Methane emission from Danish biogas plants

Quantification of methane losses

REPORT

Project report

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Quantification of methane losses

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Danish Gas Technology Centre
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1 Preface

This report is a part of reporting of the project “Methane emission from Danish biogas plants” ForskEL 2013-1-12093.
The report describes the quantification method developed for quantification of methane emissions due to leakages biogas plants.

2 Literature survey

As a part of the effort to identify and/or develop a method for quantification of methane leakages from biogas plants, Danish Gas Technology Centre has conducted a literature survey to reveal what has already been done in the field and which methods are used. This section gives an overview of the findings.

When searching for methods and techniques for measuring and quantifying methane emissions/losses/leakages two fundamentally different kinds of methods appear.

- Remote sensing methods
- On-site or point measuring techniques

Only the on-site/point measuring techniques will comply with the pre-set characteristics of and requirements to a simple, cost-efficient and easy-to-operate method which also gives a possibility to find and repair the individual leaks.

A list of sources on detection and quantification found is given in Appendix A.

2.1 Remote sensing methods

The remote sensing methods are characterised by measuring the (average) concentration of the total number of sources covered by the path of measurement. The individual source is not quantified as the method detects the component in the plume. Up- and downwind measurements ensure correct handling of background concentration.

Open Path systems (FTIR or laser) are used with one or more meteorological stations, and the emission level can be determined by use of dispersion models. The mobile tracer method combines a controlled release of tracer gas from the facility examined (a biogas plants). Concentration measurements of tracer gas and the investigated component are performed by using a mobile high-resolution analytical instrument.

Figure 1, Figure 2 and Figure 3 show examples of remote sensing methods.

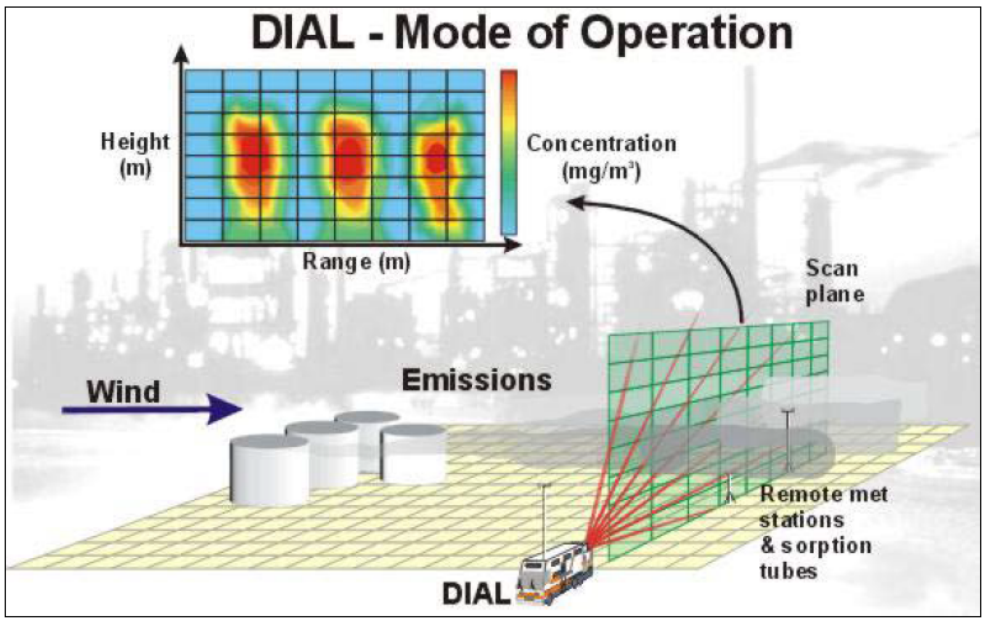


Figure 1 Principle of the LIDAR/DIAL method (Source: U. S. Environmental Protection Agency)

Figure 2 Quantification with TDLAS and inverse dispersion modelling (Source: DBFZ)

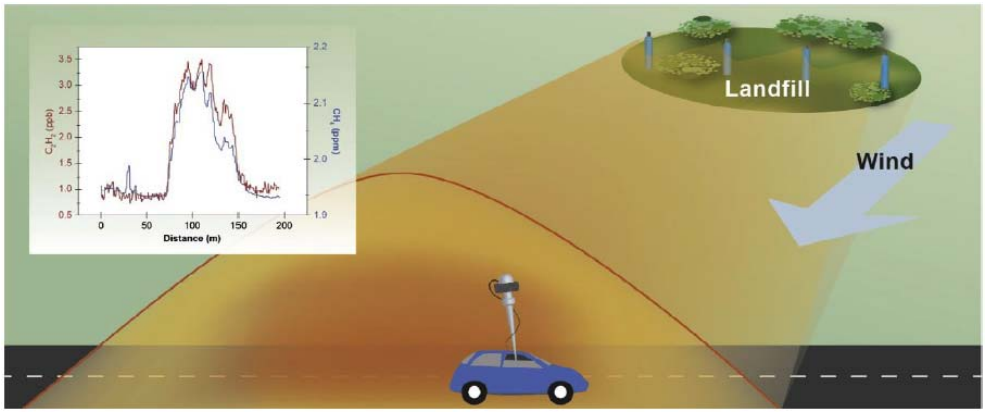


Figure 3 Quantifying methane emission from fugitive sources by combining tracer release and downwind measurements (tracer dispersion method) (Source: Technical University of Denmark, DTU Environment)

2.2 On-site measurements

Measuring methane emissions at biogas plants implies locating the emission spot and subsequently quantifying the emission rate. Locating unknown sources is referred to as "leak detection" and can be performed in several ways. Quantification of leaking biogas is done by measuring coherent values of volume flow and concentration.

Detection methods comprise:

- Smell, sound or vision
- Leak detection spray (foam)
- Portable leak detection instrument
    - Methane laser
    - Semiconductor sensor
    - Catalytic sensor
    - Infrared sensor
- IR camera

The last-mentiond is the most advanced and expensive method, but allows for quick scans of large areas. Portable leak detection instruments are cheap and can be used for systematic maintenance activities, but are time-consuming when covering large areas.

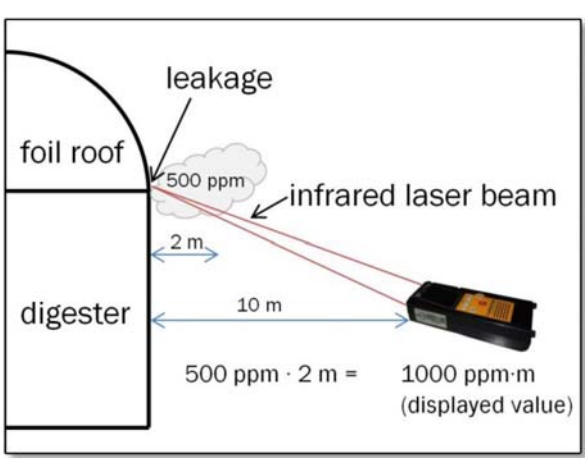


Figure 4 Leak detection instruments

Quantification methods for on-site point sources comprise the following methods:

- Calibrated bagging
- High Flow/Volume Sampler
    - With inlet device or hood
    - In combination with encapsulation of the leakage
- Flow hoods (often used in the HVAC field)
- Vane or hot-wire anemometer
- Pitot tube

The calibrated bagging technique implies filling a bag with a known volume of leaking gas while recording the filling time.

