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Analysis of linear and cyclic methylsiloxanes in water by headspace-solid phase microextraction and gas chromatography–mass spectrometry

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ABSTRACT

This paper proposes a new method for the analysis of linear and cyclic methylsiloxanes in water samples based on headspace-solid phase microextraction (HS-SPME) coupled to gas chromatography–mass spectrometry (GC–MS). The extraction efficiency of four commercially available SPME-fibres was evaluated and it was found that a 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) coating was the most suitable for the extraction of siloxanes. The method provided good linearity ($r > 0.999$) and precision (RSD % <17%), and low limits of quantification ranging from 0.01 to 0.74 ng L^{-1} for linear siloxanes and between 18 and 34 ng L^{-1} for cyclic siloxanes. The HS-SPME-GC–MS method was applied to the analysis of linear and cyclic siloxanes in river waters from Catalonia (NE, Spain) and the results showed concentrations of linear and cyclic siloxanes ranging from 0.09 to 3.94 ng L^{-1} and 22.2 to 58.5 ng L^{-1}, respectively.

1. Introduction

Cyclic and linear methylsiloxanes represent a new group of compounds proposed as priority chemicals following environmental risk assessments. This is due to their widespread use, their physicochemical properties – which have the potential to persist in the natural environment – and their bioaccumulation capacity [1]. Over the last three decades, these compounds have been used widely in the industrial production of silicon polymers and in consumer goods such as electronics, health and personal care products, cleaning agents, cookware and medical devices [2,3]. Due to their high volatility, these compounds have been detected in both outdoor and indoor environments [4–10] as they are released into the atmosphere during manufacturing processes and by the use of consumer products. In addition, due to their high affinity to the organic matter [11], these compounds have also been found in effluents and sludges from wastewater treatment plants (WWTPs) [11–13]. Several reports indicate that these compounds cause toxic effects on wildlife, such as estrogen mimicry, connective tissue disorders, adverse immunologic responses, and liver and lung damage [14–17]. Although information about their toxicity is still limited it is important to have an understanding of the occurrence and distribution of these compounds in the environment.

The analysis of linear and cyclic siloxanes in the environment is not easy due to their high volatility and the potential sources of background contamination that affect their final determination [2]. Linear and cyclic methylsiloxanes have been found in environmental samples, such as air [4–9], biota [1,5,6,18,19], sediment [5,6,13,20], sludge [5,6,12,13], soil [5,6,21], water [5,6,11] and dust [22], and also in landfill biogas samples [23,24]. Headspace (HS) [11] and purge and trap [5,6,18,25] techniques combined with gas chromatography–mass spectrometry (GC–MS) are the methods commonly used for the analysis of these compounds in solid and water samples. Among the siloxanes, decamethylcyclopentasiloxane (D5) has been the most abundant compound in all matrices [6]. Nevertheless, limited information about the occurrence of siloxanes in natural water has been reported because they are present at very low concentration levels (<100 ng L^{-1}). In a recent study, Sparham et al. [11] proposed the use of HS–GC–MS which would constitute a method with enough sensitivity to analyse these compounds at these concentration levels. This method was applied to the analysis of D5 in river water and treated wastewater. Another simple and solvent free method that could improve the detection limits is headspace-solid phase microextraction (HS-SPME), which is frequently used to analyse environmental samples [26]. To date, HS-SPME has not been applied to the analysis of methylsiloxanes, although it has been used to study the volatile composition of polysiloxane rubber [27].

The aim of the present paper was to develop an HS-SPME method combined with GC–MS for routine analysis of linear and cyclic methylsiloxanes in water samples. To achieve maximum sensitivity and selectivity, the HS-SPME parameters that affect the

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Table 1
Quantification and confirmation ions selected for the analysis of linear and cyclic siloxanes by HS-SPME–GC–MS.

