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Linear and cyclic methylsiloxanes in air by concurrent solvent recondensation–large volume injection–gas chromatography–mass spectrometry

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ABSTRACT

In the present work, a simple and fast method for the analysis of linear and cyclic methylsiloxanes in ambient air based on active sampling combined with gas chromatography – mass spectrometry (GC–MS) was developed. The retention efficiency of five sampling sorbents (activated coconut charcoal, Carbopack B, Cromosorb 102, Cromosorb 106 and Isolute ENV+) was evaluated and Isolute ENV+ was found to be the most effective. A volume of 2700 L of air can be sampled without significant losses of the most volatile methylsiloxanes. To improve the sensitivity of the GC–MS method, concurrent solvent recondensation – large volume injection (CSR–LVI), using volumes up to 30 μl of sample extract, is proposed and limits of quantification down to 0.03–0.45 ng m^{-3}, good linearity ($r > 0.999$) and precision (RSD % < 9%) were obtained. The developed method was applied to the analysis of ambient air. Concentrations of linear and cyclic methylsiloxanes in indoor air ranging from 3.9 to 319 ng m^{-3} and between 48 and 292668 ng m^{-3}, were obtained, respectively, while levels from 6 to 22 ng m^{-3} for linear and between 2.2 and 439 ng m^{-3} for cyclic methylsiloxanes in outdoor air from Barcelona (Spain), were found.

1. Introduction

Volatile methylsiloxanes (VMS) constitute a group of chemicals that are widely used in a great variety of industrial products and consumer goods, including personal care products, household products, cleaning agents, sealants, and in the manufacture of biomedical devices [1–3]. Due to their high volatility [4], these compounds are released into the atmosphere during industrial manufacturing and by the use of siloxane-based consumer goods [5]. Additional sources of VMS emissions are landfills and wastewater treatment plants [6]. Atmospheric half-lives for cyclic VMS have been estimated to be approximately from 10 to 30 days, while for linear VMS are around 9 days [7–9], which are considered to be enough for long-range transport [10,11]. Due to their widespread use, these compounds have been found in outdoor air from industrialised and urban areas [12–16], sewage treatment plants [2,6,15], rural sites [15,17,18], and even in Arctic areas [10,11]. The occurrence of these compounds has also been reported in indoor ambient air from industrial [16] and office buildings [19–22], homes [2,22], supermarkers [22] and also in indoor dust [23]. Most of these studies showed that the predominant VMS found in urban sites and indoor environments is decamethylcyclopentasiloxane (D5) followed by octamethylcyclotetrasiloxane (D4) and dodecamethylcyclohexasiloxane (D6), which are the most abundant in personal care products [24]. Several studies performed in mammalians suggest that D4 can impair fertility and cause liver damage [25–29] and D5 is a potential carcinogenic compound [2,3,30]. Toxicity assays carried out on aquatic environments showed that D4 is very toxic to sensitive aquatic organisms, while D5 and D6 do not exhibit adverse effects on fish [3,31–35]. Several risk assessment programs conducted in Canada [36–38], the UK [39], Sweden [40] and in a consortium of Nordic countries [2], showed that methylsiloxanes are ubiquitous at concentrations that may have harmful effects on the environment.

Sampling methods for the analysis of VMS in air are relatively new and limited. Active sampling using tubes filled with Tenax TA [2], or with a combination of sorbents (silica gel, carbon-sieve and charcoal [12], Tenax TA/carbon-sieve [21] or Tenax GR/graphitised carbon black [22]) followed by two-stage thermal desorption coupled to gas chromatography–mass spectrometry have been proposed. Isolute ENV+ commercial SPE cartridges [11,13–18] and passive air samplers with sorbent – polyurethane – foam disks impregnated with polystyrene–divinylbenzene copolymeric resin [6,10,15] followed by Soxhlet extraction have also been employed. The main difficulties in the analysis of these

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compounds are their high volatility, and their occurrence in the laboratory air, GC instruments, laboratory facilities, reagents and materials, and to the use of personal care products [41]. Procedural blanks make the determination of linear and cyclic methylsiloxanes difficult particularly from background locations. To ensure reliable results, there must be a thorough control of the blanks and avoid concentration steps to prevent losses of the most volatile compounds during sample preparation and processing, although it results in a decrease in sensitivity. To overcome this problem, several large volume injection (LVI) techniques combined with GC have been recently proposed for the GC analysis of VMS [41,42]. Among them, concurrent solvent recondensation–large volume injection (CSR–LVI) allowed the injection of up to 30 μL of sample extract with good peak shapes and minimising volatilisation losses of VMS [42].

The aim of this work was to develop a simple, effective and reliable method for the analysis of VMS in ambient air using sorbent traps for active sampling and CSR–LVI combined with GC–MS for their determination. For this purpose, the efficiency of several sorbents for the sampling of linear and cyclic VMS from air was evaluated. Quality parameters such as linearity, recovery, limits of detection and quantification, and intra-day precision were established, and the proposed method was applied to the analysis of indoor and outdoor air samples.

