Journal of Chromatography A, 1217 (2010) 7024–7030

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Determination of cyclic and linear siloxanes in soil samples by ultrasonic-assisted extraction and gas chromatography–mass spectrometry

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ARTICLE INFO

Article history:
Received 12 July 2010
Received in revised form 9 September 2010
Accepted 10 September 2010
Available online 17 September 2010

Keywords:
Gas chromatography–mass spectrometry (GC–MS)
SAESC
Siloxanes
Soil

ABSTRACT

A rapid method, based on sonication-assisted extraction in small columns (SAESC) and subsequent quantification and identification by gas chromatography–mass spectrometry (GC–MS), was developed for the determination of cyclic and linear siloxanes in soil. In the experiments with spiked samples (10–50 ng g^{-1}), the recovery of cyclic and linear siloxanes ranged from 87.7 to 108.0% and from 84.9 to 107.6%, respectively. The validated method was used to determine the levels of these compounds in various types of soil samples collected from different locations in Spain. The cyclic siloxanes, decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) were detected in all the soil samples analyzed at concentrations from 9.2 to 56.9 ng g^{-1} for D5 and from 5.8 to 27.1 ng g^{-1} for D6 in agricultural soils and from 22 to 184 ng g^{-1} for D5 and from 28 to 483 ng g^{-1} for D6 in industrial soils. The total linear siloxanes concentrations (L5–L14) (sum of the 10 congeners) ranged from 191 to 292 ng g^{-1} in agricultural soils and from 1411 to 8532 ng g^{-1} in industrial soils.

1. Introduction

Siloxanes are widely used in consumer products such as paints and cosmetics, as well as in medical products. Siloxanes are characterized by their high stability, physiologic inertness and lubricating properties. The stability of siloxanes makes them to be, in general, very persistent once released in the environment. In recent years, various studies pointed out that some siloxanes may have endocrine disrupting properties and effects on the reproduction, which may cause concern about their effect on humans and the environment [1–3].

Siloxanes form a large group of chemicals with molecular weights from a few hundreds to several hundred thousands. These chemical compounds consist on chains of alternating silicon (Si) and oxygen (O) atoms with aliphatic chains attached to Si atoms, and their properties depend on the length of the Si–O backbone. Silicon and oxygen atoms may be linked into cyclic or linear structures and, according to IUPAC, these compounds are named as cyclic or linear siloxanes, however, they are commonly known as silicones.

The most common linear siloxanes are polydimethylsiloxanes (PDMS), and the most studied cyclic siloxanes are octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5). Smaller molecules such as D3 (hexamethylcyclotrisiloxane) volatilize rapidly and are not present in environmental samples. Some of the key physico-chemical properties of D4, D5 and D6 (dodecamethylcyclohexasiloxane) are summarized in Table 1 [4–6]. The high Henry's law constant combined with low water solubility suggest that cyclic siloxanes may have a strong tendency to partition from water to air and it can be predicted that the atmospheric compartment will be the main environmental sink for cyclic siloxanes. Siloxanes may enter the soil compartment through direct and indirect routes, including spreading of treated sludge, spills and landfills.

Silicones have been measured in water, sediments and fish by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and high-performance liquid chromatography (HPLC) coupled with ICP [7–9]. Several studies have determined cyclic and linear siloxanes in personal care and household products by gas chromatography with mass spectrometry (GC–MS) [10] and in biological tissues by GC with atomic emission detection (AED) or GC–MS [11]. PDMS is the most common siloxane polymer used in medical products, including breast implants and it has been reported that silicones can bleed from breast implants [12] and be found in certain tissues such as plasma and blood [13–15].

Some authors have described analytical methods to determine siloxanes from biological matrices, but references of the analysis of siloxanes in environmental samples are, however, scarce [7,8,16]. To the best of our knowledge, analyses of linear and cyclic siloxanes in different types of soils (agricultural, sludge-amended and industrial) have not so far been reported. The main objective of this work was to develop a sensitive method using a low volume of extraction solvent for the analysis of a wide range of siloxanes (cyclic and

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doi:10.1016/j.chroma.2010.09.031

Table 1
Physico-chemical properties of cyclic siloxanes.

IUPAC name	INCI[a] name	Abbreviation	Boiling point (°C)	Vapor pressure (Pa, 25 °C)	Water solubility (mg l^{-1}, 23 °C)	Log k_{ow}	Henry's law constant (Pa m^3 mol^{-1})
Octamethylcyclotetrasiloxane	Cyclotetrasiloxane	D4	175.7	132	0.056	6.49	1.21×10^6
Decamethylcyclopentasiloxane	Cyclopentasiloxane	D5	211.2	33.2	0.017	8.03	3.34×10^6
Dodecamethylcyclohexasiloxane	Cyclohexasiloxane	D6	245.1	4.6	0.005	9.06	4.94×10^6

[a] INCI: International Nomenclature of Cosmetic Ingredients.

linear) in different soil samples collected in Spanish fields. In this study, linear siloxanes L4 to L14 and cyclic siloxanes including D4, D5 and D6 were determined by GC–MS detection.

