

Biomethane/biogas - Determination of siloxanes

1 Scope

This document gives general guidance for the sampling and analysis of siloxanes in biomethane/biogas. The method focuses on the following siloxanes:

- Silanol, trimethyl-
- Disiloxane, hexamethyl-, referred as L2
- Trisiloxane, octamethyl-, referred as L3
- Tetrasiloxane, decamethyl-, referred as L4
- Pentasiloxane, dodecamethyl-, referred as L5
- Cyclotrisiloxane, hexamethyl-, referred as D3
- Cyclotetrasiloxane, octamethyl-, referred as D4
- Cyclopentasiloxane, decamethyl-, referred as D5
- Cyclohexasiloxane, dodecamethyl-, referred as D6

The total siloxanes content expressed in mg Si/m³ is then calculated from the concentration of individual siloxanes and the fractional amount of silicon present in a particular siloxane.

2 Term and definition

3 Principle

A measured volume of sample air is drawn through one sorbent tube where siloxanes are retained while highly volatile organic compounds as methane pass through. Analysis of the tubes is then carried out by thermal desorption (TD) in which the adsorbed substances are released with heat and then transferred into a gas chromatograph (GC) equipped with a capillary column and a mass spectrometer (MS). The mass spectrometer is set to scan a few selected ions, which increases the selectivity and detection limit.

The use of the specific ions in addition to the retention time insures positive identification of a siloxane.

4 Chemicals and materials

4.1 Siloxanes (silanol, trimethyl, L2, L3, L4, L5, D3, D4, D5, D6), for calibration purposes

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4.2 **Dilution solvent**, for preparing blend solutions for liquid spiking. This should be of chromatographic quality.

4.3 **Sorbents**, each sorbent should be preconditioned and kept in a clean atmosphere. Example of sorbent: Tenax TA 60/80 mesh (2,6-diphenylphenylene oxide polymer).

4.4 Solutions for liquid spiking

4.4.1 Solution containing approximately 1 mg/ml of each component

Accurately weigh approximately 50 mg of each of the 9 compounds into 50 ml a volumetric flask, starting by the least volatile compound. Make up to 50 ml with dilution solvent.

4.4.2 Solution containing approximately 0.2 mg/ml of each component

Accurately weigh approximately 10 mg of each of the 9 compounds into 50 ml a volumetric flask, starting by the least volatile compound. Make up to 50 ml with dilution solvent.

4.4.3 Solution containing approximately 0.04 mg/ml of each component

Introduce 25 ml of dilution solvent into a 50 ml volumetric flask. Add 10 ml of solution described in 5.5.2. Make up to 50 ml with dilution solvent, stopper and shake to mix.

4.4.4 Solution containing approximately 0.01 mg/ml of each component

Introduce 25 ml of dilution solvent into a 50 ml volumetric flask. Add 2.5 ml of solution described in 5.5.2. Make up to 50 ml with dilution solvent, stopper and shake to mix.

4.5 Standard tubes loaded by liquid spiking

Prepare loaded tubes by injecting aliquots of solutions for liquid spiking onto clean sorbent tubes, typically 1 μ l and 2 μ l aliquot. Tubes are purged under a flow of inert gas to eliminate most of the dilution solvent from the tube.

4.6 **Field tube blanks**, a conditioned tube with seals transported to field sites and then returned to the laboratory for analysis

5 Apparatus

5.1 **Sorbent tubes**, compatible with the desorption apparatus to be used (6.7), typically containing 200 mg sorbent. The tubes are sealed with for example screw-cap fittings with polytetrafluoroethylene. Blank levels of siloxanes on unspiked, conditioned tubes should be determined.

5.2 **Syringes**, a 5 or 10 μ l liquid syringe readable to 0.1 μ l

5.3 **Sampling system**, capable of accurately and precisely drawing biomethane/biogas flow of 50-100 ml/minute through the sorbent tubes.

5.4 **Tubings**, silicon-free

5.5 **Gas chromatography/mass spectrometer**, EI mode

5.6 **Capillary column**, for gas chromatography. Example of column: 95% dimethylpolysiloxane, 5% diphenyl, 50 m long, 0.32 mm inner diameter and 1 µm film thickness.

5.7 **Thermal desorption instrument, preferably two-stage thermal desorption** in which the adsorbed substances are first released with heat and then transferred to a cooling trap for focusing. The cooling trap is reheated quickly and the substances are released and transported on to the gas chromatography column for separation.

6 Sampling

Collection of an accurately known volume of biomethane/biogas is critical to the accuracy of the results. Prior to sampling, insure that the sampling flow rate has been calibrated over a range including the rate to be used for sampling (typically 50-100 ml/min), with a test tube. The flow must be stable over some minutes. The seal of the tubes are removed just prior to initiation of the sampling. Operate the sampling for the desired time (typically 1 to 4 minutes) and record the following parameters on an appropriate data sheet: sampling location, sample name, flow rate and time, rotameter reading (if applicable), tube number, any other relevant information. Remove the tube and seal it. At least 3 replicates should be taken for one site.

The use of a field tube blank (a conditioned tube with seals transported to field sites and then returned to the laboratory for analysis) is recommended.

7 Sample handling

Contamination of the Tenax tube with the compound(s) of interest shall be avoided. The user must be careful in the storage and handling of the tubes throughout the entire sampling and analysis process to minimize this risk. Make sure that the gas to analyse does not come in contact with silicon containing materials (tubings, greases...).

8 Procedure

8.1 Desorption and analysis

The mass spectrometer is tuned in accordance with the manufacturer's instructions. Chromatograms are recorded in full scan (typically 32 to 450 absolute mass units (amu)) and selected ion monitoring/recording mode (SIM/SIR). A list of diagnostic ions are given in Table 1.

Table 1 — Characteristic masses of siloxanes

	Diagnostic ion 1 m/z	Diagnostic ion 2 m/z
Silanol, trimethyl-	75	45

L2	147	73
L3	221	73
L4	207	73
L5	281	73
D3	207	96
D4	281	73
D5	73	267
D6	73	341

Analyse tubes collected in field, field tube blanks and standard tubes loaded by liquid spiking by thermal desorption and gas chromatography with the same desorption conditions. Desorption conditions should be chosen such that desorption from the sample tube is complete, and no sample loss occurs in the secondary trap. Typical parameters are:

Desorption temperature: 250-300°C

Desorption time: 5 to 10 minutes

Carrier gas: helium

Desorption flowrate: 30 to 60 ml/min

Split ratios: Split ratios between the sample tube and secondary trap and between the secondary trap and the column should be selected dependent on expected concentration.

8.2 Calculations

Data from calibration standards (5.4) is used to calculate a response factor (area/nanogram injected) for each component of interest. Analyte quantities in nanograms on a sample tube are calculated as the area of the analyte characteristic ion for the sample tube divided by the response factor.

The concentration of the each siloxane in the sampled biomethan/biogas, c_m , expressed in $\mu\text{g}/\text{m}^3$, is calculated by means of equation (1):

$$C_m = \frac{m_s - m_{sb}}{V}$$

Where:

m_s is the mass of a siloxane present in the actual sample in nanograms

m_{sb} is the mass of a siloxane present in the blank tube, in nanograms

V is the volume of sample taken, in litres.

The total siloxanes content expressed in $\text{mg Si}/\text{m}^3$ is calculated as the sum of the individual siloxanes each corrected by the fractional amount of silicon present in a particular siloxane.

9 Bibliography

ISO 16017-1:2000, Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography, part 1: Pumped sampling.

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