Determination of linear and cyclic volatile methyl siloxanes in biogas and biomethane by solid-phase microextraction and gas chromatography-mass spectrometry

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ABSTRACT

A new method based on solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS) was developed for the analysis of seven linear (L2 – L5) and cyclic (D3 – D5) volatile methyl siloxanes (VMS) in biogas and biomethane, directly collected into Tedlar® bags (Tedlar SPME) from anaerobic digesters and wastewater treatment plants. The method was employed to monitor VMS content in biomethane produced by biogas upgrading with a pilot-plant membrane unit and provided adequate limits of quantification (< 0.05 mg m⁻³) to detect trace siloxane impurities. Tedlar SPME was validated against a standard procedure based on indirect sampling of gas streams with sorbent tubes followed by solvent extraction and GC-MS. Method precision (RSD) on total and individual VMS concentrations was lower than 10%, while RSD values of the standard procedure were higher than 20%. Tedlar SPME suitably revealed high VMS levels, expressed as total volatile silicon (> 1 mgSi m⁻³), in wastewater biogas and provided a more efficient sampling of heavier VMS in comparison to the sorbent tubes method. At low values (< 0.1 mg Si m⁻³) typical of wood waste biogas and biomethane, no statistically significant differences were observed between the two methods. Overall, Tedlar SPME simplified the analytical procedure by reducing the procedural steps, avoiding the use of solvents and demonstrated its applicability for testing the quality of biomethane as advanced biofuel.

1. Introduction

Siloxanes are silicon-based organic compounds used in a wide range of applications encompassing industrial, household and personal care products [1,2]. The increasing production and consumption of these products is causing a growing concern about their uncontrollable release in all the environmental compartments, where they can be persistent with potential risk of bioaccumulation [3]. Wastewater treatment plants represent a reservoir of siloxanes because they tend to accumulate on the sludge flocs, due to their low solubility and resistance to chemical and biological degradation [1]. Siloxanes can be degraded into low molecular weight species with linear or cyclic structure, also named as volatile methyl siloxanes (VMS), characterised by high vapor pressure and low aqueous solubility [4–6]. When the biomass of wastewater treatment plants is converted into biogas through anaerobic digestion, VMS can accumulate in the gas phase, favoured by the mesophilic conditions inside the digesters [1]. During biogas combustion, VMS oxidation generates abrasive microcrystalline silica, that can be deleterious for engines and related equipment [1]. Besides, the presence of VMS can impair the quality of biomethane obtained by biogas upgrading. Technical standards of biomethane quality comprise a set of specifications regarding its use as a fuel for vehicle engines or in the natural gas network that include the concentration of impurities such as VMS [6–8]. Tolerable siloxanes content is reported as total silicon with a recommended maximum between 0.3 and 1 mgSi m⁻³. These values reflect the limit of quantification (LOQ) of available analytical methods. However, some gas combustion turbines can be particularly vulnerable to silica and require silicon contents below 0.1 mgSi m⁻³ [6], while values above 0.1 mgSi m⁻³ can severely harm oxygen sensors of automotive vehicle engines [7]. Therefore, analytical methods that improve the quantification limit can be helpful to check biomethane quality. VMS determination represents an analytical challenge due to their presence in personal care products as well as laboratory equipment (chromatographic columns, septa), that can lead to cross contamination and false positives. Moreover, biogas and biomethane sampling is a critical step, because the risk of losses,

