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Suitability of Tedlar® gas sampling bags for siloxane quantification in landfill gas

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ABSTRACT

Landfill or digester gas can contain man-made volatile methylsiloxanes (VMS), usually in the range of a few milligrams per normal cubic metre (Nm^3). Until now, no standard method for siloxane quantification exists and there is controversy with respect to which sampling procedure is most suitable. This paper presents an analytical and a sampling procedure for the quantification of common VMS in biogas via GC–MS and polyvinyl fluoride (Tedlar®) bags. Two commercially available Tedlar bag models are studied. One is equipped with a polypropylene valve with integrated septum, the other with a dual port fitting made from stainless steel. Siloxane recovery in landfill gas samples is investigated as a function of storage time, temperature, surface-to-volume ratio and background gas. Recovery was found to depend on the type of fitting employed. The siloxanes sampled in the bag with the polypropylene valve show high and stable recovery, even after more than 30 days. Sufficiently low detection limits below $10\,\mu g\,Nm^{-3}$ and good reproducibility can be achieved. The method is therefore well applicable to biogas, greatly facilitating sampling in comparison with other common techniques involving siloxane enrichment using sorption media.

1. Introduction

1.1. Siloxanes in biogas

Landfill and digester gas may contain a large number of trace components [1]. Among the most important to remove prior to biogas combustion are volatile methylsiloxanes (VMS). During oxidation, siloxanes can convert to silicon dioxide (SiO_2), leading to abrasion in gas engines and the build-up of solid layers that inhibit essential lubrication or heat conduction. The consequences can be as far-reaching as fatal engine damage and failure to comply with emissions standards. Maintenance intervals may have to be shortened and machine lifetime decreases, leading to a rise in operational cost [2]. Concentration ranges of the linear hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), and cyclic hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) in biogas as reported by several authors are given in Fig. 1.

The predominant species in landfill gas appears to be D4, in digester gas D5. L2 is present in greater amounts only in landfill gas. Digester gas, on the other hand, contains significantly more L4. A survey was conducted by the authors in October 2008, questioning more than 40 sewage treatment plants in North-Rhine Westphalia, Germany, which were treating wastewater amounting to a total of about 6,550,000 population equivalents and operating gas engines on digester gas. It revealed that about one-third of the sites operated with gas purification technology. Of these, 70% used activated carbon without on-site regeneration to remove siloxanes. Forty percent of the operators registered an increase of problems related to siloxanes since 2003. Fifteen percent of the operators stated that maintenance frequencies were increased in the last five years explicitly due to siloxanes, 25% keep maintenance intervals even shorter than suggested by the engine producers. Digester gas of a thermal equivalent of 1021 $GWh_{thermal}$ was used for electricity production in Germany in 2008. This represents a sharp increase of about 39% compared to 2001 [7]. Moreover, siloxane emissions into wastewater will probably rise. Despite studies pointing out the dangers some siloxanes may pose to humans and the environment, especially with respect to persistence and bioaccumulation [8], the annual worldwide production of siloxanes was estimated at over one million tons [9]. Over 250,000 tons per year are produced in Germany alone [3]. The pathways of siloxanes into wastewater are reviewed in Dewil et al. [10]. Siloxanes can originate from personal care products, such as deodorants, cosmetics or shampoos. With regard to landfill gas, the degradation of silicone wastes is believed to form siloxanes. Demand for siloxanes has risen steadily and an

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Abbreviations: Nm^3, normal cubic metre at $T_N = 273.15\,K$ and $p_N = 100\,kPa$; VDI, Ger. Verein Deutscher Ingenieure, The Association of German Engineers.

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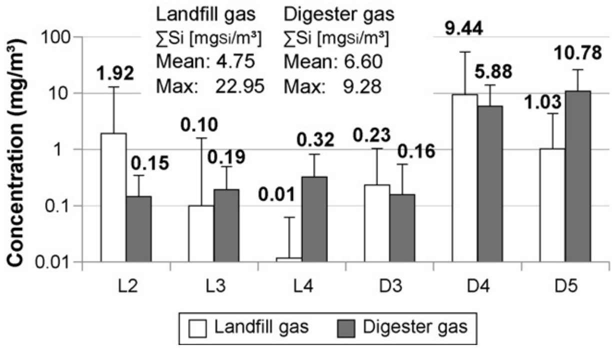

Fig. 1. Volatile methylsiloxane concentrations in landfill gas as stated in [3–5] and digester gas [3,5,6].