2. Experimental

2.1. Chemicals 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). For quantification, methyltris(trimethylsiloxy) silane (SS-1) and tetrakis(trimethylsiloxy) silane (SS-2) were used as surrogate internal standards, while bis(trimethylsiloxy) methylsilane (IS) was employed as injection internal standard. All these standards were also purchased from ABCR (> 97% purity). Individual stock standard solutions of each target compound and internal standard of 2000 μg ml^{-1}, except for SS-2 which was 10000 μg ml^{-1}, were prepared in *n*-hexane from their respective pure standards. Two standard mixtures of the target compounds containing L2, L3, L4, L5 and D3, at 0.8 μg ml^{-1}, and D4, D5 and D6 at 3 μg ml^{-1} were prepared in *n*-hexane from individual secondary standard solutions of 80 μg ml^{-1}. All standard solutions were prepared monthly and stored at -18°C. A set of seven calibration solutions containing L2, L3, L4, L5 and D3 at concentrations ranging from 0.05 to 200 ng ml^{-1}, and, D4, D5 and D6 at concentrations ranging from 0.05 to 500 ng ml^{-1}, were prepared daily by dilution of the corresponding standard mixtures in *n*-hexane. In addition, appropriate amounts of internal standard (IS) and the surrogates (SS-1 and SS-2) were added to each calibration solution to give a concentration of 50 ng ml^{-1}. For quantification, a standard mixture containing the surrogates SS-1 (30 μg mL^{-1}) and SS-2 (5700 μg mL^{-1}), prepared daily from the individual stock standard solutions, was added to the upper frit of sorbent cartridge (20 μl) prior to air sampling. In addition, a standard solution of IS at a concentration of 1000 ng ml^{-1} in *n*-hexane was used for recovery determination and was added to the final extract to give a concentration of 50 ng ml^{-1}. *n*-Hexane and dichloromethane of residue analysis grade were obtained from Fluka (Bucks, Switzerland). Carbopack B (60/80 mesh), activated coconut charcoal (80/120 mesh), and Cromosorb 102 and 106 (60/80 mesh) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Empty polypropylene SPE cartridges with polyethylene frits were also supplied from Sigma-Aldrich. Isolute ENV+ SPE cartridges (100 mg, 1 ml) were obtained from Supelco (Bellefonte, PA, USA).

2.2. Sampling locations

Air samples were collected from six indoor and two outdoor environments of urban origin located in Barcelona city (NE Spain) between March and April 2011. Indoor air samples were taken from different sites, including offices, chemical laboratories and apartments. The offices contain a large amount of office equipment, such as personal computers, laser and ink-jet printers and office furniture, and are regularly occupied by 10–15 persons. Laboratories are dedicated to the sample treatment of environmental and food matrices and include a great variety of laboratory equipment which contains some silicone-based components, such as tubes and connections, small equipment, facility sealing, etc. In addition, two apartments located in different areas of Barcelona city were also studied. In this case, the samples were taken from the living room and the bathroom of the apartments during the weekend, which is the time period of maximum occupancy. All indoor samples were collected at least 1.5 m above the floor to minimise the presence of dust and particulate matter. Outdoor air samples were collected at the university campus area in Barcelona city, where there are located several faculties and apartment buildings. Two sets of air samples were taken at 12 m above the ground.

2.3. Air sampling

All samples were collected using two sampling trains connected in parallel to a dual-head micro-diaphragm pump (Thermo Fisher Scientific, Barrington, IL, USA) [17]. Each sampling train consists of two SPE cartridges assembled in series with the inlets facing down and was connected to the pump by PTFE tubes (Fig. S1 in Supplementary material). The first cartridge was used for the sorption of the target compounds, while the second or backup cartridge was employed to check the breakthrough of the compounds. Each pump head operated independently to pull air through the cartridges at a selected flow rate. Each set of parallel samples (duplicate analyses) was accompanied by a field blank cartridge which was treated identically as the samples. At each sampling location, a field blank was collected by turning the pump on for few seconds to determine the contribution of the background contamination. The temperature and the relative humidity were measured in each sampling site and the mean values during the sampling ranged from 15 to 22 °C and between 61% and 84%, respectively.

2.4. Sampling process optimisation

Several stationary phases: activated coconut charcoal, Carbopack B, Cromosorb 102 and 106, and Isolute ENV+ were used to select the appropriate sorbent for sampling the target compounds from air samples. Polypropylene SPE cartridges (1 ml) filled with 100 mg of each sorbent and also the commercial Isolute ENV+ cartridge (100 mg/1 ml), rinsed with 10 ml of *n*-hexane and 10 ml of dichloromethane, and dried using purified nitrogen (> 99.999%) for 30 min were used. The sorbents were spiked with 20 μl of a standard solution of the target compounds at 10 μg ml^{-1} (in *n*-hexane) and 20 μL of a surrogate standard mixture, containing SS-1 and SS-2 at 10 μg ml^{-1}, on a plug of silanized glass wool positioned immediately ahead of the sorbent bed [45]. After spiking, 20 L of air from a clean room was drawn through the cartridge at a flow rate of 0.2 L min^{-1}. For the elution of the target compounds, several solvents such as

n-hexane, dichloromethane and mixtures of them were tested. A procedural blank was carried out for each sorbent to subtract the background contribution from the methylsiloxanes responses. The extracts obtained were analysed by GC–MS.

