

Direct Analysis of Volatile Methylsiloxanes in Gaseous Matrixes Using Atmospheric Pressure Chemical Ionization-Tandem Mass Spectrometry

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Atmospheric pressure chemical ionization-tandem mass spectrometry (APCI-MS/MS) was applied for the first time to the direct analysis of octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) in gaseous matrixes without extraction or prior chromatographic separation. Mass spectrometric characteristics of both compounds under APCI conditions and their fragmentation behavior in MS/MS were investigated. Unlike the classical gas chromatography/mass spectrometry (GC/MS), which involves solvent extraction before gas chromatography, the proposed approach prevents contamination from GC system components and provides unambiguous structural assignments. The method performs well achieving good linearity ($R^2 > 0.997$), low limits of detection ($4\text{--}6\text{ }\mu\text{g}/\text{m}^3$), good precision (RSD < 10%) and accuracy (>93%), and a wide dynamic range. Its applicability to real-world samples was evaluated through measurements of D4 and D5 concentrations in air and biogas samples. The high sensitivity, selectivity, and reliability of this method render our approach a good alternative to the commonly used GC/MS method.

Octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5), shown in Figure 1, are cyclic volatile methylsiloxanes (VMS) with a relatively low molecular mass (296 and 370 amu), high vapor pressure (1 and 0.2 mmHg), low water solubility (0.6 and 0.2 mg/L), and low pK_{ow} (4.45 and 5.2).^{1,2} D4 and D5 are widely used as replacement solvents for the tropospheric ozone forming volatile organic compounds (VOCs) in industrial processes and consumer products. They find applications in various fields such as fuel additives, personal care products, cleaning agents, adhesives, binding agents, surface treatment

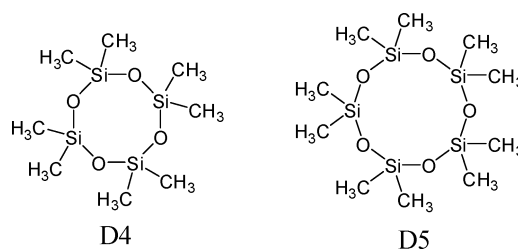


Figure 1. Structure of octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5).

agents, construction materials, paints, lacquers, and varnishes.³ These VMS are mainly released in the atmosphere during the manufacturing process and product formulation, as well as through the normal use of siloxane-containing consumer products. The growing consumption of such siloxanes contributes to their ubiquitous presence in air samples from outdoor and indoor environments.^{2–8} This raises the need to understand their health and safety incidence from both occupational and environmental exposures. Such studies require qualitative and quantitative determination of these compounds at trace levels.

On the other hand, the increasing interest in the utilization of biogases to generate renewable energy (production of heat or electricity)⁹ has created significant concerns about the presence of siloxanes in the biogas obtained during the anaerobic degradation of organic materials. When concentration of siloxanes exceed critical limits (engine warranties quoted in the range 2.8–15 mg/m³),¹⁰ combustion of biogases produces abrasive microcrystalline silica that causes serious damage to heat exchangers and gas engines, thus reducing the economic benefits of using

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biogas.^{1,11} Hence, it is essential to be able to measure the concentration of such siloxanes in biogases by a reliable analytical method.

A number of procedures have been reported for the analysis of VMS in gaseous matrixes, and recently, a review on the analytical methods for the determination of polymethylsiloxanes was published.¹² Electron impact ionization mass spectrometry coupled to gas chromatography (GC/EI-MS) was found to be the most sensitive method, but it is vulnerable to misinterpretation resulting from background and interference peaks.^{1,12} In GC/EI-MS analysis of VMS, there is a potential difficulty for the correct structure assignments due to the identical mass spectral characteristics of siloxanes and siloxanediols. For example, the EI spectrum of D4 is identical to that of octamethyltetrasiloxanediol.¹³ An additional GC/MS analysis employing a softer ionization technique such as chemical ionization (CI) would be needed in order to provide a positive identification of these compounds. Moreover, a potential for background contamination from GC system components also exists. For example, the commonly used polysiloxane-based stationary phases in GC/MS have the potential to generate low molecular mass VMS as a result of thermal and/or oxidative degradation.

