Rapport SGC 243

Impurities in biogas: Validation of methodology of analysis for siloxanes

Karine Arrhenius, SP
Bertil Magnusson, SP
Eskil Sahlin, SP

November 2011

Rapport SGC 243 • 1102-7371 • ISRN SGC-R-243-SE

SGC
Svenskt
Gastekniskt
Center AB

SGC:s FÖRORD

FUD-projekt inom Svenskt Gastekniskt Center AB avrapporteras normalt i rapporter som är fritt tillgängliga för envar intresserad.

SGC svarar för utgivningen av rapporterna medan uppdragstagarna för respektive projekt eller rapportförfattarna svarar för rapporternas innehåll. Den som utnyttjar eventuella beskrivningar, resultat eller dylikt i rapporterna gör detta helt på eget ansvar. Delar av rapport får återges med angivande av källan.

En förteckning över hittills utgivna SGC-rapporter finns på SGC:s hemsida www.sgc.se.

Svenskt Gastekniskt Center AB (SGC) är ett samarbetsorgan för företag verksamma inom energigasområdet. Dess främsta uppgift är att samordna och effektivisera intressenternas insatser inom områdena forskning, utveckling och demonstration (FUD).

SGC stakeholders:
Energigas Sverige, E.ON Gas Sverige AB, E.ON Sverige AB, Göteborg Energi AB, Lunds Energikoncernen AB (publ) och Öresundskraft AB.

The following partners made this project possible:

Borås Energi och Miljö AB
Energimyndigheten
EU - Europeiska Unionen
Gryaab AB
MittSverige Vatten AB
NSR AB
Ragn-Sells Heljestorp AB
SP Sveriges Tekniska Forskningsinstitut
Surahammars KommunalTeknik AB
Svensk Biogas
Umeå Vatten och Avfall AB

SVENSKT GASTEKNISKT CENTER AB

Jörgen Held

AUTHORS’ ACKNOWLEDGEMENT

The authors want to thank everyone that have contributed to the project:

Irene Bohn, NSR AB

Ola Fredriksson, Gryaab

Håkan Kimming, Ragn-Sells Heljestorp AB

Rakel Martinsson, Borås Energi och Miljö AB

Sören Nilsson Påledal, Tekniska Verken i Linköping AB

Malin Tuvesson, Anna-Carin Hagström, MittSverige Vatten AB

Johanna Westlund, UMEVA (Umeå Vatten och Avfall AB)

Åsa Wievegg, Surahammars Kommunalteknik AB

SAMMANFATTNING

Biogas producerad genom rötning och från deponi innehåller föroreningar som kan vara skadliga för komponenter som kommer i kontakt med biogas under dess användning. Några av de mest omtalade föroreningar i biogas är siloxaner. Under förbränning konverteras siloxaner till kiseldioxid som ansamlas på varma ytor i förbränningsutrustning vilket medför skaderisker för motorkomponenter. Därför är det viktigt att kunna bestämma halten av siloxaner i biogas.

I den första delen av rapporten redovisas valideringen av en analysmetod för siloxaner i biogas och rengas. Provtagningen utfördes direkt på plats i anläggningar genom att låta en liten volym biogas under en kort tid passera ett adsorbentrör. Dessa rör skickades sedan till laboratoriet för analys. Metodens spridning och riktighet kontrollerades mot rimliga krav som ställdes och mätosäkerheten beräknades.

I den andra delen av rapporten redovisas hur metoden tillämpades i olika anläggningar (reningsverk, avfallsanläggningar, rötning av jordbruksrester) och resultat från bestämning av siloxaner i rågas och rengas presenteras. Som förväntat innehöll rågaser från reningsverk betydligt mer siloxaner än rågaser från avfallsanläggningar, från rötning av jordbrukrester och från deponi. Siloxanhalterna som återfanns i rengaser oavsett vilket substrat som rötades och vilken uppgraderinsgteknik som användes var låg.

SUMMARY

Biogas produced from digester or landfill contains impurities which can be harmful for component that will be in contact with the biogas during its utilization. Among these, the siloxanes are often mentioned. During combustion, siloxanes are converted to silicon dioxide which accumulates on the heated surfaces in combustion equipment. Silicon dioxide is a solid compound and will remain in the engine and cause damages. Consequently, it is necessary to develop methods for the accurate determination of these compounds in biogases.

In the first part of this report, a method for analysis of siloxanes in biogases was validated. The sampling was performed directly at the plant by drawing a small volume of biogas onto an adsorbent tube under a short period of time. These tubes were subsequently sent to the laboratory for analysis. The purpose of method validation is to demonstrate that the established method is *fit for the purpose*. This means that the method, as used by the laboratory generating the data, will provide data that meets a set of criteria concerning precision and accuracy. At the end, the uncertainty of the method was calculated.

In the second part of this report, the validated method was applied to real samples collected in waste water treatment plants, co-digestion plants and plants digesting other wastes (agriculture waste). Results are presented at the end of this report. As expected, the biogases from waste water treatment plants contained largely higher concentrations of siloxanes than biogases from co-digestion plants and plants digesting agriculture wastes. The concentration of siloxanes in upgraded biogas regardless of which feedstock was digested and which upgrading technique was used was low.

TABLE OF CONTENT

1 INTRODUCTION

1.1 Background

The production and use of biogas as an energy source increases. Sweden produced the year of 2009 approximately 1.4 TWh of biogas from about 230 digestion plants [1]. The goal for 2012 is 3 TWh. The main use of biogas today is the production of heat. In 2009, 49% of the produced biogas was used for heating, 5% for electricity, 36% was upgraded to automotive fuel (CNG) and 10% reported to have been flared. Most notable is the increasing proportion of biogas upgraded to automotive fuel. In 2008 26% of the biogas was upgraded to automotive fuel[1]. A prerequisite for continued growth is to limit the problems that can occur with the use of biogas as an automotive fuel. The problems were caused by unwanted substances in the gas such as corrosive acids, hydrogen sulfide, halogenated substances and volatile silicon compounds.

If the combustion gases contain silicon impurities microsilica may be formed. This crystalline silica have similar physical and chemical properties as glass and can not be easily removed. Its hardness causes abrasion of engine surfaces. As a thermal insulator, it contributes to subjecting sensitive engine parts to high temperature. As an electrical insulator, it inhibits spark plug function. This can lead to serious damage and the formation of deposits on the spark plugs, pistons, cylinder heads, exhaust after treatment systems, among others. It is mainly siloxanes that can form silica. Therefore, it is important to check siloxane content in biogas.

A siloxane is a chemical compound containing silicon, oxygen and methyl groups (CH3). Siloxanes do not occur naturally: there are no known biological processes that lead to a bond between a silicon atom and a methyl group. They are man-made substances manufactured because of their manifold positive properties. Among other things, they exhibit high compressibility, low water solubility, low flammability, low surface tension, water resistance, high thermal stability, low toxicity and they are not allergenic. Some are biodegradable [2]. They are used in many different applications such as the manufacture of hygienic and cosmetic products (deodorant, shampoo, conditioner, hair spray, shaving gel), products for removing paint from brushes, food additives, implants in the cosmetic surgery, coating of needles, pacemakers, manufacture of feeding bottle teats, as additives in paints, oils, and in dry cleaning applications. The annual production of siloxanes is estimated to be one million tons [2] and rising. Siloxanes are thus important performance chemicals whose areas of use make them end up in the biogas plants.

They can be adsorbed on certain solid materials such as sewage sludge. During the anaerobic digestion of substrates they volatilize and they end up in the raw gas. Another source of siloxanes in the raw gas are additives used in the digester to prevent foaming. Antifoam agents may contain silicones. Some are broken down to siloxanes.

Several studies have estimated the proportion of siloxanes from consumables that can be found in the biogas substrates after treatment in sewage treatment plants. It is estimated that approximately 3 to 10% of the siloxanes ends up in the substrates for biogas production, the rest is emitted into the atmosphere. When they are emitted into the atmosphere several reactions starts, leading to almost complete degradation.

1.2 Analysis methodology of siloxanes

There are currently no national or international standardized method for the determination of siloxanes in biogas. For the measurement itself is gas chromatography (GC) appropriate, a separation method coupled to a suitable detector such as a flame ionisation detector (FID), an atomic emission detector (AED) or a mass spectrometer (MS). The critical part of the analysis method is the sampling. For sampling, the following methods have been proposed:

- Adsorption on active carbon, ion exchange membranes (XAD-2, XAD-4)
- Adsorption on a polymer based adsorbent (Tenax, ORBO®706, ORBO®43, ORBO®402)
- Adsorption on a carbon based adsorbent (ANASORB®747, ORBO®32, ORBO®101) [3] Absorption through bubbling in gas washing bottles containing solvents such as methanol, hexane, diesel
- Sampling in gas bags
- Sampling in canisters [4]

Gas-tight bags are not suitable for all siloxanes (especially for the heaviest that can adsorb irreversibly on the inner wall of the bags). Furthermore, a relatively large number of organic substances affecting the blank measurement are emitted from the walls. Use of a canister [5,6] is considered costly and impractical. The method of gas washing bottles filled with methanol gives good yields but is time consuming and quite impractical [5,6]. Approximately 20 liters must be sampled to achieve an acceptable detection limit. The recommended flow rate for sampling is about 110 ml / min [7] which means that the sampling time is 180 minutes.

However, methods based on adsorbent have often been regarded as simple and quick. Adsorption of siloxanes on Tenax or ANASORB®747 have been compared with the methanol gas washing bottle method [3]. The results were promising, though they could be slightly different from each other.

In a study of Narros [8] the sampling on Tenax tubes was compared with the sampling in a gas bag and in gas washing bottles. Results on samples obtained from biogas production show that these three methods give similar results but light siloxanes such as hexamethyldisiloxane (L2) and hexamethylcyclotrisiloxane (D3) are somewaht discriminated in the gas washing bottle method. The conclusion of this study was to recommend Tenax tube sampling on site.

In this project we have chosen to use Tenax-filled tubes for sampling on site followed by GC/MS analysis. Advantages of the method are that it is simple, requires low sample volumes and allows for simultaneously detection and possibly quantification of some other volatile organic compounds (VOCs) present in the biogas.