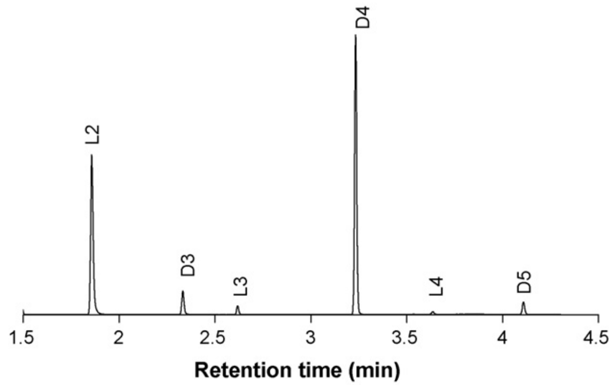

Fig. 2. Chromatogram of linear and cyclic siloxanes in selected ion monitoring.

annual growth in production of 3–5% was estimated in 2003 [11]. This tendency will intensify the need for effective siloxane removal technology, especially as more and more biogas is recovered to produce electricity.

1.2. *Tedlar bag sampling*

In order to effectively evaluate gas purification installations at landfills and sewage treatment plants, the correct quantification of siloxane levels in biogas is essential. However, there is no standardised procedure [12] and results can vary considerably with the application of different methods [13] and from laboratory to laboratory [14,15]. Whereas analysis via GC–MS is widely agreed upon, there is no consensus on the most suitable sampling technique. Common sampling methods include drawing gas through sorption tubes [16] or impingers. In both cases, siloxanes are enriched so that even very low siloxane concentrations can be determined. However, sampling is time-consuming and relatively complicated. Moreover, siloxanes may not absorb completely due to the complex landfill gas matrix [5]. There is a risk of siloxane breakthrough, for example, as a result of competing adsorption with a wide range of less volatile VOCs present in landfill gas [3]. In the case of solid sorbents such as activated carbon or resins, the siloxanes must be transferred into a solvent prior to analysis and it can be difficult to obtain complete desorption [13,17]. The disadvantages associated with siloxane enrichment can be overcome by direct sampling. Especially gas sampling bags have great advantages with respect to handling and ease of sampling. The personnel do not need to be particularly trained for the sampling procedure. It requires little or no additional sampling equipment like coolants, pumps or flow meters, and there is no risk of analyte breakthrough. Both sampling over several hours as well as sampling within seconds is possible. The price of a Tedlar bag with a nominal volume of 1 L lies below 20€. Given these advantages, Tedlar bags are by far the most widely used biogas sampling method in Germany and have recently been included in the VDI-guidelines for the measurement of landfill gas [18]. Yet no detailed information has been found in the international literature about recommended procedures implying Tedlar bags to sample biogas for siloxane quantification.

This paper presents an analytical routine, used to determine the concentrations of common siloxanes L2, L3, L4, D3, D4 and D5 via GC–MS. It was applied to landfill gas samples, collected in 1 L-Tedlar bags. The routine implies the use of external standard gas bags filled with a methane–carbon dioxide gas mixture and spiked with a stock solution containing defined amounts of siloxanes dissolved in n-hexane. The analytical routine was used to measure siloxane concentrations in two types of sampling bags equipped with different fittings (polypropylene and stainless steel). In a series of experiments, the dependence of siloxane recovery on temperature, surface-to-volume ratio and background gas as well as the siloxane stability over 30 days was investigated.

2. Materials and methods

2.1. *Chemicals and gas sampling bags*

The six siloxanes were obtained from ABCR (Karlsruhe, Germany): L2 (99.9%), D3 (95%), L3, L4, D4 and D5 (all 97%). The n-hexane was from Merck (Darmstadt, Germany), and the gas mixture of carbon dioxide (2.5) 50 vol% and methane (3.0) 50 vol% was provided by Westfalen AG (Münster, Germany). The Tedlar sampling bags were produced by SKC (USA) and were acquired from Analyt-MTC (Müllheim, Germany). Two bag types made from 50 μm thick Tedlar film were investigated. One has a single polypropylene fitting with integrated septum and is predominant in Germany (type 232), the other, older model is equipped with a dual port stainless steel fitting (type 231). All bags had nominal volumes of 1 L.

2.2. *Analytical set-up*

The set-up used for siloxane quantification included a forced-convection oven, in which the sample bag and the three external standard bags were stored during analysis. The oven door was replaced by a Plexiglas® screen (8 mm thick), through which the valves of the bags were accessible for gas withdrawal keeping the oven and sample temperature constant at 50 °C. This temperature was chosen, in order to avoid potential condensation of biogas components in the sample bag. The respective Tedlar bag was connected to the injection loop of the GC–MS system by a polytetrafluoroethylene (PTFE) capillary (i.d. 0.8 mm, length 1 m). PTFE was found to be particularly less adsorptive to higher molecular siloxanes D5 and L4 in comparison with stainless steel, copper or Tygon®. Before every measurement, the injection loop and the PTFE tubing – beforehand disconnected from the bag – were flushed with nitrogen (5.0) for 3 min at ambient temperature and at a primary pressure of 2 bar. It was found that this procedure reduced siloxane traces in the system beyond detection. A volume of 12 mL was drawn out of the gas bag through the capillary and the injection loop (1 mL). The operating conditions and instrument control parameters of the GC–MS system are shown in Table 1. The mass detector parameters for the targeted siloxanes are also given. Except for L4, the siloxanes were identified by the mass ratio of three ions and quantified by the ion with the highest response. The mass detector was operated in SIM (selected ion monitoring) modus. A typical chromatogram is given in Fig. 2.

