EMPIR 16ENG05 Metrology for Biomethane
Deliverable D11

Test methods for the conformity assessment of biomethane

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Contents

Notice to the reader

One of the aims in the project "Metrology for Biomethane" was "to develop and validate novel test methods, based on existing calibration methods, for the regular conformity assessment of biomethane during which the content of total silicon and siloxanes, total fluorine and chlorine, ammonia, terpenes, compressor oil, amines, and biogenic methane (based on determining the ^{14}C content in biomethane and blends of biogas and natural gas) are measured."

Altogether nine methods have been proposed and evidence of their validation has been provided:

- An instrumental method for measuring the total concentration silicon in biomethane. A liquid impinger is used to trap the silicon-containing species. Metrological traceability is achieved by calibrating with an aqueous silicon solution.
- For siloxanes, a method based on gas chromatography with ion mobility spectrometry has been developed and validated. The instrument is calibrated using static gas standards containing the relevant siloxanes.
- For hydrogen fluoride and hydrogen chloride, a method based on ion-exchange chromatography has been developed and validated.
- A method for measuring the amount fractions of volatile organic hydrocarbons has been developed using gas chromatography with a barrier ionisation detector. Also methods with other detectors have been developed and evaluated. Calibration is performed with either static gas standards or adsorption tubes.
- For ammonia, spectroscopic methods using Optical Feedback Cavity-Enhanced Absorption Spectroscopy and UV/vis spectroscopy have been proposed. A multipoint calibration is required using dynamic or static gas standards to obtain results with metrological traceability.
- For terpenes, a method using a micro-gas chromatograph has been developed. This method can be used in the field. Static gas standards can be used for the calibration of the instrument.
- For compressor oil concentration, a sampling and analysis method have been developed using gas chromatography. The instrument can be calibrated by standards prepared as dilutions of compressor oil.
- For amines concentration, a gas chromatography method involving thermal desorption has been developed. Calibration is performed by using spiked adsorption tubes.
- For biogenic methane content, a radiocarbon method has been validated. The method involves converting the biomethane into carbon dioxide, which is then analysed for its radiocarbon content. The method is well-aligned with similar methods for other materials.

This document collates the descriptions of the said methods. At the time of writing, these methods are under consideration by ISO/TC193/SC1/WG25 "Biomethane" to be processed to become ISO standards.

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Disclaimer

1 Determination of amines content

1.1 Scope

This document specifies tests methods involving Thermal Desorption Gas Chromatography with Flame Ionization and/or Mass Spectrometry detectors (TD-GC-MS/FID) for the analysis of five amines in biomethane, natural gas and biogas, namely:

- Monoethanolamine (MEA)
- Diglycolamine (DGA)
- Diethanolamine (DEA)
- N-methyldiethanolamine (MDEA)
- Piperazine (PZ)

The described method was specifically developed for these five compounds. Information about the compounds is given in Annex A. No information is given about biomethane sampling.

1.2 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 13443 *Natural gas -- Standard reference conditions*

ISO 14532, *Natural gas — Vocabulary*

ISO 19229, *Gas analysis — Purity analysis and the treatment of purity data*

1.3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14532 and the following apply.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

1.3.1

amine

chemical compound consisting nitrogen atoms bound to hydrogen and/or carbon atoms having the general formula R_3N

[SOURCE: ISO/TR 27912:2016, 3.5]

1.3.2
Gas chromatography-mass spectrometry (GC-MS)

method that combines the features of gas-liquid chromatography and mass spectrometry to qualitatively and quantitatively analyse volatile compounds within a test sample (Annex A)

[SOURCE: ISO/TS 16550:2014, 2.3]

1.4 Reference conditions

Unless stated otherwise, all volumes are for the real dry gas at ISO Standard Reference conditions of 15 °C and 101,325 kPa (see for other conditions ISO 13443).

1.5 Principle

A known volume of biomethane is actively sampled on a sorbent Tenax TA® tube. Amines compounds are then trapped on the sorbent and tubes are analysed in laboratory. Analysis is performed by thermal desorption at high temperature. When desorbed, compounds are sent on a cold trap prior to their transport in the gas chromatograph column and their detection by flame ionisation detector and/or mass spectrometry.

1.6 Materials

1.6.1 Amines standards

Pure amine components should be used, and their purity be analysed based on ISO 19229.

Amines (except DGA) should be at least 99% purity grade. For DGA, purity should be at least 98%,

1.6.2 Dilution solvent

Methanol (chromatographic quality) shall be used as dilution solvent for the preparation of calibration standards.

1.6.3 Tenax TA® tubes

Sorbent tubes shall be Tenax TA® based polymer (2,6-diphelylene oxide polymer). Commercial Tenax TA® contain many impurities that must be removed before any sampling. Thus, tubes should conditioned at high temperature under inert flow gas. It is also recommended to use stainless steel tubes with proper coating treatment (amines are photosensitive).

1.6.4 Gas chromatograph (GC)

Gas chromatograph must be equipped with a flame ionization detector (FID) and/or a mass spectrometer (MS). Moreover, the GC should be supplied with a thermal desorption system associated to a cryogenic trap. If FID is used, the selectivity of the method regarding amines should be established. Indeed, other components present in biomethane might interfere with amines peaks on the chromatogram.

