



Research paper

Evaluation of sampling techniques for gas-phase siloxanes in biogas

Clara M.A. Eichler^a, Yaoxing Wu^{a,b}, Steven S. Cox^{a,*}, Stephanie Klaus^a, Gregory D. Boardman^a^a Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, VA 24061, USA^b Department of Environmental Engineering, Texas A & M University-Kingsville, Kingsville, TX 78363, USA

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ABSTRACT

Biogas from landfills and wastewater treatment facilities typically contain siloxane contaminants that can cause severe operational problems in engines and boilers when biogas is used as fuel. Likely due to their relatively low volatility, reliable siloxane sampling and analysis has proven challenging, and no standard sampling technique for gas-phase siloxanes exists, leading to high variability in analytical results. This study evaluates four techniques commonly used for sampling gas-phase siloxanes. Samples of a reference gas containing decamethylcyclopentasiloxane (D5) were taken using these techniques and measured D5 concentrations were compared to the reference gas D5 concentration. Methanol impingers and thermal desorption tubes proved to be most accurate and reliable, whereas Tedlar® bags and SUMMA canisters yielded lower D5 recovery rates due to adsorption to container surfaces. Based on these results, the methanol impinger and thermal desorption tube sampling methods appear to be more suitable for the quantitative analysis of gas-phase siloxanes in biogas.

1. Introduction

Biogas produced by anaerobic digestion of sludge from wastewater treatment plants (WWTPs) and of organic waste in landfills is frequently used for energy production because it contains large amounts of methane. Recently, organosilicon compounds, often referred to as volatile methyl siloxanes, have become of great concern because they can cause severe operational problems when combusted in energy production processes which use biogas as fuel. When oxidized in combustion engines or boilers, siloxanes form microcrystalline silicon dioxide, which deposits as a sand-like residue on engine parts and can result in catastrophic engine failure. Silicon dioxide can also deposit on boiler tubes, causing inhibition of heat transfer, thereby resulting in reduced process efficiency [1,2].

Siloxanes are typically added to consumer products such as cosmetics, soaps, shampoos, paints and sealants to improve lubricity. The use of siloxanes in these products has grown rapidly in recent years [3]. Siloxanes find their way into waste streams when personal care products are rinsed to drains and when containers containing product residue are disposed in landfills. During anaerobic digestion processes, siloxanes can then be volatilized into the biogas [2].

Although siloxanes are often referred to as volatile organic compounds (VOCs), they possess significantly different mass-transfer properties as compared with common VOCs due to their relatively high molecular weight and low vapor pressure. In particular, low volatility makes siloxane sampling and analysis more challenging. One example

is the very commonly found decamethylcyclopentasiloxane (D5, CAS 541-02-6) whose vapor pressure is cited to be in the range of 20 Pa to 53 Pa at 25 °C [1,2,4–11].

Because siloxanes have highly negative impacts on operational costs and the overall efficiency of biogas-to-energy projects, removal strategies are required. To facilitate development and evaluation of effective siloxane removal processes, sensitive and reliable methods for the identification and quantification of siloxanes need to be established. In a recent review on siloxanes in biogas, it was concluded that GC-MS is the most established method for the analytical determination of siloxanes in biogas, although other detectors such as FIDs are sometimes used successfully [12]. More problematic is the selection of a sampling method for gaseous siloxanes. Although the need for an approved method is great, no standard method has yet been agreed upon [12,13].

For many sampling techniques, advantages and disadvantages have been described. Ajhar et al. [13] examined the suitability of Tedlar® bags for siloxane sampling in landfill gas and concluded that the bags were a viable option, as long as they had non-adsorptive fittings such as polypropylene. However, they also reported that losses were highest for D5 using the bags, which is among the siloxanes most often found in biogas [13]. The advantages of using Tedlar® bags cited in this work were ease of handling and low risk of leakage [13]. In a comparison of Tedlar® bags, adsorbent tubes, and impingers, Raich-Montiu et al. [14] found no significant differences between the methods, although the standard deviations of recoveries for octamethylcyclotetrasiloxane (D4) and D5 with the Tedlar® bag were higher than for the two other

* Corresponding author. 1145 Perry Street, 418 Durham Hall, Virginia Tech, Blacksburg, VA 24061, USA.
E-mail address: stcox2@vt.edu (S.S. Cox).

methods. It was concluded that adsorbent tubes filled with an activated carbon charcoal matrix were most reliable [14]. However, because the adsorbent tube method required removal of the adsorbent, extraction, and replacement of the adsorbent prior to the next sampling event, it was considered to be rather impractical for monitoring of siloxane removal in WWTPs. Tansel and Surita [15] investigated the suitability of activated carbon as sorbent and found that the affinities of different siloxanes for the carbons varied strongly. Rasi et al. [2] sampled siloxanes with Tenax GR-filled sorbent tubes, but had difficulty comparing their results with studies in which other techniques were used. Schweigkofler and Niessner [16] used stainless steel canisters for the analysis of siloxanes in landfill and digester gases. After introducing a pure, 30-compound standard mixture for an equilibration time of 2 h, the recovery rates were above 90% for all common siloxanes except for D5 (85–90%) and dodecamethylpentasiloxane (L5) (35%). Longer storage times lowered the average recovery rates to 85% [16]. This confirmed that analyte loss due to surface adsorption increases with increasing boiling point and decreasing vapor pressure, and that the storage stability of high molecular weight gas-phase analytes must be taken into account when selecting an appropriate sampling method. Saeed et al. [17] reached a similar conclusion when comparing siloxane capture with impingers and canisters. Although the canister method is simpler and faster than impinger sampling, D4, D5, and D6 could not sufficiently be recovered from the canister and the impinger proved to be more reliable and sensitive [17].