1.3 Project goal

The goal of the project was to validate the Tenax/GC/MS method to determine the content of siloxanes in biogas and using the validated method on real samples submitted from participating plants.

1.3.1 Validation

The principle of the validation performed in this project basically follows the guidance documents that have been developed by international organizations [9]. Method validation aims to show that the method is suitable for the measurements in question. Validation [10] entails stipulating a set of different requirements that the method must satisfy, and then verify that the method meets these requirements.

For the analytical method for determining the content of siloxanes in biogas, we have chosen to set the following requirements: - The method should show a low spread between the results - The method should quantitatively capture siloxanes, ie show a good yield. Tentative minimum 90% - The method should be selective or separative: detect only siloxanes alt. be able to separate and selectively identify siloxanes from other components present in the gas - The method should be sensitive, with the desired quantification at 20-50 ppb by volume for individual siloxanes and a measuring range that covers also large concentrations up to 20 mg/m3. Therefore, it is necessary to minimize contamination.

Furthermore, it is desirable that the method is simple and not time consuming. Sampling should not take more than a few minutes since it is easier to achieve stable conditions in the facilities with respect to gas flow only for short periods.

1.3.2 Measurement

The validated analytical method was then used to analyze samples obtained from biogas production and purified gas. The biogas is produced through digestion of various substrates and the siloxane content in biogas is directly dependent on the substrates. In this study, the biogas samples from sewage treatment plants, waste facilities, and from the anaerobic digestion of agricultural residues have been analyzed. A total of eight plants contributed samples. Sampling was mostly handled directly by the plants as per instructions.

1.4 Siloxane properties

Siloxanes that are relevant in a biogas context can either be linear (Fig. 1.1) or cyclic (Fig. 1.2).

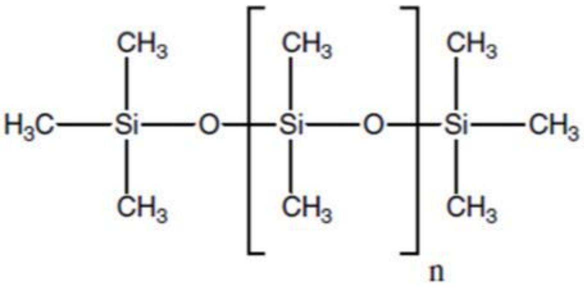


Figure 1.1. Structure of linear siloxanes

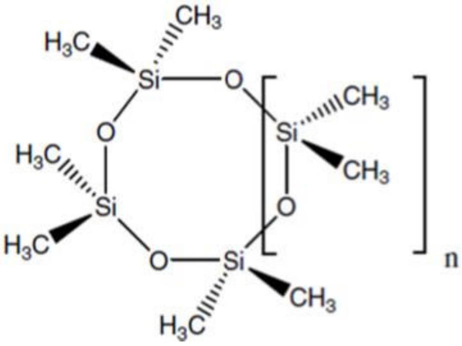


Figure 1.2. Structure of cyclic siloxanes

I detta projekt har vi studerat nio siloxaner eftersom de är de vanligast förekommande i biogas. Andra siloxaner eller kiselföroreningar har hittats i biogas från reningsverk [11] är butoxytrimetylsiloxan, methoxytrimetylsilan, 1,1,3,3,-tatremetyldisiloxan, pentametyldisiloxan, tetrametylsilan, trimetylfluorosilan och trimetylpropoxysilan. Dock enbart en gång var på de 50 anläggningar som testades och deras halter var i varje fall försumbara i förhållande med de siloxanerna som har valts i den här studien. Dessa kiselföreningar redovisas i tabell 1.1 tillsammans med sina egenskaper.

Tabell 1.1: Siloxane properties, name, designation, chemical formula and structure

	Designation	Formula	Chemical structure	Boiling point T (°C)	MW (g/mol)	Vapor pressure (Pa) [12]	Water-sol. mg/l [12]	Density g/ml
Hexametyldisiloxan	L2	$C_6H_{18}OSi_2$		100	162,4	4133	0,93	0,764
Octametyltrisiloxan	L3	$C_8H_{24}O_2Si_3$		153	236,5	520	0,035	0,82
Dekametyltetrasiloxan	L4	$C_{10}H_{30}O_3Si_4$		194	310,7	73	*	0,854
Dodekametylpentasiloxan	L5	$C_{12}H_{36}O_4Si_5$		230	384,8	9,3	*	0,875
Tetradekametylhexasiloxan	L6	$C_{14}H_{42}O_5Si_6$		245	459,0	*	*	*
Hexametylcyklotrisiloxan	D3	$C_6H_{18}O_3Si_3$		134	222,5	1333	1,56	1,02
Oktametylcyklotetrasiloxan	D4	$C_8H_{24}O_4Si_4$		175	296,6	173	0,056	0,956
Dekametylcyklopentasiloxan	D5	$C_{10}H_{30}O_5Si_5$		210	370,8	53	0,017	0,958
Dodekametylcyklohexasiloxan	D6	$C_{12}H_{36}O_6Si_6$		245	444,9	2,7	0,005	0,959

* *Data missing*

2 Sampling and analytical methods

2.1 Bag/ICP-MS

In nature most elements exist as a mixture of several so-called stable isotopes. Isotopes are atoms of different mass of one and the same element. By ICP-MS (inductively coupled plasma - mass spectrometry) the different isotopes of the elements are always measured separately. A content can be calculated in principle from each of the various elemental isotopes. Determinations of the total silicon (Si) was made with Element2 from ThermoFinnigan which is a double focusing magnetic sector field instrument. Silicon (Si) is determined with mass resolution 4000 (medium resolution) to avoid interferences between 28Si (m = 27.97693 u) and the species 12C16O (m = 27.99491 u) or 14N14N (m = 28.00614 u) that can be formed from methane (CH4) and nitrogen (N2) as shown in Figure 2.1.

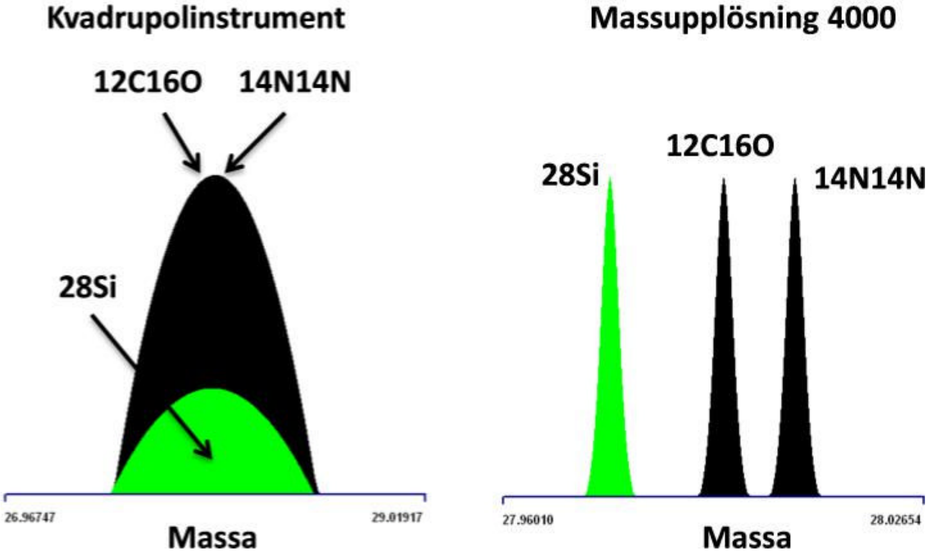


Figure 2.1. Schematic representation of the signals from the species 28Si (m = 27.97693 u), 12C16O (m = 27.99491 u) and 14N14N (m = 28.00614 u) at the mass resolution of a typical quadrupole instrument and with a double focusing magnetic sector field instrument with mass resolution 4,000.

Injection from a gas bag

To the spray chamber on the ICP-MS instrument was coupled a proprietary injection chamber through a 2 m long tube as shown schematically in Figure 2.2. In this manner, air will be continuously drawn into the plasma.

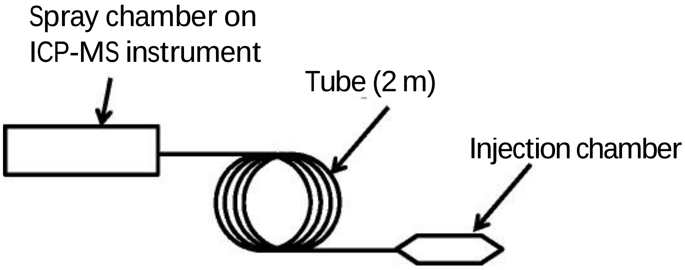
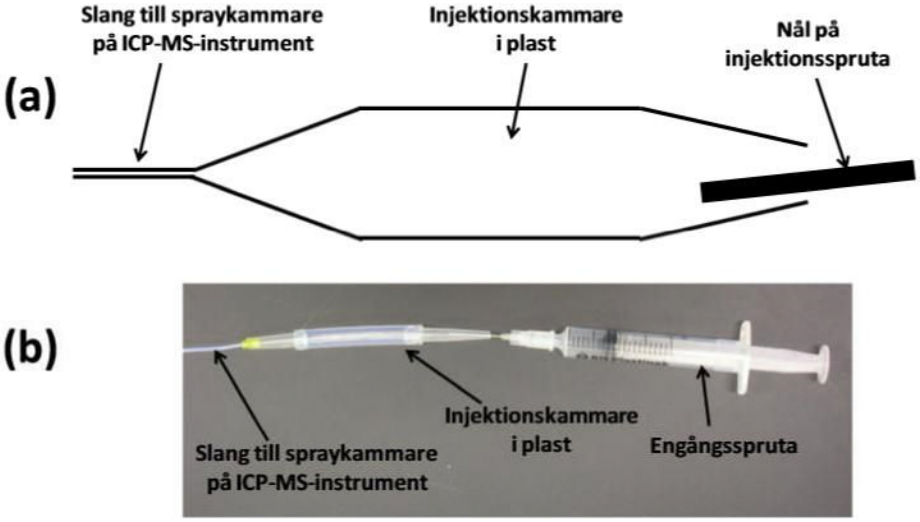


Figure 2.2. Schematic of ICP-MS instrumentation when the injection is done from the gas bag.

