INTERNATIONAL STANDARD

ISO 2613-2

First edition
2023-11

Analysis of natural gas — Silicon content of biomethane —

Part 2:
Determination of siloxane content by gas chromatography with ion mobility spectrometry

Analyse du gaz naturel — Teneur en silicium du biométhane —

Partie 2: Détermination de la teneur en siloxanes par chromatographie en phase gazeuse avec spectrométrie de mobilité ionique

Reference number
ISO 2613-2:2023(E)

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Published in Switzerland

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 408, *Natural gas and biomethane for use in transport and biomethane for injection in the natural gas grid,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

A list of all parts in the ISO 2613 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document describes a method for the determination of the siloxane content of biomethane that is applicable to both laboratory and online analyses.

Siloxanes are a common contaminant in biogas, caused by their extensive use in common household products such as cosmetics and detergents. These products eventually become entrained in waste streams that are used to generate biogas. Additionally, siloxanes are sometimes added to digesters as anti-foaming agents to improve generation efficiency.

If not effectively removed, siloxanes can cause damage to gas processing and vehicle injection equipment through formation of silica deposits at high temperatures. Many gas distributors require measurement reports to demonstrate that the resultant biomethane conforms with their requirements, which typically includes siloxane content due to its potential to cause damage. Additionally, producers may wish to monitor siloxane content for process optimisation purposes.

The technique described in this document is commercially available and tailored specifically to measuring siloxanes within biomethane at low concentrations (for instance, as specified in EN 16723-1[10] and EN 16723-2[11]). It is suitable for use both in the laboratory and field.

Analysis of natural gas — Silicon content of biomethane —

Part 2:
Determination of siloxane content by gas chromatography with ion mobility spectrometry

1 Scope

This document describes a gas chromatography – ion mobility spectroscopy (GC-IMS) method for the determination of the concentration of siloxanes in biomethane. The method is applicable to the following siloxanes:

- hexamethyldisiloxane (L2);
- octamethyltrisiloxane (L3);
- decamethyltetrasiloxane (L4);
- dodecamethylpentasiloxane (L5);
- hexamethylcyclotrisiloxane (D3);
- octamethylcyclotetrasiloxane (D4);
- decamethylcyclopentasiloxane (D5);
- dodecamethylcyclohexasiloxane (D6).

This document describes suitable calibration and measurement strategies to quantify siloxanes in (bio) methane around and above the 0,3 mg m^{-3} (14 µmol mol^{-1}) level and applies to analyses within absolute pressure ranges of 1 bar – 2 bar[1], temperatures of 0 °C – 40 °C and relative humidity < 90 %.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 6142-1, *Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures*

ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 6144, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric method*

ISO 6145-1, *Gas analysis — Preparation of calibration gas mixtures using dynamic methods — Part 1: General aspects*

ISO 7504, *Gas analysis — Vocabulary*

ISO 10715, *Natural gas — Gas sampling*

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[1] 1 bar = 0,1 MPa =10^5 Pa; 1 MPa = 1 N/mm^2.

ISO 10723, *Natural gas — Performance evaluation for analytical systems*

ISO 14532, *Natural gas — Vocabulary*

ISO 14912, *Gas analysis — Conversion of gas mixture composition data*

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/IEC Guide 98-3, ISO 7504, ISO 14532 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

3.1
ion mobility spectrometry
IMS
analytical method used to separate and identify ionised molecules in the gas phase based on their mobility in a carrier gas under an electric field

4 Principle

A gaseous biomethane sample is drawn into a sample loop via a vacuum pump. The sample is injected onto a GC column, which separates the individual components in the gas mixture. As they exit the column, the components are ionised and passed into a drift tube. The drift tube applies a defined electric field, and a flow of inert nitrogen drift gas causes the ions to drift at different rates based on their mass and geometric structure onto a detector.

The instrument is calibrated by sampling an appropriate range of siloxane concentrations and using the detector output to generate a calibration function. The function can then be applied to unknown samples to calculate the concentration of siloxanes. This can then be summed to calculate total siloxanes and total silicon.

The method is applicable to siloxanes within the concentration ranges provided in Table 1.

Table 1 — Application ranges

Component	Abbreviation	Formula	Lower limit (mg m^{-3})	Upper limit (mg m^{-3})
hexamethyldisiloxane	L2	$C_6H_{18}OSi_2$	0,1	10,0
octamethyltrisiloxane	L3	$C_8H_{24}O_2Si_3$	0,1	10,0
decamethyltetrasiloxane	L4	$C_{10}H_{30}O_3Si_4$	0,1	10,0
dodecamethylpentasiloxane	L5	$C_{12}H_{36}O_4Si_5$	0,1	10,0
hexamethylcyclotrisiloxane	D3	$C_6H_{18}O_3Si_3$	0,1	10,0
octamethylcyclotetrasiloxane	D4	$C_8H_{24}O_4Si_4$	0,1	10,0
decamethylcyclopentasiloxane	D5	$C_{10}H_{30}O_5Si_5$	0,1	10,0
dodecamethylcyclohexasiloxane	D6	$C_{12}H_{36}O_6Si_6$	0,3	10,0

NOTE Trimethylsilanol and trimethylsilane are outside of the scope of this document, but these silicon-containing compounds can also be found as impurities within biomethane.