2. Experimental

2.1. Reagents and standards

Ethyl acetate, acetone, methanol, and n-hexane, residue analysis grade, were purchased from Scharlab (Barcelona, Spain). Anhydrous sodium sulfate, obtained from Aldrich (Steinheim, Germany), was heated for 24 h at 180 °C and then allowed to cool down in a desiccator before use. Cyclic siloxane standards (D4, D5, D6, purity >98%,), linear siloxanes (L4, L5, mixture linear PDMS (L4–L14)) and tetrakis(trimethylsilyloxy)silane (M4Q), used as internal standard (IS), were provided by Sigma–Aldrich (St. Louis, MO, USA). Separate stock solutions of individual compounds were made at 5 μg ml^{-1} in ethyl acetate. From these solutions, two different working standard solutions were prepared weekly to spike samples by dilution with n-hexane of the stock solutions: standard A contained L4, D4, D5, L5, D6 and M4Q at 500 ng ml^{-1}, and standard B contained the mixture of linear PDMS (L4–L14) and M4Q at 500 ng ml^{-1}. All the standard solutions were stored in glass bottles at 4 °C prior to use.

2.2. Apparatus

Sample extraction was performed in glass columns (20 ml) of 10 cm × 20 mm i.d. (Normax, Portugal), containing Whatman No. 1 paper circles of 2 cm diameter (Whatman, Maidstone, UK). An ultrasonic water bath (Raypa, Barcelona, Spain) was used in the extraction step. The generator of this ultrasonic water bath has an output of 150 W and a frequency of 35 kHz. A vacuum manifold (Supelco, Visiprep, Madrid, Spain) was employed to collect the eluates.

GC–MS analysis was performed with an Agilent 6890 (Waldbronn, Germany) gas chromatograph equipped with an automatic injector, Model HP 7683, and a mass spectrometric detector (MSD), Model HP 5973N, equipped with an inert ion source. A fused silica capillary column ZB-5MS, 5% phenyl polysiloxane as nonpolar stationary phase (30 m × 0.25 mm i.d. and 0.10 μm film thickness) from Phenomenex (Torrance, CA), was used. Operating conditions were as follows: injector port temperature 200 °C; helium (purity 99.995%) as carrier gas at a flow-rate of 1.0 ml min^{-1} and pulsed splitless mode (pulsed pressure 45 psi = 310 kPa for 1.5 min) with the splitless injector purge valve activated 1.5 min after sample injection (2 μl), in a double-taper glass liner with a nominal volume of 800 μl. The chromatographic conditions for the analysis of compounds of standard A were the following: the column temperature was maintained at 40 °C for 2 min, then programmed at 10 °C min^{-1} to 220 °C and held for 1 min, the total analysis time was 21.00 min and the equilibration time 2 min. For compounds of standard B, the column temperature was maintained at 40 °C for 2 min, then programmed at 20 °C min^{-1} to 220 °C; increased to 280 °C at a rate of 5 °C min^{-1}, and held for 7 min, the total analysis time was 24.00 min with an equilibration time of 2 min.

The mass spectrometric detector was operated in electron impact ionization mode with an ionizing energy of 70 eV, scanning from m/z 100 to 750 at 3.62 s per scan, an ion source temperature of 300 °C and a quadrupole temperature of 150 °C. The electron multiplier voltage was maintained 100 V above autotune with a solvent delay of 3 min.

Table 2 lists the siloxanes of standard A and the internal standard along with their retention times, the selected ions and their corresponding relative abundances. For the linear siloxanes, L6–L14, contained in standard B, m/z 221 was considered the target ion whereas m/z 281, 282 and 369 were considered as qualifier ions with qualifier to target ratios of 60, 35 and 30%, respectively. The selected ion monitoring (SIM) program (Table 3) used to determine and confirm standard A compounds in soil has three acquisition windows with an ion dwell time of 100 ms and 1.69 cycles s^{-1} whereas for compounds of standard B, the SIM program consisted on one acquisition window starting at 6.20 min in which the ions indicated above were monitored.

The target and qualifier abundances were determined by injection of standards under the same chromatographic conditions using full-scan. The analytes were confirmed by their retention times, the identification of target and qualifier ions and the determination of qualifier to target ratios. Retention times must be within ±0.3 min of the expected time and qualifier-to-target ratios within a 20% range for positive confirmation. The mass spectra were compared against the NIST 98 Mass spectral Library (match quality greater than 90%). The quantification of the selected siloxanes was based on their relative response factor to the internal standard.