A direct sampling mass spectrometry (DS-MS) method would minimize this background contamination. The ability to sample a gaseous matrix via an atmospheric pressure inlet without sample preparation or chromatographic separation prior to MS analysis would therefore provide more reliable and faster measurements.¹⁴ However, to the best of our knowledge, no DS-MS-based methodologies have yet been investigated for the analysis of gas-phase D4 and D5.

The present article describes a novel and highly sensitive and selective approach for the direct determination of D4 and D5 in gaseous matrixes. This is the first report on direct gas sampling through an atmospheric pressure chemical ionization (APCI) source followed by tandem mass spectrometry (APCI-MS/MS) for VMS analysis. The technique is based on the sampling of air or biogas via an atmospheric pressure inlet directly into the APCI corona discharge region. The geometry of the direct sampling system used is designed and the sampling flow rate is optimized so that the transfer of protons from the primary reagent ions to vapor-phase molecules occurs with high efficiency. The proposed method was validated and successfully applied to the analysis of air and biogas samples from a municipal landfill site in Montreal (Canada).

EXPERIMENTAL SECTION

Mass Spectrometry. All experiments except for accurate mass measurements were carried out on a TSQ Quantum Ultra AM triple quadrupole mass spectrometer (Thermo Fisher Scientific, Waltham, MA) equipped with a laser diode thermal desorption LDTD-APCI interface (Phytronix Technologies, Quebec, QC, Canada). The system was operated in positive ion mode without

using the laser diode. The Thermo Fisher Scientific Xcalibur 2.0 software was used to adjust experimental parameters in order to maximize ionization for D4 and D5 and to optimize ion fragmentation and transmission for each compound. Ion source conditions as well as compound-specific parameters such as collision energy and tube lens offset, all important parameters for sensitive detection in the selected reaction monitoring (SRM) mode, were evaluated. The following experimental parameters were chosen: discharge current 3 μ A, capillary temperature 350 °C, sweep gas (nitrogen) pressure 0.3 mTorr, and collision gas (argon) pressure 1.5 mTorr. The peak-width of precursor and product ions was set to 0.7 u at half-height.

For identification of the D4 and D5 fragmentation ions, accurate mass measurements were performed^{15,16} on a 6210 liquid chromatography time-of-flight (TOF) mass spectrometer (Agilent Technologies, Wilmington, DE) operated in the positive APCI mode. Experimental parameters were set as following: gas and vaporizer temperature at 350 and 400 °C, respectively, drying gas (nitrogen) flow at 5 L/min, and nebulizer pressure at 50 psig. The instrument was tuned and calibrated using the standard calibration solution provided by the manufacturer, and the TOF analyzer resolution was at least 6000 full width at half maximum (fwhm) for m/z 322. Two calibration standards were infused along with the samples and their masses used for internal calibration. Both the D4 and D5 were in-source fragmented by applying 350 V on the fragmentor, and scans were performed over an m/z range of 70–1000 with an acquisition cycle of 1.03 spectra/s. The Agilent Technologies Mass Hunter software was used for accurate mass calculations and empirical formula confirmation. Mass accuracies in the low-part per million range were achieved.

Direct Sampling. The direct atmospheric sample inlet system used in the following experiments was designed and fabricated to allow introduction of gaseous samples through the LDTD-APCI interface directly into the corona discharge region, where analytes are ionized and then transmitted into the mass analyzer. A schematic diagram of the instrumental setup is shown in Figure 2. The system includes a sampling line, a Teflon-coated sampling pump, a gas flow controller inside an electronic control box, and a 3 mm i.d. glass transfer tube. The sampling line consisted of a 3 mm i.d. Teflon tube in order to avoid analyte adsorption.¹² The sampling pump was computer controlled by the Phytronix Technologies LazSoft 2.0 software. The system is designed so that an incoming gaseous sample must pass near the corona discharge needle, which must be properly positioned at the end (~2 mm) of the transfer tube. The sample is then vented outside through a purge pump system. It is important to note that although the laser diode was not used, a LazWell sample plate must be present because of software built-in safety routines and for the atmospheric pressure inlet of the LDTD-APCI interface to be functional.