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compounds discrimination, or contaminations with other unwanted species need to be minimised. Several containers were tested for gas sampling. Canisters present high equipment costs and showed poor recovery of higher molecular weights VMS due to wall adsorption, while impingers require the handling of solvents on the field [8]. The use of sorbent tubes is more advantageous given their simplicity and easiness of transport. However, it is necessary to set up a sampling train in which the flow has to be carefully monitored within a certain range to avoid analytes breakthrough and sampling can be time consuming [9]. Direct sampling with Tedlar® bags allows to overcome analytes breakthrough, with no requirement of equipment such as flowmeters or pumps and can be performed by non-trained personnel [9]. Indirect biogas sampling from wastewater treatment plants by means of activated carbon cartridges was compared to direct sampling with Tedlar bags and no statistically significant differences were observed in VMS concentrations [10]. Solid-phase microextraction (SPME) in the headspace mode (HS) was employed in the analysis of linear and cyclic VMS in river water samples and the PDMS/DVB fibre suitably detected ng L−1 levels [11]. HS-SPME was also tested to trace VMS concentrations in wastewater and sludge samples along two parallel secondary treatment processes in a municipal wastewater treatment plant [12]. On this basis, it is worth investigating SPME as a rapid and solventless procedure to determine VMS in biogas and biomethane. In a comprehensive chemical characterisation of biogas from municipal solid waste landfills, SPME successfully sampled several classes of volatile organic compounds (VOCs), including VMS [13]. However, method optimisation and its detailed analytical performance were not carried out for VMS. In this study, SPME followed by GC-MS analysis in selected ion monitoring (SIM) was evaluated to determine VMS in biogas and biomethane, directly sampled with Tedlar bags (Tedlar SPME). The principal figures of merit of the method were examined in comparison with a standard procedure based on solvent extraction of sorbent tubes. Tedlar SPME method performance was verified by the analysis of real samples from wood waste anaerobic digestion and wastewater treatment plants.

2. Materials and methods

2.1. Materials

The following pure VMS standards were used: hexamethyldisiloxane (L2, 98%), hexamethylocyclotrisiloxane (D3, 98%), octamethyltrisiloxane (L3, 98%), octamethylocyclosiloxane (D4, 98%), decamethyltetrasiloxane (L4, 98%), decamethylcyclopentasiloxane (D5, 97%), dodecamethylpentasiloxane (L5, 97%). Tetra(trimethylsilyloxy)silane (97%) was used as internal standard and pentane (anhydrous, 99%) as solvent. 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) SPME fibre was used for method development. Charcoal sorbent tubes (ORBO-32, 400/200 mg) were used for indirect gas sampling. Tedlar bags of 1 L capacity with thermogreen® LB-2 septa were used for direct gas sampling. All the materials used in this study were purchased by Sigma-Aldrich.

2.2. Tedlar SPME adsorption kinetics

Tedlar bags were inflated with a measured amount of pure nitrogen dispensed by a calibrated flowmeter at 0.5 L min−1 for 2 min. The bags were spiked with 1 µL of a solution containing a mixture of seven VMS standards (1 mg mL−1) in pentane, to obtain a standard gas with total VMS concentration of 7 mg m−3. This value is within the range observed in raw biogas [8,9]. The bags were also spiked with 1 µL of internal standard solution 1 mg mL−1 in pentane. The PDMS/DVB SPME fibre was exposed to the standard gas inside the Tedlar bag by piercing the septum with the SPME holder. Five different exposure times were tested, 1, 5, 10, 20 and 50 min respectively. The fibre was then retracted and inserted into the GC injection port. The experiment was performed in triplicate. A comparison of different SPME fibres indicated that the PDMS/DVB provided the best extraction efficiency for linear and cyclic VMS in river water samples, therefore the same fibre was used in this study [11].

2.3. GC-MS conditions

The PDMS/DVB fibre was thermally desorbed into the inlet of an Agilent 6850 gas chromatograph at the temperature of 250 °C for 10 min. Splitless injection was performed into a HP-5 column (poly(5% diphenyl-co-95% dimethyl)siloxane, 30 m length, 0.25 mm i.d, 0.25 µm film thickness) with helium flow of 1 mL min−1. The temperature program was started at 36 °C for 5 min, then ramped to 200 °C at 7.5 °C min−1 and to 300 °C at 100 °C min−1. Mass spectra were acquired with a quadrupole mass spectrometer Agilent 5975 operating under electron ionisation at 70 eV with acquisition at 1 scan s−1. For each VMS, two qualifier ions and one quantitation ion were acquired (Table 1) in selected ion monitoring mode (SIM).

2.4. Figures of merit

All Tedlar bags were flushed five times with pure nitrogen prior to use. Procedural blanks were performed to test potential background contamination from Tedlar bags, SPME fibre, GC septum and column. Tedlar bags inflated with 1 L of pure nitrogen were spiked with 1 µL of internal standard 1 mg mL−1 and increasing amounts of VMS solution 0.01, 0.1 and 1 mg mL−1 in pentane, to obtain a calibration curve over the concentration range corresponding to 0.01 – 10 µg m−3. Limits of detection and quantification were calculated from linear regression parameters [14].