Table 1
Operating conditions of the GC–MS system.

System	Model	Agilent technologies 6890N
Capillary Column	Model	HP-5MS 5% phenyl methyl siloxane
	Nominal length	30 m
	Nominal diameter	250 µm
	Nominal film thickness	0.25 µm
	Total run time	4.3 min
Oven	Temperature program	70 °C for 1.0 min, then ramp at 25 °C per minute to 160 °C where held for 0.3 min
	Post-run	No post-run
Inlet parameters	Temperature	160 °C (constant)
	Pressure:	0.598 bar
	Volume of gas loop:	1 mL
	Temperature gas loop:	120 °C
	Load time gas loop:	0.20 min
	Inject time gas loop:	4.00 min
	Split	Split ratio: 20:1, split flow: 19.8 mL/min, total flow: 23.5 mL/min
	Gas type:	helium
MS-detector	Model	Agilent Technologies 5975
	Mode	Selected ion monitoring (SIM)

Siloxane	Retention time (min)	Ion 1 (quant.)	Ion 2 (qual.)	Ion 3 (qual.)
L2	1.8687 ± 0.05%	147.1	149.1	73.1
D3	2.3427 ± 0.09%	207.1	209.1	96.1
L3	2.6269 ± 0.10%	221.1	223.1	73.1
D4	3.2398 ± 0.06%	281.1	283.1	133.1
L4	3.6358 ± 0.04%	207.1	295.1	–
D5	4.1034 ± 0.04%	73.1	355.2	267.1

2.3. Landfill gas sampling procedure

Prior to use, every sampling bag was subjected to the following procedure. The bag was inflated with nitrogen (5.0). The valve and the septum were closed so that hand-tight and optically inspected for gas tightness by submerging it into water. The nitrogen was then discarded and the bag was re-filled and flushed another three times before it was evacuated and sealed. Gas samples were taken from the pressurised line (approx. 1060 mbar) of a compressor station on the landfill “Vereinigte Ville” in Erftstadt-Liblar, southwest of Cologne, Germany. The landfill gas is known for relatively high silicon concentrations of approximately 25 $\mathrm{mg_{Si}}\,\mathrm{Nm}^{-3}$. PTFE tubing of roughly 5 cm length was used to connect the sampling port with a needle valve. Another 5 cm of PTFE tubing connected the valve to a bubble flow meter, which was used to measure the adjusted volume flow (roughly 200 NmL min^{-1}). Prior to sampling, the set-up was flushed with landfill gas for 5 min in order to reduce siloxane losses due to adsorption on the valve and tubing. The bags were then filled with landfill gas for approximately 4 min, resulting in sampled volumes of 800 NmL.

2.4. Standard preparation

A 100 mL-stock solution was prepared in n-hexane, as all considered siloxanes were found to be stable in this solvent. Prior use of methanol was abandoned, as it showed significant decomposition of the lower molecular siloxanes after 23 days of storage at 4 °C: D3 concentrations were reduced to 16%, L2 to 57% and L3 to 76%. Interestingly, methanol is a common solvent used to sample siloxanes by absorption in impingers [14]. As the use of a presumably more inert perfluoroalkoxy polymer flask (novodirect, Germany) did not lead to higher siloxane recoveries, the stock solution was prepared in a Duran®-glass flask (Hirschmann, Germany). Upon adding the solid D3 to 50 mL of n-hexane, the flask was closed with a PTFE-coated septum, through which all other (liquid) siloxanes were injected in reverse order of their volatility. Finally, n-hexane was added to a total of 100 mL and the solution was stored at 4 °C. Three sampling bags were used as calibration standards. They were always of the same type as the bag containing the gas sample to be analysed, i.e. were equipped with the same fitting. The bags were filled with 800 NmL of the methane–carbon dioxide mixture using a mass flow controller (Brooks, Germany) and weighed volumes of 2, 5 and 10 µL of stock solution were injected in the respective bag after flushing the syringe (HP, Australia) threefold in sets of 10 flushes. Liquid injection or injection by droplet evaporation on the tip of the syringe’s needle showed no difference in later siloxane quantification, so the stock solution was injected as a liquid, which evaporated into the gas mixture within minutes. The errors linked to the preparation of the stock solution and injecting weighed volumes into the calibration standards are given in Table 2.