1.6.5 Capillary column

A GC capillary column adapted for the separation of ethanolamines shall be selected, such as:

- Volatile amines, 30 m, 0.32 mm ID, 5 µm
- Rtx-5 Amine, 30 m, 0.25 mm ID, 0.50 µm

1.6.6 Thermal desorption (TD) system

A typical apparatus shall be characterized by the features listed below:

- An automatic sample-tube loading

- A thermal desorption unit able to heat the tubes: the desorption temperature and time should be adjustable, as is the carrier gas flow rate
- A cryogenic trap able to concentrate the desorbed compounds, and able to reach -40 to -100°C
- A direct connection to the GC

1.6.7 Precision syringes

Precision syringes intended for tubes spiking shall be readable to 0.1 µL or better. The capacity shall be in agreement with the volume to be deposited on the sorbent. For example, a 20 µL syringes shall be used if the spiking volume is of 20 µL.

1.6.8 Conditioning of the sorbent tubes

Tenax TA tubes should be conditioned before any usage. Conditioning should be performed at 300°C for at least 120 minutes under inert gas flow rate of approx. 50 ml min^{-1} in order to remove any potential impurities present on the sorbent.

1.6.9 Preparation of the calibration tubes

Prior to any sample analysis, a calibration of the five amines should be performed. As no gas standard for the targeted amines is commercially available, the user shall generate himself gas standards in the form of Tenax TA tubes. After preparing the liquid calibration solutions containing the five amines at different concentrations (one solution per calibration point), a proper volume (below 100 µL) of solution should be directly deposited on the sorbent tube (preliminary conditioned).

The following procedure describes the preparation of calibration standards for amines:

First a concentrated liquid mixture containing desired amounts of MEA, DEA, DGA, MDEA, PZ and n-octane is prepared (with mass/volume concentration), then this mixture is diluted with high purity methanol to obtain desired low concentrations of amines (end-mixture). The end-mixture should then be spiked onto sorbent tubes with known volume and calculated mass.

The sorbent tubes can then flushed with nitrogen for proper duration (for example 20 min) to remove major amount of methanol. Then the measurement standards for amine components are ready to be analysed.

Five levels of amine contents shall be prepared as calibration standards, *i.e*. each level contains 100ng, 500ng, 1000ng, 2000ng, and 4000ng (cover the range of the EN16723-1 requirements) of each amine component.

1.7 Analysis

1.7.1 Thermal desorption

Prior to their analysis, sampled tubes are thermally desorbed. Typical conditions for the desorption of amines spiked on sorbent tubes are summarized on the table 1.

Table 1 – thermal desorption conditions

Desorption duration	15 min
Desorption gas flow rate	
Minimum temperature of the cryogenic trap (during the desorption)	-30°C
Maximum temperature of the cryogenic trap (at the end of the desorption)	290°C

Nature of the cryogenic trap sorbent	Tenax TA®
Transfer line temperature	
Split ratio	Split ratios between the sample tube and secondary trap and between the secondary trap and analytical column should be selected dependent on expected concentration

1.7.2 Program temperature of the GC separation

As biomethane is a complex matrix containing potentially several compounds at trace levels, a program temperature is recommended for the separation. The separation method dedicated to amines shall be tested against any potential interfering peaks corresponding to compounds present in biomethane.

1.7.3 Sample analysis

Analysis of the samples shall be performed within 4 weeks after the sampling. Calibration standards, blanks and samples should be analysed in the same sequence. Identification of amines is performed by MS detection and quantification with the chromatograms obtained by FID and/or MS.

1.7.4 Quantification method

Quantification of the five amines, namely MEA, DEA, MDEA, DGA and PZ is performed using areas of the peaks, required to determine a calibration curve. A calibration shall be performed for each amine before any sample analysis. The lowest concentration used shall be at or below the lowest sample concentration.

1.8 Performance characteristics

Before this method is used, its performance characteristics should be determined in accordance with ISO/IEC Guide 98-3 or Fitness for Purpose of Analytical Methods guide from Eurachem. This determination should include, as a minimum, the estimation of uncertainty components from the following steps:

- Sampling
- Desorption efficiency
- Calibration
- Analysis

The accuracy and repeatability of the measuring method are important factors, which shall be determined in order to evaluate the results and the suitability of the method for the intended purpose.

For the calculation of the measurement uncertainty, the following sources of uncertainty shall be considered:

- the purity of the amine chemicals, the uncertainty on the weighing data during preparation of the spiking solution, the miscibility of the solution,
- precision of the analysis.

1.9 Calculations

In order to assess the performances of the developed method, precision of the method should be evaluated i.e. repeatability, intermediate precision and reproducibility. Measurement uncertainties should as well be determined. Detailed description of the calculation method is given in part 6.6.2.1.

In order to determine the amines concentration in the analysed biomethane, the following calculations shall be used:

Calibration curves shall be determined for each amine, with the aim to obtain a relationship between the peak area y and the mass of amines x (see Equation (1)). A linear regression shall be performed do determine a and b (Equation (1)). The mass x is directly linked to the volume of amines solution deposited on the tube.