2.3. Samples

2.3.1. Sample collection

Soil used in the recovery assays was collected from the plough layer (0–10 cm) of an experimental plot located in the region of Madrid (Spain). Soil samples were air dried, sieved (2 mm) and stored frozen (−18 °C) in glass containers. The characteristics of the soil were: pH 7.69, total organic matter content 0.97%, sand 44.34%, silt 37.44% and clay 18.22%

Surface soil (0–10 cm) was sampled from agricultural fields (horticultural and forested, soils 1–8) located in different Spanish regions: cornfields in Albacete, tomato fields in Badajoz, and forested fields in Badajoz and Toledo. Soil amended with sewage sludge at 12 Tn/ha (0.36% dry weight of sewage sludge, soils 9 and 10) and industrial soil from the area of Bilbao (soils 11–15) were also sampled.

2.3.2. Sample preparation

The extraction method was adapted from a procedure developed in our laboratory for the analysis of pesticides in soil, based on sonication-assisted extraction in small columns (SAESC) [17]. Two filter paper circles of 2 cm diameter were placed at the end of a glass column and anhydrous sodium sulfate (2 g) was added as a layer over the paper filter, then sieved soil (5 ± 0.001 g) was weighed and placed in the column. For recovery studies, soil samples were previously spiked with the mixture of siloxanes (standard A or standard B) and M4Q, as IS, to reach final concentrations of

Table 2
Retention times (t_R, min), molecular weight (MW), target ion (T), qualifier ions (Q_1, Q_2, Q_3) and abundance ratios of qualifier ion/target ion (Q_1/T, Q_2/T, Q_3/T)[a] of the siloxanes of standard A.

IUPAC name	Abbreviation	t_R	MW	T	Q_1	Q_2	Q_3	Q_1/T (%)	Q_2/T (%)	Q_3/T (%)
Octamethyltetrasiloxane	L4	6.21	310.0	281	207	194	267	80	18	15
Octamethylcyclotetrasiloxane	D4	6.39	296.6	281	282	283	249	40	35	6
Decamethylcyclopentasiloxane	D5	9.0	370.8	355	356	267	268	30	90	17
Tetrakis(trimethylsilyloxy)silane	M4Q	9.49	384.9	281	282	283	369	27	22	20
Dodecamethylpentasiloxane	L5	10.30	384.8	281	282	283	369	26	20	18
Dodecamethylcyclohexasiloxane	D6	11.49	444.9	341	429	342	325	40	39	35

[a] Q/T (%) are the results of abundance values of the qualifier ion (Q_1, Q_2, Q_3) divided by the abundance of the target ion (T) × 100.

10, 20 and 50 ng g^{-1} and left at room temperature for 2 h to allow solvent evaporation.

Soil samples were extracted with 5 ml of n-hexane for 15 min in an ultrasonic water bath at room temperature. The water level in the bath was adjusted to equal the extraction solvent level inside the columns, which were supported upright in a tube rack and closed with 1-way stopcocks. After extraction, the columns were placed on a multiport vacuum manifold and the solvent was collected in graduated tubes. Soil samples were extracted again with another 5 ml of hexane (15 min). The extracting solvent was collected and soil samples washed with 1 ml of additional solvent. The total extract, collected in 10 ml graduated tubes, was concentrated with a gentle stream of nitrogen to an appropriate volume, 1 ml.

2.4. Quality assurance/quality control

The quality assurance and quality control criteria used for this method included analyses of procedural blanks, laboratory control samples (LCS) and IS recoveries. The procedural blank is carried through the entire analytical procedure in the same manner as a sample. LCS are evaluated to assess overall method performance and are the primary indicators of laboratory performance. In general, LCS are similar in composition as samples, containing known concentrations of all the analytes of interest, and undergo the same preparatory and determinative procedures as the samples. One procedural blank was run with each set of samples to check for contamination from the preparative steps and to demonstrate laboratory background levels. LCS were used in the recovery assays and the concentration of the studied compounds found in blank samples was subtracted.

For the IS recoveries, a 100 μl of a standard mixture containing 30 ng of IS was added to each LCS prior to analysis. The average recovery of the IS in these samples, as measured by the external standard method, was 101.0 ± 6.6%.

3. Results and discussion

3.1. Optimization of the SAESC method

It must be emphasized that the determination of siloxanes required rigorous clean-up of the material used due to the widespread application of silicones in consumer goods. Hence, only glassware rinsed several times with acetone was used.