The retention efficiency of the target compounds at high sampling volumes using the polymeric materials (Cromosorb 102, Cromosorb 106 and Isolute ENV+), was evaluated by sampling from 50 to 500 L of clean air at a flow rate of 0.2 L min^{-1} after spiking the sorbents. After sampling, the sorbents were eluted with 12 ml of dichloromethane and the sample extracts were analysed by GC–MS. The sampling flow rate on the retention efficiency of Isolute ENV+ was studied by sampling volumes of 500 L at different flow rates (0.2–1.5 L min^{-1}). The sampling breakthrough volume of the Isolute ENV+ sorbent was determined by pumping several air volumes (500–5300 L) at a flow rate of 1.5 L min^{-1} through the cartridges spiked with 20 μL of a 10 μg mL^{-1} of standards. After each sampling experiment, the primary and backup cartridges were eluted with 12 ml of dichloromethane and the extracts were analysed by GC–MS.

2.5. Sampling and sample treatment method

For sampling atmospheric target compounds, a commercially available Isolute ENV+ SPE cartridge (100 mg/1 ml) was selected. To prevent any contamination before and after sampling, the cartridges were sealed with PTFE end caps and stored frozen at −18 °C in a closed glass jar. Prior to the sampling, 20 μL of a surrogate standard mixture, containing SS-1 at 30 μg ml^{-1} and SS-2 at 5700 μg ml^{-1}, were added to the cartridge upper frit (silanized glass wool). For air sampling, a known volume of air (2700 L) was pumped through the cartridge tube at a flow-rate of 1.5 L min^{-1}. After sampling, the sample and field blank cartridges were immediately sealed at both ends with PTFE endcaps, stored frozen at −18 °C and analysed within 24 h. The elution of the target compounds was performed with 3 ml of n-hexane. Before GC–MS analysis, 50 μl of a standard solution of bis(trimethylsiloxy) methylsilane (1000 ng ml^{-1}), used as injection internal standard, was added to an aliquot of 1.0 ml of the extract to obtain a concentration of 50 ng ml^{-1}. For the analysis of the cyclic methylsiloxanes D4, D5 and D6, a dilution of the extract (1:200, w/w) was required for quantification.

2.6. GC–MS determination

The GC–MS analysis of the linear and cyclic methylsiloxanes was carried out on a Trace GC 2000 Series gas chromatograph (ThermoFisher, Milan, Italy) coupled to a DSQ II mass spectrometer (ThermoFisher). 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, Folsom, CA, USA) of 60 m × 0.25 mm I.D., with a film thickness of 0.25 μm. The oven temperature was programmed from 60 °C (held for 5 min) to 285 °C at 15 °C min^{-1} (held for 15 min). Helium (Abelló Linde, S.A., Barcelona, Spain) with a purity of 99.999% was used as carrier gas at a constant flow-rate of 1 ml min^{-1} held by electronic flow control. For optimisation of air sampling and comparison of sorbent efficiency, 2 μm of sample extracts and standards were injected in splitless mode (1 min) at an injector port temperature of 200 °C. For the CSR-LVI injection, an AS2000 autosampler (ThermoFisher) equipped with a 50 μl syringe (Hamilton, Bonaduz, Switzerland) was used. The syringe needle was inserted in the injector to a depth of 30 mm from the top and the injection was performed at 100 μl s^{-1}. A glass liner of 105 × 5 mm ID filled in its base with 5 mm of deactivated glass wool (Panreac, Barcelona, Spain) and a 23-gauge Merlin Micro-seal septum (a high temperature resistant fluorocarbon elastomer, Supelco, Bellefonte, PA, USA) were used in the injector port. In addition, the chromatographic column was fitted with an uncoated fused – silica deactivated column of 5 m × 0.32 mm ID (J&W Scientific) installed at 2 mm from the injector port. A volume of 30 μL of sample extracts and standards in *n*-hexane was injected for CSR–LVI–GC–MS analysis. The injector temperature was kept at 200 °C and the split and the septum purge outlet were closed during 1.5 min.

The MS was operated in electron ionisation (EI) mode at electron energy of 70 eV and 100 μA of electron emission. Transfer line and ion source temperatures were set at 280 and 200 °C, respectively. For MS acquisition, selected ion monitoring (SIM) mode was employed 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 methylsiloxanes. The quantification was carried out using methyltris(trimethylsiloxy)silane (SS-1) for the determination of L2 – L5 and D3, and tetrakis (trimethylsiloxy)silane (SS-2) for D4, D5 and D6 as surrogate internal standards. For recovery determination, bis(trimethylsiloxy)methylsilane (IS) was used as injection internal standard. Xcalibur version 2.0 software was used for data acquisition and processing of the results.