Example 1 µL of a solution at 100 mg/L of DEA in methanol corresponds to 100 ng of DEA on the sorbent.

$$y = ax + b \quad (1)$$

The integrations of the amines peaks on the biomethane sample chromatogram will lead to the determination of y(amine in biomethane). Using equation (1), the mass of amine on the sorbent is determined:

$$mass\ of\ amine = \frac{y-b}{a} \quad (2)$$

To get back to the concentration of amine in the original gas, the gas volume is required. It corresponds to the volume V of biomethane that crossed the sorbent tube. The final concentration can then be determined using equation (3):

$$y = \frac{mass\ of\ amine}{gas\ Volume} \quad (3)$$

1.10 Test report

The test report shall contain at least the following information:

a) Purpose of the measurements;

b) Description of the sampling location;

c) Precisions about the process method used to upgrade biogas into biomethane;

d) Time and date of the sampling (at the beginning and at the end of the sampling);

e) Sampling conditions (temperature, relative humidity, flow rate, duration);

f) Full description of the sampling procedure;

g) Full description of the analytical procedure;

h) Detection and quantification limits of the analytical method;

i) Concentrations of identified amines, provided with CAS numbers, including calculation and calibration principles used;

j) Uncertainty of the reported results;

Annex A: Characteristics of the amines to be quantified

Table A.1 – Amines to be quantified

Name	Abbreviation	CAS No.
Monoethanolamine	MEA	141-43-5
Diglycolamine	DGA	929-06-6
Diethanolamine	DEA	111-42-2
N-methyldiethanolamine	MDEA	105-59-9
Piperazine	PZ	110-85-0

2 Determination of the ammonia content

2.1 Scope

This document describes several test methods for measuring the amount fraction ammonia in natural gas and biomethane at the trace level (μmol mol^{-1}). The suitable handling and sampling of pressurised mixtures of ammonia in methane that are applied to several different ammonia measurement systems are described. The measurement systems comprise of readily available commercial spectroscopic analysers that are specific to ammonia. These analysers are considered as a *black box* in terms of their operation, which is dependent on the instructions of the manufacturer. The document describes suitable calibration and measurement strategies to quantify ammonia in (bio)methane around the 10 mg/m^3 (14 μmol mol^{-1}) level.

This document makes references to additional standards that are applied either to Natural Gas analysis and Air Quality measurements. In this document the matrix gas is always methane and the measurand is the amount fraction NH_3.

2.2 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 5725-2:1994, Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method

ISO 6141, Gas analysis — Requirements on certificates for gases and gas mixtures.

ISO 6142, Gas analysis — Preparation of calibration gas mixtures — Gravimetric method.

ISO 6143, Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods.

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

ISO 6145-10, Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 10: Permeation method

ISO 6146, Gas analysis — Preparation of calibration gas mixtures — Manometric method.

ISO 6147, Gas analysis — Preparation of calibration gas mixtures — Saturation method.

ISO 6879, Air quality — Performance characteristics and related concepts for air quality measuring methods.

Note: Amount fraction ammonia is considered as the measurand in this standard which can be used in place of air quality characteristic in ISO 6789:1995

ISO 9169, Air quality — Determination of performance characteristics of measurement methods.

ISO 10715:1997, Natural gas — Sampling guidelines

ISO 10723:2012, Natural gas - Performance evaluation for analytical systems

ISO 14532:2014, Natural gas — Vocabulary

EN ISO 17179:2016, Stationary source emissions — Determination of the mass concentration of ammonia in flue gas — Performance characteristics of automated measuring systems

ISO 14912:2006, Gas analysis — Conversion of gas mixture composition data

2.3 Terms and definitions

For the purposes of this document, the terms and definitions given in

[ISO 4224:2000, ISO 14532, IEC 61207-7:2013, ISO 19739:2004] and the following apply.

2.3.1
diode laser

semiconductor laser which is formed from a p-n junction and powered by injected electric current

[IEC 61207-7:2013, definition 3.2]

2.3.2
tuneable diode laser absorption spectroscopy
TDLAS

Spectroscopy which utilizes a tuneable diode laser as radiation source, tunes the emission wavelength of the laser over the characteristic absorption lines of measured species in the laser beam path, detects the reduction of the measured signal intensity, and then determines the gas concentration

2.3.3
cavity enhanced absorption spectroscopy
CEAS

Spectroscopy which utilizes the resonance of laser beam in high-finesse optical cavity to prolong the effective path lengths

[IEC 61207-7:2013, definition 3.11]

2.3.4
ultraviolet visible spectroscopy
UV-Vis

absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region

Note 1 to entry: This means it uses light in the visible and adjacent [near-UV and near-infrared (NIR)] ranges.

[ISO/TS 16550:2014(en)definition 2.15]

2.3.5
span gas

gas or gas mixture used to adjust and check a specific point on a calibration curve

Note 1 to entry: Adapted from ISO 12039:2001, 3.4.1.

[ISO 13199:2012, 3.13]

2.3.6
span point

value of the output quantity (measured signal) of the automatic measuring sytem for the purpose of calibration, adjustment, etc. that represents a correct measured value generated by reference material

[ISO 13199:2012, 3.14]

2.3.7
measurand

particular quantity subject to measurement

[ISO/IEC Guide 98-3:2008, B.2.9]

2.3.8
performance characteristic

one of the quantities assigned to equipment in order to define its performance

[ISO 13199:2012, 3.9]

2.3.9
zero gas

gas or gas mixture used to establish the zero point on a calibration curve within a given concentration range

[ISO 12039:2001, 3.4.2]

2.3.10
zero point

specified value of the output quantity (measured signal) of the AMS and which, in the absence of the measured component, represents the zero crossing of the calibration line

[ISO 13199:2012, 3.19]

2.3.11
response time

time interval between the instant when a stimulus is subjected to a specified abrupt change and the instant when the response reaches and remains within specified limits around its final stable value, determined as the sum of the lag time and the rise time in the rising mode, and the sum of the lag time and the fall time in the falling mode

[ISO 9169:2006, 2.2.4]

2.3.12
interference

negative or positive effect upon the response of the measuring system, due to a component of the sample that is not the measurand

[ISO 13199:2012, 3.4]

2.3.13
interferent

interfering substance

substance present in the air mass under investigation, other than the measurand, that affects the response

[ISO 9169:2006, 2.1.12]

2.3.14
lack of fit

systematic deviation, within the range of application, between the accepted value of a reference material applied to the measuring system and the corresponding result of measurement produced by the measuring system

[ISO 9169:2006, 2.2.9]

2.3.15
mass concentration

concentration of a substance in a waste gas expressed as mass per volume

Note 1 to entry: Adapted from ISO 12039:2001,[3] 3.10.