Compound	Abbreviation	Retention time (t_R) (min)	Time window (min)	Molecular ion (m/z)	Quantification ion (m/z)	Confirmation ion (m/z)
Hexamethyldisiloxane	L2	5.40	5:00–7:00	162	147 $[M–CH_3]^+$	131, 117
Hexamethylcyclotrisiloxane	D3	7.78	7:00–8:50	222	207 $[M–CH_3]^+$	191, 177
Octamethyltrisiloxane	L3	8.83	8:50–10:00	236	221 $[M–CH_3]^+$	205, 189
Octamethylcyclotetrasiloxane	D4	10.76	10:00–11:40	296	281 $[M–CH_3]^+$	265, 249
Methyltris(trimethylsiloxy)silane	IS-1	11.71	11:40–12:50	310	295 $[M–CH_3]^+$	207, 281
Decamethyltetrasiloxane	L4	11.98	11:40–12:50	310	207 $[M–CH_3–Si(CH_3)_4]^+$	295, 191
Decamethylcyclopentasiloxane	D5	13.32	12:50–13:60	370	355 $[M–CH_3]^+$	267, 339
Tetrakis(trimethylsiloxy)silane	IS-2	13.83	13:60–15:20	384	281 $[M–CH_3–Si(CH_3)_4]^+$	369, 265
Dodecamethylpentasiloxane	L5	14.65	13:60–15:20	384	281 $[M–CH_3–Si(CH_3)_4]^+$	369, 265
Dodecamethylcyclohexasiloxane	D6	15.84	15:20–16:50	444	341 $[M–CH_3–Si(CH_3)_4]^+$	429, 325

extraction and desorption processes were optimised. The method was applied to the determination of cyclic and linear volatile methylsiloxanes in river water samples.

2. Experimental

2.1. Chemical and materials

Hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5), hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6) were obtained at a purity of over 97% from ABCR (Darmstadt, Germany). Methyltris(trimethylsiloxy)silane (IS-1) and tetrakis(trimethylsiloxy)silane (IS-2) were used as internal standards for linear and cyclic methylsiloxanes, respectively. They were also purchased from ABCR at a purity of over 98%.

Individual stock standard solutions of each compound and internal standards of 2000 mg L^{-1} were prepared in acetone for residue analysis (Merck) from their respective pure standards. Secondary individual standard solutions were prepared by successive dilution of the stock standard solutions in acetone to give concentrations of 10 mg L^{-1} for cyclic siloxanes and 1 mg L^{-1} for linear siloxanes. A standard mixture of all the compounds at concentrations ranging from 0.01 to 20 μg L^{-1} for linear siloxanes and between 10 and 150 μg L^{-1} for cyclic siloxanes was prepared in acetone by dilution from the secondary individual standard solutions. This solution was stored at 0 °C and was prepared monthly. For siloxane determination, six calibration water standard solutions were prepared by adding of 20 μL of the standard mixtures into a 40 ml screw-cap glass vial fitted with black Viton septa (Supelco, Bellefonte, PA, USA) containing 20 ml of bottled natural mineral water at concentrations between 0.01 and 20 ng L^{-1} for linear methylsiloxanes and between 10 and 150 ng L^{-1} for cyclic methylsiloxanes. In addition, appropriate amounts of the internal standard solutions were added to each calibration solution to give a concentration of 1 ng L^{-1} for IS-1 and 70 ng L^{-1} for IS-2. By using this procedure for the preparation of water calibration solutions, the amount of acetone in all vials was kept constant, which prevents changes in the selectivity of the SPME fibre. To evaluate the internal standard method, standard addition was used for quantification of a river water sample. For this purpose, replicate analyses ($n = 3$) of this sample were carried out spiking the sample with an adequate amount of standard solution of linear and cyclic siloxanes at 0%, 50%, 100%, 150% and 200% of the estimated concentrations and using IS-1 and IS-2 as internal standards at a concentration of 1 ng L^{-1} and 70 ng L^{-1}, respectively. All standards and samples were prepared in a laminar flow cabinet of a clean room (Class 100). Acetone and sodium chloride for residue analysis were purchased from Merck. All glassware was treated with chromosulphuric acid, solvent rinsed and heated to 400 °C before use. Nylon syringe filters (0.2 μm) were supplied by Filter-Lab (Barcelona, Spain). Natural mineral water was obtained from Font Vella (San Hilari Sacalm, Spain).