2.7. Quality control

Because the methylsiloxanes are present in a great variety of consumer products, the analyst took care to avoid the use of personal care products or other possible contamination sources. For every set of five samples, a procedural blank covering both instrumental and sample treatment procedures was performed in order to evaluate the contribution of background levels, which was subtracted from the analyte response for quantification. For each sampling site, a field blank was used to determine the contribution of the background contamination during the storage and transportation. The contribution of sampling and storage, sample treatment and instrumental measurement to the blank has been evaluated (Fig. S2 in Supplementary material) and the sample treatment is the most important. So, a thorough control of this step is recommended. The preparation of standard solutions, procedural blanks, sample treatments, and the experiments for the optimisation of the sampling conditions were carried out into a laminar flow cabinet of a clean room (class 100) to avoid any contamination of ambient air [43]. Retention times, peak areas and asymmetry factor control charts were used to assess the performance of the GC-column during the CSR–LVI injection. In addition, the glass wool of the GC liner was systematically replaced after 200 injections to avoid contamination problems during the GC–MS analysis of real samples. The instrumental limits of quantification, typically ranging from 0.01 to 0.03 ng ml^{-1}, were periodically tested. In addition, quality parameters of the method such as the limits of detection (LOD) and quantification (LOQ), precision (RSD% < 10%) and linearity (ranging from 0.05 to 500 ng ml^{-1}), were routinely checked to ensure the quality of the results. All glassware materials were treated with chromium sulphuric acid for 24 h, solvent rinsed and dried at 200 °C before use. To confirm the identification of methylsiloxanes, the following restrictive criteria were applied: (a) the ion abundance 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.

3. Results and discussion

3.1. Optimisation of air sampling procedure

Recently, a solid-phase extraction method using hydroxylated polystyrene–divinylbenzene copolymer as sorbent (Isolute ENV+)

Table 1
Quantification and confirmation ions selected for the determination of linear and cyclic methylsiloxanes by CSR–LVI–GC–MS.

Abbreviation	Name	Time window (min)	Selected ion for monitoring (relative abundance, %)	
			Quantification ion (*m/z*)	Confirmation ion (*m/z*)
L2	Hexamethyldisiloxane	8.40–9.20	147 (100)	131 (45), 117 (5)
D3	Hexamethylcyclotrisiloxane	9.20–10.35	207 (100)	191 (27), 177 (5)
IS[a]	Bis(trimethylsiloxy)methylsilane	9.20–10.35	207 (100)	221 (13), 191 (10)
L3	Octamethyltrisiloxane	10.35–11.30	221 (100)	205 (10), 189 (6)
D4	Octamethylcyclotetrasiloxane	11.30–12.00	281 (100)	265 (10), 249 (8)
SS-1[b]	Methyltris(trimethylsiloxy)silane	12.00–12.80	207 (100)	295 (30), 281 (12)
L4	Decamethyltetrasiloxane	12.00–12.80	207 (100)	295 (19), 191 (7)
D5	Decamethylcyclopentasiloxane	12.80–13.50	355 (100)	267 (75), 339 (10)
SS-2[b]	Tetrakis(trimethylsiloxy)silane	13.50–14.80	281 (100)	369 (14), 265 (7)
L5	Dodecamethylpentasiloxane	13.50–14.80	281 (100)	369 (21), 265 (9)
D6	Dodecamethylcyclohexasiloxane	14.80–16.00	341 (100)	429 (41), 325 (24)

[a] IS: Internal standard.
[b] SS-1 and SS-2: surrogate standards.

has been proposed for the analysis of cyclic and linear VMS in air samples [15,17,18]. However, studies comparing the efficiency of Isolute ENV+ with that of other sorbents have not been performed. In this paper, the behaviour of several stationary phases, such as activated coconut charcoal, Carbopack B and Cromosorb 102 and 106, currently used for adsorption of volatile organic compounds [44], is studied. The first step of the study was the selection of the solvent to elute the compounds from the sorbents. Among the solvent tested (*n*-hexane, dichloromethane and mixtures of them), dichloromethane (12 ml) was selected since it was the only solvent that provided the quantitative elution of the target compounds, mainly for activated coconut charcoal. Recoveries ($n=4$) of the linear and cyclic methylsiloxanes from spiked clean air samples using the studied sorbents are given in Fig. 1A. Quantitative recoveries were obtained for all the compounds using Cromosorb 102, Cromosorb 106 and Isolute ENV+, while low recoveries were achieved for the most volatile methylsiloxanes using activated coconut charcoal (L2: 18% and D3: 30%) and Carbopack B (L2: 38% and D3: 53%). These low recoveries are probably due to the adsorption of water on the surface of the sorbents that reduce their retention capacity. To evaluate this effect, experiments using humidified (relative humidity ~70%) and dried nitrogen were carried out for activated coconut charcoal and Carbopack B. Recoveries higher than 95% were obtained for all the compounds when dried nitrogen was used, while values ranging from 15% for L2 to 40% for D3 were achieved using humidified nitrogen. These findings confirmed that carbon-based sorbents are seriously affected by the moisture of the air and therefore the use of Carbopack B or activated coconut charcoal was discarded for further experiments.