At the high-flow/volume sampler technique, the leaking gas is evacuated from the emission point together with surrounding air. The volume flow of the gas/air mixture is measured as is the concentration of the gas component of interest, e.g. methane.

Vane and hot-wire anemometers are used to measure flow, and they excel in situations of well-defined cross-section areas.

The main method for measuring volume flow in ducts and channels is using pitot tubes. This method is described in “DS/EN ISO 16911-1 Stationary

source emissions – Manual and automatic determination of velocity and volume flow rate in ducts – Part 1: Manual reference method".

Measuring concentration is a choice of several principles, e.g. FID (Flame Ionization Detector), GC (micro GC), photo acoustic infrared spectroscopy, NDIR (Non-Dispersive InfraRed sensor) and FTIR (Fourier Transform InfraRed).

If capital cost is important, concentration measurements can be made by inexpensive gas "sniffers", which will provide indicative measurements sufficient for decision making, see Figure 4.

Figure 5 Quantifying emissions using calibrated bagging

Figure 6 Example of a portable HiFlow Sampler for measuring leaking objects – in the picture to the right in combination with encapsulation of the leakage

2.3 Conclusion on quantification methods

The remote sensing methods have some obvious advantages like determination of total emission rate, no influence on plant operation/design, no need for leakage search and encapsulation and the time effort is independent of plant size.

On the other hand, the equipment needed is costly and requires highly skilled operators. Furthermore, the method depends on weather conditions and topography near the plant. And a very important issue is that the method does not detect individual leaks, which is needed for subsequent repair.

The high-volume sampler technique is flexible, portable and suited for quantifying individual leakages. However, the leakages found at biogas plant installations (digestate storage tank, digesters, gas storage, upgrading plant etc.) are often characterised by a larger physical size than indicated in Figure 6.

In this project, a larger - but still flexible and transportable - high-volume sampler is developed. This system is built using an ATEX blower and standard components for flow measurement and ducts. It is described in detail in section 3.

3 Quantification

3.1 The applied principle

When a biogas leakage is detected by the IR camera, see Figure 7, the amount of leaking gas must be determined. This is done by collecting the leaking gas using a blower and a sampling device that partly covers the location of the leakage.

Figure 7 FLIR GF320 infrared camera used for detection leakages at biogas plants

The sampling device is partly open to the surroundings thus preventing the pressure inside the sampling device from being affected by the blower, see the sketch in Figure 8. The blower must deliver a flow that is sufficient to prevent leaking gas from escaping to the surroundings.

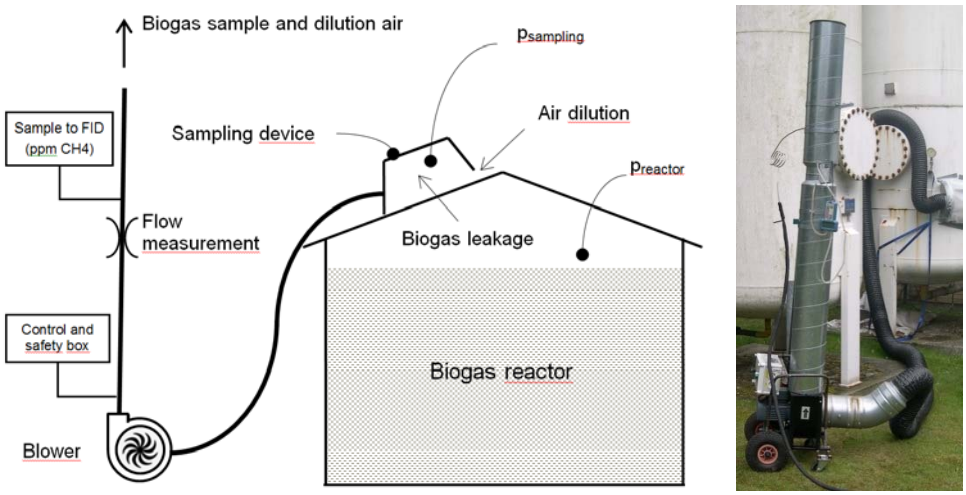


Figure 8 Sketch of the method applied for quantification of a leakage. To the left is a picture of the first version of the "high-volume sampler".

The amount of leaking gas is subsequently determined by measuring the flow of gas, which is a mixture of biogas and air, and the concentration of methane in gas, see Figure 8.

The flow of methane is calculated as

$$Q_{CH_4} = Q_{gas} \cdot C_{CH_4} \qquad \text{Eq. 1}$$

Where

Q_{CH_4} is the flow of leaking methane

Q_{gas} is total flow air and biogas removed by the blower

C_{CH_4} is the methane concentration in the air/biogas mixture

The entire system shown in Figure 8 is referred to as a "high-volume sampler" and consists of:

- Sampling hood/sampling device
- Antistatic ventilation hose
- ATEX approved blower
- Control box including safety circuit in case of too high concentration of methane in the sample gas (alarm is set at 10,000 ppm methane equivalent to 25 % of LEL[1])
- Flow measurement (calibrated orifice)
- FID instrument equipped with a non-methane hydrocarbon cutter

3.2 Determination of flow

Although the purpose of this project is to develop a method specifically for quantification of leakages at biogas plants, other applications of the method may become useful.

If the measurements are intended to document the total amount of biogas/methane emission from the plant, it is necessary to determine both unknown leakages and the anticipated methane contribution from building vents, breather valves and tubes etc. A major part of these known sources of

[1] LEL: Lower Explosion Limit

biogas emission can be quantified by using the high-volume sampler described in section 3.1.

In some cases, however, the high-volume sampler technique cannot be used:

- Buildings with forced ventilation where exit air emits through wall-mounted grilles
- Biogas/methane emissions venting through ducts, pipes or chimneys where the air flow is larger than the high-volume sampler flow capacity

The examples above are not included in this report's purpose, but are described generally in the sections below.

3.2.1 High-volume sampler air flow measurement

The flow of the air/biogas mixture evacuated from the leakage is measured by a built-in orifice located downstream the blower. The orifice can be custom-made for a specific flow and pressure range or purchased as a commercially available item at a specific flow range.

The volumetric flow is calculated by:

$$Q = CA_2\sqrt{\frac{2(p_1 - p_2)}{\rho\left(1-(A_2/A_1)^2\right)}} \qquad \text{Eq. 2}$$

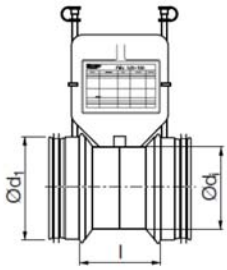
where

Q volumetric flow rate (at any cross-section), m³/s
C orifice flow coefficient, dimensionless
A_1 cross-sectional area of the pipe, m²
A_2 cross-sectional area of the orifice hole, m²
p_1 fluid upstream pressure, Pa
p_2 fluid downstream pressure, Pa
ρ fluid density, kg/m³

A LINDAB FMU 200 orifice was used in the specific high-volume sampler in this project, see *Figure 9*. For this orifice, Eq. 2 can be reduced to

$$Q = 29{,}4\sqrt{\Delta p} \ \text{l/s} \qquad \text{Eq. 3}$$

$$Q = 105{,}8\sqrt{\Delta p} \ \text{m}^3/\text{h} \qquad \text{Eq. 4}$$



Ød1 nom	Ødi nom	l mm	m kg	K-faktor [l/s]	K-faktor [m3/h]
200	160	129	0,83	29,4	105,8

Figure 9 LINDAB FMU 200 orifice

The response from the orifice should be controlled or calibrated using a standard reference method, i.e. a pitot tube, see Figure 10.

