Development of measurement techniques for siloxanes in landfill gas

M. Wzorek[1] M. Kaszubska[1]

[1] Opole University of Technology, Department of Process Engineering, Opole, Poland.
email: m.wzorek@po.opole.pl
email: mirka424@op.pl

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Abstract: In Poland, the biogas obtained from municipal solid waste landfills is most frequently used in biogas systems. In combustion of biogas contaminated with siloxanes, they transform and decompose to silica and silicate deposits, which affect the proper operation of power supply devices, i.e. electric generation systems or boilers.

The study aimed to determine the optimal methods for the collection of representative biogas sample for gas chromatography (GC) analysis. The main tasks included the selection of the most favourable sampling conditions for siloxane sorption in a given sorbent, i.e. sampling time, gas flow speed and sorbent volume.

The study regarded the landfill gas from the Municipal Landfill located in the city of Opole in Poland. Research showed the presence of organosilicon compounds in the tested biogas but their concentration was low. That's way the landfill gas can be successfully used for energy purposes without compromising the equipment caused by the presence of siloxanes.

INTRODUCTION

The economic and commercial development results in increasing need for power, and the sources of fossil fuels keep shrinking. Therefore, important aspects for the contemporary world and future generations are care for the natural environment, search for new and renewable sources of energy as well as observance of sustainable development rules in waste management.

Biogas may be the key to solve these problems. It is a product of fermentation process taking place in organic matter. Its content differs, depending on the type of reactants participating in the process. We can distinguish the following types of biogas generated from [1]:

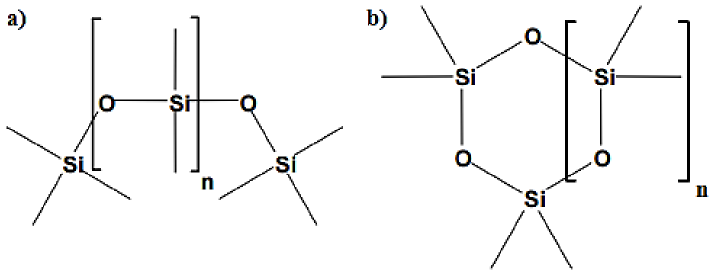
- landfill gas,
- wastewater treatment plants ,
- agricultural waste.

The landfill gas is a renewable fuel source formed from organic matter present in the waste mass collected on landfills. It is composed mostly of methane and carbon dioxide as well as various trace contaminants, e.g. organosilicon chemical compounds. These compounds, referred to as siloxanes, manifest multiple valuable properties, resulting in high willingness to use them in the industry.

Since the use of siloxanes is becoming more and more common, their concentration in the waste and, in consequence, in the biogas increases. In case of use of biogas for power generation purposes, their valuable properties become a threat for the devices using biogas as their fuel. They can cause, inter alia, increased inspection, failure and damage rate. Furthermore, siloxanes have a negative effect on the natural environment and living organisms [2,3]. Therefore, studies of siloxanes as well as continuous improvement of the methods of sampling, determination and removal of siloxanes are essential not only for the industry.

Siloxanes characteristics

The distinctive feature of siloxanes is their specific structure containing alternating atoms of oxygen and silicon. Functional groups can be bound to the silicon atoms. In terms of structure, siloxanes can be divided into chain and cyclic types. Figure 1 presents the linear and ring structure of these chemical compounds.



n=0 – hexamethyldisiloxane (L2)
n=1 – octamethyltrisiloxane (L3)
n=2 – decamethyltrisiloxane (L4)

n=1 – hexamethylcyclotrisiloxane (D3)
n=2 – octamethylcyclotetrasiloxane (D4)
n=3 – decamethylcyclopentasiloxane (D5)

Figure 1 Siloxanes structure: a) chain, b) cyclic

Organosilicon chemical compounds manifest hydrophobic properties, low water solubility and high non-polar solvent solubility. They are characterised with high vapour pressure, low viscosity, low surface tension and, furthermore, high oxidation resistance, high attenuation properties and resistance to UV radiation. They preserve their properties even in temperature increase conditions. They are high volatility substances, thus penetrating from the waste mass or sewerage to the biogas. Moreover, volatility of siloxanes significantly hinders their sampling and determination. Review of the parameters of the most common siloxanes is presented in Table 1.

