



Analytical methodology for sampling and analysing eight siloxanes and trimethylsilanol in biogas from different wastewater treatment plants in Europe



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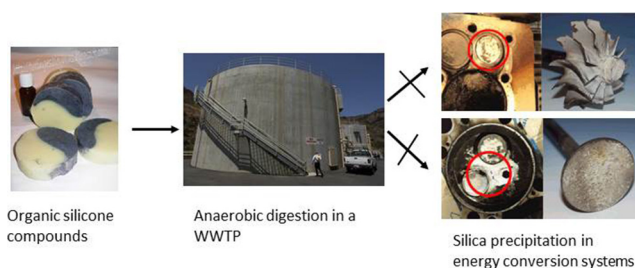
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HIGHLIGHTS

- Siloxanes cause adverse effects on biogas utilisation for energetic purposes.
- Sampling and quantification of siloxanes in biogas were assessed.
- Reliable and robust analytical methodology was developed.
- Biogas from different WWTPs of different European countries was analysed.
- Siloxanes were over the limit of tolerance for most of energy recovery technologies.

GRAPHICAL ABSTRACT



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ABSTRACT

Siloxanes and trimethylsilanol belong to a family of organic silicone compounds that are currently used extensively in industry. Those that are prone to volatilisation become minor compounds in biogas adversely affecting energetic applications. However, non-standard analytical methodologies are available to analyse biogas-based gaseous matrixes. To this end, different sampling techniques (adsorbent tubes, impingers and tedlar bags) were compared using two different configurations: sampling directly from the biogas source or from a 200 L tedlar bag filled with biogas and homogenised. No significant differences were apparent between the two sampling configurations. The adsorbent tubes performed better than the tedlar bags and impingers, particularly for quantifying low concentrations. A method for the speciation of silicon compounds in biogas was developed using gas chromatography coupled with mass spectrometry working in dual scan/single ion monitoring mode. The optimised conditions could separate and quantify eight siloxane compounds (L_2 , L_3 , L_4 , L_5 , D_3 , D_4 , D_5 and D_6) and trimethylsilanol within fourteen minutes. Biogas from five waste water treatment plants located in Spain, France and England was sampled and analysed using the developed methodology. The siloxane concentrations in the biogas samples were influenced by the anaerobic digestion temperature, as well as the nature and composition of the sewage inlet. Siloxanes D_4 and D_5 were the most abundant, ranging in concentration from 1.5 to 10.1 and 10.8 to 124.0 mg Nm^{-3} , respectively, and exceeding the tolerance limit of most energy conversion systems.

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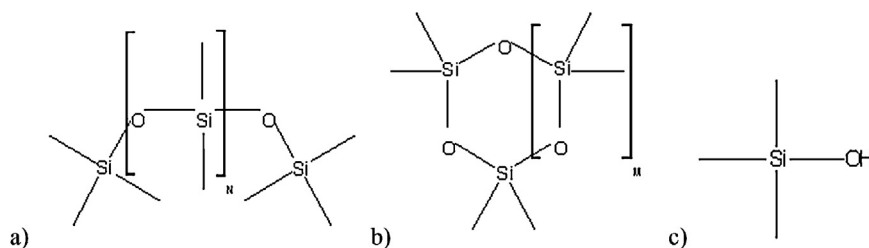


Fig. 1. General structure of siloxanes (a) linear compounds, (b) cyclic compounds and (c) trimethylsilanol.

1. Introduction

Due to the need to reduce greenhouse gas (GHG) emissions and the demand for renewable resources, using biogas is a relevant alternative for producing green energy [1]. Biogas is produced using farm biogas plants, mechanical biological treatment of municipal solid waste and, most commonly, waste water treatment plants (WWTPs) and landfills.