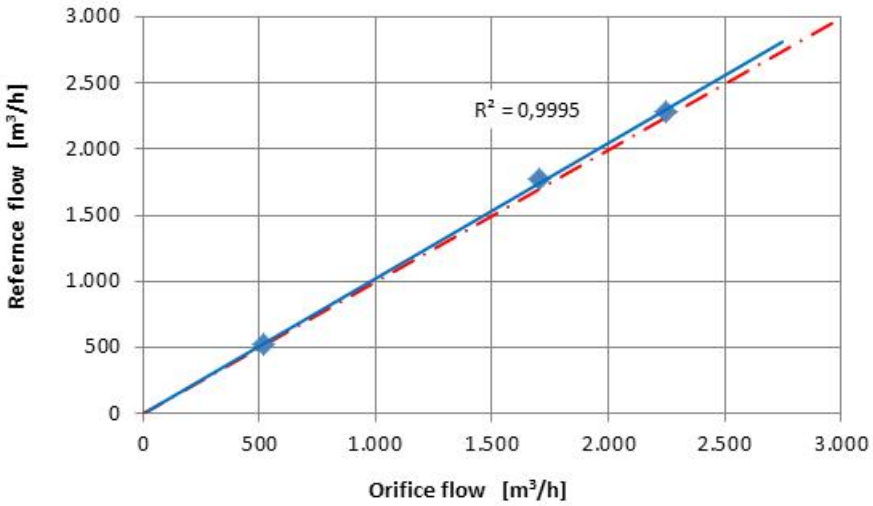


Figure 10 Example of calibration of the FMU 200 orifice using an L-type pitot tube

3.2.2 Flow measurement at ventilation grilles in buildings

In some cases, methane emissions originate from forced or natural venting of buildings, e.g. compressor houses, filter houses and other buildings housing technical installations at the biogas plant. The methane emission from these buildings is not defined as leakages, but does contribute to the overall methane loss from the biogas plant and should be documented.

If natural ventilation occurs, the high-volume sampler can be used by mounting the sampling device to completely cover a ventilation exit grille. The high-volume sampler forces an air flow through the building from the intake ventilation grilles to the exit grille and further through the sampler's orifice for flow determination as described in section 0. The higher the volume flow, the shorter the stabilization time for achieving the necessary constant methane concentration.

In situations with forced ventilation of buildings, the obvious way of determining the methane emission is to measure the volumetric air flow and methane concentration quite close to the ventilation grille exit. Flow determination can be done by using a vane or hot-wire anemometer traversing the entire area of the grille, see Figure 11. This method can be prone to large uncertainty and, if possible, the forced ventilation should be turned off and the high-volume sampler should be used instead.

Figure 11 Example of vane and hot-wire anemometer (Source: TSI)

Another option for measuring the flow from a vent grille is to remove the part of the duct with the orifice from the high-volume sampler and attach a flow hood large enough to cover the ventilation exit grille. Mounting the flow hood/orifice system on the building wall covering the grille makes it possible to measure the air flow with the same accuracy as using the high-volume sampler.

The principle of using flow hoods is well known in the HVAC field where this technique is used for commissioning, clean-room certification, trouble-shooting, testing and balancing HVAC systems. See Figure 12.

Figure 12 Example of flow hoods for measuring air volume flow at diffusers and grilles (Source: Swema and TSI)

3.2.3 Ventilation outlets through ducts and pipes

Quantification of methane emission arising from ducts and pipes can be difficult. If there is no access to the outlet of the pipe it may be impossible to place the sample device to cover the duct outlet. Another obstacle is when the air flow from the duct outlet is larger than the capacity of the high-volume sampler blower.

In this situation, the air volume flow should be determined by the primary manual method for measuring volume flow in ducts and channels. This is done by use of pitot tube and a differential pressure gauge. The method is described in the standard “DS/EN ISO 16911-1 Stationary source emissions – Manual and automatic determination of velocity and volume flow rate in ducts – Part 1: Manual reference method”.

3.2.4 Correcting flow to standard conditions

When measuring air volume flow it is important to use correct units to reflect the physical condition of the measurand. Calculating volume flow using Eq. 3 or Eq. 4 in section 3.2.1 will give an air volume flow result at actual conditions at the place of the orifice with respect to pressure, temperature and humidity of the air.

The mass flow of methane is calculated as the product of the methane concentration in the sample flow and the sample air volume flow. The concentration and volume flow must be converted to the same physical property, usually standard condition (dry gas, 101325 Pa and 0 °C), before calculating the mass flow.

Air volume flow measured by the orifice in the high-volume sampler is converted to standard conditions by:

$$Q_{std} = Q_{act} \frac{p_{atm}}{1013} \frac{273{,}15 - T_s}{273{,}15} \frac{100 - x'''}{100} \qquad \text{Eq. 5}$$

where

Q_{std} volumetric flow rate at standard conditions, m³/s
Q_{act} volumetric flow rate at actual conditions, m³/s
p_{atm} atmospheric pressure, hPa
T_s sample gas temperature at the orifice, °C
x''' sample gas humidity, % volume

Taking Eq. 5 into consideration, measuring the secondary parameters of atmospheric pressure, sample gas temperature and humidity becomes mandatory for further calculations.

3.2.5 Uncertainty of air flow measurements

The uncertainty associated with a measurement of air volume flow depends on the method used and the conditions on the measuring location. One of the advantages of the high-volume sampler is the nature of the volume flow measurement, which is performed under optimal and constant conditions at every measurement.

Using prescribed straight lengths of duct upstream and downstream the FMU 200 orifice, LINDAB indicates a measurement accuracy of ± 5%. This value was verified during the calibration using an L pitot tube, see Figure 10. The deviation of the response between the orifice and the pitot tube was in the range of -3.6 percent to -0.5 percent, which is well within the ± 5 % range.

According to DS/EN ISO 16911-1, an uncertainty of 2.2-5 % is achievable depending on type of pitot tube.

Measurement uncertainty using a vane anemometer or a hot-wire anemometer depends to a very large degree on the surrounding conditions. Especially

wind conditions and flow area will affect the accuracy of the measurement. It is estimated that the measurement uncertainty associated to a result obtained by a vane anemometer amounts to approx. 15-40 % although lower values may be obtained under good conditions.

3.3 Determination of concentration

3.3.1 Measuring methods

Methane concentration in a sample gas flow or a vent air stream can be measured by analysers with several detection principles:

- FID (Flame Ionization Detector)
- GC (micro GC)
- Photo-acoustic infrared spectroscopy
- NDIR (Non-Dispersive InfraRed sensor)
- FTIR (Fourier Transform InfraRed)

Each principle has advantages and drawbacks regarding selectivity, continuous or semi-continuous operation, precision and accuracy, calibration, cross sensitivity, ruggedness for field use etc.