HS-SPME experiments were performed with a manual fibre holder supplied from Supelco. Four commercially available SPME fibres were tested: 100 μm polydimethylsiloxane (100 μm-PDMS), 65 μm polydimethylsiloxane/divinylbenzene (65 μm-PDMS/DVB), 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (50/30 μm-DVB/CAR/PDMS) and 85 μm carboxen/polydimethylsiloxane (85 μm-CAR/PDMS) purchased from Supelco. Before use, each fibre was conditioned in the GC injection port under helium flow according to the manufacturer's recommendation. After conditioning, fibre blanks were run periodically to ensure there were no contaminants or carryover present.

2.2. Water samples

Twelve water samples were collected in the Llobregat and Besós Rivers (Barcelona, NE Spain) in May of 2011. These rivers are located in the northeast of Spain and flow into the Mediterranean Sea near the city of Barcelona. The lower sections of these rivers run through very densely populated and industrialized areas, receiving extensive urban and industrial waste water discharges from more than 3 million inhabitants. Sampling sites in the Llobregat River were located downstream of the towns of *Martorell*, *Molins de Rei*, *Sant Boi de Llobregat* and el *Prat de Llobregat* (one sample each). In addition, three surface water samples were collected before the intake of the *San Joan Despí* drinking water treatment plant (DWTP), the biggest DWTP supplying water to the city of Barcelona. Five water samples from the Besós River were collected at the towns of *Montcada i Reixach*, *Santa Coloma de Gramanet* and *Sant Adriá de Besós*. Glass bottles (100 ml) fitted with black Viton septa were filled with water without headspace and stored in the dark at 4 °C before being analysed. Field blanks consisting of 100 ml of natural mineral water were prepared at the same sampling points and they were analysed along with the real water samples. Before analysis, the river water samples were filtered using nylon syringe filters (0.2 μm) to avoid the presence of particulate matter.

2.3. HS-SPME method

The HS-SPME procedure was carried out as follows: 20 ml water sample was placed in a 40 ml screw cap glass vial fitted with black Viton septa containing a 10 mm × 5 mm PTFE-coated stir bar and an appropriate amount of the internal standards was then added by weight through the septum of the sample vial. The final internal standard concentrations were 70 ng L^{-1} for cyclic siloxanes and 1 ng L^{-1} for linear siloxanes. To prevent any losses of the analytes through the septum hole, a stainless steel rod (0.55 mm O.D. × 15 mm of length) was used for closing the septum hole just after addition of internal standard. Moreover, to avoid the possible adsorption of analytes the steel rod was not exposed to

the headspace vapours. Before the HS-SPME analysis, the sample vial was vortex mixed for 3 min and conditioned for 10 min in a thermostatic water bath at the extraction temperature. Then the sample and the calibration solutions were extracted with a 65 μm-PDMS/DVB fibre at 25 °C for 40 min using a constant magnetic agitation rate of 750 rpm. Finally, thermal desorption of the analytes was carried out by exposing the fibre in the GC injector port at 240 °C for 5 min. The fibre was kept in the injector port for an additional time of 5 min, with the injector port in split mode (purge on) to prevent possible carryover. Further details about the optimisation of the HS-SPME procedure are given in Section 3.1.

2.4. GC–MS determination

The determination of the linear and cyclic siloxanes by GC–MS was carried out on a trace GC 2000 Series gas chromatograph (ThermoFisher, Milan, Italy) coupled to a DSQ II mass spectrometer (ThermoFisher, Milan, Italy). The chromatographic separation of the target compounds was performed on a DB-5 MS (5% phenyl, 95% methyl polysiloxane) fused silica capillary column (J & W Scientific, Folson, USA), 60 m × 0.25 mm I.D., 0.25 μm film thickness. The oven temperature was programmed from 40 °C (held for 2 min) to 250 °C at 10 °C min^{-1} (held for 5 min). Helium was used as a carrier gas at a constant flow-rate of 1 ml min^{-1} held by electronic flow control. The injector temperature was maintained at 240 °C and the splitless injection mode (2 min) was used for the HS-SPME experiments. An SPME glass inlet liner (I.D., 0.75 mm, SGE Europe) and a 23-gauge Merlin Micro-seal septum (Supelco, Bellefonte, PA, USA) were used for the SPME analysis. The MS was operated in electron ionisation (EI) mode with 70 eV and 100 μA. Transfer line and ion source temperatures were set at 280 °C and 250 °C, respectively. For data acquisition, the selected ion monitoring (SIM) mode was used at a dwell time of 100 ms and a delay time of 20 ms. Table 1 shows the ions selected for quantification and confirmation of the linear and cyclic methyl siloxanes using the GC–MS method. Quantification of siloxanes was carried out by internal standard method, using methyltris(trimethylsiloxy)silane (IS-1) and tetrakis(trimethylsiloxy)silane (IS-2) as standards for cyclic and linear siloxanes, respectively. Xcalibur version 2.0 software was used for data acquisition and results processing.