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>L2</th>
<th>D3</th>
<th>L3</th>
<th>D4</th>
<th>L4</th>
<th>D5</th>
<th>L5</th>
<th>I.S</th>
</tr>
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<tr>
<td>m/z</td>
<td>117, 131, 147</td>
<td>177, 191, 207</td>
<td>189, 205, 221</td>
<td>249, 265, 281</td>
<td>191, 207, 295</td>
<td>267, 239, 355</td>
<td>265, 239, 369</td>
<td>265, 281, 369</td>
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<tr>
<td>retention time (min)</td>
<td>2.93</td>
<td>6.97</td>
<td>8.94</td>
<td>12.1</td>
<td>13.7</td>
<td>15.5</td>
<td>17.3</td>
<td>16.2</td>
</tr>
<tr>
<td>calibration range (ng m−3)</td>
<td>0.01, 0.6</td>
<td>0.01, 1</td>
<td>0.01, 6</td>
<td>0.01, 6</td>
<td>0.01, 1</td>
<td>0.01, 10</td>
<td>0.01, 1</td>
<td>–</td>
</tr>
<tr>
<td>number of calibration points</td>
<td>16</td>
<td>25</td>
<td>31</td>
<td>25</td>
<td>18</td>
<td>34</td>
<td>27</td>
<td>–</td>
</tr>
<tr>
<td>sensitivity</td>
<td>0.220</td>
<td>1.03</td>
<td>0.966</td>
<td>1.68</td>
<td>1.36</td>
<td>0.940</td>
<td>1.00</td>
<td>–</td>
</tr>
<tr>
<td>SEsensitivity</td>
<td>0.0060</td>
<td>0.0041</td>
<td>0.0031</td>
<td>0.0051</td>
<td>0.015</td>
<td>0.0035</td>
<td>0.015</td>
<td>–</td>
</tr>
<tr>
<td>intercept</td>
<td>0.00032</td>
<td>0.0011</td>
<td>0.000094</td>
<td>–0.00076</td>
<td>–0.00027</td>
<td>–0.035</td>
<td>–0.00096</td>
<td>–</td>
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<td>SEm intercept</td>
<td>6.9 × 10−8</td>
<td>4.0 × 10−7</td>
<td>2.2 × 10−7</td>
<td>1.1 × 10−6</td>
<td>1.9 × 10−7</td>
<td>1.0 × 10−6</td>
<td>1.9 × 10−8</td>
<td>–</td>
</tr>
<tr>
<td>Rs</td>
<td>0.9949</td>
<td>0.9996</td>
<td>0.9977</td>
<td>0.9977</td>
<td>0.9980</td>
<td>0.9997</td>
<td>0.9977</td>
<td>–</td>
</tr>
<tr>
<td>LOD (ng m−3)</td>
<td>0.0036</td>
<td>0.0084</td>
<td>0.0075</td>
<td>0.0091</td>
<td>0.0031</td>
<td>0.015</td>
<td>0.0050</td>
<td>–</td>
</tr>
<tr>
<td>LOQ (mg m−3)</td>
<td>0.011</td>
<td>0.026</td>
<td>0.023</td>
<td>0.028</td>
<td>0.0095</td>
<td>0.047</td>
<td>0.015</td>
<td>–</td>
</tr>
<tr>
<td>Precision (%RSD)</td>
<td>9</td>
<td>6</td>
<td>4</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>7</td>
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</tbody>
</table>
2.5. Application to real samples

Biogas produced by the anaerobic digestion of wood waste from urban tree pruning was sampled at the pilot-plant anaerobic digester of the Interdepartmental Centre for Industrial Research “FRAME”, University of Bologna (Ravenna, Italy). Gas samples were collected by installing an in-house built Tee sampling port made of steel hydraulic tube fittings at the outlet of the gasometer (Fig. S1A). The use of Teflon for tube fittings was avoided to prevent adsorption and/or cross contamination during sampling. The gas streams to be sampled were calibrated by means of a portable flowmeter to the value of 0.5 L min\(^{-1}\). Contamination during sampling. The gas streams to be sampled were calibrated by means of a portable flowmeter to the value of 0.5 L min\(^{-1}\). Tedlar bags were inflated for 2 min and biogas in turn analysed by SPME-GC-MS within the same day of sampling. Biogas samples were collected from the digester six times over one month and each measurement was performed in triplicate. Samples from sewage sludge anaerobic digestion were collected at the wastewater treatment plant of Roncocesi (Reggio Emilia, Italy), equipped with a pilot-plant membrane unit for upgrading raw biogas to biomethane. Each gas stream (raw biogas, purified biomethane and the CO\(_2\)-enriched off-gas) along the upgrading unit was sampled in triplicate (Fig. S1B).