The mass of L4 in the stock solution is particularly low; the weighing error therefore has a comparably high impact. This can easily be remedied by adding greater amounts of L4 to the stock solution (at least 20 mg), however, this induces higher L4-concentrations than typical for landfill gas. Another way to reduce this error is to add elevated amounts of L4 to n-hexane, and a small volume of this mixture can subsequently be diluted to yield a second, separate stock solution. With regard to spiking the bags, volumes equal or below 5 µL cause noticeable errors above 4% for any siloxane, again, due to the weighing error. This can also be avoided by using dilutions of more concentrated stock solutions and injecting volumes no less than 10 µL. Of course, the above measures lead to an increase in time and effort, and depending on the gas to be analysed, there may be no practical need for high precision, e.g. with regard to L4, a siloxane hardly present in landfill gas.

2.5. GC–MS calibration

The integrated peak-signals of three calibration standards were plotted against the known siloxane contents in the bag. Forced through the origin, the calibration curves were distinctly linear for all siloxanes studied (R^2 > 99%). The calibration levels were chosen to mirror siloxane concentrations in the landfill gas sampled. The lowest calibrated concentration range was for L4 between 50 and 250 $\mu\mathrm{g}\,\mathrm{Nm}^{-3}$, the highest for D4 ranging from 10 to 50 $\mathrm{mg}\,\mathrm{Nm}^{-3}$. As a result of the high and repeated linearity of the calibration curves, it was decided to quantify siloxane concentrations using

Table 2
Standard preparation: error estimation.

	L2	D3	L3	D4	L4	D5
Stock solution[a]						
Added amounts (mg)[b]	126 ± 0.1	35 ± 0.1	18 ± 0.1	400 ± 0.1	2.0 ± 0.1	128 ± 0.1
Concentrations ($g\,L^{-1}$)	1.26 ± 1.0%	0.35 ± 1.0%	0.18 ± 1.1%	4.0 ± 1.0%	0.020 ± 5.1%	1.28 ± 1.0%
Calibration standards[c]						
Concentrations ($mg\,Nm^{-3}$), spiked vol.: 10 ± 0.15 μL[b]	15.8 ± 3.1%	4.36 ± 3.1%	2.25 ± 3.1%	50.0 ± 3.1%	0.250 ± 5.9%	16.0 ± 3.1%
Concentrations ($mg\,Nm^{-3}$), spiked vol.: 5 ± 0.15 μL	7.9 ± 4.1%	2.18 ± 4.1%	1.13 ± 4.1%	25.0 ± 4.1%	0.125 ± 6.4%	8.0 ± 4.1%
Concentrations ($mg\,Nm^{-3}$), spiked vol.: 2 ± 0.15 μL	3.15 ± 8.1%	0.87 ± 8.1%	0.45 ± 8.1%	10.0 ± 8.1%	0.050 ± 9.5%	3.19 ± 8.1%

[a] Prepared in n-hexane, total volume: 100 ± 1 mL.

[b] A weighing error of 0.1 mg is assumed. With n-hexane at 20 °C, this corresponds to an error volume of approximately 0.15 μL.

[c] Prepared in 1 L-Tedlar sampling bags filled with a CH_4–CO_2 gas mixture, total volume: 800 ± 20 NmL.

a 2-point calibration line forced through the origin and incorporating the signals of only the calibration standard with the highest siloxane concentrations.

3. Results and discussion

3.1. Short-term stability and temperature variation

A 10 L-Tedlar bag (type 232 SKC, USA) was filled with 8 NL of the methane–carbon dioxide mixture and spiked with 50 μL of stock solution before it was set aside over night at ambient conditions. Assuming all siloxanes to go into the gas phase, theoretical siloxane concentrations were 8.3 mg Nm^{-3} L2, 1.4 mg Nm^{-3} D3, 650 μg Nm^{-3} L3, 15.2 mg Nm^{-3} D4, 180 μg Nm^{-3} L4 and 1.4 mg Nm^{-3} D5. The next day, the gas was analysed at 20 °C and two 1 L-Tedlar bags (equipped with a polypropylene, respectively stainless steel fitting) were symmetrically connected to the 10 L-bag using a T-piece and tubing as short as possible. Gas was then transferred to the two smaller bags by pressing around 800 mL into each. This procedure was chosen to assure identical initial siloxane concentrations in both bags. Immediate analysis confirmed that the siloxane concentrations in both bags were practically equal (error below one relative standard deviation). The 1 L-bags were then alternately analysed. Both bag types showed stable L2 and D3 signals; L3 signals decreased only slightly. D4, L4 and particularly D5-losses, however, were more pronounced, especially in the bag equipped with the stainless steel fitting.