2.5. Quality control

Criteria for ensuring the quality of the data included specific tests for checking the GC separation, the sensitivity of the GC–MS system using standards and a quality control water sample (a river water sample spiked at 1 and 40 ng L^{-1} for linear and cyclic methylsiloxanes, respectively), the validity of the calibration, and the possible carryover between samples. Procedural blanks covering both the instrumental and the HS-SPME procedure were routinely performed every three samples to evaluate the contribution of background levels on the siloxane response. In addition, each water sample was accompanied by a field blank to ensure the accurate tracing of any contamination. The mean value of the area of each analyte in the field blanks was used for subtraction. The personnel involved in this work refrained the use of personal care products to minimize the contamination before or during the sampling and analysis. The preparation of standards, procedural blanks, and samples were carried out in a clean air cabinet under a laminar flow. Limits of detection (LODs) and quantification (LOQs) were set as the amount of analyte that provides a response in the field blank equal to the mean plus three and ten times the standard deviation, respectively. To confirm the identification of siloxanes, the following restrictive criteria were applied: (a) the isotope ratios between the selected ions monitored should be within ±15% of the theoretical value, and (b) the retention times should be within ±2 s of those observed for the standards.

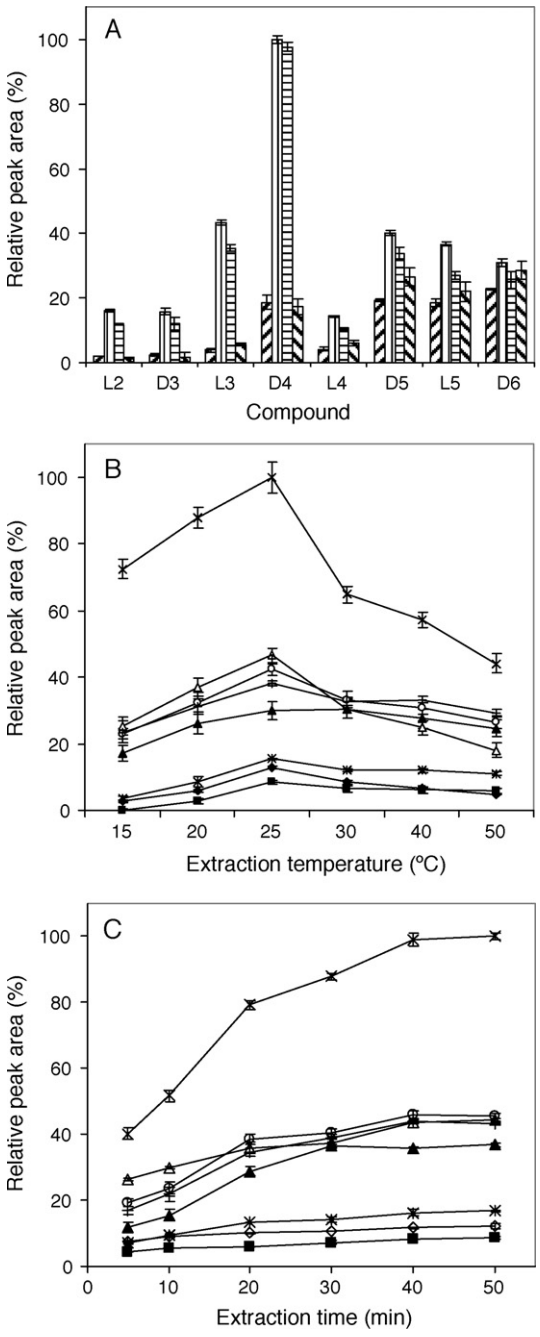

Fig. 1. Behaviour of the commercially SPME fibres (A): (▨) 100-μ PDMS, (▥) 65-μm PDMS/DVB, (▤) 30/50-μm CAR/DVB/PDMS, and (▧) 65-μm CAR/PDMS, on the extraction of linear and cyclic siloxanes. Effect of extraction temperature (B), and time (C) on the extraction efficiency of linear and cyclic siloxanes by HS-SPME. Compounds: (◊) L2, (△) L3, (✳) L4, (|) L5, (■) D3, (×) D4, (○) D5, (▲) D6 (conditions: 65-μm DVB-PDMS fibre, extraction time 50 min and desorption time 5 min).

3. Results and discussion

3.1. Headspace-SPME optimisation

The presence of siloxanes in procedural blanks as background contamination produced by the instrument, laboratory products

and reagents, and also ambient air, are the major difficulty in the analysis of siloxanes in environmental samples [2,11,28]. This contamination affects quantification and requires a thorough control of the blanks to ensure the reliability of the results. In the present work, some actions were taken into account to reduce the contribution of background contamination to the procedural blanks. For instance, the use of a Merlin micro-seal septum instead of a silicone septum in the GC injector port and black Viton septa in the SPME vials allowed a reduction of 90% of the background levels of cyclic siloxanes in the instrumental blanks. However, the main sources of contamination of procedural blanks came from the ambient air and the ultrapure water used for preparing blanks and standards. Experiments carried out using bottled natural mineral water and the use of a laminar flow cabinet for sample handling and standard preparation allowed a substantial reduction in the background levels of linear siloxanes (96–99%), although for cyclic siloxanes this reduction was slightly lower (62–92%). Therefore, to minimize the contribution of siloxanes to the procedural blanks, we recommend the use of a laminar flow cabinet and bottled natural mineral water for preparing of both procedural blanks and standards.