In order to check for contamination, various organic solvents or mixtures, such as ethyl acetate, ethyl acetate-methanol and hexane, were assayed. Trace quantities of D4 (11–16 ng ml^{-1}) and D5 (25–31 ng ml^{-1}) were detected in procedural blanks when ethyl acetate and ethyl acetate–methanol were used, while no contamination was detected with hexane. This agrees with Flassbeck [13], who detected traces of D4 and D6 using solvents such as tetrahydrofuran (THF) and ethyl acetate. Therefore, hexane was the most suitable solvent in order to avoid contamination. Procedural blanks were run between samples to check for siloxane levels, and the levels in blanks, if found, were subtracted from sample values.

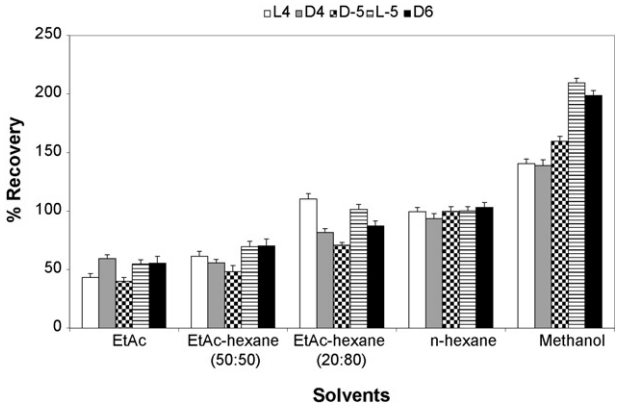

Fig. 1. Comparison of extraction efficiencies obtained for compounds of standard A after 30 min ultrasonic extraction of soil samples using different solvents, $n = 4$ replicates.

Various organic solvents, such as THF [18], hexane [13,14,19], ethyl acetate [11], ethyl acetate–methanol [12], ethyl acetate–hexane [18] and petroleum ether [7,8] have been used in the extraction of siloxanes from different matrices. In our case, methanol, hexane, ethyl acetate and mixtures of ethyl acetate–hexane (50:50 and 20:80, v/v) were initially assayed. Recoveries obtained from soil samples, at the 20 ng g^{-1} fortification level, with ethyl acetate or ethyl acetate–hexane (50:50, v/v) were lower than 70% and although the mixture ethyl acetate–hexane (20:80, v/v) provided higher recovery results for all the siloxanes studied they were still somewhat low for D4 and D5. When the extraction was carried out with hexane, the recovery of all siloxanes was higher than 92% (Fig. 1). However, the recoveries obtained with methanol were higher than 180% due to solvent contamination and a possible matrix effect, and consequently, methanol cannot be used as extraction solvent. Therefore, hexane was the solvent selected for the extraction of siloxanes. This is in

Table 3
SIM program used to analyze the siloxanes of standard A in soil.

Group	Time	Siloxane	m/z	Dwell time (ms)	Scan rate (cycles s^{-1})
1	2.00	L4, D4	193, 207, 221, 249, 267, 281	100	1.91
2	8.00	D5	267, 268, 355, 356	100	2.36
3	9.30	M4Q, L5	221, 281, 283, 369	100	2.36
4	11.00	D6	325, 341, 342, 429	100	2.36