After 26 h, D4-signals decreased by roughly 25% (Fig. 3A), L4-signals dropped by 40% (Fig. 3C) and D5-signals even decreased by approximately 50% (Fig. 3B). In order to assess whether losses were reversible, the bags were heated to 50 °C (taking roughly 20 min). The losses in the bag with the stainless steel fitting were partly recovered, with D5 and L4-signals remaining steady at about 85% and D4-signals at around 90%. Nevertheless, at any point during the experiment, the siloxane concentrations in the bag sealed with the polypropylene fitting were higher. Reducing temperatures back to 20 °C, again, resulted in significant losses in the bag equipped with the stainless steel fitting and signals were lower than previously observed at 20 °C. The decreasing signals can be fitted to a logarithmic decay function. This function describes the siloxane losses with time at a constant analytical temperature of 20 °C.

It is clearly visible that the bag with the polypropylene fitting exhibits better siloxane stability. D4, L4 and D5-signals decreased mainly in the first 20 min after sampling and then remained relatively steady. At the end of the investigation (193 h), recoveries were still above 85%. This clearly shows that losses are dependent on the fitting with which the bag is equipped [19].

3.2. Surface-to-volume ratio

During the above experiment, 30 volumes of 12 mL were drawn from each bag. The total volume decrease of 360 mL per bag increased the bag surface-to-gas volume ratio of the samples by 81%. High surface-to-volume ratios A/V may lead to lower signals due to adsorption (compare Eqs. (1)–(4)).

An experiment was conducted to visualise the adsorption of siloxanes on the interior surfaces of the gas sampling bags at 50 °C. As previously described in the section *GC–MS calibration*, a clearly linear dependence between MS-signal and siloxane gas concentration was observed during calibration. This linearity was given in both types of sampling bags and over the entire concentration range typical for the respective siloxane in biogas. If adsorption occurred on the interior surfaces of the Tedlar bag (including the fittings), this would therefore suggest a linear sorption isotherm (Eq. (1)), since the percentage of the analyte adsorbed does not depend on concentration. It is stressed, that surface concentration $c_{i,ads} = n_{i,ads}/A$ is not physically precise, as the exact adsorption area A of the sampling bag is not known and consists of different materials (Tedlar foil, o-rings, steel or polypropylene). If the partition coefficients k_i are high, the surface-to-volume ratio of the samples will have little effect on the measured MS-signal. Eq. (2) states that of the total amount of a specific siloxane sampled $n_{i,tot}$, one part stays in the gas phase $n_{i,gas}$, while the other adsorbs $n_{i,ads}$. Combining Eq. (2) with Eq. (1) yields Eq. (3), which relates the amount of the respective siloxane in the gas phase to its total amount in the bag. Assuming $n_{i,tot}$ to remain practically unchanged during the experiment, a 1 L-Tedlar bag was filled with $V_0 = 200$ NmL of landfill gas and inflated step-wise with 4 more 200 NmL-volumes of the siloxane-free methane–carbon dioxide mixture. The initial concentrations in the 200 NmL samples were not quantified directly, however, a respective 800 NmL sample was taken in parallel and exposed siloxane concentrations of approximately 13 mg Nm^{-3} L2, 2 mg Nm^{-3} D3, 800 μg Nm^{-3} L3, 23 mg Nm^{-3} D4, 100 μg Nm^{-3} L4 and 4 mg Nm^{-3} D5. After each filling, the sample bag was allowed to equilibrate for 1 h before it was analysed threefold at 50 °C. As the volumes, used to dilute the landfill gas sample, were at room temperature, 1 h was ample time to assure constant 50 °C in the Tedlar bag.

In case of negligible adsorption, siloxane concentrations should decrease in proportion with the relative increase in gas volume. However, in the bag equipped with the stainless steel fittings, D5, L4 and D4 concentrations decreased disproportionally less after dilution. Equation 4 gives the amount of siloxane in the gas phase after dilution relative to the undiluted base case. Rewritten as a MS-signal ratio R/R_0 and normalised to 1 with the dilution ratio V/V_0, Eq. (4) can be plotted to visualise siloxane adsorption, Fig. 4.