The first step in the optimisation of the HS-SPME procedure was the selection of the appropriate fibre for the analysis of siloxanes. The following four SPME fibres were tested to obtain the best sensitivity and selectivity for siloxane determination: 100 μm PDMS, 65 μm PDMS/DVB, 50/30 μm DVB/CAR/PDMS and 85 μm CAR/PDMS. For this purpose, a long extraction time (50 min) and a pre-equilibration time of 15 min were applied to ensure that maximum amounts of cyclic and linear siloxanes were extracted. In addition, the extraction temperature and desorption time were fixed to 30 °C and 2 min, respectively. The desorption temperature was 250 °C for all fibres, which is within the recommended operating temperature range. For this study, 10 ml of a bottled mineral water sample spiked with 200 ng L^{-1} of each compound was analysed using the five fibres. No carryover on second desorption was found for any of the fibres, indicating that the complete removal of analytes at these conditions was achieved. Fig. 1(A) shows the relative peak area obtained for cyclic and linear siloxanes using the studied fibres. The 65 μm PDMS/DVB fibre and CAR/DVB/PDMS fibre provided the highest extraction yields for all the compounds. The PDMS/DVB coating was selected for all subsequent experiments due to the slightly higher extraction efficiencies obtained.

After the fibre was selected, several HS-SPME parameters related to the extraction and desorption steps were optimised. Initially, the effect of temperature on the siloxane extraction yield was examined using a sampling time of 50 min and a desorption temperature and time of 250 °C and 5 min, respectively. As Fig. 1(B) shows, maximum relative responses were obtained for all the compounds at an extraction temperature of 25 °C. At temperatures above 25 °C lower responses were obtained because of the decrease in the distribution constants of the analytes between the headspace and the fibre coating. Sodium chloride (NaCl, 0–30%, w/w) was used to study the effect of the ionic strength. In our case, the addition of NaCl did not significantly improve the amount of siloxane extracted. This could be attributed to both the high volatility of these compounds that allowed a rapid migration from the aqueous solution to the headspace, and to their low solubility in water. We also studied the influence of the headspace and aqueous solution volume ratio (V_h/V_w) on the siloxane extraction yield using a 40 ml vial. An aqueous volume of 20 ml ($V_h/V_w = 1$) was chosen since it provided the best results. Larger aqueous volumes were not tested because when reducing the headspace volume the complete spreading of the fibre was not possible. The extraction time required to reach the equilibrium between the fibre coating and the headspace was evaluated. This parameter was studied from 5

Table 2
Quality parameters of the HS-SPME–GC–MS method and analysis of a spiked river water sample by internal standard and standard addition methods.