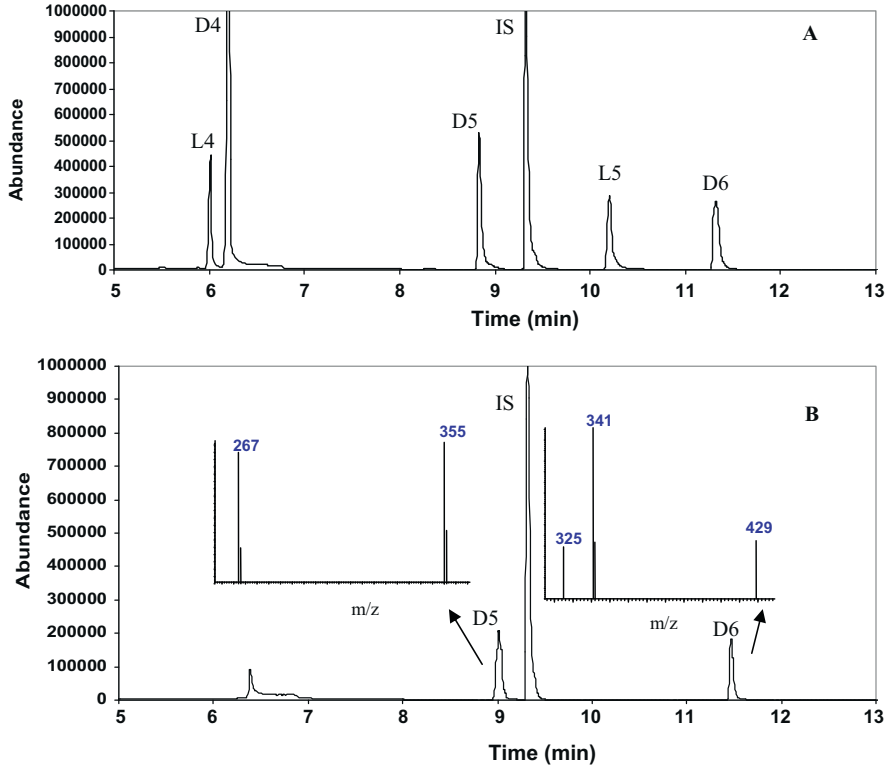

Fig. 2. (A) GC–MS-SIM chromatogram of a standard A solution containing 50 μg l^{-1}. (B) GC–MS-SIM chromatogram of a soil extract containing D5 (9.2 ng g^{-1}) and D6 (5.8 ng g^{-1}) with the main ions of their mass spectra.

agreement with the use of hexane to extract cyclic siloxanes from plasma reported by Flassbeck et al. [13].

Another parameter subsequently considered was the ultrasonic-assisted extraction. The effect of sonication on the extraction was studied analyzing a set of soil samples spiked at 20 ng g^{-1} with and without sonication. When the extraction was carried out with the assistance of sonication the recoveries were 20% higher than in absence of ultrasound radiation and therefore, extraction was performed with sonication. The effect of temperature on extraction was studied at 50 °C. The recovery of D4 was lower than for the other compounds due to its higher volatility. Therefore, the experimental conditions selected were SAESC at room temperature.

3.2. Gas chromatographic determination

Prior to the analysis of samples, contamination arising from the presence of siloxanes in certain parts of the gas chromatograph, such as the inlet septum and the stationary phase of the capillary column was studied. To reduce the possible bleeding of siloxanes, low-bleed septa and a low-bleed capillary columns, ZB-5MS, were used. Several inlet temperatures were also tested and it was observed that background levels of siloxanes decreased when lower inlet temperatures were applied. Everyday, prior to the analysis of samples, the inlet was flushed by heating at 300 °C for 30 min and procedural blanks were analyzed after every four samples. No siloxanes were detected in these blanks. In addition, quality controls of standards and n-hexane were analyzed after four sample runs to check for instrumental background and stability. A SIM chromatogram of standard A is shown in Fig. 2A and the corresponding chromatogram of linear siloxanes (standard B) is depicted in Fig. 3A. Eleven peaks were detected in standard B. Although the molecular ions were specific for each peak, the eleven peaks contained common ionic fragments at *m*/*z*, 221, 281 and 369 and these ions were chosen for their determination in SIM mode.

Matrix effect has a negative impact on the accuracy of the generated results in the GC analysis of some organic compounds. The study on matrix effect was performed by comparing the response obtained for the analytes in neat solvent with that in soil extracts. At the levels studied, 50 and 20 ng g^{-1}, the matrix effect was <10% and an internal standard was used to overcome any possible matrix effect and improve reproducibility and accuracy.

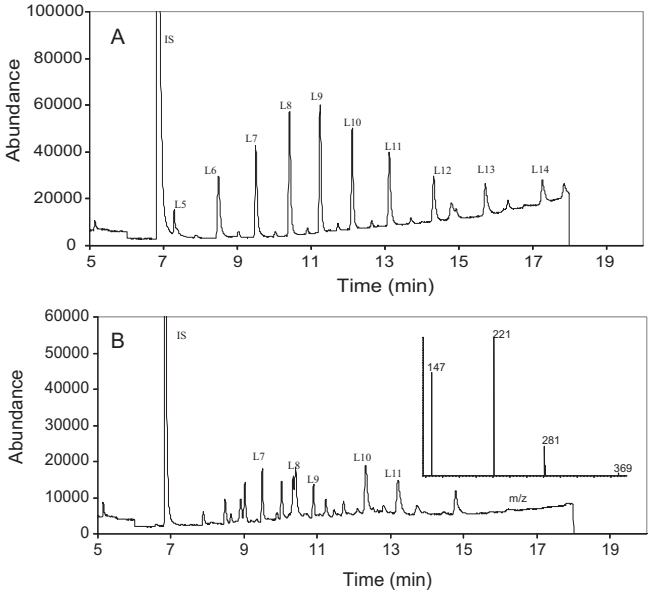

Fig. 3. (A) GC–MS-SIM chromatogram of a standard B solution containing 100 μg l^{-1}. (B) GC–MS-SIM chromatogram of a soil extract with the main ions of the mass spectrum. The levels of siloxane encountered in this sample are summarized in Table 6 (Soil 1).