Gaseous Standard Preparation. Gas-phase standards were generated by mixing saturated headspace samples of each compound with ambient air, used as the diluent gas, to account automatically for any matrix effects. D4 of 98% purity and D5 of 97% purity (Sigma-Aldrich, Oakville, ON, Canada) were used as

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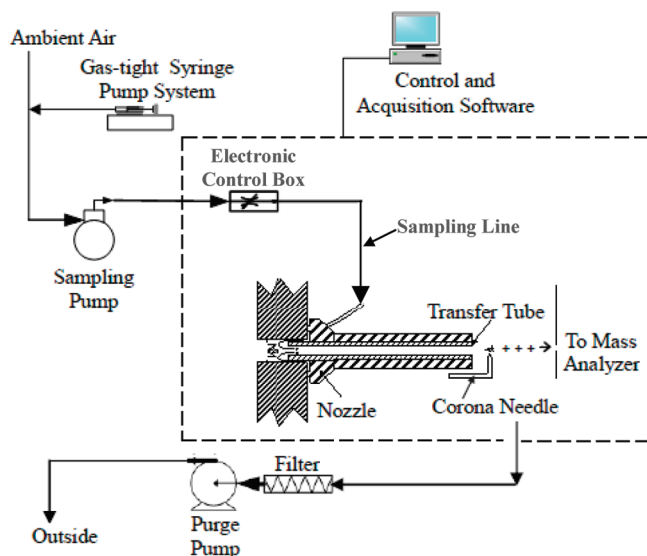


Figure 2. Schematic flow diagram of the instrumental setup.

sources of primary standards. An aliquot of ~2 mL of each analyte was placed into a sealed 40 mL volumetric bottle and maintained at 25 °C for over 1 h to allow liquid–vapor equilibrium to be reached. Direct sampling of the ambient air was performed at a flow rate of 2.5 L/min via the atmospheric pressure inlet through the LDTD-APCI interface. The saturated samples were dynamically diluted into the ambient air stream via a 500 μ L gauge gastight syringe (Hamilton Co., Reno, NV) mounted in a syringe pump model 22 (Harvard Apparatus, Holliston, MA). The flow rates of the headspace samples were controlled by the speed of the syringe pump to provide analyte concentrations up to 3200 μ g/m³. The standard concentrations were calculated based on the known analyte vapor pressure¹ and the chosen dilution factors. Octamethyltetrasiloxane-1,7-diol and decamethylpentasiloxane-1,9-diol were obtained as standards from Dow Corning Analytical Solutions (Midland, MI).

Method Validation. Validation of the direct APCI-MS/MS method for the determination of D4 and D5 in gaseous matrixes was conducted according to the procedure DR-12 VMC of the Centre d'Expertise en Analyse Environnementale du Québec.¹⁷ This document details the performance characteristics required for the development of analytical chemistry methods. Quality parameters, including linearity, limit of detection (LOD), limit of quantification (LOQ), repeatability, reproducibility, and accuracy, were assessed to validate this method under the optimized conditions.