Note 2 to entry: Mass concentration is often expressed in milligrams per cubic metre (mg/m3).

[ISO 13199:2012, 3.7]

2.3.16
amount fraction

amount fraction, *x*, quotient of the amount of substance of a specified component and the sum of the amounts of substance of all components of a gas mixture

NOTE The amount fraction is independent of the pressure and the temperature of the gas mixture.

[ISO 14912:2006, 2.1.1]

2.3.17
measurement system

complete set of measurement instrumentation and associated equipment used for the determination of a specified measurand

[ISO 11771:2010, 2.4]

2.4 Principle

A biomethane sample or calibration mixture is introduced into a measurement system which comprises of a gas delivery/vent system and a spectroscopic analyser.

The spectroscopic analyser is specific to NH_3 detection and shall be characterised by certified calibration materials specified to meet the requirements of EN 16723:2016.

The calibration gas and sample gas shall be analysed using the same measurement system and measurement conditions.

The amount fraction NH_3 in the sample is determined from a calibration function.

2.5 Apparatus

2.5.1 NH_3 analyser

The analyser shall consist of a NH_3 specific instrument based on the spectroscopic detection and quantification of NH_3. The analyser shall be suitable for measuring trace amounts of NH_3 in a methane matrix. See annex A for example analyser performance characteristics.

2.5.2 Gas Delivery System

A gas delivery system shall be constructed to safely deliver gas from the supply sources to the NH_3 analyser. The system shall include outlets to the vent, before and after the analyser, to allow the safe removal of sample/calibration and purge gas mixtures from the measurement system. It is recommended to include a rotameter at the analyser outlet as an external monitor of the flow rate through the analyser in case the flow meter (see 5.5.3) becomes faulty. The design shall include consideration of the construction materials (see 8.1).

2.5.3 Temperature sensor

Temperature sensor, capable of measuring sample gas temperature to ± 0.5 °C.

2.5.4 Pressure sensor

Pressure sensor, capable of measuring sample gas pressure to ± 0.6 kPa.

2.5.5 Calibration equipment

The two acceptable methods for dynamic multipoint calibration of NH_3 analysers are:

a) the use of individual certified standard cylinders of NH_3 for each concentration needed;

b) the use of one certified standard cylinder of NH_3, diluted as necessary with methane, to obtain the various calibration concentrations needed.

Both methods require the following equipment.

2.5.5.1 Pressure regulators for the NH_3 cylinders

A two-stage regulator with inlet and delivery pressure gauges will be required for the NH_3 calibration standard cylinder. Procure regulators for each cylinder if individual cylinders are to be used for individual calibration points. Ensure the cylinders have a non-reactive diaphragm and suitable delivery pressure. Consult the supplier from whom the NH_3 cylinders are to be obtained for the correct cylinder fitting size required for the regulator.

2.5.5.2 Flow controller

The flow controller can be any device (valve) capable of adjusting and regulating the flow from the calibration standard: If the dilution method is to be used for calibration, a second device is required for the zero-air. For dilution, the controllers shall be capable of regulating the flow to ± 1 %.

2.5.5.3 Flow meter

A calibrated flow meter capable of measuring and monitoring the calibration standard flowrate. If the dilution method is used, a second flow meter is required for the zero-methane flow. For dilution, the flow meters shall be capable of measuring the flow with an accuracy of ± 2 %.

2.5.5.4 Mixing chamber (dynamic dilution only)

A mixing chamber is required only if the calibrator concentrations are generated by dynamic dilution of a NH_3 standard. Design the chamber to provide thorough mixing of NH_3 and methane.

2.5.5.5 Output manifold

The output manifold should be of sufficient diameter to ensure an insignificant pressure drop at the analyser connection. The system shall have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

2.6 Reagents and materials

2.6.1 Methane

Use a pressurized cylinder of pure methane certified to contain less than the LOD of the measurement system of NH_3. Methane is used as the zero point gas and diluent gas in the case of calibration by dynamic dilution.

2.6.2 Calibration gases

Use pressurized cylinders containing concentrations of NH_3 in methane corresponding to the instrument operating range, that is, 10 %, 20 %, 40 % and 80 % of full-scale range. They shall be certified to a traceable national standard.

Alternatively, if a dilution calibration method is used, a single calibration standard pressurized cylinder may be used as a parent. However a second calibration gas cylinder at the level that is not related to the parent should be used in parallel to check for bias in the calibration curve

Span gas comprising of a NH_3 in methane certified reference gas mixture meeting the requirements of EN 16723:2016

2.6.3 Inert Gas

A dry inert gas shall be used to purge the measurement system before and after use to remove ambient air or flammable gases and residual NH_3 and moisture from the measurement system.