The retention efficiency of the target compounds at high sampling volumes was evaluated using the polymeric materials (Cromosorb 102, Cromosorb 106 and Isolute ENV+) which were spiked as described above (Section 2.4). Significant losses were found for some of the sorbents when 500 L was used (Fig. 1B). For instance, losses from 42% to 63% were obtained for L2 using Cromosorb 102 and 106. The better sorption capacity of Isolute ENV+ could be attributed to the higher specific surface area of the hypercrosslinked resine (1100 $m^2 g^{-1}$) [46] in comparison with the conventional macroporous polymers Cromosorb 102 (350 $m^2 g^{-1}$) and Cromosorb 106 (750 $m^2 g^{-1}$) [47]. Therefore, in order to maximise the sampling volume Isolute ENV+ was selected for further work. Then, the effect of the sampling flow rate (from 0.2 to 1.5 L min^{-1}) on the retention efficiency of Isolute ENV+ was studied. Recoveries higher than 95% were obtained for all the compounds demonstrating that the flow within the tested range did not cause a significant effect on the retention efficiency of the sorbent. Hence, a flow rate of 1.5 L min^{-1} was chosen as optimal value to decrease analysis time and prevent potential losses and degradation of the analytes. Finally, the breakthrough volume of the target compounds was determined by drawing air volumes (500–5300 L) through Isolute ENV+ cartridges at a flow rate of 1.5 L min^{-1}. Figure1C shows the recoveries obtained for the more volatile compounds, L2, L3 and D3. As can be seen, L2 showed a significant loss above 2700 L, while for D3 and L3 considerable losses were observed at air volumes above 3300 and 4100 L, respectively. For the less volatile compounds (L4, L5, D4, D5 and D6), the breakthrough volume was not achieved up to 5300 L. In view of the results obtained and with the aim of establishing a general method for the analysis of all the compounds, a sampling volume of 2700 L was chosen.

3.2. CSR–LVI conditions for GC–MS analysis

Due to the high volatility of some linear and cyclic methylsiloxanes, the use of concentration steps before GC–MS analysis resulted in a partial loss of the target compounds by volatilisation. For instance, L2 was completely lost and the recovery for D3 was only of 30% when a standard mixture (200 ng ml^{-1}) in dichloromethane was concentrated from 12 ml to 0.5 ml using rotary evaporation. Losses also occurred when using a gently stream of nitrogen. To increase sensitivity of the method avoiding concentration steps, CSR–LVI was applied at the conditions given in the experimental section. However, when a high volume (30 μl) of a standard mixture in dichloromethane (20 ng ml^{-1}) was injected fronting peaks were obtained (Fig. 2A), while this effect was not observed when injecting the same standard using conventional splitless injection (2 μl). In contrast, when injecting a standard in *n*-hexane (30 μl) this distortion was not observed (Fig. 2B). For this reason, this solvent was selected for the elution from the Isolute ENV+ cartridge, and the minimum volume was evaluated. It was found that a volume of 3 ml was enough to obtain quantitative recoveries for all the compounds (Table S1 in Supplementary material).

3.3. Performance of the analytical method

To evaluate the validity of the developed method, quality parameters such as linearity, precision, recoveries and limits of detection and quantification, were established. The linearity on the response was examined by injecting 30 μL of standard mixtures containing the target compounds at concentrations between 0.05 and 200 ng ml^{-1} for L2, L3, L4, L5 and D3 and from 0.05 to 500 ng ml^{-1} for D4, D5 and D6, and correlation coefficients (r)