Multipoint calibration curves were constructed for D4 and D5. Calibration equations were calculated by using a linear regression method. For each compound, the LOD was determined as 3 times the standard deviation (SD) of five replicate injections of the lowest standard concentration divided by the slope of the corresponding calibration curve.¹⁸ LOQs were calculated using 10-fold the SD. The relative standard deviation (RSD) was adopted for repeatability and reproducibility assessment. The repeatability was tested

for each compound at two different concentration levels by analyzing five replicates of each level within 25 min. The reproducibility was estimated at two different concentration levels by analyzing five replicates of each level per day over 3 days. Because standard reference materials for D4 and D5 were not available, the accuracy was evaluated at two different concentration levels by analyzing standard mixtures prepared by spiking saturated headspace vapors into Teflon gas sampling bags (Jensen Inert Products, Coral Springs, FL) filled with ambient air. Standard mixtures were prepared with known nominal concentrations of each compound and were analyzed as unknown samples by our method. The background contamination in the laboratory ambient air was accounted for by subtracting background signals from analyte responses. The applicability of the method to real-world samples was evaluated through measurements of D4 and D5 in a compressed air sample (Megs, Ville St-Laurent, QC, Canada) and biogas samples taken from a municipal landfill site in Montreal (Canada).¹⁹ The landfill-derived biogas samples were collected from three extraction wells via collector pipes into 56 L Teflon gas sampling bags (Jensen Inert Products, Coral Springs, FL) using a portable peristaltic sampling pump. Biogas no. 1 was collected from a well located in a landfill zone operated from 1984 to 1990. Biogas no. 2 was collected from a well located in a landfill zone operated from 1991 to 2000. Biogas no. 3 was a composite sample taken from the compressor room located between the pumping station and the electrical power plant. The sample bags were transported to the laboratory and analyzed by direct APCI-MS/MS within 4 h after sampling. Because of the complexity of the biogas compared to ambient air, correction factors to compensate for matrix effects were first estimated by comparing the MS/MS responses of five standards of each compound spiked in ambient air at known concentrations with those spiked in a biogas sample, after correcting for the analyte intensity in the nonspiked matrix (eq 1). Signal suppression effects were weak for D5 (5%) but quite significant for D4 (~30%). However, matrix effects were constant in the studied range with a precision of 2% for both compounds in all spiked biogas samples. This outlines that the use of correction factors can be suitable to correct signal intensities for D4 and D5 quantification in the biogas with an external calibration in ambient air.

$$\text{matrix effects} = \frac{\text{spiked biogas} - \text{nonspiked biogas}}{\text{spiked ambient air} - \text{nonspiked ambient air}} \quad (1)$$

RESULTS AND DISCUSSION

The characteristics of the present direct sampling system that differentiate it from existing technologies are the capability of low sampling flow rates (0–10 L/min) without capillary restrictor or polymeric membrane,^{20–23} providing accurate laminar flows, and a simple geometry that is easy to operate. Classical direct sampling systems require large volumes of gaseous sample and thus high

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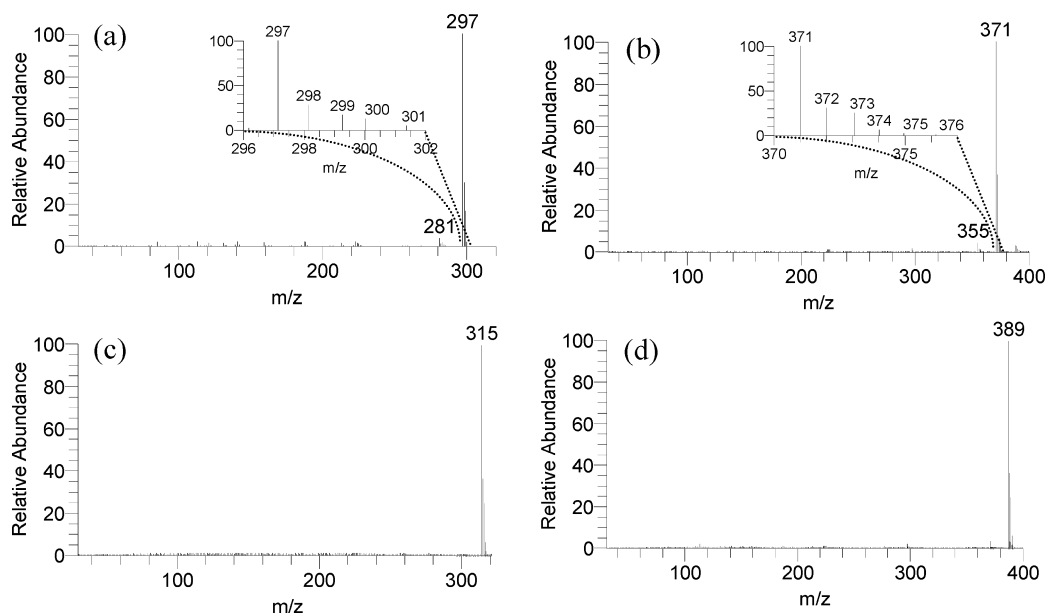