The injection of gas samples was done by withdrawing 2.0 ml gas with a disposable syringe with needle directly from the gas bag and then inject the gas directly into the injection chamber. Figure 2.3 (a) shows a schematic of the injection chamber and Figure 2.3 (b) shows a photo of the injection chamber with disposable syringe. With the help of the suction from the spray chamber in the ICP/MS instrument the sample is transported into the spray chamber.



Figur 2.3. (a) Schematic and (b)photo of the injection chamber(injektionskammare i plast) and the disposable syringe (engångsspruta).

With ICP-MS, the content of silicon (Si) and not siloxane is determined.

The mass part of Si in the different siloxanes are in the range of 0.346 to 0.379, ie the proportion of Si in siloxane is not much different (<10%) for different siloxanes. This means that a Si content can be converted to an approximate total content siloxane by multiplying Si content with 1/0.36 = 2.8 with the assumption that all volatile silicon comes from siloxanes. This means that:

a) One siloxane compound may be used for calibration of the instrument, making calibration of the instrument and its evaluation relatively simple and quick
b) The different siloxanes present in the biogas do not have to be identified
c) The lack of standard references for some siloxanes is no longer a problem

2.2 Tenax/GC/MS method

In this project we have chosen to use the adsorbent tube filled with Tenax to catch siloxanes in biogas. Tenax is the most common adsorbent to quantitatively capture the volatile organic compounds and is suitable for substances with boiling points between 70 ° C and 320 ° C. Losses during transport to the lab analysis are negligible.

Analysis of the Tenax tubes is implemented through so-called thermal desorption (TD), where the adsorbed substances released by first heating and then transferred to a cold trap for focusing. The cold trap is rapidly heated again and the compounds are released and routed to a gas chromatography ¬ column for separation. The column effluent then reaches a mass spectrometric detector.

The Tenax-filled tubes used for sampling of biogas for analysis of siloxanes must be treated before sampling. The treatment is intended to clean the pipes, to ensure that there is not remaining significant levels of adsorbed substances on Tenax. The purification is done by heating the Tenax tubes containing at 300 ° C for 5 minutes. This treatment / purification is called conditioning. All pipes must be conditioned before use.

Then those pipes were sent, together with a flow meter and a reduction valve to regulate the flow, to staff in the participating plants who took samples as instructed. Staff was asked to document the flow which had passed the pipe and the length of time the sampling took place. In this way one can calculate the volume of gas sampled. Staff would also note if the flow was stable during the sampling. At the same time a bag was filled with gas.

2.3 Bag/Tenax/GC/MS method

Sampling in Tedlar bags is recommended by the manufacturer for substances with boiling points up to about 130 °C, while Tenax tubes are recommended for substances with boiling points between 70 to 350 °C. Consequently, substances with boiling points between approximately 70 to 130 °C, preferably be sampled in bags or on adsorbent tubes. Two of the siloxanes studied in this project have boiling points in the this range: L2 with a boiling point of 100 °C and D3 with a boiling point of 134 °C. L3 has a boiling point of about 150 °C. Under these conditions, the bags can be used to determine some performance parameters included in the validation process. In these bags gas standards can be produced containing known concentrations of L2, D3 and L3 with a metrological traceability.

3 Results

3.1 Validation of Tenax/GC/MS analytical method

3.1.1 Deviation

Deviation - repeatibility

The repeatability[1] is the distribution that is observed when a sample is analyzed multiple times on the same day by the same person in a laboratory and with the same instrument. [10].

The repeatability was determined by multiple testing of the same sample sent in by the participating plants. Two to five tests per sample was performed. Results are shown in Table 3.1.

Tabell 3.1: Standard deviations (s) och coefficients of variation (CV%) for siloxanes

Siloxane	Low level (< 20 µg/m^3)	High level (> 20µg/m^3)
	s µg/m3	CV%
L2	0.4	3.7
D3	3.2	9.9
L3	0.3	6.4
D4	1.5	3.3
L4	0.7	5.5
D5	0.6	4.6
L5	2.8	10.8
D6	0.6	4.7

Deviation – intermediate precision

The intermediate precision [14] is the distribution that is observed when the method is used on a routine basis at the same laboratory. This means that factors such as operator, reagents, instrumentation, calibration, and time may vary.

To estimate the intermediate precision a control sample is prepared by injecting known concentrations of siloxanes in a gas bag. Content is 5 mg/m3 for each siloxane. This preparation is done every test week for four weeks (n = 4). Results are presented in Table 3.2:

---

[1] **Repeatability** or **test–retest reliability** is the variation in measurements taken by a single person or instrument on the same item and under the same conditions. A less-than-perfect test–retest reliability causes **test–retest variability**. Such variability can be caused by, for example, intra-individual variability and intra-observer variability. A measurement may be said to be *repeatable* when this variation is smaller than some agreed limit. (http://en.wikipedia.org/wiki/Repeatability)

Tabell 3.2: Standard deviations and coefficients of variation for siloxanes

Siloxane	s µg/m^3	s/rot(n)	CV%	CV%/rot(n)
L2	140.2	70.1	2.8	1.4
D3	176.5	88.2	3.5	1.8
L3	173.5	86.7	3.5	1.7
D4	261.9	130.9	5.2	2.6
L4	270.7	135.4	5.4	2.7
D5	222.1	111.0	4.4	2.2
L5	183.5	91.7	3.7	1.8

3.1.2 Bias

Standard addition

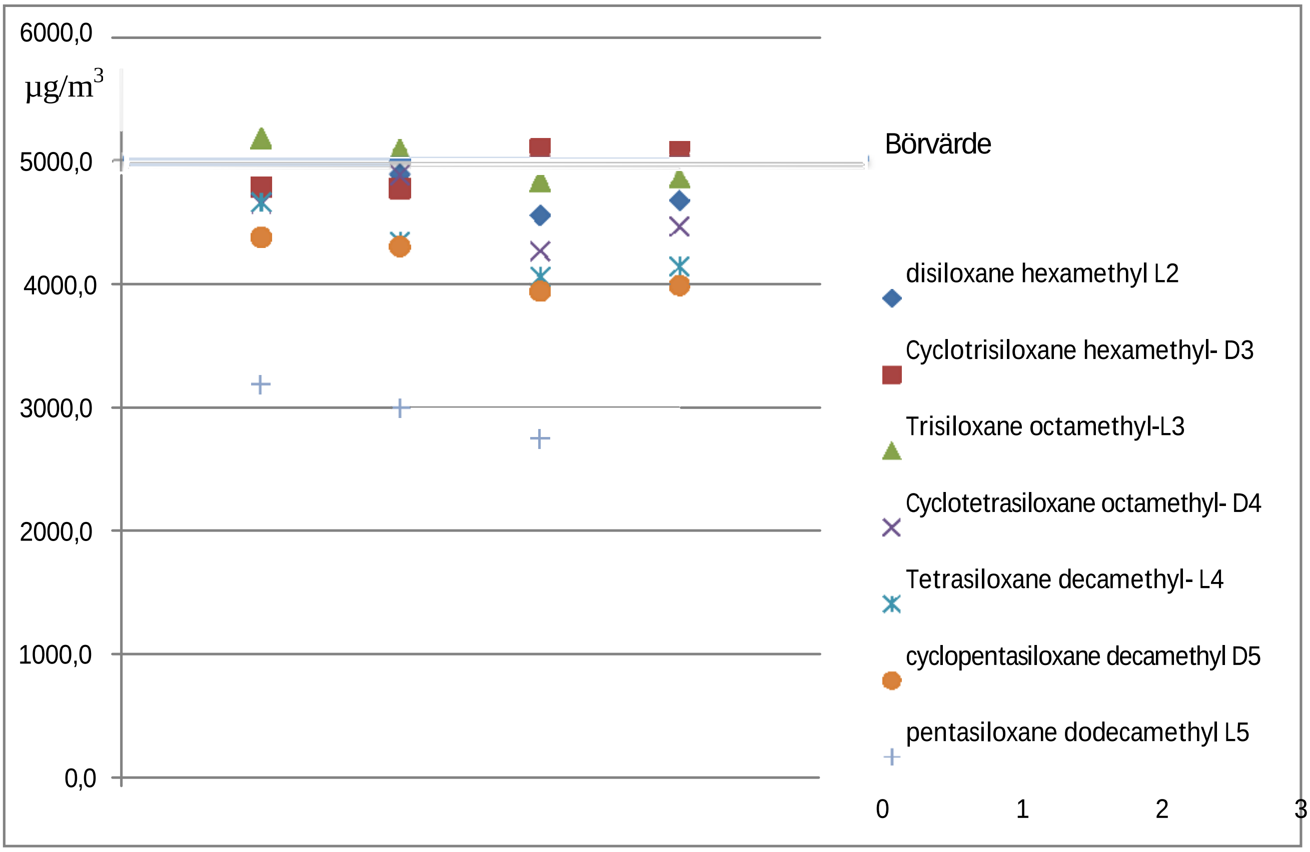
The accuracy of an analytical method describes the closeness to the "true value" an analysis result is. There are several ways to estimate the accuracy, ie the size of the bias [10]. One can use certified reference materials, but if they are not available as is the case for this type of sample, one can use so-called standard addition. By adding known amounts of siloxanes in a sample biogas you can investigate possible losses that may occur in different steps of the method. Bias may be expressed as percentage yield on addition experiments.

To estimate the bias, the following tests have been performed:

Known concentrations of siloxanes have been injected into a gas bag containing 60% methane, 39% carbon and 1% of nitrogen. A known volume of gas with additives intended siloxanes have been transferred to a Tenaxrör that have been analyzed. This bias control the whole method, both sampling with Tenax and measurement by GC / MS. The siloxanes used for bias control has another metrological traceability than those used for the calibration of the GC / MS: n Results are presented in Table 3.3 and Figure 3.1.