The most widely used instruments in Denmark for methane measurements are probably FID analysers, as this type is recommended by the Danish EPA for measuring TOC (Total Organic Carbons, which include methane) in gasses emitted from stationary sources[2].

In order to detect only methane the FID analyser is used along with a non-methane hydrocarbon cutter, see subsection 3.3.2. This method, the FID analyser in conjunction with a cutter, is described in the standard DS/EN ISO 25140:2010 Stationary source emissions – Automatic method for the determination of the methane concentration using flame ionization detection (FID). Swedish Gas Technology Centre (now Energiforsk) also prescribes using the FID and cutter method in their Handbook for measuring methane[3]. For details of the standard, please refer to Appendix B.

[2] DGC is accredited by DANAK (The Danish Accreditation Fund) to measure TOC by the use of FID.
[3] SGC rapport 227 Handbok metanmätninger.

In the present project developing a quantification method for methane leaks from biogas plants, DGC has used the FID/cutter method as the main approach to determine methane concentration. Appendix C gives an overview of the specific analyser and extractive sample system used.

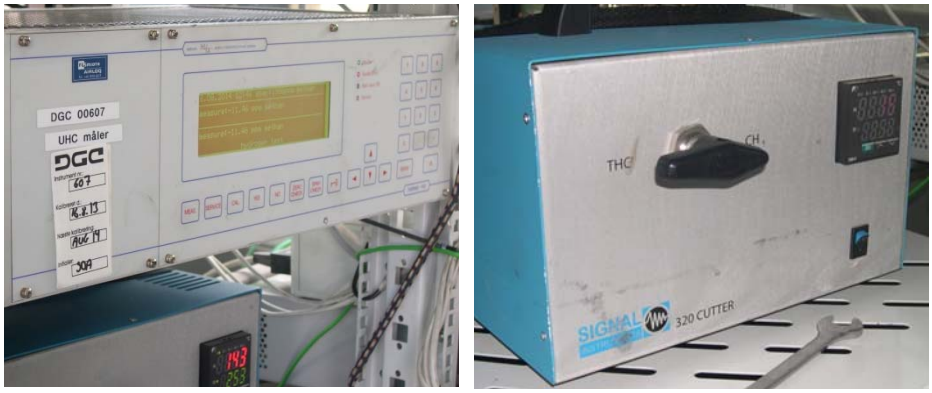


Figure 13 FID analyser and non-methane cutter used by Danish Gas Technology Centre

However it should be noted that the quantification method developed neither relies on, nor is bound to one single method of determining the methane concentration. There is a freedom of choice as long as the chosen method complies with performance characteristics which ensure reliable results.

3.3.2 Non-methane hydrocarbon cutter

A non-methane hydrocarbon cutter is a catalytic device consisting of a catalyst in a reactor designed by type of catalyst and operating temperature to combust all non-methane hydrocarbons and to leave only methane. DGC uses a Model 320 cutter from SIGNAL Instruments.

Operation of a methane cutter is based upon different combustion temperatures of methane compared to other non-methane hydrocarbon compounds. The methane cutter uses an oxidizing catalyst that is maintained at a temperature specific for the catalyst used, to selectively combust the non-methane hydrocarbons in the sample stream, while not reacting with the methane content of the sample.

As the sample stream passes through the cutter, non-methane hydrocarbons oxidize to CO_2 and H_2O, which are not detected by the FID. The FID only

measures the unreacted methane in the sample stream. By taking the difference between the methane-only measurement and the total hydrocarbon measurement, the non-methane hydrocarbon content can be determined.

DS/EN ISO 25140:2010 describes how to check the converter efficiency with ethane test gas.

3.3.3 Calibration

In general, the analyser used must be calibrated and maintained according to the manufacturer's instructions. Specific attention should be drawn to interfering substances (cross sensitivity) and field calibration suited for handling large ranges of methane concentration.

At field measurements it is good practice to calibrate the FID analyser before and after execution of the measurements with zero gas and span gas in a suitable concentration. Sometimes it is advisable to perform calibration/control between measurements. This is done during very long measuring periods (> 10 h), or if the analyser is moved between different measuring points. A new calibration is a must if the power has been switched off during relocation of the analyser.

During the execution of the measurement programme, it became obvious that the methane concentration could take very different values from close to zero and beyond 10,000 ppm which is the alarm limit programmed into the control system of the high-volume sampler. Therefore, it is recommended to operate with at least three span gases with different concentrations of methane. One gas should be of low concentration close to zero, e.g. 50 ppm. The other two could be 2.000 ppm and 9.000 ppm methane. Please note that the balance gas must be synthetic air in order to avoid oxygen cross sensitivity issues.

Which concentration values to select for span gasses depends on the selected analyser measuring range and the flow capacity of the sample blower. High methane concentrations from large biogas leaks can be avoided if the sample system is capable of operating with large air flows.

3.3.4 Uncertainty of methane concentration measurements

The uncertainty of the methane concentration measurement depends on the analyser specification, the chosen measuring range, zero and span calibration, the surrounding conditions (temperature etc.), interfering substances in the gas matrix etc.

Chapter 6 in DS/EN ISO 25140 specifies performance criteria and performance characteristics to be evaluated in order to obtain reliable measurement results and to minimize the measurements uncertainty. Table 1 of Appendix 9 in the standard shows the above mentioned criteria from which the overall uncertainty can be established by setting up an uncertainty budget.

Experience from comparative measurements indicates [1] relative standard uncertainty values in the range 3-10 %. When adding interfering compounds to the test gas, no systematic deviations were observed, but the relative standard uncertainty increased, depending on the concentration level, to a range from 4.0 % to 17.5 %.

Selecting the appropriate measuring range and suitable calibration gasses Danish Gas Technology Centre usually experiences relative uncertainties of 4-6 %.

3.4 Measurement example

This section describes the measurement on a leaking safety valve performed in two different ways. Figure 14 shows that the leak was constant during the measurement period.

Measurement #1: Sampling hose was mounted directly over/on the vent pipe. Sufficient sample flow applied and controlled by checking for back flow of leaking biogas. No sampling device/sampling hood was used.

Measurement #2: Sampling hood/device was mounted on the hose and the hood was equipped with plastic skirts to prevent wind turbulence causing leaking biogas to escape. This method resulted in less pressure loss in the sam-

pling system and consequently a larger sample flow and lower CH_4 concentration.

The table below indicates that the CH_4 emissions measured by the two different sample flows are almost identical. There is a difference in methane emission less than 2 % between measurement #1 and #2.