2.7 Safety Precautions

The handling of and sampling from high pressured cylinders of methane is potentially hazardous to personnel, the laboratory and immediate area to the laboratory. Refer to section 4 of EN ISO 10715:2001. Ensure that cylinder pressure regulators are in serviceable condition and that they are constructed of materials recommended by the producer of the calibration gas.

2.8 Sampling

The choice of sampling procedure is important in the analysis of NH_3. NH_3 has the tendency to adsorb onto the wetted surfaces of different materials, particularly stainless steel. For this reason, low amount fractions of NH_3 in gas mixtures require particular consideration to ensure that the amount of ammonia entering the NH_3 analyser is representative for both the sample and calibration gas mixtures. Sampling and sample transfer shall be in accordance with ISO 10715.

2.8.1 Construction materials

NH_3 is a sticky component and the choice of material used in the gas tubing of the measurement system can strongly affect the time for a measurement to stabilise, especially at the trace level. Materials or coatings that reduce the adsorption of NH3 onto wetted surfaces are recommended in order to reduce the amount of sample and calibration gas required for the measurement and also reduce measurement time. The general considerations of ISO 10715 should always be followed.

2.8.2 Cleanness

When a calibration or sample gas cylinder is to be connected to a gas system, always inspect visually the connection on the cylinder valve outlet. Carefully clean out any dirt, dust or particles with a dust-free cloth. Ambient air and humidity is to be purged out of the system 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 contamination. Particle filters may be helpful, but they shall only contain material proposed in ISO 10715. The effect on the NH_3 response of the measurement system from the presence of a particle filter shall also be investigated, if installed.

2.8.3 Installation of the calibration gas cylinder

The installation of a calibration or sample gas cylinder into the measurement system is necessary for off-line spectroscopic analysis of NH_3 in biomethane. It is important to minimise the interaction of NH3 with the wetted surfaces within the measurement system and therefore minimise the length of tubing between the analyser and the point of sample injection. One principle for the connection of a calibration gas cylinder in direct sampling is shown in ISO 10715:1997, Annex A.

2.8.4 Pressure control

As described for the sample handling in ISO 10715, very often a pressure reduction device is required in order to feed the calibration and sample gas to an analyser. Normally, this is a reduction valve connected directly or close to the calibration and sample gas cylinder. Only use

a pressure regulator made of the material approved by the producer of the calibration gas mixture.

Never use a calibration gas mixture with a total pressure lower than the stated minimum pressure on the calibration certificate. If no minimum is stated, contact the supplier. If the supplier cannot recommend a minimum pressure, the mixture shall no longer be used if the mixture of the total pressure is lower than 10 % of the certified filling pressure.

Always use the same reduced pressure when injecting the calibration mixture and the biomethane gas sample. Control the purge flow by a needle valve or other flow controlling device, e.g. a mass flow controller.

2.8.5 Purging of reduction valve and transfer lines

Due to the strong tendency of NH_3 to adsorb to different materials of construction, it is important to purge all wetted surfaces from the cylinder valve up to a valve before the analyser inlet. Ensure that the analyser is not at risk from exceeding its maximum pressure when performing purge. Using a pressure-reducing valve mounted directly onto the cylinder valve connection, the purging should include a number of "fill and empty" cycles as described in ISO 10715.

When analysing calibration gases with different concentration levels, always flush the transfer lines and the valves with dry N_2 or CH_4 in order to avoid memory effects.

2.8.6 Flow control

When sampling from a gas cylinder, the flow of the sample or calibration gas shall be controlled by a flow control device that is suited to the operating conditions of the measurement system. A constant flow of gas is important for maintaining a constant pressure inside the system, which is particularly important for spectroscopic measurements. The purge time should be long enough to replicate stable analytical results within the acceptable standard deviation of the analyser and is dependent on the amount of NH_3, materials used in the measurement system

2.8.7 Diffusion control

Always leak check the system with a suitable leak detector when new gas connections have been made in the system. Leaks via diffusion of ambient air or the gas mixture should be avoided by using non-permeable materials in the measurement system. Polymer tubes in gas transfer lines may cause problems related to diffusion of water vapour from ambient air.

2.9 Calibration

2.9.1 Calibration procedures using dynamic dilution methods

Use a reference standard and methane diluent gas to calibrate the instrument over the desired range of interest. The calibration should be conducted using thermal mass-flow controllers, in accordance with ISO 6145-7.

2.9.2 Calibration procedures using multiple reference standards

Use a series of reference standards to calibrate the instrument over the desired range of interest. The calibration should be in accordance with ISO 6143.

2.9.3 Frequency of calibration

2.9.3.1 Multipoint calibration

Perform a multipoint calibration when:

a) the analyser is first purchased;

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

c) the analyser shows drift in excess of specifications as determined when the zero and span calibrations are performed.

Evaluate the calibration data in accordance with ISO 6143.

2.9.3.2 Zero and span calibration

Perform zero and span calibrations before and after each sampling period. If the analyser is used continuously, calibrations should be performed before the period of time which the measurement system drifts beyond the acceptable analytical limit.

2.10 Interferences

2.10.1 Interfering Absorbers

Components that absorb within the same spectral window as NH_3 can interfere with the NH_3 signal and result in a false non-zero analyser response if present within the analysis mixture and unaccounted for. Therefore, consideration shall be given to the effect of interferences on the response of the spectroscopic analyser of the measurement system. Contact the analyser manufacturer for the specifications of the effect of any interfering components on the analyser. If any interfering component identified is listed in EN 16723, the measurement system response to that component shall also be characterised in the same manner as NH_3.