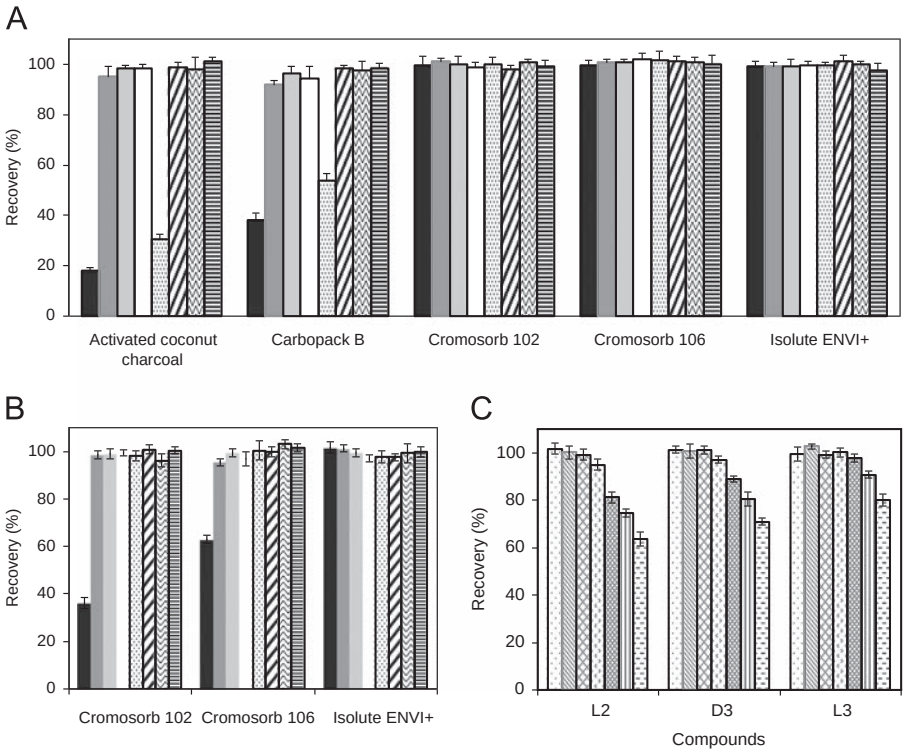

Fig. 1. Sampling efficiency of the studied sorbents (activated coconut charcoal, Carbopack B, Cromosorb 102, Cromosorb 106 and Isolute ENV+), (n=4) (A) Air volume sampled: 20 L (200 mL min^{-1}), (B) Air volume sampled: 500 L (200 mL min^{-1}). Compounds: (■) L2, (■) L3, (■) L4, (□) L5, (⁘) D3, (◪) D4, (▨) D5, (▤) D6; (C) Recoveries of L2, L3 and D3 obtained with Isolute ENV+ using air volumes of 500 L (⁘), 1300 (▨), 2200 (◪), 2700 (⁘), 3300 (▩), 4100 (▥) and 5300 (▬) at a flow rate: 1.5 L min^{-1}.

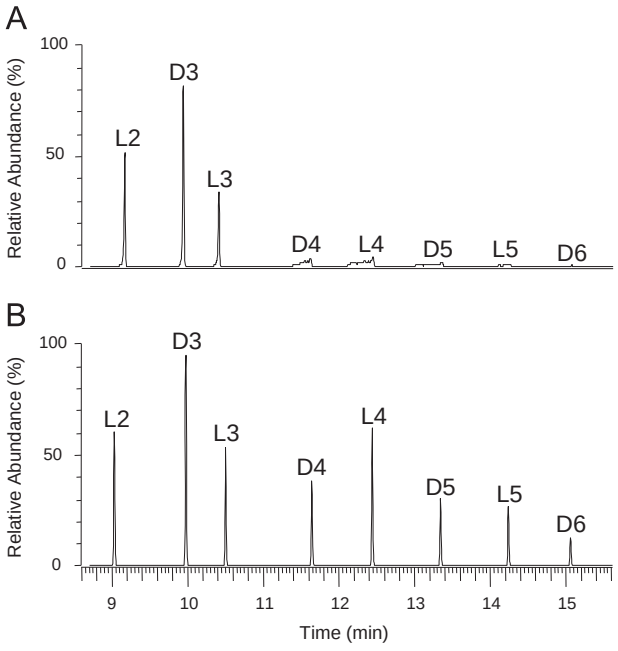

Fig. 2. CSR–LVI–GC–MS (SIM) reconstructed ion chromatograms of a mixture of linear and cyclic methylsiloxanes (20 pg μL^{-1}) obtained using: (A) dichloromethane and (B) n-hexane as injection solvents (injection volume: 30 μL).

higher than 0.999 were obtained for all the compounds. Recoveries of the whole method were studied at two concentration levels (20 and 200 ng m^{-3}) using Isolute ENV+ cartridges spiked with known amounts of an appropriate standard solution. Eight replicate analyses were carried out for each spiked level and

Table 2
Recoveries (%) and method limits of detection (mLOD) and quantification (mLOQ) of linear and cyclic methylsiloxanes (air sampling volume 2700 L at 1.5 L min^{-1}).

Compound	Recovery (%) ± sd[a]		mLOD (ng m^{-3})	mLOQ (ng m^{-3})
	Low level[b]	Medium level[c]		
L2	99 ± 8	101 ± 5	0.18	0.45
L3	98 ± 5	96 ± 4	0.02	0.08
L4	100 ± 9	99 ± 3	0.02	0.05
L5	101 ± 6	102 ± 4	0.01	0.03
D3	97 ± 6	100 ± 4	0.10	0.28
D4	98 ± 9	104 ± 3	0.15	0.40
D5	100 ± 6	101 ± 4	0.10	0.28
D6	102 ± 7	103 ± 6	0.08	0.18

[a] n=8.
[b] Low level: 20 ng m^{-3}.
[c] Medium level: 200 ng m^{-3}.

recoveries higher than 96% were obtained for all the compounds (Table 2). Precision of the method was also determined at the two concentration levels, 20 and 200 ng m^{-3}, and relative standard deviations (RSD, %) lower than 9% were obtained. The recoveries of the surrogate internal standards (SS-1 and SS-2) were also determined and ranged from 94% to 99% with a RSD (%) lower than 12%. Method LODs (mLODs) and LOQs (mLOQs) expressed as the concentration of analyte that provides a response equal to the mean of field blanks plus three and 10 times the standard deviation, respectively, are given in Table 2. mLOQs were between 0.03 and 0.45 ng m^{-3} for linear and cyclic methylsiloxanes for a sampling volume of 2700 L (Table 2). These values were 10–100 times lower than those reported by Krogseth et al. [15] using Isolute ENV+ cartridges (120 mg) and higher sampling air volumes.