Tabell 3.3: Bias for L2, D3, L3 at 5 mg/m^3

Siloxane	Result	Reference value	Bias	
	x_{Lab} mg/m^3	x_{Ref}mg/m^3	mg/m^3	%
L2	4.72	5	- 0.28	-5.6
D3	4.99	5	-0.01	- 0.2
L3	4.93	5	-0.07	-1.4



Figur 3.1. Control of accuracy at 5 mg/m3 repeated 4 times

It is clear from Table 3.1 that the yield is better than 94% for compounds with boiling points of 150 ° C or lower (L2, D3, L3). The requirement of more than 90% yield is thus satisfied for these three siloxanes. From these results it can be concluded that if the yield could be determined for the other siloxanes with higher boiling points, it would also meet the requirement because Tenax tubes is equally suitable for substances with higher boiling points up to 350 °C.

As expected (Figure 3.1) the yield for siloxanes D4, L4, D5 and L5 are significantly lower which very likely can be attributed to adsorption effects on the bag walls.

Selectivity

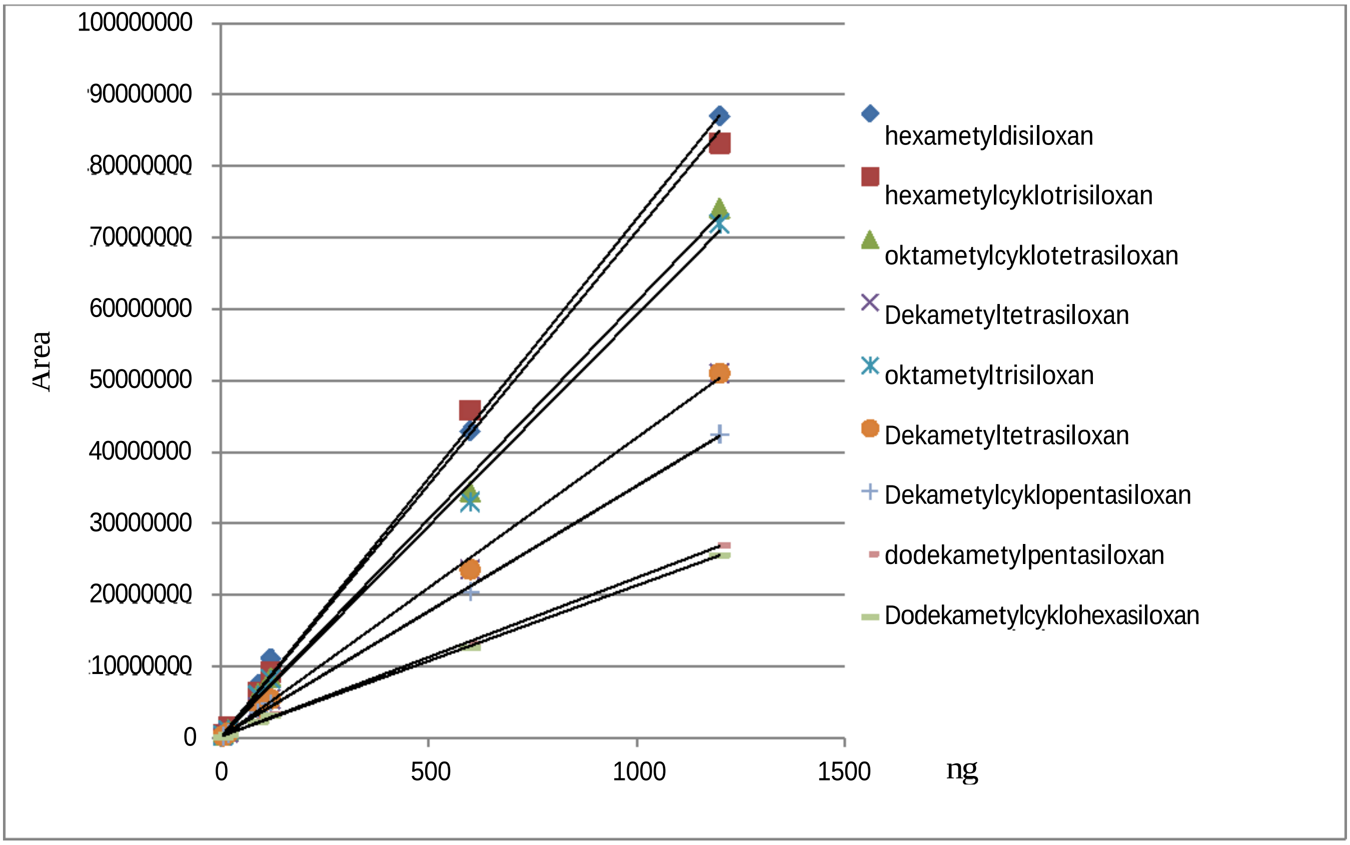
In a mass spectrometer, compounds are fragmented when bombarded by electrons. Fragmentation, registered in the form of a spectrum, is specific to each compound and independent of which instrument was used. In this way it has been possible to collect mass spectra of a large number of compounds in a library of spectra. When an unknown substance is analyzed comparing the obtained mass spectrum of all spectra in the library until it is identified. A mass spectrometer is a selective detector.

3.1.3 Measurement range

Investigation of the linear region

To determine the linearity, known amounts of the respective siloxane was injected at 6 levels between 6 ng to 1200 ng. For each level a weighed amount was dissolved in an appropriate solvent. From each of the six solutions 2µl were applied at Tenax tubes. The method shows good linearity in the range 6-1200 ng as shown in Figure 3.2. With appropriate sample volume, content ranges of 30 µg/m3 up to 20 mg/m3 are covered.

Figur 3.2. Standard curves for siloxanes in the range between 6 to 1200 ng



Limit of quantification

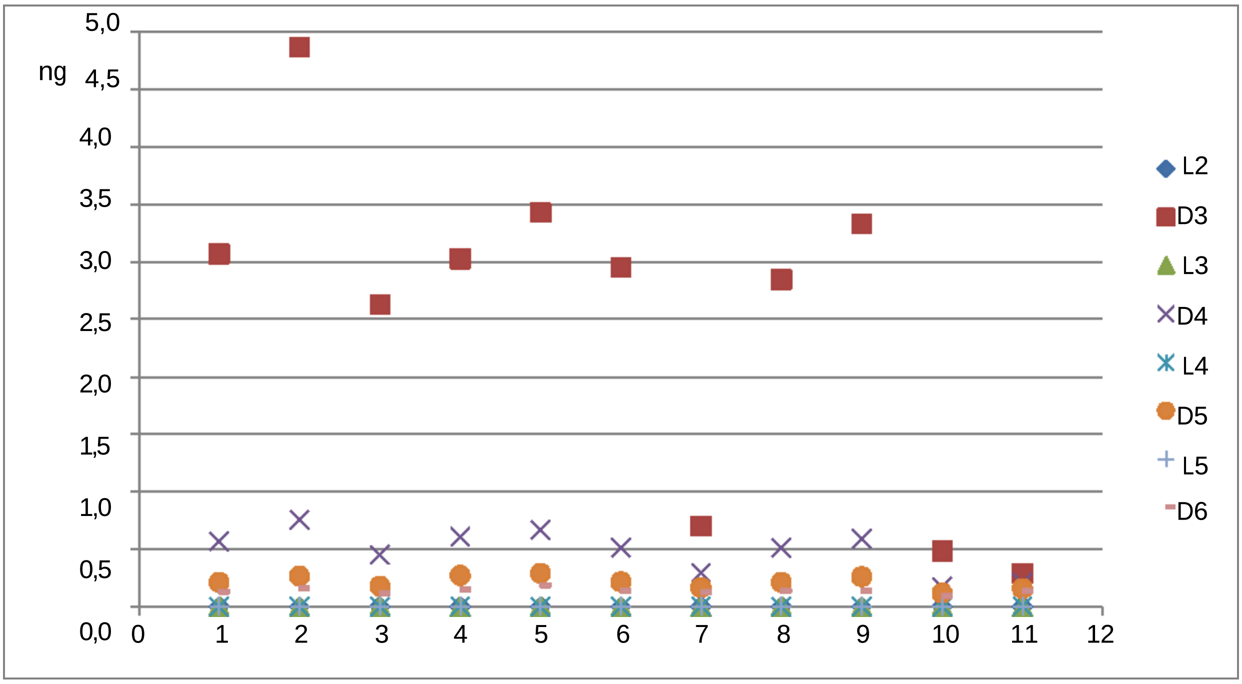
The limit of quantification LOQ is the lowest level that can be determined with acceptable uncertainty. [10] In this project, the LOQ for each siloxane has been expressed as 10 times the standard deviation that was developed for the estimation of repeatability at low level (see section 3.1.1). Results are presented in Table 3.4.

Tabell 3.4: Standard deviations at low level and LOQ

Siloxane	Low level (<20 µg/m^3)	10s µg/m^3	LOQ µg/m^3
	s* µg/m^3		
L2	0.4	4	5
D3	3.2	32	30
L3	0.3	3	5
D4	1.5	15	10
L4	0.7	7	10
D5	0.6	6	10
L5	2.8	28	30
D6	0.6	6	10

For D3 and L5 greater distribution are demonstrated than for the other siloxanes. As for D3, this is because there is already varying levels of D3 (from 0.5 ng up to 5 ng) on Tenax tubes even after conditioning. This affects the results only at low levels (less than 100 µg/m3)

To check blank levels adsorbent tubes are analyzed which has been conditioned before sampling. Results are shown in Figure 3.3. Linear siloxanes can not be detected in significant concentrations in the assay blank (all below 0.5 ng), while on the other hand cyclic siloxanes could be detected and quantified. D3 is the only siloxane present at significant concentration, ie at more than 1 ng. To try and get an explanation of why siloxanes could be detected in the assay blank the pipe without adsorbent (ie, system blank) was also analyzed and then the levels of all siloxanes was kept low (less than 0.5 ng). This indicates that the siloxanes detected in the assay blank are present on the adsorbent. Results also show that even if you follow the same approach for tube conditioning before sampling the concentrations of D3 on the adsorbent can vary from tube to tube. Most tubes demonstrate levels of D3 around 3 ng but the individual tubes can be up to 5 ng of D3, while on others it may be less than 1 ng of D3.