Table 1 Characteristics of biogas of various origin [4,5]

Organic silicon compound	**Abbreviation**	**Vapour pressure at 25°C (mmHg)**	**Boiling temperature (°C)**	**Water solubility 25°C (mg/L)**
Hexamethyldisiloxane	L2	31.00	106.67	0.9300
Hexamethylcyclotrisiloxane	D3	10.00	135.00	1.5600
Octamethyltrisiloxane	L3	3.90	152.78	0.0350
Octamethylcyclotetrasiloxane	D4	1.30	175.56	0.0560
Decamethyltetrasiloxane	L4	0.55	193.89	0.0067
Dodecamethylpentasiloxane	L5	0.07	-	0.0003
Dodecamethylcyclohexasiloxane	D6	0.02	245.00	0.0050
Decamethylcyclopentasiloxane	D5	0.40	211.11	0.0170
Trimethylsilanol	TMS	-	98.89	3500

Due to their properties, their application is becoming increasingly common in such various industries as: cosmetic, chemical, pharmaceutical and medical (Table 2). Depending on the reactants in the methane fermentation process, the amount and type of siloxanes in the biogas can vary. The highest siloxanes count can be found in biogas from sludge from wastewater treatment plants - D4 and D5 compounds account for over 90% of their concentration [6,7].

Table 2 Use of siloxanes and silicones

Sector	Products
Medical	Implants, tracheostomy tubes
Chemical	Washing agents, paper, glue, paint, shoe polish
Cosmetic	Creams, shampoos, nail polish
Automobile	Greases, varnishes

Landfill biogas is less rich in siloxanes, and D4 and D5 compounds account for slightly over 50% of their total concentration [8]. It is estimated that the siloxanes content in biogas falls within the range of 3÷400 mg/m^3. In addition, the age of the landfill has an effect on their content in biogas - the older the landfill, the lower the siloxanes concentration [8]. On the other hand, the agricultural biogas is free from this type of contamination. The exemplary concentrations of siloxanes in biogas of various origin are presented in Table 3.

Table 3 Siloxanes concentrations in different locations [7,9,10,11]

Target	Location	Total siloxanes concentration (mg/m^3)
Bioreactor	Switzerland	25.1
Bioreactor	Germany	59.8
Bioreactor	Belgium	20.0
Bioreactor	Finland	29.6
Bioreactor	UK	400.0
Bioreactor	Poland	8.5
Landfill	Poland	5.5
Landfill	Germany	36.3
Landfill	Austria	9.3
Landfill	Finland	6.69

Technological aspects of disposal of biogas contaminated with siloxanes

Combustion of biogas that is contaminated with siloxanes causes their transformation into the so-called deposits. They form a deposit layer that adheres to the hot metal surfaces of devices, causing disturbances in operation, reduction of efficiency of energy recovery from biogas as well as extensive damage. The consequences involve servicing and operating issues, entailing excessive costs of power generation from biogas. Furthermore, removal of these deposits using chemical or mechanical methods is almost impossible [11]. In general, the silicon content from deposits found in facilities utilizing biogas from anaerobic digesters was lower than those operated with landfills gas. The difference was made up with higher phosphorus, sulfur and calcium content in the deposits from the engines operated with digester gas [12].

The deposits are composed mostly of silica and silicates in form of white solids with high hardness and sand-line structure (Figure 2).

Silica deposits are good heat insulators which results in temperature increase and heat exchange process inhibition in recuperators. Due to abrasive properties of silica, the rotor blades are frequently damaged due to their excessive abrasion, with crankshaft and bearings also being exposed to potential damage.

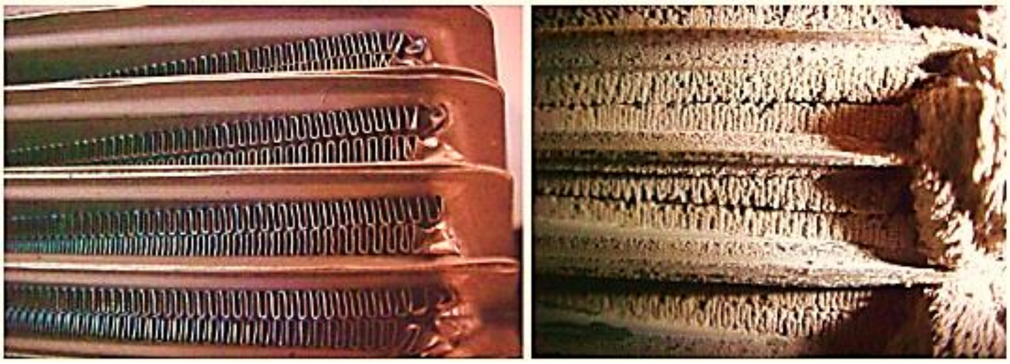


Figure 2 Silicate layers present in a microturbine [13]

In piston engines, the deposit layer covers both valves and cylinder walls. The combustion chamber can suffer from geometry distortion, causing an increase of carbon dioxide and formaldehyde emission. Hard deposits can cause scratches and cuts on the bush surface [5,7,14].