Table 4
Recoveries[a] of siloxanes from soil.

Siloxanes	Fortification levels (ng g^{-1})		
	10	20	50
Standard A			
L4	87.7 ± 5.3	98.4 ± 1.8	102.3 ± 1.0
D4	93.2 ± 7.0	96.2 ± 1.0	94.3 ± 1.1
D5	104.7 ± 8.4	108.0 ± 1.1	100.3 ± 1.2
L5	102.6 ± 7.4	102.4 ± 1.9	100.3 ± 0.4
D6	107.5 ± 5.8	103.9 ± 1.4	103.8 ± 3.1
Standard B			
L5	110.7 ± 4.8	104.4 ± 1.8	105.2 ± 1.7
L6	96.1 ± 1.8	103.3 ± 2.1	92.5 ± 2.1
L7	89.2 ± 4.8	87.2 ± 1.9	84.9 ± 3.0
L8	111.0 ± 7.3	89.9 ± 1.7	88.9 ± 2.6
L9	111.9 ± 9.0	99.9 ± 3.1	98.3 ± 0.6
L10	105.9 ± 6.3	99.5 ± 2.0	103.1 ± 1.7
L11	93.8 ± 4.7	103.9 ± 3.7	103.7 ± 2.2
L12	100.5 ± 6.4	105.2 ± 2.3	107.6 ± 2.6
L13	102.6 ± 4.0	102.4 ± 1.6	104.9 ± 3.0
L14	107.0 ± 8.8	103.6 ± 5.5	98.3 ± 0.6

[a] Results are the mean of four replicates ± standard deviation.

3.3. Method validation

3.3.1. Recovery

Recovery experiments were carried out by spiking soil samples at three levels: 10, 20 and 50 ng g^{-1}. These fortified samples were left to stand for 2 h to allow solvent evaporation before extraction following the method described above. Unspiked "blank" samples were analyzed to determine the possible presence of these compounds and the recoveries were calculated by dividing the difference between the measured concentrations for spiked and unspiked samples by the added one. D4 and D6 were present in the unspiked sample at concentrations of 5.3 and 6.7 ng g^{-1} dry weight, respectively. Recoveries of cyclic and linear siloxanes ranged between 87.7–108.0% and 84.9–107.6% for soil samples, respectively (Table 4), with standard deviations equal or lower than 9.0%, thus, fulfilling the requirements of the IUPAC [20]. The range of recoveries achieved is similar to that obtained by other authors for the analysis of siloxanes in biological matrices [10,19,21].

3.3.2. Repeatability

The repeatability of the whole analytical procedure was determined by analyzing seven soil samples spiked at 15 ng g^{-1} within a given day and the relative standard deviations (RSD) calculated ranged from 4.5 to 8.9%. The repeatability of the chromatographic determination was determined by injecting 10 times standard solutions of 50 ng ml^{-1} for cyclic siloxanes and of 100 ng ml^{-1} for linear siloxanes with an automatic injector. The RSD obtained for the retention times were equal or lower than 0.04% for both types of siloxanes, whereas for peak areas those values ranged from 2.1 to 9.3% and from 4.6 to 8.2% for cyclic and linear siloxanes, respectively (Table 5). Day to day precision, expressed as RSD, was performed injecting standard solutions in different days during 3 consecutive weeks and it was found to be lower than 12% for all of the studied compounds. The robustness of the method was determined by analyzing five replicates of soil samples on 5 different days and RSD ranging from 7.6 and 10.4% were found.

3.3.3. Linearity

The linearity was studied by performing a multipoint calibration curve in the range of levels expected in soil samples. The linear range was established by a six point calibration curve (50, 75, 100, 150, 200 and 250 ng ml^{-1}) for standard A and (100, 200, 400, 600, 800 and 1000 ng ml^{-1}) for standard B, and each calibration level was spiked with M4Q at 100 ng ml^{-1} for standard A and 200 ng ml^{-1} for standard B. The calibration data listed in Table 5 show the linear response of these compounds in the range considered with correlation coefficients equal or higher than 0.997.

3.3.4. Limits of detection (LODs) and quantification (LOQs)

The LODs and LOQs were obtained considering a signal to noise ratio of 3 and 10, respectively, using the lowest level of the calibration curves. No linear siloxanes were found in blank samples; however, all of them contained D5 and D6. Therefore, for these compounds, LODs and LOQs were calculated based on blank assays ($n = 6$) as 3 and 10 times the standard deviation of the blank signal, respectively. The limits for cyclic and linear siloxanes are shown in Table 5, and were in the lower end of the range of values previously published for cyclic and linear siloxanes in personal care and household products [10] and for linear siloxanes in biological tissues [11].