Figure 3. Background-subtracted full-scan mass spectra of (a) D4, (b) D5, (c) tetramerdiol, and (d) pentamerdiol recorded in direct APCI-MS. Insets illustrate the isotopic patterns of the precursor ions from D4 and D5.

sampling flow rates (90 L/min and more)^{24–27} to achieve low LODs. However, in APCI the high flow rate significantly reduces the residence time in the source and hampers the ionization of some organic compounds.²⁸ The geometry of the present system uses gas dynamics to optimize the sampling efficiency into the assembly formed by the corona discharge region and the MS inlet. The use of low sampling flow rates favors the kinetics of charge/proton transfer from primary reagent ions to gas-phase analyte molecules. Maximizing the number of collisions under atmospheric pressure conditions while keeping the properties of gas dynamics provides optimal opportunities for reagent ions in the reaction zone to come into contact with analyte molecules and thereby provides a greater extent of reaction.

Direct APCI-MS Analysis of D4 and D5. Research on VMS determination in gaseous matrixes has been active during recent years with the principal method being GC/EI-MS.^{2–8,29,30} However, it has been shown that EI spectra are not adequate to distinguish VMS and siloxanediols,^{12,13} important environmental and biological degradation products of polysiloxanes.² Under EI conditions, D4 and D5 molecules undergo severe fragmentation and lose methyl radicals yielding predominantly $[M - 15]^+$ ions at m/z 281 for D4 and 355 for D5.¹³ GC/EI-MS measurements of D4 and D5 therefore are usually based on the selected ion monitoring (SIM) of these major ions. Unfortunately, octamethyltetrasiloxanediol $H(OSi(CH_3)_2)_4OH$ and decamethylpen-

tasiloxanediol $H(OSi(CH_3)_2)_5OH$ whose molecular masses differ by 18 amu from those of D4 ($OSi(CH_3)_2)_4$ and D5 ($OSi(CH_3)_2)_5$, respectively, lose a molecule of water in addition to the methyl radical.¹³ Thus, EI fragmentation patterns of the tetramerdiol and the pentamerdiol are essentially identical to those of D4 and D5, respectively. Although one could rely on retention time differences to distinguish these compounds by comparison to standards, incorrect structural assignments could easily occur under certain conditions,^{12,31} leading to data misinterpretation and systematic errors in qualitative and quantitative analysis.

As shown in Figure 3a,b, direct APCI-MS of D4 and D5 predominantly produces protonated molecules $[M + H]^+$ at m/z 297 and 371, respectively. This is in accordance with the ionization mechanism of VOCs in air under positive APCI,³² which relies on the relative proton affinities (PA) of primary reagent ions (e.g., H_3O^+ , ~ 167 kcal/mol, $(H_2O)H_3O^+$, ~ 193 kcal/mol)^{33,34} and gas-phase analyte molecules. Although the proton affinities of D4 and D5 are not available from the literature, the value for the cyclotetrasiloxane ($OSiH_2)_4$, estimated at ~ 189 kcal/mol,³⁵ should serve as a good estimation for D4 and D5. It is well-known that substitution of hydrogen for a methyl group increases the PA of alkyl-substituted compounds.^{36–38} Hence, it is reasonable to expect that the PA of D4 and D5 would be higher than those of primary reagent ions, and proton transfer reactions would be energetically feasible with the protonation site at the oxygen of the Si–O bond in the monomer.³⁵ Besides the