2.10.2 Matrix Gas

The analyser response for NH_3 can change significantly between different matrix gases and measurement systems using high resolution detection methods e.g. laser spectroscopic analysers are particularly susceptible. Therefore, the calibration matrix gas shall match the sample gas matrix.

2.10.3 Humidity

Humidity can also be another interference: the measurement system response may be significantly different between calibration mixtures that are of the same nominal amount fraction but in a dry or humid matrix.

2.11 Procedure

Determine the performance characteristics in accordance with ISO 9169.

Establish calibration, check the analyser system operating parameters, and set the sample flowrate.

2.12 Analysis

Perform quantitative analysis and determine the amount fraction and uncertainty budget of NH_3 in the sample gas in accordance with ISO 6143.

Be aware of the special adsorption and/or chemical problems that can occur with the handling of NH_3. Repeated sampling of the same working reference gas mixture before and after comparison analysis may give an indication of any drift due to NH_3 adsorption during the total analytical time. Analyser drift shall also be included in the uncertainty budget by measuring the zero gas at the start and again at the end of the measurement run.

2.13 Expression of results

To meet the requirements of EN 16723-1:2016, the amount fraction of NH_3 within biomethane must be expressed in units of mass concentration (mg/m^3). The calibration of the test method is underpinned by comparison of reference standard gas mixtures that are traceable to the SI, in

units of amount fraction (μmol mol^{-1}). The analytical values shall therefore be converted from amount fraction to mass concentration correctly. To convert between different units of gas composition data, refer to ISO 14912:2006.

2.14 Test report

The test report shall include at least the following information:

a) reference to this International Standard and the analytical method used;

b) sample identification including

— time/date of the sampling,

— sample point/stream (location), and

— cylinder identification (for spot sampling);

c) reference to the calibration system used;

d) sample amount fraction and mass concentration, including the number of digits appropriate to the certificate of calibration and size of error, including the result of uncertainty calculation;

e) comments, including

— any deviation from specified procedure, and/or

— problems concerning the sample;

f) date of analysis, name of laboratory and signature of analyst.

Annex A
(informative)

Spectroscopic Analyser Performance Characteristics for NH_3 Analysis in Biomethane

Example performance characteristics of two different commercially available NH_3 spectroscopic analysers are shown in table A.1. The example NH_3 analysers are based on Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS) and Ultraviolet-visible spectroscopy (UV/vis).

Table A.1 Example performance characteristics of an OFCEAS and an UV/vis NH_3 analyser as tested in a laboratory setting.

Parameter	OFCEAS	UV/vis
NH_3 Range (µmol mol^{-1})	0 – 145	0 - 22
Repeatability (%)[a]	1	1
Reproducibility (%)[a]	1.1 (6 weeks)	1.4 (1 week)
LOQ (µmol mol^{-1})	0.5	0.5
t_{90} (minutes)[a]	36	7
Stabilisation time (hh:mm)[a]	01:30	00:50
Sample flow (ml min^{-1})	150	500
Temperature Range (°C)	Not tested	Not tested

[a]Parameters measured at 10 µmol mol^{-1} NH_3 in CH_4

[b]Initial stabilisation time: subsequent stabilisation time < 30 minutes

3 Determination of the biogenic carbon fraction — Radiocarbon (^{14}C) method

3.1 Scope

This document describes the methodological aspects of a test method for measuring the biogenic carbon fraction based on radiocarbon (^{14}C) measurements in gaseous fuel samples that contain hydrocarbons.

The method is applicable to fuel gases containing hydrocarbons that can first be sampled and then pre-treated and measured off-line.

The test method is applicable to fuel gases containing only methane, for mixtures of methane with other hydrocarbons, gases with only specific hydrocarbons other than methane and mixtures of hydrocarbons with CO and/or CO_2. It has been specifically developed for blends of biomethane and natural gas.

This test method cannot be used by laboratories that work with exposure to artificial ^{14}C.

3.2 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 14532, *Natural gas – Vocabulary*

ISO 10715, *Natural gas — Sampling guidelines*

3.3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14532 and the following apply.

Comment by first author: The terms and definitions of ASTM D6866 would apply if ASTM D6866 would be used as the main standard.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.3.1

laboratory sample

sample as prepared for sending to the laboratory and intended for inspection or testing

[Based on ISO 6206]

3.3.2

test sample

sample prepared from the laboratory sample and from which the test portions will be taken

[Based on ISO 6206]

3.3.3

test portion

the quantity of material drawn from the test sample (or from the laboratory sample if both are the same) and on which the test or observation is actually carried out

[Based on ISO 6206]

3.3.4

precision

the closeness of agreement between independent test results obtained under stipulated conditions

[Based on ISO 5725-1]

3.3.5

accuracy

closeness of agreement between a test result and an accepted reference value

NOTE The term accuracy, when applied to a set of test results, involves a combination of random components and a common systematic error or bias component.

[Based on ISO 5725-1]

3.3.6

biogenic carbon

biogenic carbon (organic or inorganic) is carbon that originates from organisms that lived after 1955 CE and that took up carbon during their lifetime originating from atmospheric CO_2 (from the time period after 1955 CE)

NOTE This definition applies specifically for the ^{14}C-based test method as described in this document.