Table 1 Measurement on leaking safety valve

Measurement	Sample flow [m3(n,t)/h]	CH_4 concentration [ppm]	Methane flow [g/h]
# 1 (13:15 - 14:08)	507,1	24.650	9.000
# 2 (14:22 - 15:03)	745,4	17.067	9.159

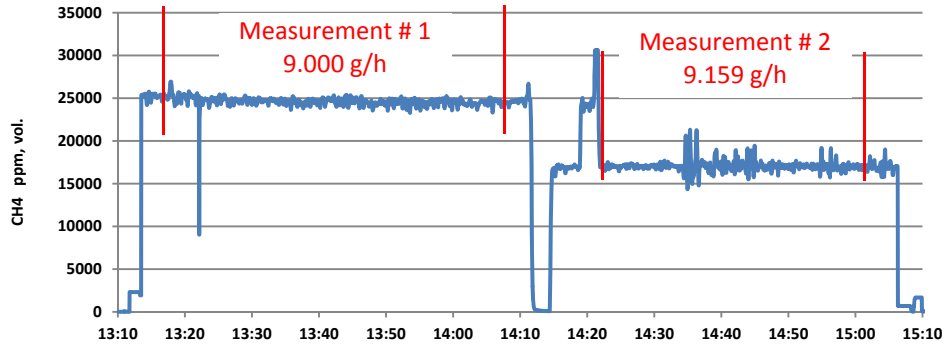


Figure 14 Pressure relief vent (safety valve leak)

For details on the measuring equipment, please refer to Appendix C.

3.5 Sampling

Methane emissions from biogas come from a number of different sources, such as safety valves and feedthrough for stirrer of substrate in the reactor. For information of the different types of leakages please refer to /4/.

Different types of leakages require different sampling devices. Examples are shown in Figure 15.

Safety valve

Crevice on curved surface

Figure 15 Examples of use of different sample devices for different types of leakages

3.5.1 Intrusion of measurement

The quantification method implies that the whole amount of leaking gas must be collected during sampling. This means that it is necessary that the blower creates a sufficient flow to prevent biogas from escaping the sampling device. To achieve this the pressure in the sampling device must be at least slightly lower than the ambient pressure.

When that is the case the flow of leaking gas is affected by the sampling. For a well-defined orifice it is possible to calculate the flow based on a measured pressure difference. The orifices through which the leakages take place are not well-defined. However, Bernoulli's principle says that the flow rate across an opening is proportional to the square root of pressure difference across the opening. This can be described mathematically as

$$Q \approx \sqrt{p_2 - p_1} \qquad \text{Eq. 6}$$

Where

Q is the flowrate (mass or volume based)

p_2 and p_1 are pressures on each side of the opening.

This means that the relation between sampling pressure relative to the pressure in the biogas reactive and amount of gas escaping through the leakage can be depicted as shown in Figure 16. The figure shows that if sampling pressure is the same as the pressure in the reactor

$p_{sampling} = p_{reactor}$ or $p_{sampling}/p_{reactor} = 1$

the effect on the outflowing gas is

$q_{affect}/q_{unaffected} = 1.4$

meaning that the measured amount of escaping gas is 40 % higher than it would be if the flow was unaffected.

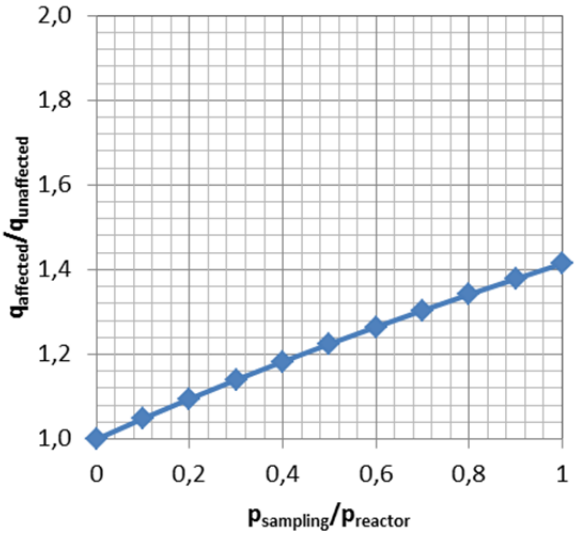


Figure 16 The effect of sampling pressure on the amount of gas escaping the biogas reactor through a leakage

If this theory is applied to assess to which extent the result of the measurement is affected by the sampling pressure in the sampling device, it requires measurement of the pressure in the sampling device as well as information of the pressure inside the reactor, or whatever the source of the gas leak. We can measure the pressure in the sample device. Often, it was not possible to measure or obtain information on pressure in the biogas reactor. By determining the amount leaking gas at two different sampling flows and thereby two different pressures in the sampling device, it was possible to calculate the pressure in the biogas reactor.

In this way it was possible to assess the effect of the measurement on the result of the measurement.

3.6 Combined uncertainty

The determined value of the methane loss from a leakage is associated with a certain uncertainty. Different factors contribute to this certainty. The most important ones are

- Methane concentration measurement, which is ± 5 %
- Gas flow measurement, which is ± 5 %
- Sample conditions, like the weather. This is estimated to be ± 5 %.

As none of these factors are correlated, the total uncertainty is approximately ± 10 %.
On top of that, there is the contribution due to intrusion as described in 3.5.1. The effect of this factor depends heavily on the individual leakages. If the leakage occurs from a safety valve at a compressor, and the pressure is high, e.g. 5 bar, the leakage is not affected by the sampling. But if it occurs at a location with a pressure close to atmospheric pressure, the leakage is sensitive to the sampling pressure. However, it is assessed that awareness of this issue during sampling can keep the uncertainty below + 5 %.

The above mentioned uncertainties are all related to quantification of the loss from the individual leakages. There is also an uncertainty related to whether all leakages are found. It is hard to estimate this. This uncertainty is very dependent on weather conditions. However, as illustrated in Figure 18, even very small leakages were detected.

4 Safety aspects

There are a number of safety aspects that must be taken into consideration when conducting this kind of measurements.
Biogas and air mixtures are flammable if the ratio between the two is in a certain range. In order to eliminate the risk of explosions and fire different precautions were made:

- The methane concentration was measured, and it was decided that it should not exceed 25 % of the lower explosion limit corresponding to 10,000 ppm.
- The plastic tube between the sampling point and the blower may cause static electricity. Therefore, the velocity of the gas should be higher than the flame speed of the gas. This means that if the gas is ignited in the tube, it will be carried to the blower instead of being moved towards the reactor.
- An ATEX approved blower is applied.
- Biogas contains H_2S, which is very toxic, see Table 2. Therefore, it is important to ensure that the collected gas is carried away from the work space of the persons conducting the measurement.
- As some of the leakages are at the top of the reactor, work must be conducted at elevated heights, see Figure 17, and adequate precautions must be taken.

Table 2 Effects of H_2S exposure at different concentrations. From www.osha.gov.