Figur 3.3. Content of siloxanes in ng on 11 different tubes which have been conditioned for sampling

Regarding L5, the distribution observed when produced standards were used (see Figure 3.1) is relatively low while the distribution observed when real samples were used is relatively high (see Table 3.1).

One can therefore suspect that the adsorption of L5 on Tenax is impaired by other substances found in real samples without understanding the process that lead to this.

3.1.4 Measurement uncertainty

The measurement uncertainty has been estimated by combining the various sources of uncertainty into a single value. [15] Measurement uncertainty is expressed as U, total expanded uncertainty with a coverage factor k = 2 which means that the confidence level is about 95%. Results of measurement uncertainty calculations and ranges are presented in Table 3.5.

Table 3.5: Measurement uncertainty and range

	Measurement uncertainty U	Range mg/m^3
L2	15% rel.	0.005 - 20
D3	20% rel.	0.030 - 20
L3	15% rel.	0.005 - 20
D4	15% rel.	0.015 – 20
L4	15% rel.	0.010 – 20
D5	15% rel.	0.010 – 20
L5	25% rel.	0.030 - 20
D6	15% rel.	0.010 – 20
Total siloxanes expressed as Si	10% rel.	0.05 - 50

From the determined concentrations for each individual siloxane can then total content of silicon be calculated by first "weighting" individual levels with the proportion, n_{Si}*M(Si)/M(siloxane), and then summing all contributions. For example D5 has a molecular weight of 370 g / mol where 140 g / mol is silicon. The proportion of silicon, n_{Si}*M(Si)/M(siloxane), is thus 38%.

The analytical requirements were met for all siloxanes except D3 and L5. For these substances the spread is higher and hence quantification limit is higher and measurement uncertainty greater. The method is still good enough for assay of siloxanes in biogas since the levels of these siloxanes normally are relatively low in the biogas.

3.2 Validation of methods based on sampling in bags

The ICP-MS method has proved to be a method which exhibits a good linearity and very low detection limit for determining total Si content. Collection of samples was however made with bags. This sampling method is not quite suitable for siloxanes, due to the adsorption effects of siloxanes with boiling point greater than 150 °C on the bag walls, as shown in Figure 3.1. An opportunity for improvement would be to use also here Tenax tubes to collect samples, but this has not been tested in the framework of this project as it requires a more or less extensive modification of our instrument to connect it to a thermal desorption unit.

3.3 Results from measurements

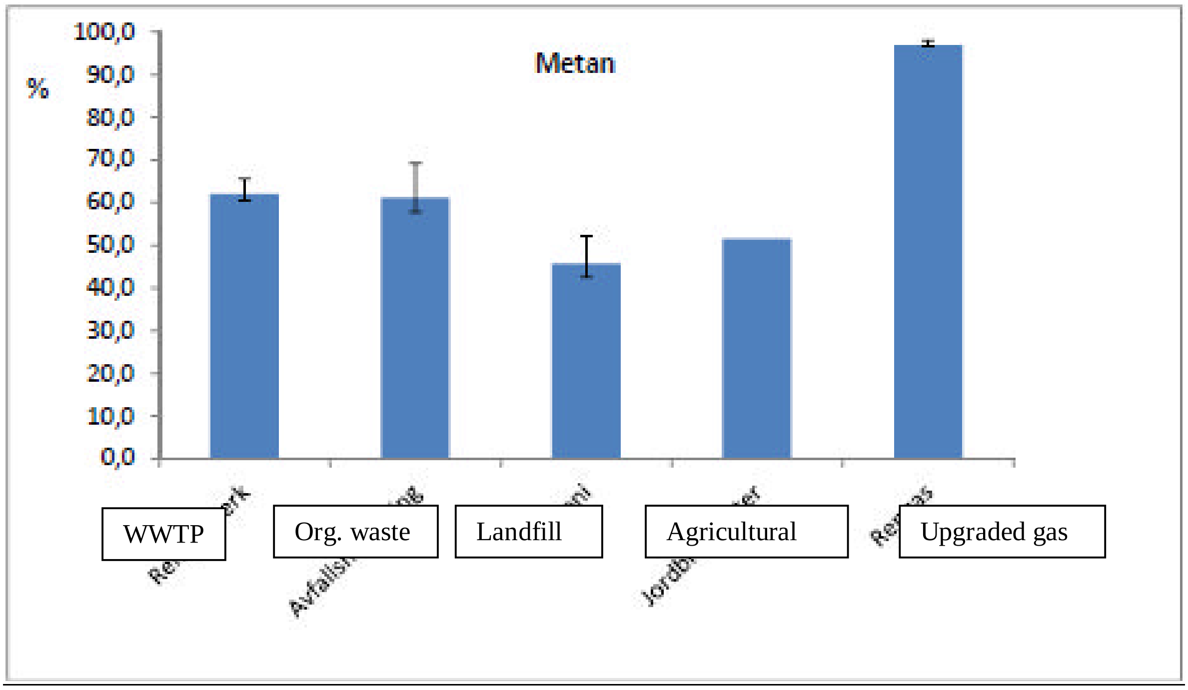
3.3.1 Main components

Measurements were performed according to the method described in section 2 Analytical Methods, 2.2 Tenax/GC/MS method. These measurements are mainly aimed at determining organic siloxanes. But the composition regarding methane, carbon dioxide, oxygen, nitrogen, hydrogen sulfide and water vapor have also been determined. Methane, carbon dioxide, oxygen and nitrogen were determined by gas chromatography / thermal conductivity detector (GC/TCD) according to method ISO6974 [16], while water vapour was determined by gas being suctioned through reagent tube of type Draeger which gives a direct reading in mg/L. Hydrogen sulfide was analyzed by an SO2 instruments where sulfide was converted to sulfur dioxide. The analytical principle is based on UV fluorescence.

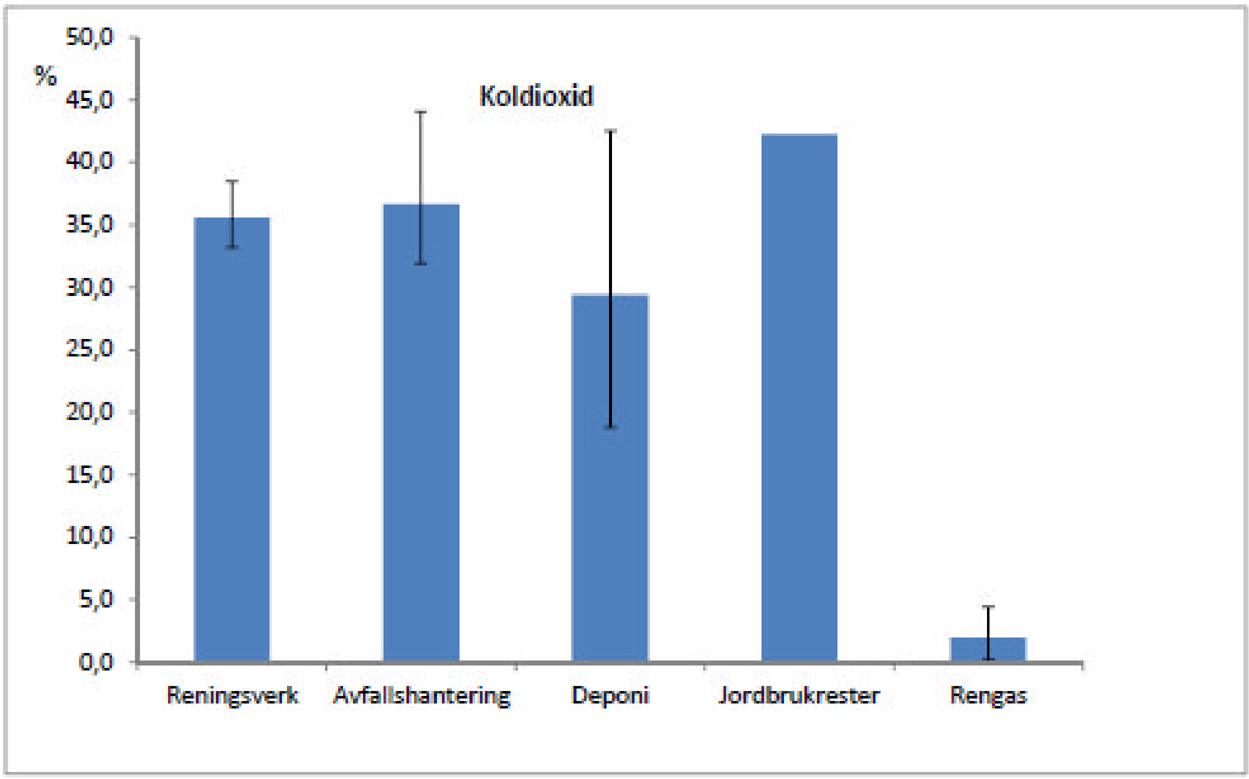
A total of 18 biogas samples were analyzed from eight different sites across Sweden:

- 7 biogas samples from wastewater treatment plants
- 3 samples biogas from organic waste treatment plants
- 1 biogas samples from the anaerobic digestion of agricultural residues
- 2 biogas samples from landfill
- 5 purified gas samples upgraded from wastewater treatment plants or organic waste treatment facilities

