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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, Carboxpack 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  $\mu\text{L}$  of sample extract, is proposed and limits of quantification down to 0.03–0.45  $\text{ng m}^{-3}$ , 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  $\text{ng m}^{-3}$  and between 48 and 292668  $\text{ng m}^{-3}$ , were obtained, respectively, while levels from 6 to 22  $\text{ng m}^{-3}$  for linear and between 2.2 and 439  $\text{ng m}^{-3}$  for cyclic methylsiloxanes in outdoor air from Barcelona (Spain), were found.

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## 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], supermarkets [22] and also in indoor dust [23]. Most of these studies showed that the

predominant VMS found in urban sites and indoor environments is decamethylcyclotrisiloxane (D5) followed by octamethylcyclotetrasiloxane (D4) and dodecamethylcyclohexasiloxane (D6), which are the most abundant in personal care products [24]. Several studies performed in mammals 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  $\mu\text{L}$  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  $\mu\text{g ml}^{-1}$ , except for SS-2 which was 10000  $\mu\text{g ml}^{-1}$ , 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  $\mu\text{g ml}^{-1}$ , and D4, D5 and D6 at 3  $\mu\text{g ml}^{-1}$  were prepared in *n*-hexane from individual secondary standard solutions of 80  $\mu\text{g ml}^{-1}$ . All standard solutions were prepared monthly and stored at  $-18^\circ\text{C}$ . A set of seven calibration solutions containing L2, L3, L4, L5 and D3 at concentrations ranging from 0.05 to 200  $\text{ng ml}^{-1}$ , and D4, D5 and D6 at concentrations ranging from 0.05 to 500  $\text{ng ml}^{-1}$ , 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  $\text{ng ml}^{-1}$ . For quantification, a standard mixture containing the surrogates SS-1 (30  $\mu\text{g mL}^{-1}$ ) and SS-2 (5700  $\mu\text{g mL}^{-1}$ ), prepared daily from the individual stock standard solutions, was added to the upper frit of sorbent cartridge (20  $\mu\text{l}$ ) prior to air sampling. In addition, a standard solution of IS at a concentration of 1000  $\text{ng ml}^{-1}$  in *n*-hexane was used for recovery determination and was added to the final extract to give a concentration of 50  $\text{ng ml}^{-1}$ . *n*-Hexane and dichloromethane of residue analysis grade were obtained from Fluka (Bucks, Switzerland). Carboxpack B (60/80 mesh), activated coconut charcoal (80/120 mesh), and Chromosorb 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  $^\circ\text{C}$  and between 61% and 84%, respectively.

### 2.4. Sampling process optimisation

Several stationary phases: activated coconut charcoal, Carboxpack B, Chromosorb 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  $\mu\text{l}$  of a standard solution of the target compounds at 10  $\mu\text{g ml}^{-1}$  (in *n*-hexane) and 20  $\mu\text{l}$  of a surrogate standard mixture, containing SS-1 and SS-2 at 10  $\mu\text{g ml}^{-1}$ , 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  $\text{L min}^{-1}$ . For the elution of the target compounds, several solvents such as

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