5 Materials

5.1 Calibration gases

Calibration gases containing siloxanes of appropriate concentrations for calibration in a methane matrix. Calibration gases shall be traceable to a national standard and certified in accordance with ISO 6142-1, ISO 6143 or ISO 6144.

The two acceptable methods for multipoint calibration of siloxane analysers are:

a) the use of individual calibration gas mixtures in the cylinders for each concentration needed;

b) the use of one calibration gas mixture in the cylinder containing siloxanes in methane, diluted as necessary with methane, to obtain the calibration concentrations needed.

5.2 Diluent gas

The diluent gas is a pressurised cylinder of pure methane or ≥ 99,999 cmol/mol purity grade, certified to contain less than the limit of detection (LOD) of siloxanes for the measurement system. Use of a diluent gas is not required if individual certified standards are used for calibration.

NOTE The method described in this document was validated using methane of ≥ 99,999 cmol/mol purity grade. The use of lower purity grades requires validation of the method prior to use.

5.3 Carrier and drift gas

The carrier and drift gas is pressurised nitrogen of at least 10 bar pressure and ≥ 99,999 cmol/mol purity grade.

NOTE 1 bar = 0,1 MPa = 10^5 Pa; 1 MPa = 1 N/mm^2. The method described in this document was validated using nitrogen of ≥ 99,999 cmol/mol purity grade. The use of lower purity grades requires validation of the method prior to use.

6 Apparatus

6.1 **GC-IMS analyser**, containing injection device, oven, regulation system for temperature and pressure control. Chromatographic column tubing should be made of a material inert to siloxane compounds (for example, passivated stainless steel or silicon-free glass). Column stationary phase in combination with the ion mobility spectrometer shall be able to separate the siloxane compounds to be analysed.

An example schematic is provided in Annex A.

6.2 **Pressure regulator**, to supply carrier and drift gas pressures from source cylinders to the analyser, as specified by manufacturer.

6.3 **Dilution device**, any device capable of diluting with methane a parent siloxanes gas mixture to a required concentration level. The dilution device shall be capable of providing thorough mixing of the parent siloxanes gas mixture and methane, and capable of providing the required pressure to the GC-IMS analyser. It shall be capable of providing the required flow rate of the calibration gas and diluent gas in order to produce the required gas mixture composition. It shall be made of or passivated with a material inert to siloxane compounds, if in contact with siloxane species. It is important that the wetted surfaces are made of appropriate materials (or have appropriate passivation) to prevent siloxane adsorption. Guidance on passivation suitability is available in open access scientific literature[12],[13],[14].

Uncertainty of the dilution factor shall be known and taken into account in the uncertainty budget. Dilution device shall be calibrated according to ISO 6145-1. Use of a dilution device is not required if individual certified standards are used for calibration.

NOTE Dilution device can be based on methods specified in the ISO 6145 series.

6.4 Auxiliary valves, tubing and accessories, for controlling the flow of biomethane into the analyser. The materials should have passivation or adsorption resistance appropriate for the measurement of siloxanes. Passivation of stainless steel using proprietary techniques is available to inhibit adsorption as demonstrated by research[12]. Results of investigations into coating suitability is available as part of research project outputs, such as EMRP ENG54 "Metrology for biogas"[13] and EMPIR 16ENG05 "Metrology for biomethane"[14].

7 Sampling

7.1 General

It is important that an appropriate sampling procedure is employed for the analysis of siloxanes, due to their tendency to adsorb on to the wetted surfaces of certain materials. Additionally, there is the potential for siloxanes to condense out of gas streams due to temperature effects. Inappropriate sampling can lead to bias in the measurements and therefore sampling considerations should be of high importance.

Carry out representative sampling in such a way that the sample represents the bulk of the gas at the time of sampling. Sampling and sample transfer shall be in accordance with ISO 10715.

7.2 Safety precautions

Safety precautions relating to personnel, equipment, flammability, personal protective equipment and transportation are described in the ISO 10715, which should be followed.

7.3 Temperature control

When a cylinder of a calibration or sample gas mixture arrives at the place of use, ensure that the cylinder temperature is kept above the condensation temperature (as stated on the certificate). If condensation has occurred during transportation or storage, contact the producer for re-homogenisation advice before usage.

Always store both calibration and sample gases at the same suitable temperature and ensure both are homogenous prior to use.