3.3.7

fossil carbon

fossil carbon (organic or inorganic) is carbon that originates from organisms that lived more than 50.000 years ago and which ^{14}C amount is below the detection limit of ^{14}C measurement techniques

NOTE This definition applies specifically for the ^{14}C-based test method as described in this document.

3.3.8

biogenic carbon fraction

the amount of biogenic carbon in the material or product as a percent of the total carbon (TC) in the product

3.3.9

pMC

percent of Modern Carbon (pMC) is the amount of ^{14}C in a sample relative to the measured and normalized amount of ^{14}C in a reference standard which has a standardized amount of ^{14}C for reference year 1950 CE

NOTE 100% biogenic carbon has a pMC value that depends on the time period when atmospheric CO_2 was taken up by organisms. Due to above ground nuclear tests atmospheric $^{14}CO_2$ values peaked to almost 200 pMC in 1963 at the Northern Hemisphere, but decreased in decreasing rate on a global scale since the ban of these tests in 1963. In 2020 the global atmospheric $^{14}CO_2$ value was around 100 pMC and its annual decrease is approximately -0.3 pMC/year. Fossil carbon does not contain ^{14}C anymore and its pMC value is therefore 0 pMC.

3.3.10

REF ^{14}C value

The REF ^{14}C value is the ^{14}C amount (pMC) representing 100% biogenic carbon

3.4 Principle

To measure the biogenic carbon fraction of gaseous laboratory samples that contain hydrocarbons, first the total carbon fraction of the test sample shall be collected. A test portion of this collected carbon fraction is then measured using a ^{14}C measurement technique. The measured amount of ^{14}C in the test portion is normalized and calibrated based on the measurement of a reference material with normalized and standardized ^{14}C amount. The ^{14}C amount (pMC) of carbon in the test portion is then compared relative to the REF ^{14}C value (pMC) representing 100% biogenic carbon. The lower the biogenic carbon fraction (and the larger the fossil carbon fraction) in the test portion, the lower the measured ^{14}C amount. The ^{14}C amount decreases to 0 pMC, proportional to the decreasing biogenic carbon fraction.

The biogenic carbon fraction, f_{bioC}, is calculated according to

$$f_{bioC} = \frac{14Csample}{REF\ 14C}$$

where

$^{14}C_{sample}$ is the ^{14}C amount (pMC) measured in the carbon of the test portion

REF ^{14}C is a reference ^{14}C amount (pMC) representing 100% biogenic carbon

NOTE that only main features that should be taken into account for fuel gases are described below Procedure, Sampling, Apparatus, Calculation, Quality Assurance and Control.

3.5 Procedure

Testing laboratories are free to use their own sample preparation and ^{14}C measurement techniques, as long as the carbon composition of the test sample does not change during the sample preparation, and the applied preparation and measurement methods are validated. Gas sampling, gas sample conservation and the pre-treatment methods in the lab shall be free of any (significant) carbon fractionation: the carbon composition of the gas should be representative for the gas to be investigated and shall therefore not change in its biogenic carbon fraction during and after sampling and/or after pre-treatment in the lab. The use of traps in gas-inlet systems and combustion systems shall only be applied during inlet and combustion of the gases if this does not result in carbon fractionation.

Applied lab methods to prepare and measure the test samples shall be validated before these are used. Reference materials containing mixtures of biogas and natural gas with known ^{14}C amounts and known biogenic carbon fraction should be used for this validation.

For identification purposes of 100% fossil carbon samples, the detection limit of ^{14}C for the applied method shall be <1 pMC (is analogue to > 37000 yrBP and <1% biogenic carbon).

Laboratory samples of gases are sampled and stored in cylinders or in gasbags. For AMS analysis 2 mg of carbon is sufficient, while for LSC measurement (method with conversion to benzene) and proportional gas counters approximately 1-4 gram of carbon is required. The amount of sample that is required for an analysis (and preferably also a duplicate) depends on the carbon content and on the applied sample preparation technique and the volumes of the used systems. In general for natural gas and biogas (or mixtures of these two), 30 ml of gas is by far sufficient for multiple AMS ^{14}C analyses, but usually more material is required in the specific systems. For LSC and proportional gas counters at least 3 liter of sample material will be required to obtain sufficient carbon for one analysis.

To measure the biogenic carbon fraction in the laboratory sample, first the carbon of this sample, which is very often a mixture of different carbon-containing molecules, should be selected and separated from most other elements in the sample. To do this, the gas sample is introduced into a combustion system and then combusted in a process in which all carbon-containing molecules are converted into CO_2. The obtained CO_2 gas is then a mixture of the original carbon-containing molecules.

Depending on the applied ^{14}C measurement technique, the CO_2 is measured as CO_2 in proportional gas counters, converted to solid carbon by graphitization for AMS measurement (direct measurement of CO_2 is not common yet, but it is also possible with some AMS instruments), or converted to benzene for LSC measurement. These conversions to graphite or to benzene and the ^{14}C measurement methods are routinely used methods by (most) ^{14}C test laboratories. These methods are usually also validated with intra-and inter-laboratory tests by the testing laboratories and will therefore not be described in this test method.

After the ^{14}C measurement of the carbon in the test sample, the measured ^{14}C amount is calculated relative to the measured ^{14}C amount in a reference standard with known and standardized (by the ^{14}C community) ^{14}C amount. Isotope fractionation correction is applied.

This is very important and necessary for fuels with methane, because the $\delta^{13}C$ values of these gases deviate considerably from the normalization value (large correction factor).

The calculated ^{14}C amount is then calculated relative to the REF ^{14}C value to obtain the biogenic carbon fraction of the test sample.