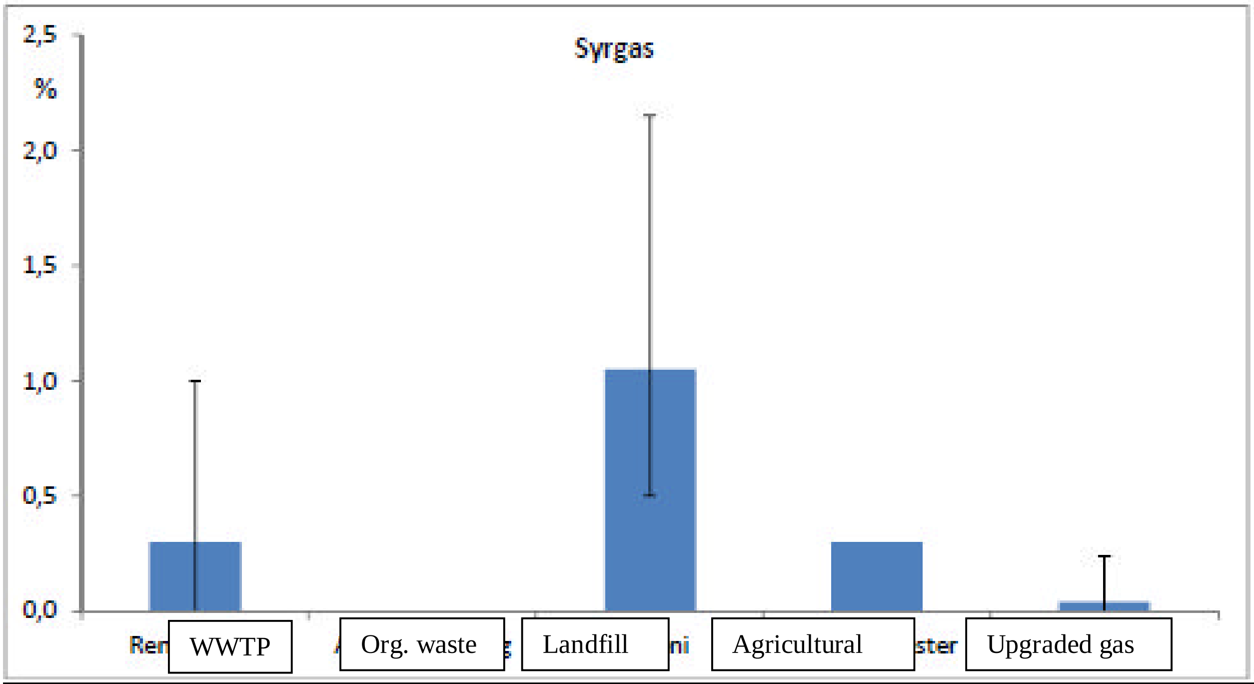
The results for the main components are shown in Figures 3.6 (methane), 3.7 (carbon dioxide), 3.8 (oxygen) and 3.9 (nitrogen). In the figures are presented the average of measurements made by type of substrate. Also shown is the span between the lowest measured value and the highest. Relative measurement uncertainty (95% confidence interval) for methane and carbon dioxide is estimated at 1.0% in the range of 6-100%. Absolute measurement uncertainty (95% confidence interval) for oxygen and nitrogen are estimated at 0.1% in the range of 0.1-6%.



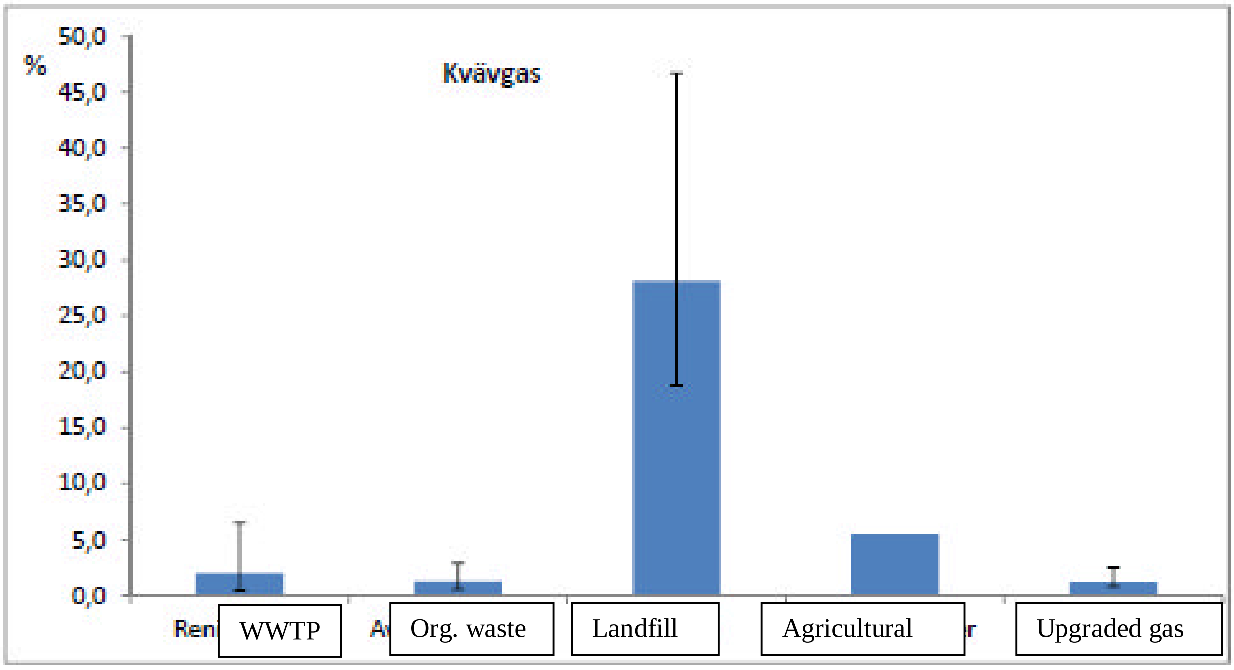
Figur 3.6:Average content of methane (%-vol) in raw gas from different substrates and in clean gas and the range of minimum-maximum measured values



Figur 3.7: Average content of carbon dioxide (%-vol) in raw gas from different substrates and in clean gas and the range of minimum-maximum measured values



Figur 3.8: Average content of oxygen (%-vol) in raw gas from different substrates and in clean gas and the range of minimum-maximum measured values



Figur 3.9: Average content of nitrogen (%-vol) in raw gas from different substrates and in clean gas and the range of minimum-maximum measured values

The result are also summarised in Table 3.6 and 3.7.

Table 3.6: Average of the main components (% vol) of raw gas from various substrates, and the range minimum-maximum measured values

	WWTP		Organic waste		Agriculture		Landfill	
n	7		3		1		2	
	Av.	Range	Av.	Range	Av.	Range	Av.	Range
CH_4	62.0	60.5-64.2	61.8	57.8-65.8	51.5	-	45.8	42.5-49.0
CO_2	35.6	33.2-36.1	33.2	31.9-39.3	42.2	-	29.4	18.8-31.9
O_2	0.3	<0.1-0.7	<0.1	<0.1	0.3	-	1.1	0.5-1.6
N_2	2.0	0.5-5.0	1.3	0.6-2.2	5.5	-	28.1	18.8-37.4

Table 3.7: Average of the main components (% vol) in clean gas and the range of minimum-maximum measured values

	Upgraded gas	
Sample no.	5	
	Av.	Range
CH_4	96.9	96.6-97.7
CO_2	2.0	0.2-2.7
O_2	< 0.1	<0.1-0.2
N_2	1.2	0.8-2.1

These values correspond well with the indicative gas specifications presented in the Marcogaz report "Injection of gases from non-conventional sources into gas networks" [17]. In this report, the authors state an indicative level of 65% of methane in biogas produced by anaerobic digestion with a range between 50 to 80%, and 45% in biogas from landfill with a range between 30 to 60%. In this study, one can see that the concentration of methane in biogas produced in wastewater treatment plants or waste facilities has an indicative value around 62% with a relatively small range from 58% to 65%. Concentration of methane in the biogas produced by anaerobic digestion of agricultural residues is a bit lower, about 52%.

It is noteworthy that the highest values measured for nitrogen and oxygen in biogas produced in wastewater treatment plants (two instances around 5% out of 7 measurements) may result from an air contamination arising during the actual sampling.

All clean gases which have been analyzed in this study satisfies the two requirements of Swedish Standard SS15 54 38 "Requirements for biogas as vehicle fuel" [18] regarding the main components ie a methane content of 97 ± 1% and the total content of carbon + oxygen + nitrogen at a maximum of 4% of which an oxygen percentage of 1% max.

3.3.2 Siloxanes

Results for siloxanes are shown in Figures 3.10 (siloxanes in raw gas from sewage treatment plants, expressed in µg/m3), 3.11 (siloxanes in raw gas from waste plants in µg/m3), 3.12 (siloxanes in rengas in µg/m3), 3.13 (total Si in the raw gas from various substrates and in the clean gas expressed in mg Si/m3). In the figures the average of measurements made by type of substrate are presented. Also shown is the span between the minimum measured value and the maximum.

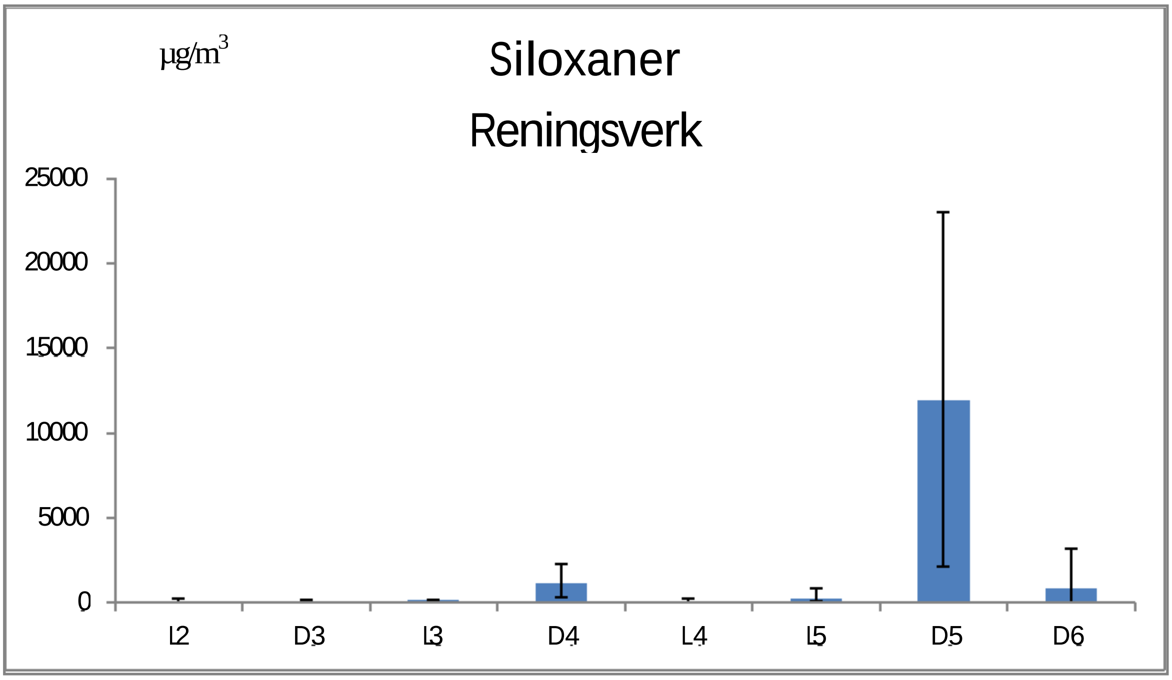


Figure 3.10: Average of siloxanes (µg/m3) of raw gas from waste water treatment plants, and the range minimum-maximum measured values