To reduce adsorption of siloxanes when using a calibration gas or a sample, the transfer lines from the cylinder and the gas chromatograph loop injection valve may be heated (according to manufacturer's guidelines).

7.4 Construction materials

Use appropriate materials or passivation that reduce siloxane adsorption to a level that will not cause analytical bias (e.g. proprietary treatments are available to produce passivated stainless steel). The general considerations of ISO 10715 should always be followed.

7.5 Cleanness

When a calibration or sample gas cylinder is to be connected to a gas system, always visually inspect the connection on the cylinder valve outlet. Carefully clean out any dirt, dust or particles with a dust-free cloth. Any trace of humidity should be purged out with dry inert gas.

Make sure that all transfer lines are free of dirt, rust, grease or other particles. Change all tubing/ fittings if there is any suspicion of impurities or damage. Particle filters may be helpful, but they shall only contain material proposed in ISO 10715 and shall not cause adsorption of siloxanes.

7.6 Sampling of biomethane into vessels

A previously evacuated vessel is used to gather the sample. This could be for example, a gas cylinder or sample cannister. It is important that the wetted surfaces are made of appropriate materials (or have appropriate passivation) to prevent siloxane adsorption. This sampling method is applicable where the biomethane pressure is either above or below atmospheric pressure, and the source temperature is either greater or less than the sample vessel temperature.

NOTE An example of this technique is described in ISO 10715.

7.7 Installation of the calibration gas cylinder

The installation of a calibration gas cylinder and use of the certified gas mixture is dependent on the method by which a gas sample is taken and is to be analysed/compared. To minimise the surface in gas contact, it is important to connect the calibration gas as near as possible to the injection point. The gas flow from the calibration cylinder may be diluted using a dilution device (see 6.3).

NOTE One principle for the connection of a calibration gas cylinder in direct sampling is shown in ISO 10715.

7.8 Pressure control

Some measurements may be carried out at close to atmospheric pressure, in which case a pump should be used to draw sample into the sample loop. If pressure reduction is necessary, only use a pressure regulator made of the material approved for use with the gas mixture in question as recommended by the regulator manufacturer.

To further minimise any adsorption effects, a regulating needle valve (of appropriate material or passivation) could be connected directly to the gas cylinder or sample point valve. Ensure that the certified pressure range of this valve suits that of the total system and that no local or national safety regulation prohibits such an arrangement.

Never use a calibration gas mixture with a total pressure lower than that recommended on the certificate. If no recommendation is stated, stop using the mixture if the total pressure is lower than 10 % of the certified filling pressure.

Always use the same pressure when injecting the calibration mixture and the biomethane sample.

It is recommended to use the same pressure or flow reducers for both the calibration gases and samples where possible, to minimise the potential for bias caused by this. If diluent gases are used, the pressure should be regulated to the same pressure that the diluent system was calibrated to.

7.9 Purging of wetted flow path

Purging of the system may be required if the wetted flow path has been exposed to gases other than those being measured (for example ambient air). Due to the strong tendency of siloxanes to adsorb to different materials, it is important to purge all wetted surfaces with the gas to be measured from the calibration cylinder or gas sample to the injection point. The purging should include a minimum number of “fill and empty” cycles as described in ISO 10715.

When analysing calibration or sample gases with different concentration levels, always flush the transfer lines and the valves with dry nitrogen or methane in order to avoid memory effects. Additional purge cycles may be required when moving from high to low siloxane concentrations.

7.10 Flow control

As stated in ISO 10715, turbulent flow is advantageous in a sampling system. The flow rate of the calibration gas with 3,175 mm (1/8 in) tubing is recommended to be between 20 ml min^{-1} and 50 ml min^{-1} as it passes through the sample loop. Other flow rates may be used, as recommended by the manufacturer. The flow rate of sample gases should be the same as the calibration gases.

For near atmospheric pressure samples, flow can be achieved through use of a sampling pump, placed after the sample loop to avoid contamination.

7.11 Diffusion control

Any leakage caused by diffusion should be avoided by using pressure regulators with non-permeable membranes.

Be aware that using polymer types of tubing in gas transfer lines can cause problems related to diffusion of humidity from the environmental air.

8 Calibration

8.1 Calibration procedure

The instrument can be calibrated over the desired range of interest using either multiple calibration gas mixtures in cylinders or one calibration gas mixture in a cylinder together with a dilution device and a diluent gas. The calibration shall be in accordance with ISO 10723. Further guidance is available in ISO 6974-1[7].

8.2 Frequency of calibration

Perform a multipoint calibration when:

a) the analyser is first installed;

b) the analyser has had maintenance that could affect its response characteristics;

c) the analyser shows drift in excess of performance specifications as determined via comparison with a calibration standard as part of routine calibration checks.