Compound	Linear range (ng L^{-1})	Correlation coefficient (r)	Intra-day precision (RSD, %) [a]	Method LOD (ng L^{-1})	Method LOQ (ng L^{-1})	Concentration (ng L^{-1})			
						Spiked concentration (ng L^{-1})	Internal standard (mean ± S.D.) [b]	Standard addition (mean ± S.D.) [b]	Significance level [c] (p-value)
L2	0.2–20	0.9998	17	0.05	0.17	0.99	0.94 ± 0.16	0.93 ± 0.14	0.949
L3	0.01–20	0.9990	16	0.003	0.01	1.03	1.16 ± 0.14	1.02 ± 0.15	0.205
L4	0.03–20	0.9998	13	0.01	0.03	1.04	0.97 ± 0.18	1.20 ± 0.17	0.225
L5	0.8–20	0.9995	14	0.25	0.74	1.02	1.05 ± 0.20	1.18 ± 0.17	0.734
D3	35–150	0.9997	5	11	34	42.2	41.8 ± 2.4	41.2 ± 3.0	0.600
D4	20–150	0.9944	4	6	19	40.2	41.5 ± 2.5	41.4 ± 2.4	0.426
D5	20–150	0.9998	4	6	19	40.4	41.6 ± 3.5	40.9 ± 1.9	0.189
D6	20–150	0.9995	6	6	18	40.8	42.3 ± 2.8	41.1 ± 2.6	0.260

[a] $n = 6$ (spiked level: 1 ng L^{-1} for linear and 40 ng L^{-1} for cyclic siloxanes).
[b] $n = 3$.
[c] Significant differences between methods for p-value < 0.05 (at 95% confidence level).

Table 3
Concentrations of linear and cyclic siloxanes (ng L^{-1}) in Llobregat and Besos river water samples by HS-SPME–GC–MS.

Compound	Concentration (ng L^{-1})									
	Llobregat river ($n=7$)					Besos river ($n=5$)				
	Detection frequency	Mean[a]	Min	Max	Median	Detection frequency	Mean[b]	Min.	Max.	Median
L2	7/7	0.77	0.33	1.53	0.43	3/5	1.32	0.93	1.65	1.37
L3	7/7	1.02	0.58	2.14	0.72	5/5	0.56	0.17	0.85	0.78
L4	6/7	0.27	0.09	0.55	0.18	3/5	0.57	0.16	0.80	0.75
L5	5/7	2.19	0.95	3.94	1.98	3/5	1.28	0.99	1.44	1.41
D3	0/7	nd	–	–	nd	0/5	nd	–	–	nd
D4	0/7	nd	–	–	nd	0/5	nd	–	–	nd
D5	2/7	22.9	22.2	23.5	22.9	1/5	58.5	–	–	nd
D6	0/7	nd	–	–	nd	1/5	21.2	–	–	nd

[a] Mean of seven river water samples (3 replicate analyses of each sample).
[b] Mean of five river water samples (3 replicates analyses of each sample).
nd: not detected, <LOD.

to 50 min using the optimal conditions previously established. As shown in Fig. 1(C), where the extraction time profiles obtained for the linear and cyclic siloxanes are given, a period of 40 min was enough to reach the equilibrium and so it was chosen as the optimal extraction time. For the desorption process, several temperatures (220, 230, 240 and 250 °C) of the GC injector port were studied, maintaining the desorption time constant at 5 min. Up to 240 °C an increase in the response was observed, so this temperature was selected. Finally, the quantitative desorption of the analytes from the fibre coating to the injector port was achieved in 2 min and no sample carryover was observed at these conditions. In summary, the HS-SPME optimal conditions for the analysis of linear and cyclic siloxanes in water using a 65 μm PDMS/DVB fibre were: an extraction temperature of 25 °C, an extraction time of 40 min, a