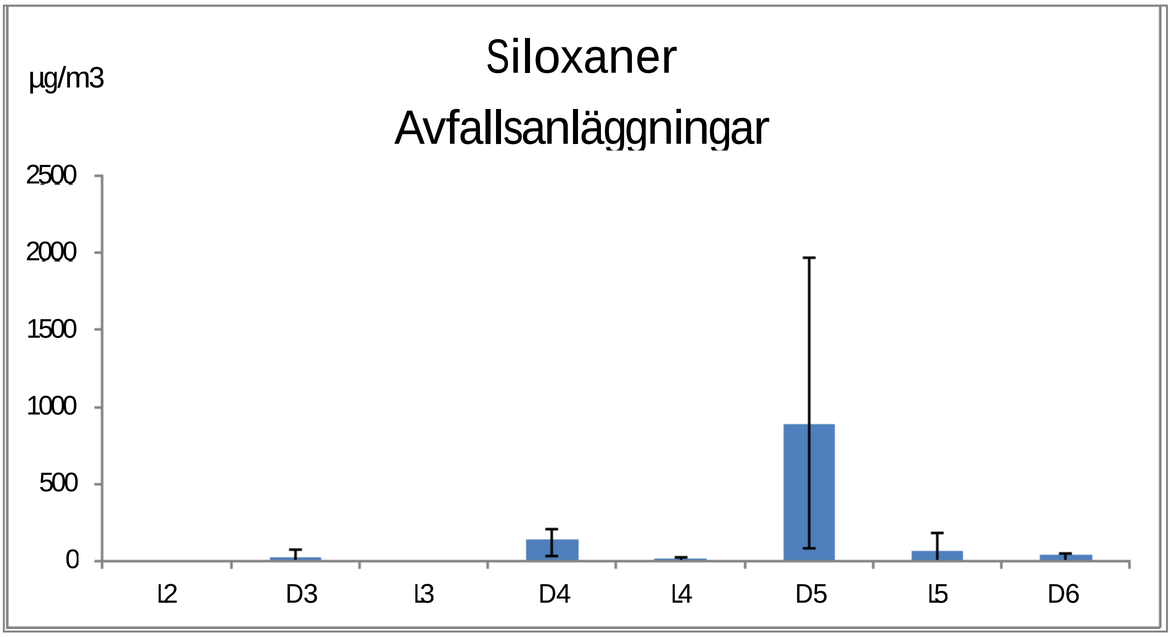


Figure 3.11: Average of siloxanes (µg/m3) of raw gas from waste treatment plants, and the range minimum-maximum measured values

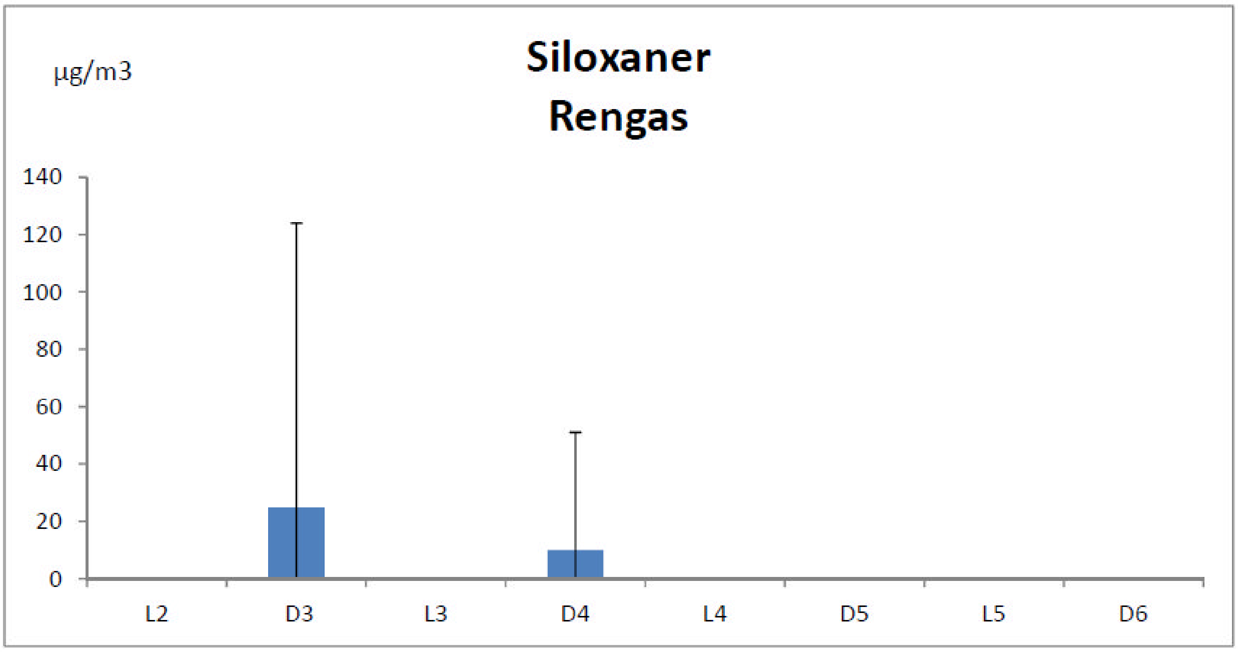


Figure 3.12: Average for individual siloxanes (µg/m3) in upgraded gases, together with maximum-minimum range of measured levels

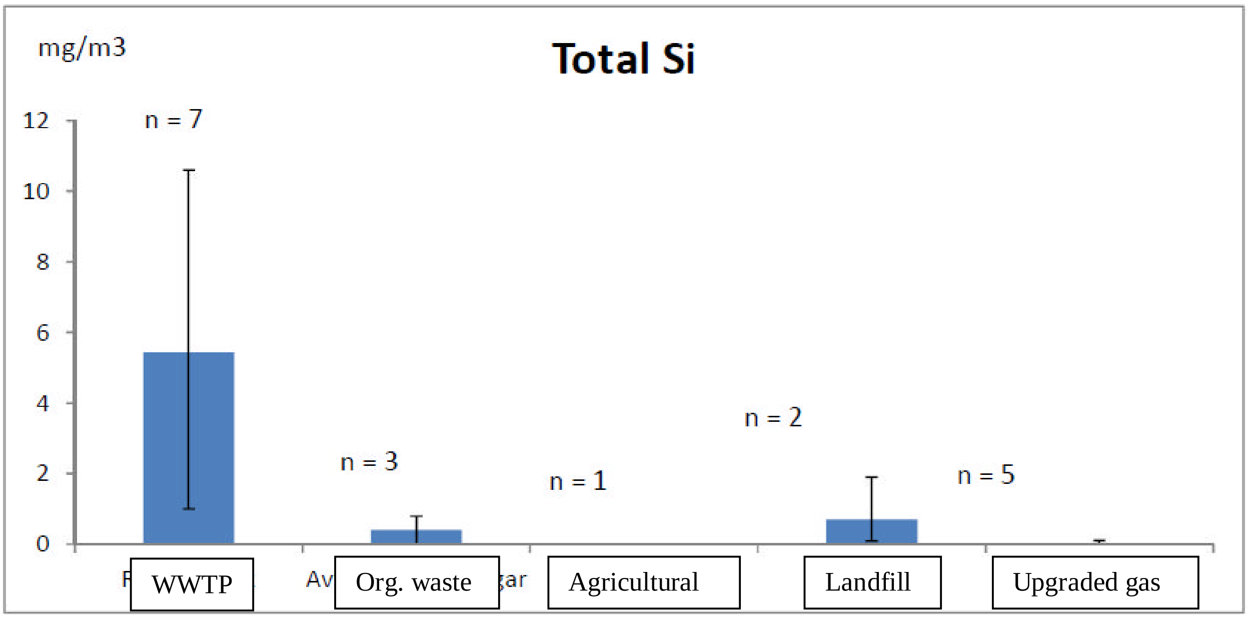


Figure 3.13: Average for siloxanes(mg Si/m3)in raw gases from different substrates and in upgraded gases, together with maximum-minimum range of measured levels

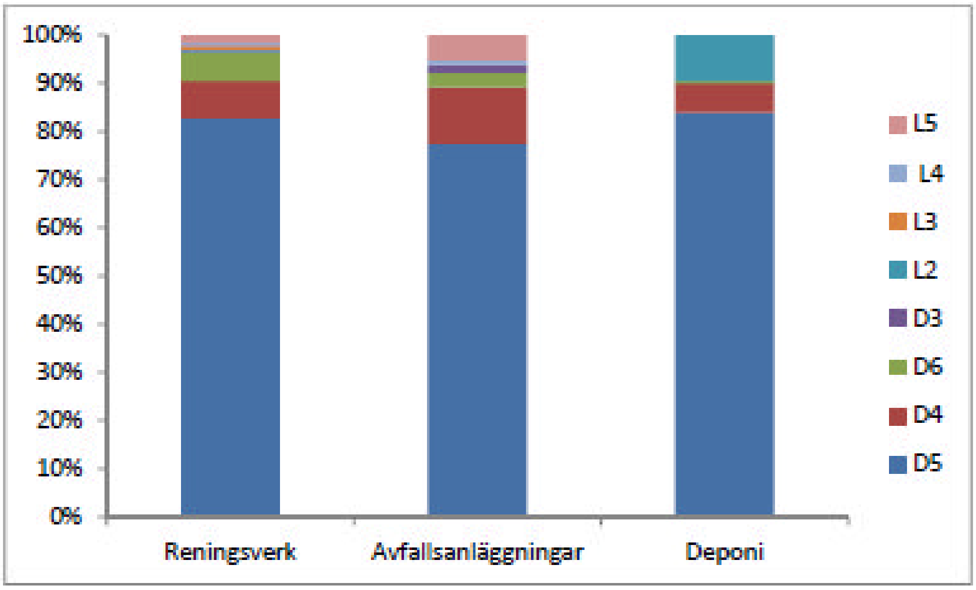
The results are also summarized in Table 3.8.