3.4. Application to real samples

The developed method was applied to the analysis of siloxanes in various types of agricultural and industrial soils collected from

Table 5
Calibration data and repeatability[a] of the siloxanes.

Compound	t_R	Calibration data		Repeatability (RSD, %)[b]		LOD (ng g^{-1})	LOQ (ng g^{-1})
		Equation	r	Peak area	t_R		
Standard A							
L4	6.21	$y = 9.48 \times 10^{-4} x - 8.19 \times 10^{-5}$	1.000	9.3	0.03	0.5	1.8
D4	6.39	$y = 3.17 \times 10^{-5} x + 2.14 \times 10^{-6}$	0.999	4.5	0.03	1.1	4.0
D5	9.00	$y = 8.98 \times 10^{-4} x + 7.39 \times 10^{-5}$	1.000	2.1	0.01	0.7	1.9
L5	10.37	$y = 1.47 \times 10^{-5} x - 1.00 \times 10^{-6}$	1.000	6.8	0.01	0.5	1.8
D6	11.49	$y = 4.91 \times 10^{-4} x - 4.19 \times 10^{-5}$	0.999	5.3	0.02	0.6	2.0
Standard B							
L5	7.29	$y = 9.81 \times 10^{-2} x + 1.87 \times 10^{-4}$	0.998	5.9	0.02	0.5	1.6
L6	8.50	$y = 2.90 \times 10^{-3} x + 6.17 \times 10^{-4}$	0.998	4.6	0.02	0.4	1.6
L7	9.50	$y = 5.83 \times 10^{-3} x - 1.49 \times 10^{-4}$	0.999	7.6	0.01	0.4	1.5
L8	10.41	$y = 4.79 \times 10^{-3} x + 1.01 \times 10^{-5}$	0.998	8.2	0.01	0.4	1.5
L9	11.24	$y = 4.25 \times 10^{-3} x + 9.03 \times 10^{-4}$	0.998	6.3	0.03	0.5	1.5
L10	12.19	$y = 3.73 \times 10^{-3} x - 6.14 \times 10^{-4}$	0.997	5.3	0.02	0.5	1.6
L11	13.12	$y = 2.61 \times 10^{-3} x - 4.67 \times 10^{-4}$	0.997	4.5	0.03	0.5	1.6
L12	14.34	$y = 1.72 \times 10^{-3} x + 8.01 \times 10^{-3}$	0.997	5.9	0.04	0.5	1.6
L13	15.74	$y = 1.20 \times 10^{-3} x + 1.17 \times 10^{-4}$	0.997	6.1	0.03	0.6	1.6
L14	17.20	$y = 8.09 \times 10^{-2} x - 2.83 \times 10^{-3}$	0.997	6.7	0.04	0.6	1.8

[a] Repeatability of the chromatographic method.
[b] RSD of retention times and peak areas ($n = 10$).

Table 6
Concentration[a] of the studied compounds (ng g^{-1} dry weight) in soils collected in various areas of Spain.

	Agricultural								Sludge-amended		Industrial					
	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8	Soil 9	Soil 10	Soil 11	Soil 12	Soil 13	Soil 14	Soil 15	
D4														58.6 ± 2.9		
D5	9.2 ± 0.5	11.4 ± 0.4	25.9 ± 0.9	56.9 ± 1.8	12.3 ± 0.9	16.4 ± 0.5	14.8 ± 0.9	11.3 ± 0.4	37.5 ± 1.7	30.8 ± 1.7	128.0 ± 4.9	22.3 ± 6.3	35.0 ± 0.5	184.1 ± 9.0	119.5 ± 12.1	
D6	5.8 ± 0.7	7.6 ± 0.2	26.7 ± 0.8	27.1 ± 1.0	7..5 ± 0.4	17.4 ± 0.3	7.8 ± 0.3	6.8 ± 0.1	22.5 ± 1.2	32.0 ± 1.5	482.6 ± 12.3	33.7 ± 5.8	28.2 ± 0.4	175.0 ± 10.3	67.6 ± 9.9	
$\sum$D4–D6	15.0 ± 0.9	19.0 ± 0.4	52.6 ± 1.2	84.0 ± 2.1	19.8 ± 1.0	23.8 ± 0.6	22.6 ± 0.9	18.1 ± 0.4	60.0 ± 2.1	62.8 ± 2.3	610.6 ± 13.2	56.0 ± 8.6	63.2 ± 0.6	417.7 ± 14.0	187.1 ± 15.6	
L4																
L5																
L6											47.5 ± 3.4			204.2 ± 6.2		
L7	33.4 ± 1.8								27.2 ± 1..2		200.4 ± 8.3		127.6 ± 2.9	980.8 ± 8.7	18.5 ± 1.5	
L8	12.7 ± 0.9			10.2 ± 0.7					50.3 ± 3..9		150.0 ± 7.6			1304..5 ± 5.4	12.6 ± 0.9	
L9	18.9 ± 1.3			19.3 ± 1.0					32.1 ± 1.6	90.0 ± 5.8	114.2 ± 6.8		22.9 ± 1.2	1256.5 ± 6.3	1124.8 ± 7.6	
L10	13.7 ± 1.0			44.6 ± 2.5					39.2 ± 3.4	108.5 ± 5.9	423.2 ± 8.1		67.0 ± 3.8	524.8 ± 6.9		
L11	59.9 ± 2.1			52.9 ± 3.0					41.7 ± 4.5	128.2 ± 6.2	321.1 ± 7.5		82.9 ± 4.1	2903.4 ± 10.5	1752.5 ± 5.8	
L12				64.6 ± 3.7					57.8 ± 4.3	133.4 ± 7.2	153.1 ± 4.7		131.0 ± 5.4	1359.1 ± 10.9		
L13				100.8 ± 5.8												
L14																
$\sum$L5–L14	138.5 ± 3.3			292.4 ± 8.0					170.8 ± 7.3	537.3 ± 11.4	1410.6 ± 18.1		431.4 ± 8.4	8532.2 ± 15.9	2908.6 ± 9.7	