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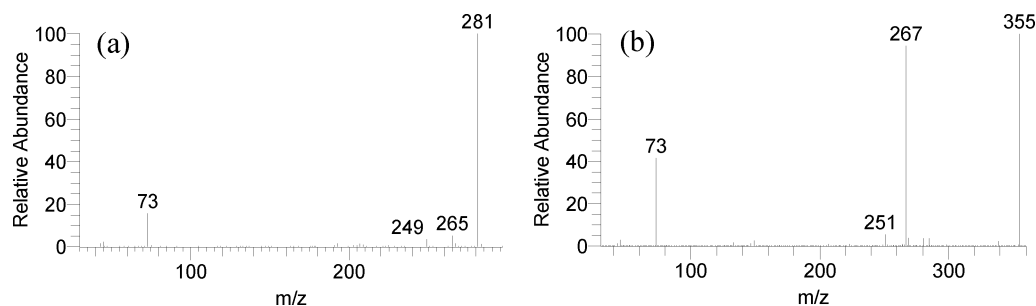


Figure 4. MS/MS spectra of the monoisotopic species of APCI produced ions (a) m/z 297 from D4 and (b) m/z 371 from D5.

Table 1. MS/MS Product Ions of Protonated Molecules from D4 and D5 Identified Using the APCI-TOF

compounds	experimental m/z	theoretical m/z	molecular formula	error (ppm)
D4	281.0516	281.0511	$C_7H_{21}O_4Si_4^+$	-1.57
	265.0204	265.0198	$C_6H_{17}O_4Si_4^+$	-2.22
	248.9891	248.9885	$C_5H_{13}O_4Si_4^+$	-2.11
	73.0463	73.0468	$C_3H_9Si^+$	7.26
D5	355.0701	355.0699	$C_9H_{27}O_5Si_5^+$	-0.44
	267.0004	266.9991	$C_5H_{15}O_5Si_4^+$	-4.97
	250.9696	250.9678	$C_4H_{11}O_5Si_4^+$	-7.25
	73.0471	73.0468	$C_3H_9Si^+$	-3.59

monoisotopic species, D4 formed a cluster of silicon-related isotopologous ions in the m/z range 298–301, while D5 formed a cluster of isotopologous ions in the m/z range 372–376 (see insets in Figure 3a,b). Small amounts of in-source fragment ions at m/z 281 for D4 and m/z 355 for D5, arising from the neutral loss of methane from the protonated molecular ions, were also observed.

Direct APCI-MS predominantly produces from the tetramerdiol and the pentamerdiol $[M + H]^+$ ions at m/z 315 and 389, respectively (see Figure 3c,d), distinct from those of D4 and D5, thus proving to be an interesting alternative for unambiguous structural assignments.

Direct sampling for D4 and D5 quantification in gaseous matrixes is another strength of the present approach. Analyte loss or degradation usually associated with sample preparation steps such as extraction or preconcentration is therefore avoided. Moreover, potential contamination from GC system components (syringe lubricants, o-rings, septa, glass liner containing silanized glass-wool in the injection port, stationary phases based on polysiloxane) is also prevented. Therefore, the proposed method provides reliable measurements with low background interferences.

MS/MS Analysis of APCI Produced Ions from D4 and D5.