Concentration (ppm)	**Symptoms / Effects**
0.00011-0.00033	Typical background concentrations
0.01-1.5	Odor threshold (when rotten egg smell is first noticeable to some). Odor becomes more offensive at 3-5 ppm. Above 30 ppm, odor described as sweet or sickeningly sweet.
2-5	Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep. Airway problems (bronchial constriction) in some asthma patients.
20	Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.
50-100	Slight conjunctivitis ("gas eye") and respiratory tract irritation after 1 hour. May cause digestive upset and loss of appetite.
100	Coughing, eye irritation, loss of smell after 2-15 minutes (olfactory fatigue). Altered breathing, drowsiness after 15-30 minutes. Throat irritation after 1 hour. Gradual increase in severity of symptoms over several hours. Death may occur after 48 hours.
100-150	Loss of smell (olfactory fatigue or paralysis).
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary edema may occur from prolonged exposure.
500-700	Staggering, collapse in 5 minutes. Serious damage to the eyes in 30 minutes. Death after 30-60 minutes.
700-1000	Rapid unconsciousness, "knockdown" or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes.
1000-2000	Nearly instant death

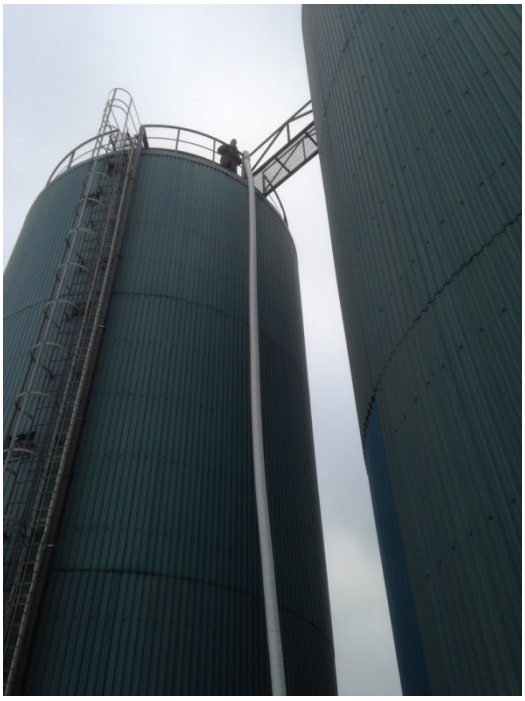


Figure 17 Sampling of leaking gas at the top of a biogas reactor

5 Results

Ten biogas plants were selected for quantification of methane emission. See /4/ for information on the background of the selection.
From the beginning, two rounds of measurements were planned. In the first round, all selected plants were analyzed for leakages, and the amount of methane leaking from each of the found leakages was quantified. One of the ten plants, that was initially interested in participating in the project, changed their mind when we came to conduct the quantification. Therefore, no measurements were conducted for plant #10.

Afterwards, the examined plants were informed about the found leakages and the amount of leaking methane. They were all offered a second measurement after they had been given time for repairing the leakages found in the first round. Six plants participated in the second round.

As mentioned above, each plant was scanned by an IR camera for leakages, and the flow from each leakage was subsequently quantified. Table 3 shows the results of the measurements conducted at one of the examined plants. For that specific plant, seven different leakages were found, and for each of them the flow rate of air and leaking biogas and the concentration of methane in the air/biogas mixture were determined. For this plant, the flow rate varied from 402 to 482 m^3_n/h, and the methane concentration varied from 33 to 2,077 ppm. Based on these measurements, it was calculated that the total methane loss was 8,839 m^3_n/year. The loss from the individual leaks varied from 129 to 6,677 m^3_n/year. This means that one leak contributed with 75 % of the whole methane loss from that plant.

In order to be sure that all biogas escaping from a leakage is collected and included in the quantification, it is necessary to have pressure below atmospheric pressure in the sampling device. This means that the amount of leaking gas is affected by the measurement itself to some extent, as described in section 3.5.1. The pressure in the sample device was measured during sampling in order to assess the influence of the measurement. The plant informed us that the pressure in reactor was 4 mbar(g).
For one of the leakages, the measurements were conducted twice at different sampling rates. Based on the two measurements, the reactor pressure was calculated to be 3.4 mbar(g).

With this reactor pressure and the pressure in the sampling device, the effect of sampling the amount of leaking gas was assessed for each of leakages. It was found that the measured amount was overestimated by 0.1 – 16 % for the individual leakages. For the leak where 16 % of leaking gas was caused by the suction of the blower, the leaking gas contributed to 19 % of the total amount of gas leaking from that plant. For the whole plant 3.3 % of the quantified leakage wass caused by the measurement itself, see Table 3.

Table 3 Measurement results for one of the examined plants

	Measurement			Calculated	Estimated error due to suction	
Leakage	CH4 conc.	Sampling pressure	Flow	Methane loss		
	ppm.	Pa	m^3/h	m^3/year	m^3/year	-
#1	54	-0,3	422	180	0,8	-0.4 %
#2	62	-2,9	402	187	7,9	-4.2 %
#3	49	-0,1	417	163	0,2	-0.1 %
#4	33	-2	482	129	3,8	-2.9 %
#5	65	-5	473	222	16	-7.2 %
#6	507	-12	423	1272	210	-16 %
#7	2077	-0,5	469	6677	49	-0.7 %
Total				8830	288	-3.3 %

5.1 Round 1 before modification

Measurements were conducted for nine of the 10 selected plants.
The number of leakages varied from 0 – 14 for the different plants. For one of the plants the methane loss corresponded to 10 % of the whole biogas production. The amount of leaking methane was in the worst case 276,000 m^3(n)/year. See Table 4 for further details.

Table 4 Results of the first round of measurements

Biogas plant #	Type of plant	Number of leakages	Total annaul methane emission	Annual methane production	Methane loss
			[1000 m^3]	[10^6 m^3]	[percent]
1	Farm scale	10	1,6	0,3	0,6%
2	Farm scale	5	3,9	0,5	0,9%
3	Farm scale	0	0	0,1	0,0%
4	Farm scale	4	4,4	0,5	0,9%
5	Farm scale	2	10,1	0,9	1,1%
6	Centralised	3	28	1,3	2,1%
7	Centralised	14	276	4,9	5,7%
8	Centralised	3	123	1,2	10%
9	Centralised	11	131	3,9	3,4%
10	Centralised	----------No measurement----------			
total		**52**	**579**	**14**	

The total methane loss due to the found leakages on the nine examined plants constituted 4.3 % of the total biogas production.

The loss from the individual leakages varied a lot. This is shown in Figure 18 which shows the amount of methane leaking from the found leakages on the examined plants. For the plants examined in the first round, it was found that 15 % of the leakages contributed with 85 % of total methane loss.

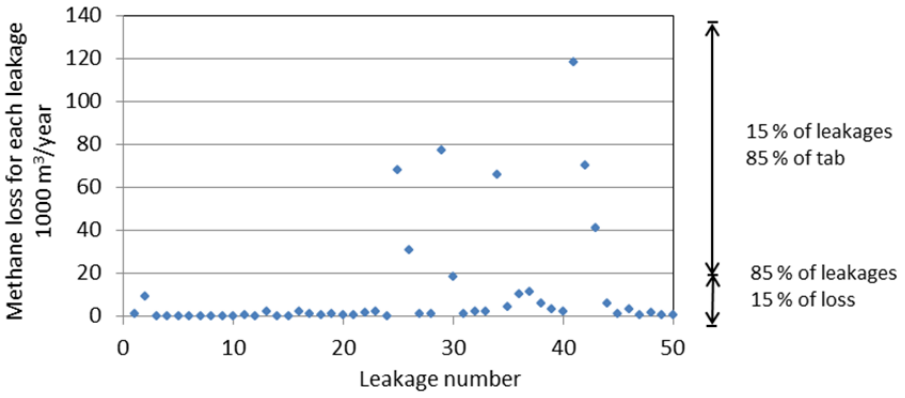


Figure 18 The methane loss for each leakage found on the nine examined biogas plant in the first round of measurement.