$$c_{i,gas} = k_i c_{i,ads} \Rightarrow k_i = \frac{n_{i,gas}/V}{n_{i,ads}/A} \quad (\mathrm{m^2\,Nm^{-3}}) \tag{1}$$

$$n_{i,ads} = n_{i,tot} - n_{i,gas} \quad (\mathrm{mol}) \tag{2}$$

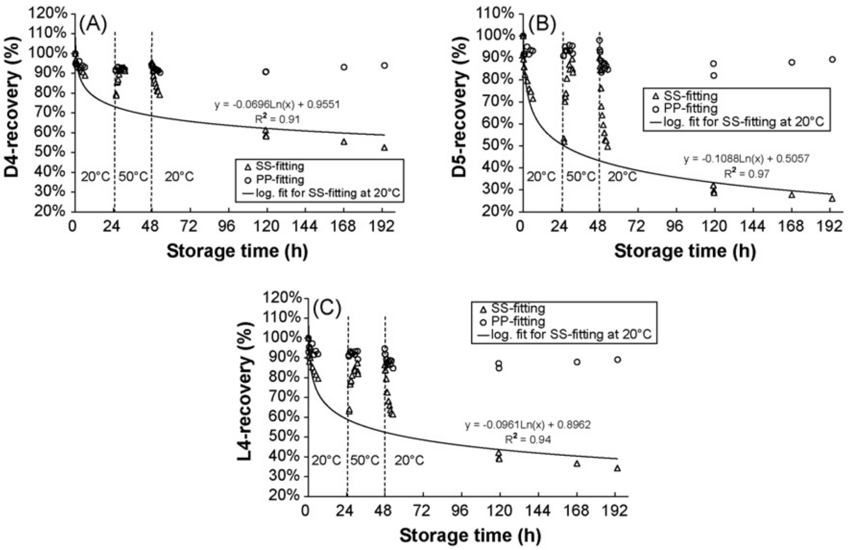

Fig. 3. The stability of (A) octamethylcyclotetrasiloxane, D4, (B) decamethylcyclopentasiloxane, D5 and (C) decamethyltetrasiloxane, L4 in two 1 L-Tedlar bags equipped with different fittings (SS, stainless steel and PP, polypropylene). After 26 h, the samples were heated from 20 to 50 °C and after 48 h the samples were re-cooled to 20 °C.

$$\frac{n_{i,tot}-n_{i,gas}}{n_{i,gas}} = \frac{1}{k_i}\frac{A}{V} \Rightarrow n_{i,gas} = \frac{n_{i,tot}}{(1+(1/k_i)(A/V))} \quad (\mathrm{mol}) \tag{3}$$

$$\frac{n_{i,gas}}{n_{i,gas0}} = \frac{c_{i,gas}V}{c_{i,gas0}V_0} = \frac{R_i}{R_{i,0}} \times \frac{V}{V_0} = \frac{1+(1/k_i)(A/V_0)}{1+(1/k_i)(A/V)} \tag{4}$$

The dashed line, around which all data points of L2, L3 and D3 are closely located, indicates no adsorption. The bag with the polypropylene fitting shows negligible adsorption. In the case of the bag equipped with the stainless steel fitting, the values of L4, D4 and D5 are above the dashed line and can be well fitted by equation 4, varying the unknown term A/k_i (full lines). As previously mentioned, the exact calculation of k_i is not possible, because the adsorption surface of the bag must be known and the sealing is made from different materials.

Nevertheless, the experiment clearly show that the stainless steel fitting causes D5, L4 and D4 losses due to adsorption. Although siloxane concentrations in a 800 NmL-Tedlar bag did recover at 50 °C (Fig. 3), some degree of adsorption seems inevitable, especially in samples with higher surface-to-volume ratios, as shown in Fig. 4. Both fittings have parts which are lubricated with grease containing silicone [20]. However, in contrast to the polypropylene fitting which seals the bag via a PTFE-coated septum, the stainless steel fitting contains an o-ring that is in direct contact with the sampled gas during storage. The adsorption on the fitting material itself, stainless steel, is perhaps also relevant. As prior experiments revealed, a steel capillary connecting sampling bag and injection loop was exchanged for PTFE, because it adsorbed siloxanes prior to analysis. D5, the least volatile of the siloxanes studied, adsorbs most readily on the sample bag interior. In addition, it is the most common methylsiloxane in digester gas and with five silicon atoms per molecule, it contributes strongly to the total silicon content of the biogas. Given these disadvantages and the alternative of the polypropylene fitting, the bag model equipped with stainless steel was no further investigated.

3.3. *Sample stability*

Measured molar fractions of CH_4, CO_2, and air inside a reference Tedlar bag indicated that during storage, ambient air permeates into the samples, but faster counter permeation of CO_2 and CH_4 occurs into the surroundings. This effect leads to a minor decrease in sample volume with time and if no siloxane losses were assumed, higher siloxane signals would be registered. This trend was observed using the Tedlar bags with the polypropylene valve. An 800 NmL land fill gas sample was drawn. Upon retrieval to the laboratory, it was stored at room temperature and a calibration standard was prepared. Both sample and standard were analysed over a period of 32 days, the first analysis was performed 3 h after sampling. Moreover, directly prior to each GC–MS analysis, a new calibration standard (800 NmL) was prepared with which the sample was quantified. On the one hand, "new" standards were used for quantification (Fig. 5A), on the other hand, siloxane concentrations were determined using the initial standard throughout, Fig. 5B.