Use of piston engines requires proper lubrication between the bush surface and the piston ring. The deposits absorb the lubricant, thus preventing formation of the lubrication layer which can result in adhesion wear and tear. Silicon compounds can also accumulate under the outlet valves, which can cause valve burns and, thus, decrease of engine capacity [15].

Measurement methods

The interest in siloxanes has begun relatively recently, both in terms of their application and impact on industrial devices, natural environment and living organisms. There is no golden method to sample these compounds from the biogas stream or a perfect analytical method of their determination. The research in this area is still being conducted and the best solution is yet to be found.

Table 4 presents the most common methods used to collect siloxanes from the biogas stream.

Table 4 Sampling techniques of gaseous siloxane [8,12,16]

Method	Material	Advantages	Disadvantages
Adsorbent	Activated carbon Tenax XAD	Sample concentration possible, simple, acceptable D4 recovery	Time consuming, additional devices required
Impinger	Methanol n-hexane Acetone	Perform better than canisters for less volatile compounds (D4, D5, D6), 80% recovery for L2 and L3	Time consuming, additional devices and ice bath required
Canister	Metal canister	Simple, quick passive sampling, better D3 recovery performance than impingers	Sample concentration not possible, erratic readings for D4, D5, D6
Tedlar bags	Tedlar® bag	Low purchase/shipping cost, availability	Sample concentration not possible

These methods can be divided into direct and indirect methods. The former ones involve sorption processes with use of a solid sorbent - adsorption, or liquid sorbent - absorption. In terms of sample collections, the direct, for example canister method is simple and fast requiring only 16 seconds to passively fill a 6L canister. The indirect, for example impinge method requires experience with solution sampling and patience since sampling intervals can last up to three hours [15]. It is recommend to employ intermediate methods due to the possibility of sample enrichment. Moreover, the most common sorbents are organic solvents as they manifest higher affinity to silicon compounds than solid sorbents. An important element affecting the efficiency of intermediate methods employing liquid sorbents is their continuous optimization, i.e. providing for the gas flow, sampling time and volume of the applied sorption solvent [11,16].

The analytical methods employed to determine trace contamination present in the biogas involve atomic absorption spectrometry and gas chromatography combined with various types of detectors, e.g.:

- mass spectrometry - MS,
- flame ionization detection - FID,
- photoionization detection - PID.
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MATERIALS AND METHODS

Biogas sampling locations

The study regarded the landfill gas from the Municipal Landfill located in the city of Opole, Poland. It was obtained from a landfill with area of 6.4 ha. Biogas is used to generate electricity about 2,200 MWh/year. Averaged parameters of the examined biogas are presented in Table 5.

Table 5 Averaged composition of the tested environmental biogas

Ingredient	Unit	Value
CH_4	vol. %	47.8
CO_2	vol. %	24.0
O_2	vol. %	1.9
H_2S	ppm	79.0

Samples collection

The adsorption method was used for the purpose of collection of environmental samples. XAD2 polymer resin was used as the solid sorbent, filling the glass tubes. Furthermore, the sampling installation consists also of a biogas pump, gas meter and cooler. The sampling parameters are presented in Table 6.

Table 6 Sample collection specification

Specifications	Adsorbent Method
Utilities	Glass tube, size 155x5 mm XAD2 polymer resin
Impinger solution	24 – 100L
Sampling Volume	35 – 90L/h
Sampling rate	20 – 60min
Sampling time	Closed tubes, room temp.

Analytical detection of siloxanes

The analytical evaluation of the samples was performed using the gas chromatograph System 7890B Agilent Technoligies combined with a flame ionizing detector. Instrument and standard specification was presented in Table 7.