It was assessed whether there is a relation between the age or the size of the plants and the share of the gas production that escapes through leakages.

Some of the plants had been renovated and expanded with an additional reactor. Therefore, the methane loss is depicted both versus the year the plant was commissioned and the year of the renovation or the expansion. If the plant had not been renovated or expanded, the year of commissioning was used for the comparison. See Figure 19. Apparently, there is a tendency that the older plants have the highest methane losses. But apparently, there is no correlation between the methane losses and the year of renovation or expansion.

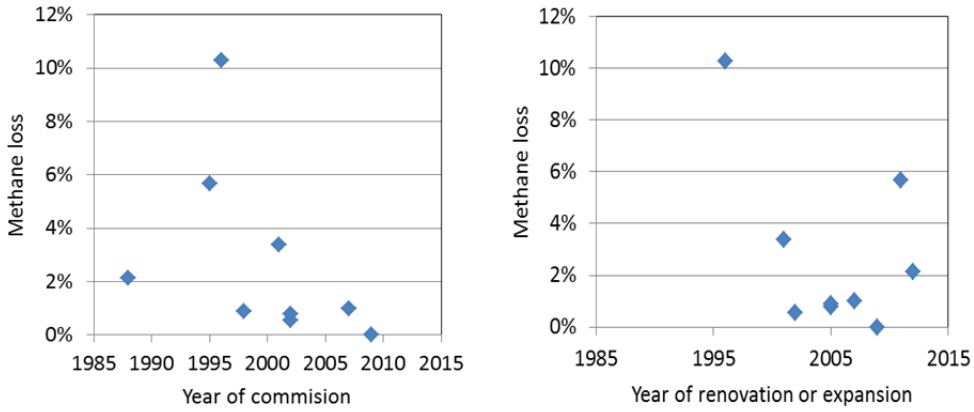


Figure 19 The methane loss as percentage of the production depicted versus the year of commissioning and the year of renovation or expansion respectively

Apparently, there is a correlation between the fraction of the methane production that is lost and the production capacity of the plants. Figure 20 shows that the lowest loss came from the smallest plant, and that the loss was higher for the larger plants. However, the highest loss came from one of the smaller plants.

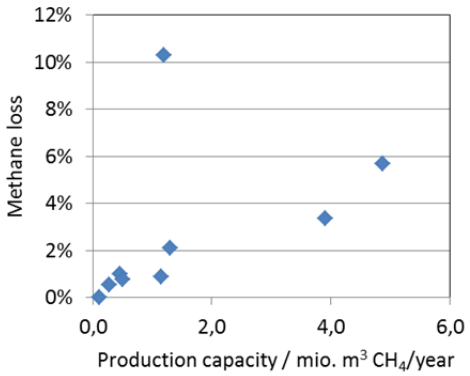


Figure 20 The methane loss as percentage of the production depicted versus the production capacity

5.2 Round 2 after modification

After the first round of measurements, the plant owners were informed about the leakages found on their plant. On six of nine plants an effort was made the repair the leakages. On two plants the opinion was that the losses were so small that it was not worth the effort to reduce them. On the last plant, no leakages were found in the first round.

Table 5 shows the results obtained from the second round of measurements. On plants #1, 2 and 3 the measurements were not repeated after repairing leakages. For these plants, it is assumed the methane losses are the same as during the first round. Therefore, the data stated in Table 5 for these plants are the same as shown in Table 4.
As shown in Table 5, the amount of leaking methane was reduced dramatically by the efforts made to reduce the methane losses. After the second round of measurements, the total methane loss from the examined plants was reduced from 579,000 m^3_n/year to 110,000 m^3_n /year. The results are shown graphically in Figure 21. The figure shows that for plant #4 the amount of leaking gas increased from the first to the second measurement.

Table 5 Results of the second round of measurements.

Biogas plant #	Type of plant	Number of leakages	Total annaul methane emission	Annual methane production	Methane loss
			[1000 m^3]	[10^6 m^3]	[percent]
1	Farm scale	10	1,6	0,3	0,6%
2	Farm scale	5	3,9	0,5	0,9%
3	Farm scale	0	0	0,1	0,0%
4	Farm scale	4	22,0	0,5	4,4%
5	Farm scale	2	9,7	0,9	1,1%
6	Centralised	1	0,9	1,3	0,1%
7	Centralised	15	60	4,9	1,2%
8	Centralised	7	9,3	1,2	0,8%
9	Centralised	3	2,3	3,9	0,1%
10	Centralised	----------No measurement----------			
total		**47**	**110**	**14**	

After repairs, the total methane loss due to the found leakages was reduced by 80 % from 4.3 % to 0.8 % of the total biogas production.

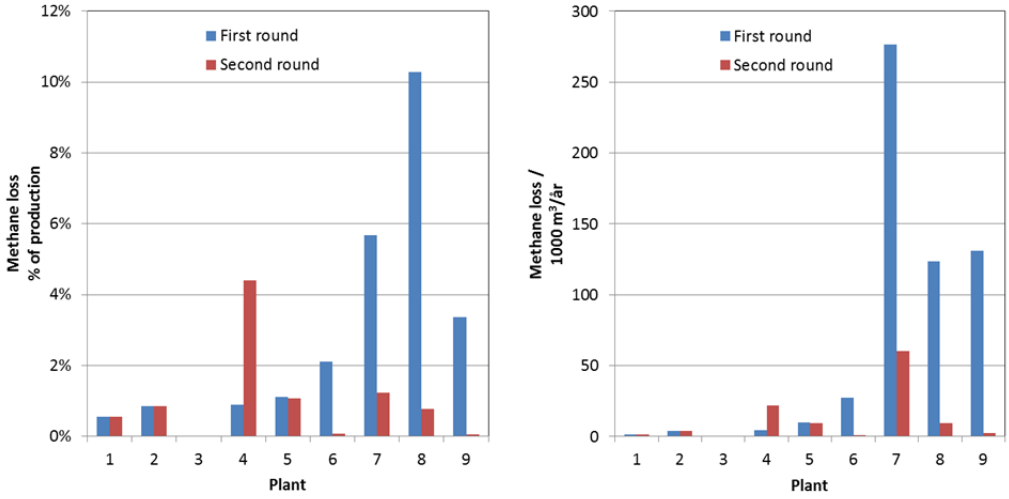


Figure 21 The results of the measurements of the methane loss for the examined biogas plants for the two rounds of measurements. The methane loss is given both as m^3 and as share of the biogas production.

6 References

/1/ DS/EN ISO 25140:2010 Stationary source emissions – Automatic method for the determination of the methane concentration using flame ionization detection (FID)

/2/ DS/EN 12619:2013 Stationary source emissions – Determination of the mass concentration of total gaseous organic carbon - Continuous flame ionisation detection method

/3/ SGC, Rapport SGC 227, Handbok metanmätninger, 2011.