3.4. Analysis of indoor and outdoor air samples

To examine the applicability of the developed method, two outdoor air samples of urban origin (Barcelona, Spain) and six indoor air samples were analysed in duplicate using the optimised sampling conditions (2700 L at 1.5 L min^{-1}). To guaranty that breakthrough volume of the sampling cartridges was not surpassed, the second cartridge coupled online was analysed and the amount of target compounds found in this cartridge was always lower than 3%. Recoveries of the surrogate internal standards were always higher than 95%. Table 3 shows the concentration mean values with their corresponding standard deviations found for linear and cyclic methylsiloxanes in the analysed air samples. As an example, Fig. 3 shows the CSR–LVI–GC–MS (SIM) chromatograms obtained of an indoor air sample (laboratory 1). Generally, concentrations of cyclic methylsiloxanes were up to three orders of magnitude higher than those of linear methylsiloxanes in both environments, indoor and outdoor air. These findings are in agreement with data reported in the literature [2,10,40], and can be associated to the high production and uses of cyclic compounds in the European Union [2,3,40]. D5 was the compound detected at the highest concentrations, followed by D4 and D6. This distribution pattern of cyclic VMS has also been found in urban air from different cities located in United States, Canada, France and Switzerland [10,13,14].

For indoor air, the cyclic methylsiloxanes D5 followed by D4 and D6 were found to be the most abundant chemicals, with concentrations ranging from 156 ng m^{-3} to 292.7 μg m^{-3} (Table 3). D5 accounted routinely for more than 53% (laboratory air) of the total VMS with a maximum of 92% at home environments. The predominance of D5 is in accordance with the data reported in several studies which determined the content of cyclic methylsiloxanes in a

Table 3
Mean concentrations (ng m^{-3}) of linear and cyclic methylsiloxanes found in indoor and outdoor air samples.

Compound	Concentration (mean ± sd) (ng m^{-3})[a]							
	Indoor air						Outdoor air	
	Office 1	Office 2	Laboratory 1	Laboratory 2	Home 1	Home 2	Urban air 1	Urban air 2
L2	26 ± 2	33 ± 4	89 ± 9	319 ± 27	12 ± 1	18 ± 2	22 ± 3	12 ± 1
L3	9.5 ± 0.4	10.6 ± 0.6	13 ± 1	17 ± 2	15 ± 2	17 ± 2	16 ± 2	14 ± 1
L4	10.5 ± 0.4	11 ± 1	< 0.05[b]	13.4 ± 0.7	15 ± 1	20 ± 2	17 ± 2	16 ± 2
L5	3.9 ± 0.3	4.5 ± 0.3	4.2 ± 0.5	6.7 ± 0.9	265 ± 18	129 ± 11	8 ± 1	6.0 ± 0.5
D3	122 ± 6	48 ± 3	471 ± 30	508 ± 36	170 ± 12	126 ± 11	5.0 ± 0.5	2.2 ± 0.2
D4	416 ± 25	226 ± 12	641 ± 45	833 ± 75	3052 ± 115	1592 ± 75	79 ± 5	73 ± 6
D5	2415 ± 168	1704 ± 166	2854 ± 263	2320 ± 195	229114 ± 7388	292668 ± 8974	439 ± 24	375 ± 18
D6	393 ± 25	156 ± 11	569 ± 51	380 ± 30	84562 ± 4012	23123 ± 1029	60 ± 4	45 ± 4

[a] $n=2$.
[b] < mLOQ (ng m^{-3}).