2.6. Method validation

Charcoal sorbent tubes (ORBO-32) were connected to the calibrated flowmeter during sampling at the digesters in Fig. S1A and S1B until 30 L of gas passed through the cartridges, as described in a standard method for VOCs analysis in waste gas (CEN/TS 13649:2014) [15]. The sorbent inside the cartridges was collected into a GC vial (2 mL), spiked with 0.1 mL of internal standard 1 mg L\(^{-1}\) in pentane, extracted with 0.9 mL of pentane under sonication (15 min) and centrifugated afterwards. The extracts were injected into GC-MS under the same conditions used for SPME-GC-MS. A solvent delay of two minutes was added due to the injection of 1 mL of pentane extract. The method was internally calibrated over the concentration range 0.01 – 10 mg L\(^{-1}\). The figures of merit were also determined for comparison with Tedlar SPME.

2.7. Statistical analysis

Linear regression of VMS calibration curves was performed with PAST (Palaeontological Statistics vers. 3.16). The linear models of each VMS were considered adequate when the following statistics on the residuals were fulfilled at the significance level of 5%: no positive autocorrelation according to Durbin-Watson test, homoscedasticity according to Breusch-Pagan test and normal distributions according to Shapiro-Wilk test. Parametric (t-test) and non-parametric (Mann-Whitney test) statistics were performed for comparing the means and medians of individual and total VMS concentrations between direct Tedlar SPME and indirect (sorbent tubes) gas sampling methods.

3. Results and discussion

3.1. Determination of SPME conditions

The selection of fibre exposure time is a fundamental step in SPME due to its effect on method sensitivity. To this purpose, the peak areas of each VMS and the internal standard (tetrasil(isotriethylsiloxyl)silane) were plotted versus the time (minutes) in which the fibre was exposed into a Tedlar bag filled with N\(_2\) and spiked with a mixture of VMS (Fig. S2, adsorption kinetics). Interestingly, each VMS exhibited a different adsorption behavior. The curves of L2 and D3 peaked at 5 min thereafter the signal decreased with increasing exposure time. Similar trends were observed for L3 and D4, whose highest peak areas were achieved at 10 min. Contrarily, the peak areas of I4, D5, L5 and that of the internal standard increased with exposure time, without reaching fibre saturation even after 50 min. These trends highlight the occurrence of analytes displacement due to competitive adsorption onto the SPME fibre. In fact, higher molecular weight (HMV) VMS (L4, L5, D5) were sampled more efficiently than lower molecular weight (LMW) homologues (L2, L3, D3, D4), for which a decrease in peak area was observed after 10 min. Analogous results emerged from HS-SPME experiments on a multi-component solution of carboxylic acids and phenols with low Henry’s Law constants [16]. The extraction efficiency decreased after the adsorption maximum with Carboxen-PDMS fibre, and the displacement occurred at the expenses of the LMW components of the mixture [16]. In another study dealing with aromatic hydrocarbons determination, species with stronger affinity for the PDMS/DVB fibre, such as ethylbenzene and p-xylene tended to displace other homologues less strongly adsorbed to the fibre, such as benzene and toluene [17]. The PDMS/DVB fibre consists of a porous polymer (DVB) with uniform micro-porosity, that performs better for the extraction of semi-volatile and HMW volatile compounds [18]. These species with higher affinity for the fibre can thus displace those with less affinity [18]. According to these findings, the displacement highlighted in Fig. S2 was more pronounced for L2, D3, L3 and D4, being the VMS with lower molecular weight (162, 222, 236 and 296 Da respectively, Table S1), compared to L4, D5 and L5 (310, 370 and 384 Da respectively, Table S1). Similarly, VMS with lower K\(_{ow}\) values (LogK\(_{ow}\) < 7, Table S1) exhibited adsorption curves with a maximum peak at short exposure times in comparison to VMS with higher K\(_{ow}\) values (LogK\(_{ow}\) > 8, Table S1), suggesting that the latter had higher affinity for the PDMS-DVB fibre. Previous studies reporting mass discrimination by the SPME fibre indicated that a reduced sampling time and non-equilibrium conditions are suitable options to overcome analytes displacement [16–19]. In the case of VMS in gaseous matrices, exposure times higher than 10 min would be suitable only for HMW VMS. Conversely, at low exposure times it is possible to obtain a favorable detection of LMW VMS and assure a good response of the HMW homologues. Therefore, a sampling time of 5 min was chosen to obtain the maximum response of L2 and D3, while maintaining the signals of the other VMS comparable or higher under the same concentrations (Fig. S2) [16].