/4/ Methane emission from Danish biogas plants, Main report. AgroTech, June 2015

Appendix A
Source list for the literature survey

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15. **Livscykelanalys av biogas från avloppsreningsverksslam.** Swedish Gas Technology Center. *Rapport SGC 219-1102-7371*. 2010.
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17. **MEASURING FUGITIVE EMISSIONS OF HYDROCARBONS AT GAS PROCESSING PLANTS**. Chambers, Allan. *15th Annual Emission Inventory Conference*. 2006.
18. **Measuring methane emissions on biogas plants.** Schillig, Frank. *BiogasWorld, Berlin, 24th February 2012*. 2012.
19. **Meeting emission targets under uncertainty – the case of Finnish non-emission-trading sector.** Hast, A.; Ekholm, T.; Savolainen, I.. *Mitig Adapt Strateg Glob Change (2013)*. 2012.
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Appendix B
Performance criteria of the methane measuring system according to standard

The table below is copied from the standard *DS/EN ISO 25140 Stationary source emissions - Automatic method for the determination of the methane concentration using flame ionisation detection (FID*) and indicates the performance criteria of the analyser and measuring system used for determination of methane according to the standard.

Table 1 Relevant performance criteria of the analyser and the measuring system to be evaluated during the general performance test and by means of ongoing QA/QC in the laboratory and during field operation

Performance characteristic	Performance criterion	General performance test	QA/QC in the laboratory	Field application
Response time	⩽ 60 s	×	×	×[f]
Repeatability standard deviation at zero point	⩽ 1,0 % of upper limit of the lowest measuring range used[a]	×	×	—
Repeatability standard deviation at span point	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	×	—
Lack of fit	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	×	—
Influence of atmospheric pressure[b], for a pressure change of ± 2 kPa	⩽ 1,0 % of upper limit of the lowest measuring range used[a]	×	—	—
Influence of sample volume flow	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	—
Influence of sample gas pressure at span point, for a pressure change of 3 kPa	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	—
Influence of ambient temperature, for a change of 10 °C	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	—
Influence of voltage, at −15 % below and at +10 % above nominal supply voltage	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	—
Influence of inorganic interference gases[c]	⩽ 4,0 % of upper limit of the lowest measuring range used[a]	×	×	—
Oxygen interference	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	×	—
Converter efficiency, tested with ethane	⩾ 98,0 %	×	×	—
Methane loss[d]	⩽ 15,0 %	×	—	—
Zero drift[e], within 24 h	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	×
Span drift[e], within 24 h	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	×	—	×
Period of unattended operation for permanently installed AMS	⩾ 8 days	×	—	×
Losses and leakage in the sampling line and conditioning system	⩽ 2,0 % of upper limit of the lowest measuring range used[a]	—	—	×

[a] The upper limit of the lowest measuring range used should be selected depending on the application such that the measured values lie within 20 % to 80 % of the analyser range.

[b] The tested sample pressure is defined in the manufacturer's recommendations.

[c] See Table B.1.

[d] The temperature dependent methane loss is compensated for in the calibration process.

[e] The frequency of zero and span checks is specified in Table 2.

[f] If sampling line length exceeds the length applied in the general performance test.

Appendix C
Measuring equipment used during quantification tests

FID detector

Instrument supplier:	Mess & Analysentechnik Thermo FID
Range:	0 – 1.000.000 maximum
	(Arbitrary range can be selected)

Uncertainty contributions

Basic uncertainty	1 % FS
Temperature	2 % relative
Linearity	1 % FS
Repeatability	1 % FS
Calibration gas	2 % relative

Technical Data

Main Power 115 - 230Volt/50-60Hz (model MK & cat.heater 115V or 230V)
Power consumption 250VA
Additional temperature controller for external heated sample probe 1000VA
1 x analog INPUT (for H2 – control) 4 - 20mA
1 x serial printer interface RS232 EPSON compatible
1 x serial interface, Remote Control/Service RS232/485 on COM2
1 x standard analog OUTPUT measurement reading 0/4-20mA, 600 (not galvanic isolated)
Optional 4 x analog OUT (readings/alarms) 0/4-20mA, 600, galvanic isolated
OUTPUT Engineering Units (selectable) ppm, mg/m³, g/m³, Vol.%, %UEG
Instrument Range (Full Scale) 0-1...500 000 mg org.C/m³
Measurement Range (free selectable) Linear to Full Scale
Lower Detectable Limit < 0.01mg org.C/m³
Response Time T_{90} (90%-reading, gas input at instrument) < 0.5 sec. @reading >20mg org. C/m³
[TÜV requirement T_{90} = less than 5 seconds]
Response time T_{90} (model „MK“ probe length 0.5m) < 3 sec. @reading >20mg org. C/m³
[TÜV requirement T_{90} = less than 7,5 seconds]
Sample Flow (ejector pump driven) 2, 5, 25 or 90l/hr (@1013mbar)
Ejector pump pressure 800 - 1600mbar abs.
Gas pressure using external/internal membrane sample pump 800 - 1200mbar abs.
Detector temperature (free selectable) 95°C - 200°C (203°F-392°F)

Probe temperature range (free selectable) 60°C - 200°C (140°F-392°F)
Probe temperature controller Pt100, 230V/50Hz, 4 Amp
Environmental temperature (model PT, TG, ES, 19") -5°C to +40°C (23°F -104°F)
(for other temp. range consult factory)

Methane cutter

Model 320 Specification

SPECIFICATION

- **Converter Chamber**
  Fully Heated
- **Wetted Materials**
  316 Stainless Steel
  Catalyst
  PEEK
- **Gas Connections**
  ¼" Stainless Steel
- **Gas Change Over Valve**
  Heated Ball Valve
- **Chamber Temperature**
  Fully Adjustable
- **Temperature Control**
  Accurate PID Controlled
- **Warm Up Time**
  60 minutes
- **Sample Settle Time**
  <30 minutes
- **Drift**
  <20ppm Methane Equivalent in 1hr
- **Filter**
  Stainless Steel Sintered Disk
- **Sample Flow**
  2 L/min maximum
- **Inlet THC Concentration**
  2000ppm C_3H_8 (Propane) equivalent maximum HC cutting ability
  Unlimited CH_4 (Methane) measurement (THC analyser permitting)
- **Power Requirements**
  320W
- **Weight**
  Approx. 10Kg

320 EXTERNAL CUTTER CHECK LIST

Serial Number 19540	**Customer** Duotek		
Works Order 21754	**Date** 17 December 2013		
	115V ☐	**230V** ☒	
Signature	**Initials** G.D.	**QA**	

Section	Test	Results	
Visual Inspection	Assembly	OK	
	Wiring	OK	
	Works Order Form	Yes	
	Sales Order Form	No	
	Serial Number	19540	
Initial Safety	Earth Continuity	< 0.25 Ω	
	Mains Isolation	> 10 MΩ	
Temperature	Time to Temperature	11 Minutes	
	Confirm Set Temperature	253 °C	253 °C
Flow Rates	Flow	1.0 l/min	2.0 l/min
Cutter Efficiency	Methane Concentration Factor	1.010 %	1.020 %
	Propane Cut (>98%)	>99 %	>98 %
Calibrated Gas Type	Supplier	Bottle Certificate №	
1000ppm C_3H_8 in Air	BOC	123335	
500ppm CH_4 in Air	BOC	1231380	
Final Safety	PAT Test	Pass	
Completion	Sales Order Form	No	
	Visual Inspection	Pass	
	Documentation Complete	Yes	