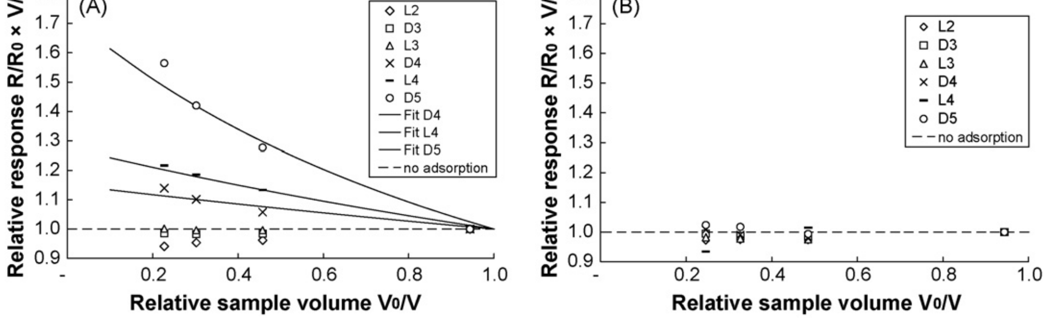

Fig. 4. Siloxane adsorption visualised by diluting a 200 NmL landfill gas sample in a 1 L-Tedlar bag at 50 °C. (A) Stainless steel fitting: 1 L nominal volume, type 231 SKC, USA and (B) polypropylene fitting: 1 L nominal volume, type 232 SKC, USA.

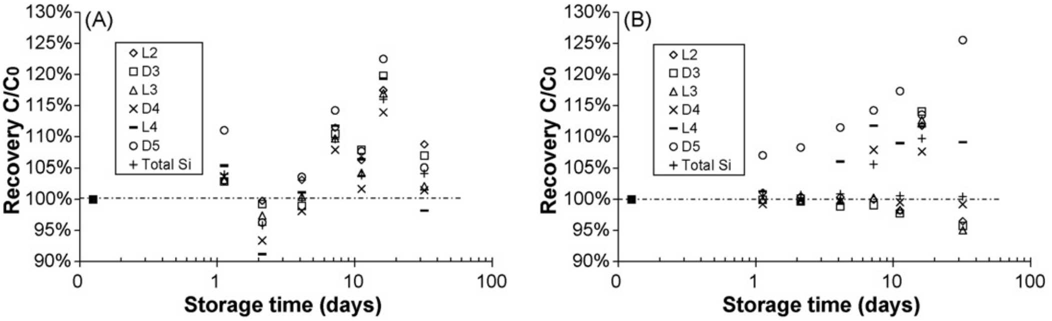

Fig. 5. Siloxane stability in Tedlar sampling bags (1 L nominal volume, type 232 SKC, USA). (A) Quantified with new calibration standards, (B) quantified with the initial standard, prepared directly after sampling. Storage temperature: 20 °C, analysis at 50 °C.

In any case, all siloxane concentrations remain markedly stable. The concentrations exposed a relative standard deviation (RSD) below 9% of the mean concentration and there was no statistical difference between the mean concentrations of any day and day 32 (deviation was within one SD). The mean silicon content attributed to the 6 siloxanes considered was $17.27 \pm 1.03\,\mathrm{mg_{Si}\,Nm^{-3}}$ when quantified with new standards and $16.96 \pm 0.58\,\mathrm{mg_{Si}\,Nm^{-3}}$ with the initial standard.

Quantification with new standards leads to more fluctuating recoveries, probably due to the predominance of statistical errors (Table 2) associated with weighing and injecting the spike volumes for every new calibration standard.

Quantification with the initial external standard exhibited a lower RSD for every compound, in average by 25%. Siloxane recovery as a function of time generally shows a higher degree of continuity. The deviations are more specific to the siloxanes, and are possibly linked to the minor, but still present effect of selective adsorption in the bag or siloxane diffusion out of the bag during long-term storage. These phenomena are either more or less pronounced in the sample than in the initial standard, probably as a consequence of the different gas matrix. In contrast to the sample, the less volatile siloxanes D5 and L4 in the calibration standard tend to adsorb better and/or diffuse faster out of the bag, possibly because there is no competing adsorption with other landfill gas components in the standard. The other siloxanes show no clear tendency in this regard.

For practical purposes, recovery is high and stable enough to allow sufficiently correct sample analysis even weeks after sampling.