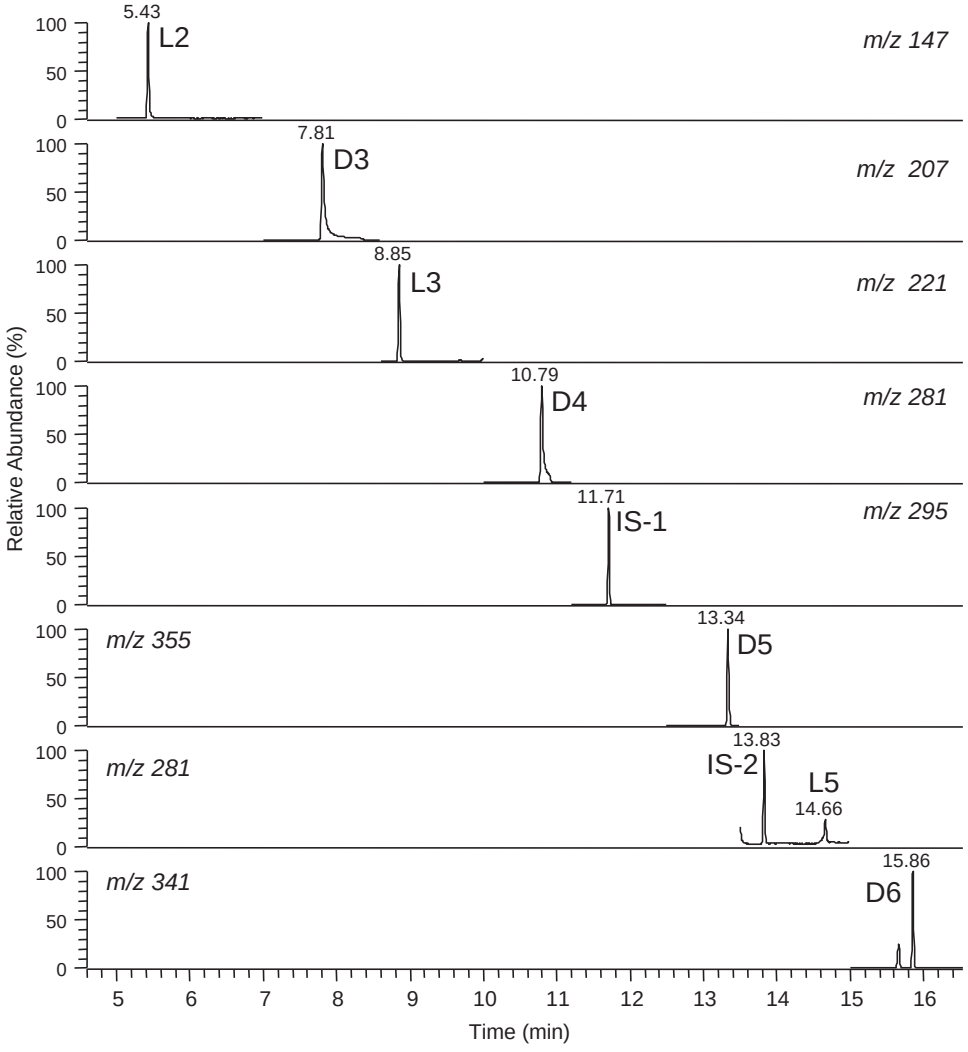

Fig. 2. GC–MS (SIM) chromatogram of a water sample from the Besós River analysed by HS-SPME–GC–MS.

headspace/aqueous volume ratio of 1 (20 ml/20 ml) in a 40 ml glass vial, a desorption temperature of 240 °C, a desorption time of 2 min and no salt addition.

