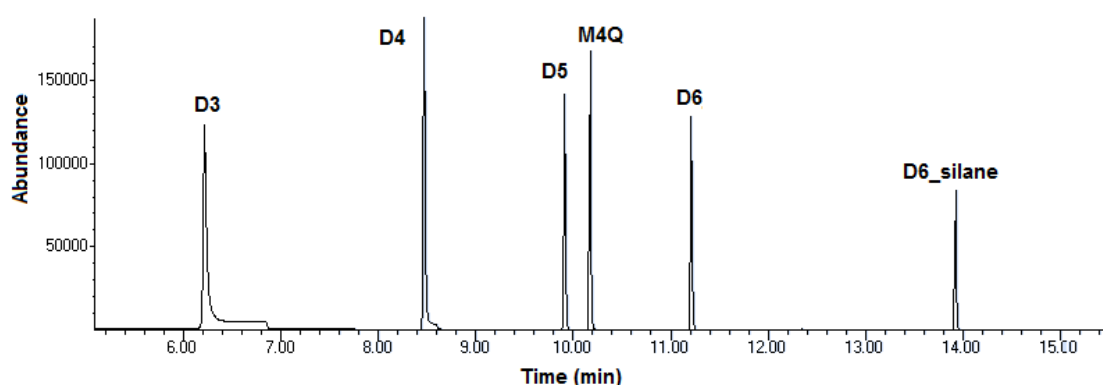


Figure 1: Chromatogram of a standard solution containing 0.3 mg L^{-1} of the target siloxanes and the surrogate (M4Q) in SIM mode.

Pentane was chosen among different solvent which were tested (pentane, hexane, heptane, octane) since resulted in the less contribution to the total background. Extraction of several siloxanes using pentane has been reported by other authors as well (Wang *et al.*, 2013). To evaluate the best mass spectral data for each siloxane, injection of every individual compound

was performed in full scan (mass range from 50-500) and the most abundant ions were selected from its spectrum. The chosen ions for SIM mode were 207, 191, 96 for D3, 281, 265, 349, 133 for D4, 355, 267 for D5, 348, 201, 215 for D6, 281, 147, 369 for D6-silane and 341, 429, 325 for M4Q. The selected ions are in agreement with those reported in the open literature (Bletsou *et al.*, 2013).

3.2. Validation of the analytical methods

Satisfactory linearity was observed all along the tested area of concentration for all the compounds both during instrumental and matrix matched calibrations with coefficients of correlation (R^2) > 0.99. The obtained LODs varied from 2.2 (D4) to 4.6 (D6_siloxane) ng mL⁻¹ and from 0.1 (D4) to 1.8 (D5) ng mg⁻¹ for wastewater and sludge, respectively. These values are higher compare to other authors (Bletsou *et al.*, 2013). However, it should be taken into account the lower preconcentration factors in the present study (only 10 mL of wastewater and 85 mg of sludge were extracted) compared to others. The precision experiments have shown acceptable repeatability and reproducibility of the analytical procedures, both during the same day and between days. According to the results, RSDs less than 10% were observed in all cases for both types of matrices. Regarding the trueness experiments, the modified analytical method for wastewater resulted in satisfactory recoveries almost for all the tested siloxanes, ranging from 68% (D4) to 108% (D6_silane) with RSDs ≤ 13 % in all cases. D3 was the only compound for which low recoveries (<40 %, RSDs <16 %) were observed. Sanchís *et al.* (2013) also reported low recovery of D3 (around 40%), probably due to the high vapour pressure of this compound. As for the sludge samples, recoveries varied between 67% (D3) and 110% (D6_siloxane) and the observed RSDs were less than 11%. D5 was the only compound for which too high recoveries (up to 150%) were observed but with good repeatability (RSDs < 11%). Results are comparable with those reported by other authors, although much lower amounts of wastewater and sludge sample were extracted (Bletsou *et al.*, 2013; Sanchís *et al.* 2013).

3.3. Hydrolysis experiments

According to the results, all tested siloxanes undergo hydrolysis. D3 found to be the most sensitive among the five compounds. About 70% of its initial concentration was disappeared after 15 h even at 4 °C and the elimination was increased with the increase of temperature (90% loss at 55 °C after 15 h). Hydrolysis of other target compounds was much slower. D4 loss due to hydrolysis reached 53%, 70%, 91% and 96% at 4, 20, 35 and 55 °C, respectively, after 12 d of experiment. D5 reduction was evident after the 3rd day of the experiment and at the end of the experiment varied between 59% and 98% at 4 and 55 °C, respectively. As for D6, no loss of the compound was observed throughout the experiment at 4 °C, whereas its removal ranged up to 50% at 55 °C (12 d). Finally, D6 silane concentration loss varied from 15% (4 °C) to 38% (55 °C) during the experiment (12 d).

4. Conclusions

A fast and efficient LLE-GC-MS analytical method was modified and fully validated during the present study, which was able to meet the needs for the simultaneous determination of the selected cyclic siloxanes. Results indicated satisfactory recoveries and LODs with acceptable RSDs for all the compounds except D3 for which low recoveries were observed for wastewater. Regarding hydrolysis experiments, results showed that all compounds are removed due to this abiotic process. As the temperature increases the loss is greater. Furthermore, it seems that the smaller the molecule is, the more sensitive to hydrolysis is.

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