[a] Results are the mean of four replicates.

different areas of Spain. Fifteen samples were analyzed for cyclic and linear siloxanes and these samples were grouped into three categories according to the soil types: agricultural, sludge-amended and industrial. Table 6 shows the concentrations of siloxanes found expressed as ng g^{-1} dry weight.

In agricultural soils, all of the examined samples contained D5 and D6, with concentrations ranging from 9.2 to 56.9 ng g^{-1} and from 5.8 to 27.1 ng g^{-1}, respectively. In contrast, D_4 was not found in any of the agricultural soil samples. No information on concentrations of cyclic siloxanes in agricultural soils has been found in the literature. Due to their widespread use, siloxanes may enter the soil through direct and indirect routes, including biosolids, spills and gaseous deposition from the atmosphere. In soil amended with sewage sludge, D5 and D6 were detected at concentrations ranging from 30.8 to 37.5 ng g^{-1} and from 22.5 to 32.0 ng g^{-1}, respectively. Regarding industrial soils, all of the examined samples showed detectable amounts of siloxanes with concentrations ranging from 22.3 to 482.6 ng g^{-1}. In this type of soil, D5 and D6 were found in higher concentrations than in agricultural and sludge amended soils, which is in agreement with the results reported in other papers for sediment [7,8]. D4 was detected in only one soil at a concentration of 58.6 ng g^{-1}. A chromatogram of an agricultural soil extract containing D5 (9.2 ng g^{-1}) and D6 (5.8 ng g^{-1}) with the main ions of the mass spectrum are depicted in Fig. 2B.

Skin lotions, cosmetics, and hair care products contain high concentrations of D5 and D6 [10]. Siloxanes enter wastewater treatment plants will be adsorbed by sludge and thus they may enter soil directly by land application of the sludge.

In our study, the most frequent linear compounds found were L10 to L13 (8 out of 15 samples, 8/15), L8 (7/15), L9 (6/15), and L7 (2/15); Table 6. L5 and L6 were not detected in any of the analyzed samples. The total linear siloxanes concentration (sum of L5 to L14) ranged from 170.8 to 8532.2 ng g^{-1}. A GC–MS-SIM chromatogram of a soil extract with the main ions of the mass spectrum is depicted in Fig. 3B. The soil sample 14 was the most contaminated, with a total linear siloxanes concentration of 8532.2 ng g^{-1}.

To our knowledge, this is the first work reporting the simultaneous determination of linear and cyclic siloxanes in soils by GC–MS.

4. Conclusions

The developed method allows a rapid determination of cyclic and linear siloxanes in agricultural and industrial soils, based on ultrasonic-assisted extraction of siloxanes with n-hexane and subsequent analysis of the extract by GC–MS. The method uses a low volume of extraction solvent (10 ml), and the evaporation of low volumes of solvent reduces the loss of volatiles.

The validated method was applied to the determination of siloxanes in real samples. D5 and D6 were the main cyclic siloxanes found in all soil samples and the concentration of the total linear siloxanes (sum of L5 to L14) ranged from 171 to 8532 ng g^{-1}.

Acknowledgements

This study was financed by the Ministry of Science and Innovation-National Institute for Agricultural and Food Research and Technology, INIA, Project number “RTA 2008-00040”.

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