Table 3.8: Average of siloxanes (µg/m3) of raw gas from various substrates, and the range minimum-maximum measured values

	WWTP		Organic waste		Agriculture		Landfill	
Antal prov	7		3		1		2	
	Av.	Range	Av.	Range	Av.	Range	Av.	Range
L2	40	<5 - 220	<5	<5	< 5	-	280	70 – 500
D3	30	<30 - 150	20	<30 - 70	< 30	-	< 30	< 30
L3	110	30 - 160	<5	<5	< 5	-	<5	<5
D4	1110	300 - 2300	130	30 - 200	< 15	-		
L4	100	20 - 200	10	<10 - 20	< 10	-	< 10	< 10
D5	12000	2100 -23000	890	80 – 1980	< 10	-	2500	300 - 4700
L5	240	100 - 860	60	<30 - 180	< 30	-	< 30	< 30
D6	860	< 10- 3200	30	<10 - 50	< 5	-	15	<10 – 30

3.4 Sammanfattning

As expected, the raw gas from wastewater treatment plants contains significantly more siloxanes than the raw gases from landfills, from anaerobic digestion of agricultural residues and from landfill. As is shown in figure 3.14, D5 is clearly dominant in all raw gases and is usually about 80% of all siloxanes. D4 is the second most common siloxanes and D5 + D4 together contribute to about 90% of siloxanes in the raw gas, which is consistent with other studies [11, 19]. Raw gases from landfills are also significant levels of L2.



Figur 3.14: Ratio of different siloxanes (%)in raw gas from different substrates (average values)

Despite a relatively small base (n = 7), the mean siloxane levels were calculated to be 14.4 mg/m3, in biogas from wastewater treatment plants in this study. This can be compared with results from the Tower Study (USA), where mean siloxane levels in the raw gas from wastewater treatment plants (n = 50) was 38 mg/m3, or the Beese study [20] (Germany), where mean siloxane levels of raw gas from wastewater treatment plants (n = 308) was 14.9 mg/m3. In the Beese study, measured the highest levels in an area were adjacent to a factory of cosmetic products that use silica containing materials Some suppliers of combustion engines place requirements on gas quality. MAN Nutzfahrzeuge AG for example sets a requirement that the gas should contain less than 5 mg/Nm3 methane silicon (total concentration Silicon). This corresponds to about 3 mg total Si/m3 biogas methane content of the biogas is 60%. Virtually all of biogas from wastewater treatment plants samples analyzed in this study exceed 3 mg total Si/m3 biogas while all other samples from other substrates meets the requirement.

The siloxane levels found in upgraded gas regardless of the substrate being digested and the upgrading technology used is very low in this study (maximum 450 µg/m3 total content siloxanes ie 0.1 mg Si / m3). However, it is important to note that the base (n = 5) is very limited, and that it in this study do not reflect all combinations substrate / upgrade technology currently available in Sweden. In the current situation, there are limits on siloxanes in the gas injected into the natural gas grid only in Austria, where the content of siloxanes may not exceed 10 mg/m3. The content of siloxanes in upgraded gases tested in this study is well below this limit.

Henceforth, it would be interesting to identify the levels of siloxanes in the raw biogas produced from various substrates as well as the upgraded gas in Sweden through the analysis of a statistically representative sample. This material can be used for comparison with other countries (with the condition that the same analytical method is used) where other substrates may be digested anaerobically as well as a tool to put demands on siloxane levels in raw biogas suitable for a particular application and for vehicle gas resulting from the upgrading of biogas.

4 REFERENCES

[1] www.biogasportalen.se och rapporten ”Produktion och användning av biogas år 2009”, ES2010:05, Energigas Sverige

[2] ”Energy use of biogas hampered by the presence of siloxanes”, Energy Conversion and Management, 2006, 47, 1711-1722, Dewil R., Appels L., Baeyens J.

[3] “Siloxane Analysis in Landfill biogas: study of sample capture method and identification - quantification by HRGC-MS”, Broto-Puig F., Microphilox project, 2007, http://www.microphilox.com/pdf/FBrotoIQSMICROPHILOX.pdf

[4] “Determination of Siloxanes and VOC in Landfill Gas and Sewage Gas by Canister Sampling and GC-MS/AES Analysis”**.** Environmental Science and Technology, 1999, 33(20), 3680-3685, Schweigkofler M., Niessner R.. Institute of Hydrochemistry, Technical University, Munich, Germany.

[5] “Comparison of Impinger and Canister Methods for the Determination of Siloxanes in Air”, 2002, AWMA Symposium on Air Quality Measurement Methods and Technology, San Francisco, CA, S. Saeed, S.F. Kao, G.J. Graening

[6] “A Summary of available Analytical Methods for the determination of Siloxanes in Biogas”, H.C. Hayes, S. Saeed, G.J. Graening, S. Kao, Air Toxics Ltd, 2002

[7] ATL (Air Toxics Ltd) method 71 for siloxanes, http://www.airtoxics.com/cinfo/services/landfillgas.html

[8] “Determination of siloxanes in landfill gas by adsorption on Tenax tubes and TD-GC-MS”, 2009, Proceedings Sardinia, 12th International Waste Management and Landfill symposium”, Narros A., Del Peso M.I., Mele G., Vinot M., Fernandez E., Rodriguez M.E., http://www.otersu.es/pages/docs/383.pdf

[9] IUPAC Technical Report, The international harmonised protocol for the proficiency of (chemical) analytical laboratories, Pure Appl. Chem., 2006, 78(1), 145-196

[10] “Handbok för validering av analysmetoder inom laboratoriet”, SP rapport 2009:01, Magnusson B., Örnemark U., 2009

[11] ”New technologies for removal of siloxanes in digester gas results in lower maintenance costs and air quality benefits in power generation equipment”, WEFTEC 2003, Tower P.

[12] “ Siloxane quantification, removal and impact on landfill gas utilization facilities”, 8th annual LMOP conference and project expo, 2005, Maryland, Pierce J.L.

[13] http://webbook.nist.gov/, The National Institute of Standards and Technology (NIST)

[14]. SS-ISO 5725-1, Noggrannhet (riktighet och precision) för mätmetoder och mätresultat - Del 1: Allmänna principer och definitioner, SIS, Stockholm, 2003. Del 2: Grundläggande metod för bestämning av en standardiserad mätmetods repeterbarhet och reproducerbarhet, SIS, Stockholm, 2003. Del 3: Mellanliggande precisionsmått på en standardiserad mätmetod.

Del 4: Grundläggande metod för bestämning av en standardiserad mätmetods riktighet, Del 5: Alternativ metod för bestämning av en standardiserad mätmetods precision, Del 6: Praktisk användning av noggrannhetsvärden.

[15] Handbok för beräkning av mätosäkerhet vid miljölaboratorier, SP rapport 2003:23, översättning av NORDTEST rapporten TR537, ”Handbook for calculation of measurement uncertainty in environmental laboratories, Magnusson B. , Näykki T., Hovind H., Krysell M.

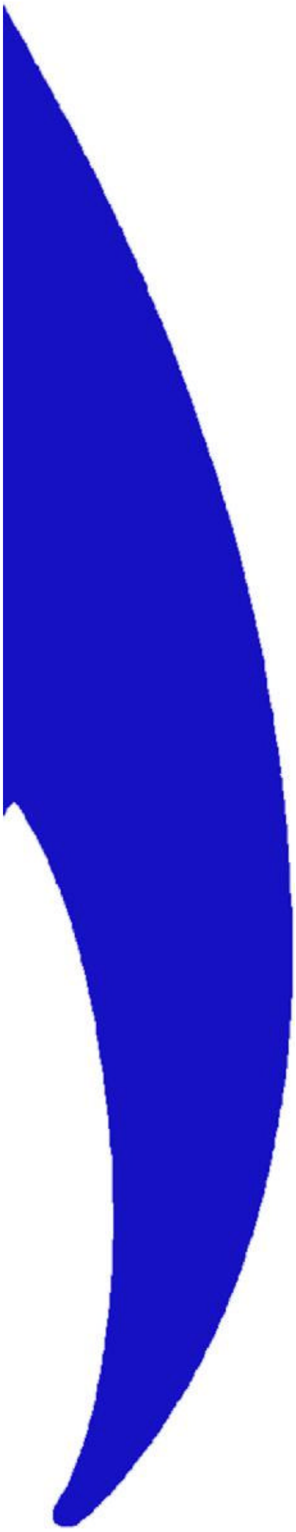
[16] ISO6974 “Natural gas. Determination of composition with defined uncertainty by gas chromatography”

[17] Marcogaz rapport ”Injection of gases from non-conventional sources into gas networks”, 2006, (hppt://www.marcogaz.org/membernet/show.asp?wat=WG-Biogas-06-18_D497_Final Recommendation.pdf)

[18] SIS, 1999, ”SS 15 54 38 Motorbränslen – Biogas som bränsle till snabbgående ottomotorer (motor fuels – biogas as fuel for high-speed otto engines)”

[19] ”Reduction and monitoring of biogas trace compounds”, VTT Research Notes, 2496, Arnold M., 2008

[20] ”Betriebsoptimierung der motorischen gasverwertung durch den Einsatz von Gasreinigungsanalagen”, 2007, Deponiegas 2007 FH Trier Saksa, Beese J.



Scheelegatan 3, 212 28 Malmö ● Tel 040-680 07 60 ● Fax 040-680 07 69
www.sgc.se ● info@sgc.se