3.4. Background gas and water vapour

A test was conducted to evaluate if nitrogen (instead of the methane–carbon dioxide mixture) could be used to prepare calibration standards. Moreover, water was added to the gas to determine whether humidity had an effect on siloxane quantification. For this purpose, six calibration standards were prepared, each with a total volume of 800 NmL. Three standards were filled with nitrogen (5.0), the other three with the methane–carbon dioxide gas mixture. For every background gas, one standard was left dry, the other two were spiked with water (0.055 μS/cm) to attain 90 RH% at 20 and 37 °C respectively. Each bag was then spiked with 10 μL of the stock solution and analysed over a period of 5 days. In relation to the calibration standard filled with the dry methane–carbon dioxide mixture (normalised to 100%), humidified gas (90 RH% at 37 °C) lead to slightly higher MS-signals. The mean increase of all siloxanes over time amounts to roughly 6% in the CH_4–CO_2 mixture and 4% in nitrogen. A possible explanation is reduced adsorption in the bag due to the presence of water vapour. There was no noticeable impact of slightly humidified gas (90 RH% at 20 °C) on any of the siloxane signals.

Conveniently, calibration standards can also be prepared with nitrogen or probably with any other available gas, as results are practically identical to the standards prepared with the dry methane/carbon dioxide mixture.

3.5. Detection limit and repeatability

The repeatability of the analytical routine was determined from 10 measurements of one landfill gas sample, analysed 2 days after sampling. With the exception of L4 and D5, repeatability exposed a relative standard deviation below 1%. A signal-to-noise ratio of three was regarded as the detection limit. A first theoretical approximation of the detection limit was achieved by analysing a landfill gas sample and calculating the respective signal-to noise ratio. The theoretical siloxane concentrations at a signal-to-noise ratio of three could then be calculated via linear extrapolation. The detection limit was then estimated experimentally (Table 3). This was done by consecutively injecting small volumes of landfill gas, sampled in another Tedlar bag and previously analysed for siloxane concentrations, into a fresh siloxane-free sample bag filled with the CO_2/CH_4-mixture. Before spiking the sample, the gas tight syringes (Hamilton, USA) were flushed with the landfill gas and allowed to equilibrate in direct contact with the landfill gas sample for 10 min.

Both the theoretical and experimental way of determining the detection limit showed that siloxane concentrations in the range of $10\,\mu\mathrm{g\,Nm^{-3}}$ could be detected. The low detection limit and the very

Table 3
Siloxane detection limit and repeatability.

	L2	D3	L3	D4	L4	D5
Repeatability[a] (RSD)	0.42%	0.60%	0.76%	0.35%	3.72%	3.55%
	(μg Nm^{-3})	(μg Nm^{-3})	(μg Nm^{-3})	(μg Nm^{-3})	(μg Nm^{-3})	(μg Nm^{-3})
Detection limit (S/N = 3), theoretical	5.33	4.80	6.31	4.23	5.94	10.19
Detection limit (S/N = 3), experimental	6.25	5.75	7.05	3.76	N/A	6.41

Tedlar bag specifications: 1 L nominal volume, type 232 SKC, USA (polypropylene fitting). The bags were kept at 50 °C during analysis and were connected to the injection loop via a PTFE-capillary (1 m length, 0.8 mm i.d.). The capillary was flushed with nitrogen (5.0) prior to every measurement.

[a] Determined from 10 trials taken from a single bag filled with landfill gas of the following siloxane concentrations: L2 17 mg Nm^{-3}, D3 2.8 mg Nm^{-3}, L3 1.16 mg Nm^{-3}, D4 37.5 mg Nm^{-3}, L4 97.5 μg Nm^{-3}, D5 3.9 mg Nm^{-3}.

good repeatability qualify the Tedlar bag with the polypropylene fitting for biogas sampling.

4. Conclusion

It was found that the combination of direct gas sampling using commercial Tedlar bags equipped with relatively non-adsorbing fittings and GC–MS analysis is a viable option for the quantification of volatile methylsiloxanes, L2, L3, L4, D3, D4 and D5 in landfill gas. The analytical method implies the preparation of a stock solution comprising the siloxanes in n-hexane. The calibration standards are Tedlar bags filled with a defined amount of gas and spiked with given amounts of the stock solution. Samples are favourably introduced into the injection loop via a PTFE-capillary which is flushed between measurements. Siloxane losses during storage are a result of adsorption on the fittings, the adsorption on the Tedlar material itself is secondary. The losses can partly be recovered by increasing the temperature of the sample to 50 °C during analysis. The samples stored in commercial Tedlar bags with polypropylene fittings (SKC, USA, type 232) were found to be stable over a period of 30 days. Other commonly used Tedlar bags are equipped with o-ring-sealed stainless steel fittings, which were shown to cause high losses of the higher molecular siloxanes D5, D4 and L4 within just a few hours after sampling. It is therefore imperative to test siloxane adsorption on fittings, before using any type of gas sampling bag for siloxane quantification. A list of suitable commercially available bags should be made available to sampling personnel.

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