3.2. Analysis of linear and cyclic siloxanes in river water samples

To examine the performance of the proposed HS-SPME–GC–MS method, quality parameters such as linearity, limits of detection (LOD), limits of quantification (LOQ) and repeatability were established (Table 2). Bottled mineral water spiked from 0.01 to 20 ng L^{-1} for linear siloxanes and between 20 and 150 ng L^{-1} for cyclic siloxanes were used to study linearity. Regression coefficients (r) higher than 0.999 were obtained for all the compounds (Table 2) at concentrations ranging from the limit of quantification to 20 ng L^{-1} for linear and 150 ng L^{-1} for cyclic siloxanes, respectively. Since no blank river water samples were found, the field blanks ($n = 12$) obtained from each sampling point were used to estimate the LOD and LOQ values of the method. Each field blank was analysed in triplicate using the developed method and the method LOD and LOQ were determined as the concentration of analyte that provides a response equal to the mean (12 field blanks × 3 replicates) plus three and ten times the standard deviation, respectively. Method LODs ranged from 0.003 to 0.25 ng L^{-1} for linear siloxanes and from 6 to 11 ng L^{-1} for cyclic siloxanes (Table 2), while the LOQs were between 0.01 and 0.74 ng L^{-1} for linear and from 18 to 34 ng L^{-1} for cyclic siloxanes. These values are lower than those reported using purge and trap method [6], but similar to that found by Sparham et al. [11] for D5 using headspace–GC–MS. The intra-day precision of the whole HS-SPME–GC–MS method was also studied by analysing a river water sample with very low concentration levels of siloxanes (<0.1 ng L^{-1} for linear and <10 ng L^{-1} for cyclic siloxanes) spiked at a concentration of 1 ng L^{-1} for linear siloxanes and 40 ng L^{-1} for cyclic siloxanes. Six independent analyses of the spiked river water sample were performed using the proposed HS-SPME–GC–MS method and relative standard deviations (RSD%) lower than 17% were obtained for all the compounds (Table 2). In addition, to assure that the matrix did not affect the reliability of the results obtained by internal standard method using as calibration solutions spiked bottled natural mineral water, quantification by the standard addition method was also applied (Section 2.1) for the analysis of water samples using HS-SPME–GC–MS. For this purpose, replicate analyses ($n = 3$) of a river water sample spiked at 1 ng L^{-1} for linear and 40 ng L^{-1} for cyclic siloxanes were carried out using both quantification methods and the results obtained are summarized in Table 2. As can be seen, good agreement between the two quantification methods was obtained and no significant differences were observed (p-value > 0.05), demonstrating the validity of the internal standard method and the absence of matrix effect using the HS-SPME–GC–MS.

In order to evaluate the applicability of the optimised HS-SPME–GC–MS method to the analysis of linear and cyclic siloxanes in waters, twelve river water samples collected at the Llobregat and Besós Rivers were analysed in triplicate and the results are summarized in Table 3. Linear siloxanes were found in Llobregat and Besós river waters at concentration levels ranging between 0.09 and 3.94 ng L^{-1} and from 0.16 to 1.65 ng L^{-1}, respectively. For cyclic siloxanes, concentrations of the D5 ranged from 22.2 ng L^{-1} (Llobregat River) to 58.5 ng L^{-1} (Besós River), while the D6 was only found in a sample from Besós River (21.2 ng L^{-1}). D3 and D4 were not detected in any of the samples analysed. Fig. 2 shows as an example the GC–MS selected ion monitoring (SIM) chromatograms of a water sample from the Besós River. The differences in the concentration levels between linear and cyclic siloxanes are in agreement with data reported in the literature [5,6] and can be attributed to the widespread use of consumer products that mainly contain D5 siloxane [4,11]. Similar concentrations for D5 have been found in water samples from two UK rivers (12.9–59.2 ng L^{-1}) [11].

4. Conclusions

A new headspace-SPME method combined with GC–MS has been developed to analyse siloxanes in water samples. The PDMS/DVB fibre (25 °C, 40 min) was found to be the most effective coating for the extraction of siloxanes. The proposed method provided low limits of quantification, from 0.01 to 0.74 ng L^{-1} for linear siloxanes and from 18 to 34 ng L^{-1} for cyclic siloxanes, and precise results (RSD < 17%) for the analysis of river water samples. The absence of matrix effect using the HS-SPME has been demonstrated allowing to propose the internal standard method with water standard solutions as calibrants for the quantification of the target compounds. The HS-SPME–GC–MS has proved to be a fast and sensitive method for the analysis of linear and cyclic siloxanes at ng L^{-1} levels in river water and can be proposed as a novel method for the routine analysis of these compounds.

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