The MS/MS spectra obtained by collision-induced dissociation (CID) of $[M + H]^+$ precursor ions from D4 (m/z 297) and D5 (m/z 371) are presented in Figure 4. The spectra displayed product ions at m/z 281, 265, 249, and 73 for D4 and at m/z 355, 267, 251, and 73 for D5. In the case of D4, MS/MS spectra generated from the isotopologous ions m/z 298–301 showed a similar cluster of ions at m/z 73–75, which corresponds to the isotopic distribution pattern of a fragment containing one silicon atom. The accurate mass of the ion m/z 73 was determined to be 73.0463 (Table 1). The only elemental composition that could explain the observed isotopic pattern and accurate mass with a reasonable mass accuracy is $C_3H_9Si^+$. Its formation likely involves extensive bond cleavages and rearrangements. In the

case of product ions m/z 281, 265 and 249, isotopologous ions observed in the MS/MS spectra of ions m/z 298–301 exhibited the distribution pattern of a species containing four silicon atoms. As confirmed by accurate mass measurements (Table 1), the product ions m/z 281 ($C_7H_{21}O_4Si_4^+$), 265 ($C_6H_{17}O_4Si_4^+$), and 249 ($C_5H_{13}O_4Si_4^+$) can easily be rationalized by the neutral loss of one, two, and three methane molecules, respectively, from the protonated molecular ion m/z 297 ($C_8H_{25}O_4Si_4^+$).

Similarly for D5, MS/MS spectra generated from the isotopologous ions m/z 372–376 showed a one silicon atom isotopic distribution pattern for m/z 73, a five silicon atom distribution for m/z 355, and a four silicon atom distribution in the case of m/z 267 and 251. The product ion m/z 355 ($C_9H_{27}O_5Si_5^+$) was formed by the neutral loss of methane from the precursor ion m/z 371 ($C_{10}H_{31}O_5Si_5^+$). The most probable elemental compositions of the product ions m/z 267 ($C_5H_{15}O_5Si_4^+$) and m/z 251 ($C_4H_{11}O_5Si_4^+$) were generated by accurate mass measurements (see Table 1).

In regard to their fragmentation behavior in MS/MS experiments, D4 and D5 show product ion patterns which are suited for SRM. Identification of these VMS in unknown samples was done by manual interpretation of the spectra based on their MS/MS fragmentation pattern. Quantification of D4 was performed with a tube lens set at 56 V by recording the transitions m/z 297 \rightarrow 281 and 297 \rightarrow 73 and using collision energies of 15 and 29 V, respectively. Quantification of D5 was performed with a tube lens set at 57 V by recording the transitions m/z 371 \rightarrow 355 and 371 \rightarrow 267 with collision energies set at 14 and 20 V, respectively. The dwell time was 300 ms per transition, and background contamination signals were subtracted from analyte responses.

Optimization of the Sampling Flow Rate. The effect of the sampling flow rate on the overall detection sensitivity of D4 and D5 by direct APCI-MS was investigated. For both species, the signal intensity of the precursor ion reached a plateau at 1 L/min and decreased at values above 3 L/min. Higher flow rates may cause turbulence which can have a direct impact on the ion transfer efficiency and therefore diminish the signal intensity. The signal showed maximum stability (RSD \sim 5%) at flow rates ranging from 2 to 3 L/min. On the basis of these considerations, a flow rate of 2.5 L/min was used for subsequent experiments.

Performance Evaluation of the Method. The linearity of the proposed method was evaluated from 25 to 3200 $\mu\text{g}/\text{m}^3$ for D4 and from 15 to 1100 $\mu\text{g}/\text{m}^3$ for D5 under the optimal experimental conditions described above. The response for each compound was found to be linear in the tested range, with correlation coefficients of 0.9980 (m/z 297 \rightarrow 281) and 0.9972 (m/z 297 \rightarrow 73) for D4 and 0.9991 (m/z 371 \rightarrow 355)

Table 2. Precision and Accuracy at Different Concentration Levels for the Proposed Method

compounds	standard concentration ($\mu\text{g}/\text{m}^3$)	repeatability (% RSD, $n = 5$)	reproducibility (% RSD, $n = 5$)	spiked concentration ($\mu\text{g}/\text{m}^3$)	measured ($\pm\text{SD}$, $n = 5$) ($\mu\text{g}/\text{m}^3$)	accuracy (%)
D4	51	2	8	54	58 ± 3	93
D4	402	4	7	1001	1020 ± 32	98
D5	99	3	5	88	93 ± 5	94
D5	400	7	10	1017	1068 ± 75	95

and 0.9981 (m/z 371 \rightarrow 267) for D5, covering at least 2 orders of magnitude. These results attest to the quantification potential for the method over a wide concentration range of D4 and D5 from low- to high-microgram per cubic meter levels.