Table 7 Instrument and standard specification [13]

GC/FID method		Unit	D4, D5, L2, L3	D3
Dispenser	Dispenser temperature	°C	110	240
	Splitless	Yes/No	Yes	Yes
Column	Flow	mL/min	4	4
	Initiation temperature	°C	40/ min	45/maintains 5 min
Furnace	Temperature change	°C/min	15	25
	Final temperature	°C	240	250
	Max. furnace temp.	°C	325	325
Autosampler	Injection volume	µl	1	1
	Detector temperature	°C	300	300
Detector	Air flow	mL/min	400	400
	Hydrogen flow	mL/min	30	30
	Carrier gas flow	mL/min	15	30

RESULTS AND DISCUSSION

According to Wheless and Pierce [17], the landfill gas contains mostly D5 and D4 compounds. Furthermore, it can contain small amounts of D3, D6 and L2 - L5 compounds [18]. The conducted analyses showed that cyclic siloxanes, i.e. D4 and D3, and then L3 and D5, have the highest share in the content of the landfill biogas. Additionally, summed up concentrations of these compounds are significantly lower than values specified by other authors (table 3). This fact can result from the old age of the landfill. Table 8 contains concentrations of siloxanes in the tested landfill gas.

Table 8 Obtained concentrations of siloxanes in the investigated landfill gas

	Sampling time	**Flow**	**L3**	**D4**	**D5**	**D3**	**Total**
	h	L/h	mg/m^3	mg/m^3	mg/m^3	mg/m^3	mg/m^3
XAD I	0.1	42	0.2520	0.1606	0.3608	0.6327	1.0814
XAD II	0.2	42	0.2766	0.2772	0.0618	0.4391	1.0548
XAD III	0.3	42	0.2491	0.3096	0.0510	0.3126	0.9223
XAD IV	0.4	42	0.1406	0.3063	0.0413	0.2241	0.7122
XAD V	0.5	42	0.3482	1.0704	0.1067	0.0200	1.5453
XAD VI	0.6	42	0.2225	0.9541	0.0683	0.2888	1.5337
XAD VIII	0.3	135	0.0009	0.0096	0.0043	ND	0.0154
XAD IX	0.4	135	0.0091	0.0211	0.0080	ND	0.0347
XAD X	0.6	135	0.0010	0.0115	0.0050	ND	0.0106

*ND - not detected

Analysing the obtained results, one might note that increase of the biogas flow from 42 L/h to 135 L/h causes substantial decreased of total siloxane concentration. Similarly, as a result of a high flow, the sorbent could fail to capture the silicon compounds or it could be saturated with these substances. During the determined flow, with increased sampling time, there is a drop in the total concentration of siloxanes. This dependence occurs if the sampling time is extended from 0.1h to 0.4h. Whereas above this value, the total count of siloxanes increases and reaches is peak count at the sampling time of 0.5h (figure 3).

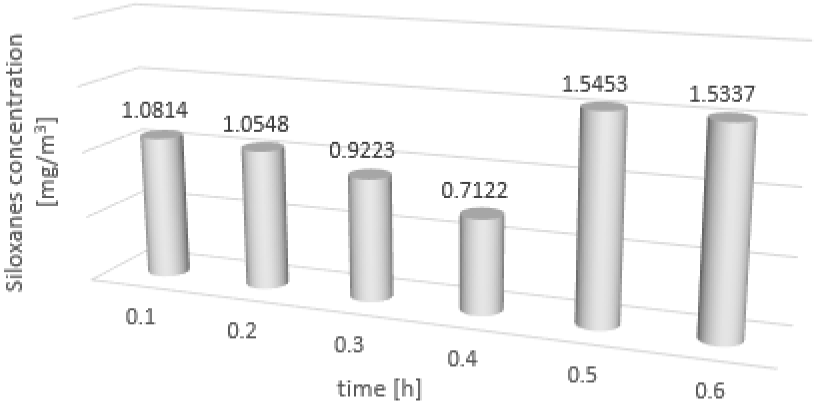

Figure 3 Change of the siloxanes concentration depending on the sampling time

CONCLUSIONS

The landfill gas obtained at the Municipal Landfill in Opole in Poland, is contaminated with a low amount of siloxanes. The adsorptive siloxane sampling method and gas chromatographic analysis coupled with the flame ionization detection allowed to determine the following silicon compounds in the examined landfill biogas: D4, D3, L3 and D5. A series of sampling activities was performed varying in terms of their sampling time and biogas flow through the sorbent. The analysis of results allowed to distinct the most advantageous sampling conditions, i.e. low biogas flow of ca. 40 L/h with sampling time of 0.5h. The total siloxane counts in the examined biogas are so low that their effect on the power devices of the bio-power plant located in the landfill area is negligible, whereas attempts of biogas treatment would be too expensive in relation to the damage caused by them.

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