9 Measurement procedure

9.1 Safety precautions

Follow all safety guidance as recommended by the manufacturer. The analyser should only be opened or altered by authorised persons as identified by the manufacturer due to potential high voltages and the presence of an ionisation source. Ensure that the environment is appropriate to carry out the procedure based on local and national safety requirements.

9.2 Analysis

Establish calibration using an appropriate number of calibration standards. “An appropriate number” of calibration standards is three for a linear function, five for a second-order polynomial, seven for a third-order polynomial, five for a power function and five for an exponential function. Requirements within ISO 6143 shall be followed for determining the analysis function.

Check the analyser system operating parameters are suitable for performing the required analysis, and set the sample flow rate.

Perform quantitative analysis and determine the mass concentration and uncertainty budget of siloxanes in the sample gas in accordance with ISO 6143 and ISO 14912 (if required to convert compositional data). Example method parameters and analytical procedure are provided in Annex A.

10 Expression of results

10.1 Quantities and units

The content of siloxanes within biomethane shall be expressed in SI units of amount fraction (e.g. μmol mol^{-1}) or mass concentration (mg m^{-3}). Composition of the calibration gas mixtures is usually expressed in units of amount fraction. The composition data shall be converted from amount fraction to mass concentration according to ISO 14912. When the results are expressed in terms of mass concentration, respective reference pressure and temperature values shall be specified.

10.2 Uncertainty

The uncertainty of the measurement shall be evaluated and reported. The first step shall identify the individual sources of random and systematic error in the method. These are then estimated and/or determined experimentally and combined in an uncertainty budget. Correlations between individual sources should be investigated and taken into account in accordance with the provided mathematical model. Finally, the combined uncertainty is multiplied by an appropriate coverage factor to produce an expanded uncertainty. A coverage factor of two is recommended, which gives a level of confidence of approximately 95 % in the calculated value.

NOTE 1 Guidance on evaluation of measurement uncertainty is available in, e.g. ISO 6974-2[8], ISO/IEC Guide 98-3 and Reference [15].

NOTE 2 Terms that contribute to the random variability of the method are generally accounted for in the measurement precision, which can be determined from quality-control data. An error associated with instrumental drift can be estimated, assuming a rectangular probability distribution, by dividing the drift permitted before the instrument is recalibrated by three.

NOTE 3 Systematic errors include, for example, those associated with analyte adsorption to sampling system.

10.3 Test report

The work carried out by the testing laboratory shall be covered by a report which accurately, clearly and unambiguously presents the test results and all other relevant information.

The test report shall contain:

a) the date, time and location of sampling;

b) the value, expanded uncertainty, and coverage factor used;

c) the reference conditions used;

d) a reference to this document.

NOTE ISO/IEC 17025[9] contains further guidance on test reports.

Annex A
(informative)

Example of application

A.1 Analytical conditions

Example analytical conditions are provided for a GC-IMS system in Table A.1.

Table A.1 — Example GC-IMS method parameters

Parameter	Setting
Ionisation source	Tritium (300 MBq - below exemption limit in EURATOM)
GC column	30 m (5 % Diphenyl, 95 % dimethyl polysiloxane) x 0,44 mm x 0,32 µm FS-SE-54-CB-1
Column temperature	80 °C isothermal
Carrier flow rate	15 ml/min
Carrier/Drift gas purity	Nitrogen 5,0 purity grade
Sample loop volume	1 ml
Method run time	60 min
Analytes measured	L2, L3, L4, L5, D3, D4, D5, D6, (+ total Si, total SiO_2, total siloxanes)

A.2 Analytical procedure

Select a suitable number of calibration gases for use in instrument calibration and connect to the GC-IMS using an appropriate regulator and connections as detailed in Clause 6.

Purge the regulator and sample lines to instrument thoroughly using the calibration gases and establish an appropriate flow through the instrument sampling loop.

Calibrate the instrument using the traceable calibration gases, ensuring that the regulator and sampling lines are thoroughly purged prior to each injection with the calibration gases.

Obtain sufficient repeat measurement of the calibration gas. A minimum of five stable repeat injections of each calibration gas is recommended (the GC-IMS response should be monitored to confirm stability has been reached).

Repeat for all remaining calibration gases. It is recommended to start from the lowest concentration to minimise the possibility of carry-over in subsequent measurements caused by siloxane compounds adsorbing and desorbing from the sampling lines.

Connect the biomethane sample to the GC-IMS and purge lines thoroughly with the sample gas.

Establish an appropriate flow of biomethane through the GC-IMS sample loop (equivalent to that of the calibration gases used during calibration step).

Obtain sufficient repeat measurements of the biomethane sample gas. A minimum of five stable repeat injections of the biomethane sample is recommended (the GC-IMS response should be monitored to confirm stability has been reached).

Use calibration function obtained from instrument calibration to calculate the content of each analyte within the biomethane sample.