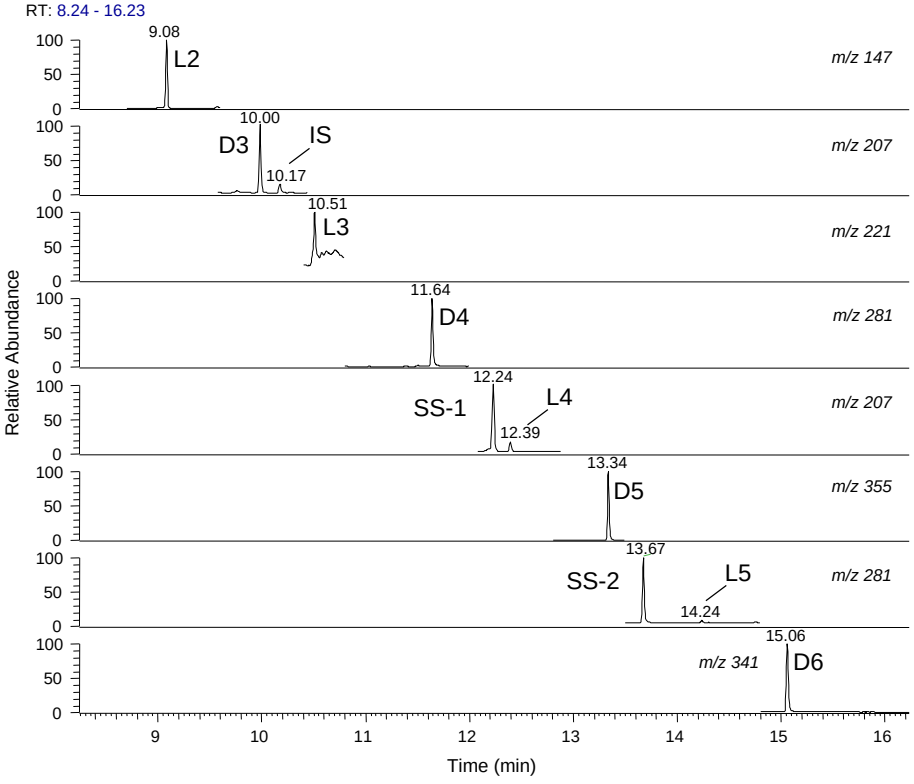

Fig. 3. CSR–LVI–GC–MS (SIM) chromatograms of an air sample obtained from Laboratory 1 (sampling air volume: 2700 L, flow rate: 1.5 L min^{-1}).

great variety of personal-care products [48–50]. For indoor air samples collected at homes, concentrations of cyclic methylsiloxanes were in line with those reported in indoor air samples from Sweden (0.6–164 μg m^{-3}) [2], UK (0.22–350 μg m^{-3}) and Italy (0.23–730 μg m^{-3}) [22], although for linear methylsiloxanes values up to two orders of magnitude lower were found [2,22]. Concentrations ranging from 3.9 to 33 ng m^{-3} for linear and between 48 and 2415 ng m^{-3} for cyclic methylsiloxanes were found in the office indoor air samples analysed in our study. These values are lower than those published by Hodgson el at. [21], who reported levels for D5 between 1.1 and 7.4 ppb (16.9–113.9 μg m^{-3}), Shield et al. [19], that found values from 2.5 to 10.2 μg m^{-3} for D4 and between 7 and 39.6 μg m^{-3} for D5, and Pieri et al. [22] (0.04–170 μg m^{-3}). In addition, the levels found for cyclic VMS in office environments were two-order of magnitude lower than those determined at home indoor air samples. These differences could be attributed to the existence of distinct emission sources of cyclic VMS. In office indoor air, the human occupants, computers and printers are the main sources of emissions of cyclic VMS, while at home environments, the siloxane-containing products are the predominant contamination source. Regarding the results obtained for laboratory air, levels of cyclic methylsiloxanes, except for D4, were lower than those reported for D5 and D6 in laboratory air from the University of Iowa, USA ($<$59–39000 ng m^{-3}) [13]. In the laboratory air samples collected our study, the cyclic VMS levels were 1.5 times higher than those found in office environments. Taking into account that the number of occupants is similar between the laboratories and the offices, these differences could be attributed to the methylsiloxane emission from the laboratory equipment and facilities (e.g., instrumentation, silicone tubes, sealants and electronics).

Regarding outdoor air samples collected in Barcelona city, levels of cyclic methylsiloxanes ranged from 2.2 to 439 ng m^{-3}. These concentrations, except for D3, were higher than those reported for urban air in cities from United States, Canada, Hawaii and France (0.13–280 ng m^{-3}) [10]. Recently, concentrations in line with those obtained in our study were reported for D5 and D6 in outdoor air from Zurich (Switzerland) (10–650 ng m^{-3}) [14] and Chicago (USA) ($<$8.5–1100 ng m^{-3}) [13], although these values were clearly lower than those found in cities located at the South of China (up to 3.3 μg m^{-3}) [12]. For the linear methylsiloxanes, concentrations ranging between 6 and 22 ng m^{-3} were detected in Barcelona urban air and these values were higher than those found in cities from North America and Europe [10,15].

4. Conclusions

A simple method for determining linear and cyclic methylsiloxanes in air using active sampling combined with CSR–LVI–GC–MS is developed. Air sampling volumes of 2700 L and Isolute ENV+ as sorbent are proposed for the quantitative sorption of linear and cyclic VMS. The use of the CSR–LVI technique for sample injection allowed increasing the detectability of the method, avoiding the use of concentration steps during sample treatment, providing method limits of detection down to 0.01–0.18 ng m^{-3}. One of the advantages of the method is its capability of determining the most volatile compounds, such as L2 and D3, which are not often analysed in other studies. The developed method has been applied to the analysis of linear and cyclic VMS in air samples and concentrations were found from 4 ng m^{-3} for L5 (office air) to 293 μg m^{-3} for D5 (home air). Concentrations of cyclic methylsiloxanes in outdoor air from urban ambient were 5–500 times lower than those found in indoor environments, indicating that emissions from indoor air could be a significant contributor to outdoor air concentrations. The method proved to be able of giving reproducible results for the analysis of linear and cyclic VMS in air samples at ng m^{-3} levels, and can be proposed for the routine analysis of these compounds in ambient air.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.10.020.

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