Biogas is composed of methane (CH_4) and carbon dioxide (CO_2), as well as other minor components, such as hydrogen sulphide, halogenated compounds and organosilicon compounds [2]. Although numerous technologies for biogas energy recovery, such as boilers, internal combustion engines (ICE), micro-turbines, fuel cells and Stirling engines have been developed, biogas contaminants hinder the efficiency and long-term performance of these systems. In particular, siloxanes adversely affect biogas usage [3], possibly damaging energy recovery technologies when silica is formed via combustion [4]. Siloxanes and trimethylsilanol (TMS) compose a family of compounds derived from the silicone derivatives widely used in cosmetics, oils, silicon production factories, electronics, paints, paper coatings and textiles. These compounds become volatile at relatively high operating temperatures ($35\text{--}55^\circ\text{C}$) during anaerobic digestion at waste water treatment plants and may be present in biogas as linear compounds, such as TMS, L_2 , L_3 , L_4 , L_5 , or cyclic compounds, such as D_3 , D_4 , D_5 and D_6 (see Fig. 1). Therefore, due to the high demand for biogas as a future energy source [5] and the extensive use of silicones, reliable analytical methodologies for analysing these compounds in biogas are critical. Currently, different analyses of the siloxanes in biogas [6–11], air [7,12–17], water [10,17–21], activated sludge [10,21–23] and soil samples [17,19,20,22,24] have already been published. Although gas chromatography–mass spectrometry (GC–MS) is most frequently used for these analyses [6,8–15,17–24], no standardised analytical methodologies have been reported in a gaseous matrix [25]. In addition, the most practical and reliable sampling technique has yet to be identified. Although several authors have already assessed using canisters [9], tedlar bags [6], sorbent tubes [8,23,24] or even on-line measurement techniques combining GC and Fourier transform infrared spectroscopy (FT-IR) [26] to analyse siloxanes, no studies have compared the different sampling techniques while analysing eight siloxanes and TMS.

This paper expands the analytical methodology used to quantify nine organic silicon compounds in biogas such as L_2 , L_3 , L_4 , L_5 , D_3 , D_4 , D_5 , D_6 and TMS generated at five different WWTPs in Europe, while avoiding any undesired interference [27]. A rapid chromatographic separation and a reliable sampling technique were pursued for the siloxanes. The sampling techniques were compared by sampling sewage biogas directly from the waste water treatment plant or indirectly from a 200-L tedlar bag filled with homogenised biogas.

In addition, this study was also devoted to gaining further knowledge regarding the presence of siloxanes in biogas from different WWTPs. These important data should strengthen decision making related to selecting energy conversion systems (ECS) and

designing biogas treatment technologies [28] used to prevent ECS breakdown. Five different WWTPs with different types of effluents, treatment processes and operational conditions were selected and studied in England, France and Spain. One site had already reported trouble with silica precipitation when biogas was used for energy production.

2. Materials and methods

2.1. Biogas samples

Biogas from five WWTPs located in Catalunya (NE of Spain), France and England was sampled in triplicate from the digester outlet streams or gas holder. The campaigns were performed during the spring and summer of 2011.

The different configurations of the sludge lines at the selected WWTPs are shown in Table 1. The role of five different parameters on siloxane concentration was studied: sludge type, sludge pre-treatment before digestion, operating temperature, retention time and sludge mixing. The type of sludge (primary, secondary or mixed sludge) strongly affects the biogas production and composition because the rate (kinetics) and extent (thermodynamics) biodegradability is different for each sludge type. Sludge is pre-treated (e.g. thermal hydrolysis) to break down organic matter before digestion to increase biogas production, converting large and non-volatile silicon compounds into lighter and more volatile compounds. The digestion temperature determines both the evaporation and stripping of silicon compounds. The retention time defines the extent of degradation for the organic matter in the reactor, linking this parameter to biogas production. Finally, the sludge mixing system (mechanical, sludge recirculation or biogas recirculation) prevents stratification, improving the anaerobic process and affecting the mechanism for siloxane transfer from the liquid to the gas phase.

2.2. Chemicals

TMS, L_2 , L_3 , L_4 , L_5 , D_3 , D_4 and D_5 were supplied by Sigma–Aldrich (Steinheim, Germany); D_6 was supplied by TCI Europe (Zwijndrecht, Belgium). All purchased compounds were more than 97% pure. Table 2 shows some of the physico-chemical properties of these compounds.

Decane- d_{22} (Sigma–Aldrich, Steinheim, Germany, 99%) and a deuterated siloxane $\text{L}_2\text{-d}_{18}$ (C/D/N Isotopes Inc., Quebec, Canada, 99.8%) were used as internal standards.

Trace substances typically found in biogas samples such as *n*-octane, *n*-decane, xylenes, ethylbenzene, cumene and α -pinene were supplied by Fluka (Steinheim, Germany), while trichloroethylene, tetrachloroethylene, and 1,2-dichlorobenzene were supplied by Merck (Darmstadt, Germany); toluene, and δ -limonene were supplied by Sigma–Aldrich and chlorobenzene was supplied by Panreac (Castellar del Vallès, Spain). All of these compounds had purities ranging from 98 to 99.5%.

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