The main figures of merit of the method were determined by the analysis of standard gas samples prepared by injection of VMS calibration solutions (in n-pentane) into known volumes of nitrogen. Nitrogen proved to be suitable for the preparation of standard calibration gases [9]. Pentane was employed as solvent for calibration solutions, in accordance to a study dealing with VMS quantification from landfill gases [20]. Pentane evaporated quickly after injection into the Tedlar bags during calibration gas preparation and did not interfere with the detection of LMW VMS in GC-MS analysis. VMS concentrations in calibration gases (Table 1) were chosen to cover a wide range of values (µg - mg m\(^{-3}\)) that might be encountered in real cases, such as high levels in biogas from wastewaters [2] and very low ones in agricultural biogas and biomethane [21]. The calibration curves of all the investigated VMS species showed good linearity expressed by the R\(^2\) coefficient (> 0.995, Table 1). Procedural blanks revealed that the signals of siloxanes from the equipment (including nitrogen gas, Tedlar bags, SPME fibre, GC septum and column bleeding) were lower than those of the lowest calibration point (Fig. S3). Thus, SPME is suitable to detect VMS in gas below 0.01 mg m\(^{-3}\), LOD (< 0.01 mg m\(^{-3}\), Table 1) and LOQ (< 0.05 mg m\(^{-3}\), Table 1) calculated from the linear regression are in accordance with this outcome. Method precision was calculated from replicated analysis of gas spiked at the 0.1 mg m\(^{-3}\) level. RSD resulted lower than 10% for all VMS (Table 1). Standard VMS solutions were directly injected into GC-MS to calibrate the method based on solvent extraction of sorbent tubes (CEN/TS 13649:2014) and the main figures of merit are reported in Table S2. LOD and LOQ were calculated after the analysis of ten blanks. VMS signals at the lowest calibration value were barely distinguished from those of the blanks, confirming a bias below 0.01 mg L\(^{-1}\). This is in line with the technical standards, that report lower sensitivity on VOCs for solvent extraction of sorbent tubes compared to thermal desorption [15].
comparison with the figures of merit of direct GC-MS analysis of VMS solutions, Tedlar SPME allowed to achieve lower detection limits and better precision, in terms of peak area RSD. Tedlar SPME sampling was considered satisfactory to the purpose of quantifying VMS at concentrations below the threshold limit that cause problems in biogas burning and meet biomethane quality requirements (0.1 mg Si m−3). Since the signal to noise of the lowest concentration levels were still high compared to the procedural blanks (Fig. S3), lower LOD and LOQ could be achieved. This highlights method applicability to monitor other gaseous matrices such as atmospheric VMS. Furthermore, the figures of merit of Tedlar SPME (Table 1) are in line with other studies reporting detection capabilities at µg m−3 levels and precision below 10%, with direct gas analysis (Tedlar bags) [9,10] and thermal desorption of sorbent tubes [10,21].

3.2. Method application to real samples

Two configurations of anaerobic digesters were selected as test bench of the Tedlar SPME method: the former (Fig. S1A) was a pilot-plant thermophilic reactor fed with wood waste from urban tree pruning, and the latter (Fig. S1B) a digester of a municipal wastewater plant, equipped with a pilot-plant upgrading unit for the purification of biogas to biomethane. These configurations were selected as indicative of the more recent advances in the research field of anaerobic digestion, that include the production of waste-derived biogas and upgraded biomethane [22].