A noticeable feature of available literature on siloxane sampling techniques is the lack of a siloxane-containing reference gas with which to compare measurements. Instead, past studies relate to an environmental sample with an unknown background matrix and use the highest concentration found as the “true” concentration [2,13,14,16], or to liquid standard mixtures which were introduced into bags or canisters without complete knowledge of the mass transfer processes involved [13,16,17].

For this study, D5 was chosen for the reference gas because it is among the most common siloxanes, generally present in high concentrations in biogas from WWTPs and at lower concentrations in landfill gas [2,13,16]. In addition, it is also one of the less volatile siloxanes with a vapor pressure of 20.4 Pa (25 °C) and more likely to adsorb to surfaces [13,14,16,17]. The sampling techniques tested were thermal desorption (TD) tubes, methanol impingers, SUMMA canister, and Tedlar® bags because they are commonly used in biogas sampling (Fig. 1) [14,16]. TD tubes and methanol impingers are direct sampling techniques in which analytes are removed from the gas stream during sampling, whereas for indirect sampling techniques, like SUMMA canisters and Tedlar® bags, gas samples are captured and stored in containers prior to analysis.

The TD method can be used for many air monitoring applications, with a wide variety of commercial sorbents, such as Tenax and graphitized carbon black. In the sampling process, a known volume of gas sample is drawn through the TD tube. The tube is then sealed and can theoretically be stored for up to several months at room temperature [18,19]. During the TD process, analytes are extracted from the sorbent and introduced to the analytical instrument in an inert gas stream.

An impinger is a solvent-filled container through which a known volume of analyte-containing gas stream is passed. Within the

impinger, analytes are absorbed by the solvent, and the solvent is then analyzed. The solvent is chosen based on the solubility characteristics of the analytes. Using the known solvent volume, gas flowrate, and sampling time, the gas-phase concentration can be calculated from the measured concentration of analyte in the solvent. The liquid sample can be stored in a sealed vial prior to analysis, depending on the properties of the target compounds.

Tedlar® bags and SUMMA canisters are mainly used for collecting, storing, and transporting a complete gas sample prior to analysis, whereas TD tubes and impingers capture and store the analyte. A critical requirement for the containers is that the loss of gas-phase analytes during storage and transportation, through leakage or surface sorption, is minimal. For analysis, a gas phase sample is transferred from the container to the analytical instrument. Due to surface adsorption, analyte concentrations in the air could be underestimated. Surface sorption tends to increase with decreasing volatility of the analyte. Storage conditions and duration could also impact analyte adsorption behavior, as well.

Accurate measurement of siloxane concentrations in biogas is critical to increasing renewable energy production and advancing sustainability in wastewater treatment processes because underestimating siloxane concentrations in biogas can lead to increased operating costs, equipment damage, and improper biogas treatment process operation. This study was conducted in order to identify the most effective biogas sampling methods by comparing gas-phase siloxane concentration estimates obtained using four commonly utilized biogas sampling techniques. This study is novel in that analytical siloxane concentration estimates were compared to a standard siloxane-containing gas stream in which the siloxane concentration was known through primary standards. The most commonly used, state-of-science sampling techniques were evaluated in this study.

2. Materials and methods

2.1. Chemicals

D5 (97% pure) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Its physicochemical properties can be found in Table 1. D4-bis(2-ethylhexyl) phthalate-3,4,5,6 (d4-DEHP, 98 atom% D), used as surrogate for the determination of the recovery rate, and d4-dibutyl phthalate-3,4,5,6 (d4-DiBP, 98 atom% D), used as internal standard (IS), were also obtained from Sigma-Aldrich. Reagent-grade methanol, used as solvent, and acetone, used for cleaning, were obtained from Fisher Scientific (Waltham, MA, USA). Nitrogen used as the gas-stream carrier was obtained from Airgas (Radnor, PA, USA).

2.2. Calibration gas generation

The calibration gas generator (CGG) used was a Dynacalibrator Model 190 (VICI Metronics Inc., Santa Clara, CA, USA). A glass diffusion vial filled with liquid D5 was placed in the Dynacalibrator at an oven temperature of 90 °C to ensure a steady mass emission rate of gaseous D5 into the nitrogen carrier gas stream (Fig. 2). The nitrogen carrier gas was controlled at a flowrate of 640 cm³/min. The D5 emission rate was measured gravimetrically by weighing the vial

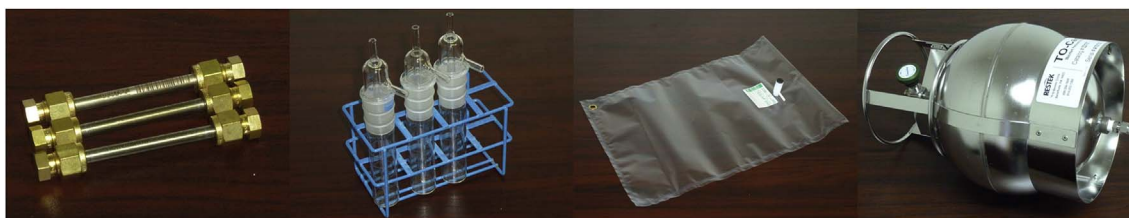


Fig. 1. The siloxane sampling techniques considered, from left to right: Thermal desorption (TD) tubes, methanol impingers, Tedlar® bag, SUMMA canister.

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