The method LODs determined for D4 and D5 were 6 and 4 $\mu\text{g}/\text{m}^3$, respectively, while LOQs were 21 and 14 $\mu\text{g}/\text{m}^3$, respectively. The sensitivity of the present method is more than 160 times higher than that reported recently for a GC/MS method (LOD 1 mg/m^3 for D4)³⁹ and 75–300 times higher than that reported more recently for a microcantilever array sensor (LOD ~ 0.3 –1.2 mg/m^3 for D5).⁴⁰ The proposed method is thus applicable for the monitoring of D4 and D5 in gaseous matrixes at trace levels, and our results confirm the quantification potential for near background levels in ambient air as well as high concentrations found in biogases.^{1–3,8,29}

Table 2 summarizes the repeatability (intraday precision), reproducibility (interday precision), and accuracy of the proposed method to determine D4 and D5 in gaseous matrixes. These results clearly demonstrate that the values are within an acceptable range, and the direct APCI-MS/MS method is precise and accurate.

Response and recovery times for the system in detecting D4 and D5 were also evaluated. Herein, response time is defined as the time to reach 90% of the signal peak height, while recovery time is the time needed for the signal to decrease to 90% of the peak height when sample flow is turned off. A response profile was obtained by analyzing three replicates of a spiked sample within 10 min and showed that response and recovery times of the system to both compounds were less than 20 s (data not shown).

Real-World Applications of the Method. D4 and D5 were successfully detected and quantified in compressed air and landfill-derived biogas samples by direct APCI-MS/MS. Concentrations measured for both VMS in these real samples are presented in Table 3. Levels of D4 and D5 in the biogases analyzed were below the threshold of 15 mg/m^3 tolerated by several engine manufacturers. It is noteworthy that our results for D4 are of the same order of magnitude as data found in the literature for landfill biogases, whereas in the case of D5 our results are lower by more than 1 order of magnitude.^{10,29,41} The difference may be assigned primarily to differences in waste composition, the stage reached in the decomposition process, and parameters

Table 3. Mean Concentrations \pm SD ($\mu\text{g}/\text{m}^3$) of D4 and D5 Measured in Compressed Air and Biogas Samples

compounds	compressed air	landfill biogas no. 1	landfill biogas no. 2	landfill biogas no. 3
D4	123 ± 1	257 ± 11	1950 ± 8	7851 ± 81
D5	22.3 ± 0.2	16.5 ± 0.5	21.0 ± 0.2	107 ± 1

such as temperature and moisture of the landfills. Although the use of correction factors has been suitable to compensate matrix effects, we suggest that the best option to quantify D4 and D5 in biogas and environmental samples using calibration curves in ambient air is to use an isotopically labeled internal standard.

CONCLUSIONS

We have developed and validated a sensitive, selective, and reliable method for the direct analysis of siloxanes D4 and D5 in gaseous matrixes. Unlike the classical GC/EI-MS, the direct APCI-MS/MS technique significantly minimizes the potential background contamination. Moreover, this method is free of interference effects from siloxanediols containing the same number of silicon atoms as the VMS. The analytical characteristics of the proposed method make it suitable for D4 and D5 monitoring of waste-to-energy biogases in determining either if a biogas purification system is needed or if the system in place is operating properly. The instrument can be installed on the spot and perform continuous in situ measurements, providing control room operators continuous information. This method is also applicable for the direct analysis of such VMS in air samples from outdoor and indoor environments and thus allows further work on potential environmental or human health risks.

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