Fig. 1A shows a representative total ion current (TIC) chromatogram obtained from the analysis of wood waste biogas. TIC chromatograms were acquired to check the presence of other species that could interfere with VMS analysis. Several VOCs were adsorbed onto the SPME fibre after 5 min exposure. The most intense peaks were attributed to monoterpenes such as α-limonene, α- and β-pinene, camphene and terpinenes. Other less intense peaks eluting at higher retention times were attributed to sesquiterpenes, principally β-caryophyllene. It is known that terpenes can be predominant VOCs in biogas produced from anaerobic digestion of biowaste containing green waste [23]. Although D5 could be revealed in the TIC chromatogram of the analysed biogas sample (Fig. 1A), selected ion monitoring (SIM) mode is more appropriate for reliable VMS determination, as evidenced in Fig. 1B showing the peaks of D3, D4 and D5.

TIC chromatograms of raw wastewater biogas, upgraded biomethane and CO2-enriched off-gas are reported in Fig. 2. Wastewater biogas featured several VOCs, but its profile diverged from that of wood waste biogas. An intense region of unresolved peaks at higher retention times was associated to aliphatic, cyclic and branched hydrocarbons (Fig. 2A). Other intense peaks included toluene, acetamide, N,N-dimethyl, and phenol. This is in accordance with previous studies that detected aliphatic and monoaromatic hydrocarbons in wastewater biogas [10,21]. After biogas upgrading, the VOC profiles of biomethane and off-gas (enriched in CO2) changed remarkably, presenting fewer peaks with lower intensities. In particular, phenol and acetamide N,N-dimethyl were not completely removed by the upgrading process (Figs. 2B and 2C). Quantitative VMS determination was performed in SIM mode, using the ions listed in Table 1. Representative SIM chromatographic traces obtained from the analysis of wood waste and wastewater biogas are shown in Figs. 1B and 2D, respectively. VMS concentrations are reported in Table 2 (wastewater biogas, biomethane and off-gas) and Table S3 (time series of wood waste biogas).

Wood waste biogas featured total VMS concentrations ranging from 0.01 to 0.2 mg m−3 (Table S3). Only cyclic VMS were detected, principally D5 and D4, while D3 concentration was always below the LOQ. A slight decreasing trend was observed over the sampling time (Table S3). These trace levels can be due to the addition of anti-foaming agents in the digester or to the degradation of silicone residues in wood waste. In agreement with the present study, cyclic VMS, especially D3, D4 and D5 were detected in biogas from the anaerobic digestion of maize, grass and grass silage under mesophilic conditions, while linear homologues were not revealed [24]. Total VMS concentrations ranged from values below 0.1–0.7 mg m−3 [24]. Overall, the average total volatile silicon content of wood waste biogas over the investigated period of time was 0.05 mgSi m−3 ± 0.02, that is lower than the threshold levels proposed for biomethane quality (< 0.3 mgSi m−3) [6,7].

Contrarily to wood waste biogas, wastewater biogas featured both linear and cyclic siloxanes with higher concentrations (Table 2). The highest contribution to total VMS was given by D5 and D4, followed by L5 and L4, while L2, L3 and D3 were below the LOQ (Table 2). Other studies reported the predominance of D5 and D4 in biogas from landfill, digesters, and wastewater treatment plants, with a wide range of concentrations from 1 up to more than 100 mg m−3 [9,10,25]. The average total volatile silicon concentrations in wastewater biogas (Table 2) exceeded the maximum values reported in technical standards (> 1 mgSi m−3), indicating that VMS abatement is necessary prior to biogas upgrading into biomethane.

As outlined in Table 2, VMS concentrations in purified biomethane were markedly reduced, with total volatile silicon lower than 0.3 mgSi m−3. This confirms the efficiency of the upgrading process in removing VMS impurities. D4 and D5 were still detected at trace levels, but in contrast with the profile of raw biogas, D4 was slightly higher than D5 (Table 2). This suggests a more efficient removal of D5 in comparison to D4, that could present lower affinity for the membrane unit. Interestingly, L2 and D3 concentrations were higher in biomethane than in raw biogas, possibly indicating a lower removal efficiency due to higher volatility and lower affinity for the activated carbon filter of the upgrading unit. The off-gas showed even lower VMS values due to a second recirculation of the gas stream in the membrane unit. In a recent study, the composition of biogas from sewage sludge, upgraded biomethane and off-gas was investigated [21]. VMS concentration in raw biogas was dominated by D5 and D4, while other VMS concentrations from 1 up to more than 100 mg m−3 [9,10,25].
accounted for less than 2% of total VMS. Critical values were observed for raw biogas (> 2 mg m\(^{-3}\)). D5 and D4 concentrations were sharply reduced in biomethane but a relative high contribution of D3 was observed. This effect was attributed to its higher volatility, that lead to a low removal efficiency \[21\]. Overall, these results supported the reliability of the proposed method to identify differences between production systems, trends in time and effects of the upgrading process in real anaerobic digesters. Tedlar SPME suitably detected high and low VMS values in real samples with satisfactory precision. RSD values of total VMS concentrations calculated from data in Table 2 and S3 resulted lower than 5% for high concentrations typical of wastewater biogas (0.2 – 3 mg m\(^{-3}\)) and lower than 10% for trace concentrations typical of wood waste biogas and biomethane (< 0.2 mg m\(^{-3}\)). Moreover, RSD of the most representative VMS contaminants, D4 and D5, showed maximum values of 10%, indicating the suitability of the method to detect individual VMS species.

### 3.3. Validation of the Tedlar SPME method

Biogas and biomethane sampling at the two digesters was performed both directly with Tedlar bags, followed by SPME-GC-MS and indirectly with activated carbon sorbent tubes, followed by solvent extraction and GC-MS (CEN/TS 13649:2014 \[15\]). Total VMS concentrations determined in the wood waste digester monitored for six days within a month (Fig. 5A) were reported in Fig. 3A, while individual VMS concentrations in Fig. S4. Trace amounts were detected.

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**Table 2**

Average VMS concentrations in wastewater biogas, biomethane and off-gas. Values of triplicate analysis were reported with standard deviations in brackets. Individual VMS concentrations were expressed as mg m\(^{-3}\), while total VMS were reported both as mg m\(^{-3}\) and total silicon (mg Sim\(^{-3}\)). Values below the quantification limit were reported as < LOQ.

<table>
<thead>
<tr>
<th>Sample</th>
<th>L2 (mg m(^{-3}))</th>
<th>D3 (mg m(^{-3}))</th>
<th>L3 (mg m(^{-3}))</th>
<th>D4 (mg m(^{-3}))</th>
<th>L4 (mg m(^{-3}))</th>
<th>D5 (mg m(^{-3}))</th>
<th>L5 (mg m(^{-3}))</th>
<th>Total VMS (mg m(^{-3}))</th>
<th>Total silicon (mg Sim(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas</td>
<td>&lt; LOQ</td>
<td>&lt; LOQ</td>
<td>&lt; LOQ</td>
<td>0.23</td>
<td>0.010</td>
<td>2.82</td>
<td>0.025</td>
<td>3.11</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>(0.024)</td>
<td>(0.00015)</td>
<td>(0.0065)</td>
<td>(0.089)</td>
<td>(0.034)</td>
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</tr>
<tr>
<td>Biomethane</td>
<td>0.077</td>
<td>0.049</td>
<td>&lt; LOQ</td>
<td>0.087</td>
<td>&lt; LOQ</td>
<td>0.031</td>
<td>&lt; LOQ</td>
<td>0.25</td>
<td>0.090</td>
</tr>
<tr>
<td></td>
<td>(0.0067)</td>
<td>(0.0019)</td>
<td></td>
<td>(0.0046)</td>
<td>(0.0016)</td>
<td></td>
<td></td>
<td></td>
<td>(0.0042)</td>
</tr>
<tr>
<td>Off-gas</td>
<td>&lt; LOQ</td>
<td>0.028(0.0071)</td>
<td>&lt; LOQ</td>
<td>0.063(0.010)</td>
<td>&lt; LOQ</td>
<td>&lt; LOQ</td>
<td>&lt; LOQ</td>
<td>0.11(0.013)</td>
<td>0.042(0.0046)</td>
</tr>
</tbody>
</table>

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Fig. 2. Total ion current chromatograms of wastewater biogas (A), upgraded biomethane (B) and off-gas (C); selected ion monitoring (SIM) chromatograms of VMS ions in wastewater biogas (D), upgraded biomethane (E) and CO\(_2\)-enriched off-gas (F).
with both methods and the results obtained by the indirect one were in line with those of Tedlar SPME (Table S3). Overall, one-way ANOVA, Kruskall Wallis and post-hoc tests indicated no statistically significant difference between the concentrations calculated with the two methods. D5 concentrations from sorbent tubes were significantly lower than those of Tedlar SPME in two days, while D3 concentration was statistically higher in three days (Fig. S4). However, D3 values were close to the detection limits of the methods, therefore higher variability is expected, due to possible background contamination.

Total VMS concentrations in raw wastewater biogas (Fig. 3B) resulted statistically significant with the t-test but not with Mann-Whitney statistic. This was related with the significantly lower amounts of D5, L4 and L5 observed with the sorbent tubes method (Fig. S5). The adsorption affinity of HMW VMS for the activated carbon could cause their incomplete recovery when solvent extracted. Moreover, the observed difference could be also related to changes in the flow during sampling, even though careful attention was paid in monitoring the flow during the indirect sampling.

Tansel and Surita [26] performed experiments in which four activated carbon sorbent tubes in series were employed for biogas sampling. Activated carbon showed higher affinity for LMW VMS and did not quantitatively capture HMW ones (D4 and D5), especially at high concentrations (> 1 mg m\(^{-3}\)) [26]. Therefore, the bias observed between the methods in raw wastewater biogas, can be also due to competitive adsorption of VMS onto the cartridges, that prevented their accurate determination [26].

Total VMS in upgraded biomethane were not significantly different (Fig. 3C), except L2, which was significantly higher with SPME. It is possible that L2, being the most volatile VMS, could be less captured by the adsorbent during sampling.

Biogas sampling with Tedlar bags was deemed reliable to analyse impurities (including VMS) when the analysis was performed shortly after sampling [27]. Other studies that focused on VMS demonstrated how Tedlar bags with polypropylene fittings provided sample stability over 30 days [9]. In a comparative study on high VMS concentrations typical of biogas from a sewage treatment plant, direct gas injection from Tedlar bags was preferred to thermal desorption of sorbent tubes, because the latter caused incomplete analytes desorption [28]. Moreover, competitive adsorption occurred in activated carbon filters for removing siloxane impurities from biogas. It was shown that light VMS such as L2 and D4 were displaced by D5 and other VOCs present in biogas such as limonene [29].

The error bars in Fig. 3 indicated that Tedlar SPME on real biogas and biomethane samples provided better precision compared to the indirect method, that required more steps in sample collection, preparation and analysis. In fact, RSD on total VMS, D4 and D5 concentrations were lower than 10% with Tedlar SPME, while those of the sorbent tubes method were always higher than 20% on average. This confirms the superior performance of Tedlar SPME, as highlighted in the comparison of the figures of merit on standard VMS compounds.

4. Conclusions

Reliable quantification of volatile methyl siloxanes (VMS) in biomethane represents a fundamental target for the determination of its possible use as advanced biofuel. VMS concentrations below 0.1 mg m\(^{-3}\) could be detrimental in engine applications, therefore, advancement in analytical methods to achieve lower limits of detection is required. A protocol based on direct sampling of gas streams with Tedlar bags with polypropylene fittings and analysis by solid-phase microextraction (SPME) and gas chromatography-mass spectrometry (GC-MS) was developed in this study. Direct biogas and biomethane collection with Tedlar bags significantly improved sampling procedure and reduced both sampling time and risk of cross contamination in comparison to the standard method with sorbent tubes, that requires the use of dedicated equipment and constant measurement of gas flow. The method was successfully applied to biogas samples from wastewater and plant-based residues, that represented a realistic scenario of anaerobic digestion products from different matrices, characterised by high and low VMS concentrations respectively. Moreover, the method highlighted differences in VMS profiles within the gas streams of biogas upgrading membrane units, offering insights into the impurity removal efficiency.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2018.11.032.

References