3.6 Sampling

Sampling shall be performed in accordance with ISO 10715. Samples can be collected in cylinders or gas bags.

For gas bags: storage conditions are important; change of carbon composition/isotope fractionation in time. Material: Tedlar is very commonly used with polypropylene fitting. In general: measurement < 1 month after sampling is recommended.

3.7 Apparatus

In case of ^{14}C measurement with LSC, proportional gas counters or $^{14}C/^{13}C$ AMS, the CO_2 fraction of the fuel gas test portion after combustion, should be measured on $\delta^{13}C$. For this measurement an instrument dedicated to measure ^{13}C and ^{12}C isotopes should be used (for instance an Isotope Ratio Mass Spectrometer (IRMS), dual inlet-IRMS, or laser technique.

For ^{14}C measurement an Accelerator Mass Spectrometer (AMS) can be used (measurement of C or in some cases is CO_2 also possible), or a Liquid Scintillation Counter (measurement of benzene), or a proportional gas counter (measurement of CO_2).

3.8 Calculation

The calculation of measured ^{14}C to a ^{14}C value (in pMC) is standardized within the ^{14}C measurement community according to Stuiver and Polach (1977) and Mook and van der Plicht (1999) and includes standardization and normalization.

^{14}C results shall always be corrected for isotope fractionation. When using measured $\delta^{13}C$ values to correct for isotope fractionation, it is the best to correct with the $\delta^{13}C$ values of the biogenic carbon in the sample (if known). For AMS measurement, correction for graphitization and AMS measurement should then also be applied, based on the measured $\delta^{13}C$ values in the CO_2 gas (IRMS) and in the pressed or CO_2 target (AMS). If this value $\delta^{13}C$ of the biogenic carbon in the sample is not known, which is usually the case for unknown gas mixtures, then the isotope fractionation correction shall be based on the measured $\delta^{13}C$ value of the test sample. For proportional gas counters, LSC and $^{14}C/^{13}C$ AMS measurement, the isotope fractionation should be based on additional $\delta^{13}C$ measurement of the test sample after combustion of the test sample to CO_2. In case of $^{14}C/^{12}C$ AMS measurements, the $\delta^{13}C$ values in the samples are measured in with the AMS in the same run as ^{14}C.

The uncertainties in $^{14}C_{sample}$ and REF ^{14}C, together determine the combined uncertainty in the calculated biogenic carbon fraction, f_{bioC}.

3.9 Quality assurance and Control

The ^{14}C results of a lab should be verified on a regular base by treating a reference gas sample as unknown laboratory sample. This reference gas should have a known ^{14}C amount and a representative (compared to the measured unknown laboratory samples) carbon composition. For gaseous laboratory samples with only one type of hydrocarbon and for the verification of biogas samples (whether these contain 100% biogenic carbon), biogas with known ^{14}C amount can be used as reference gas. For the quality assurance of mixtures of renewable gases with

natural gas, a reference gas with known ^{14}C amount should be used with 50-80% biogenic carbon. The natural gas used in this mixture should contain different hydrocarbons.

3.10 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:

1) The date, time and location of sampling.

2) The name of the testing lab. In case the sample preparation is performed by another lab, this should be mentioned as well.

3) The value of the biogenic methane fraction, expanded uncertainty, and coverage factor used.

4) A reference to this document.

5) Used 14C measurement technique, and $\delta^{13}C$ measurement technique.

6) Applied isotope fractionation correction (based on $\delta^{13}C$ sample or $\delta^{13}C$ biogenic carbon).

7) Used 14C reference value for 100% biogenic carbon.

NOTE ISO/IEC 17025 [4] contains further guidance on test reports.

4 Determination of the compressor oil content

4.1 Scope

This document gives general guidance for the sampling and analysis of oil carryover in biomethane/CNG. The oil carryover is determined by sampling on coalescing filters under defined operational conditions (the two first Nm^3 delivered at a refueling station). The oil carryover is expressed as concentration.

4.2 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.

ISO 6974-1:2012 *Natural gas - Determination of composition and associated uncertainty by gas chromatography - Part 1: General guidelines and calculation of composition*

ISO 6974-2:2012 *Natural gas - Determination of composition and associated uncertainty by gas chromatography - Part 2: Uncertainty calculations*

ISO 6974-3:2018 *Natural gas - Determination of composition and associated uncertainty by gas chromatography - Part 3: Precision and bias*

ISO 6976:2016 *Natural gas - Calculation of calorific values, density, relative density and Wobbe indices from composition*

ISO 14532:2014, *Natural gas — Vocabulary*

EN 16723-1:2016, *Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network – Part 1: Specifications for biomethane for injection in the natural gas network*

EN 16723-2:2017, *Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network – Part 2: Automotive fuels specification*

4.3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14532 and the following apply.

4.3.1
Response
Output signal of the measuring system, for a component that is measured as peak area or peak height

4.3.2
Uncertainty (of measurement)
Parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

NOTE 1 The parameter may be, for example, a standard deviation (or a given multiple of it), or the half-width of an interval having a stated level of confidence.

NOTE 2 Uncertainty of measurement comprises, in general, many components. Some of these components may be evaluated from the statistical distribution of the results of series of measurements and can be characterized by experimental standard deviations. The other components, which also can be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information.

NOTE 3 it is understood that the results of the measurement is the best estimate of the value of the measurand, and that all components of uncertainty, including those arising from the systematic effects, such as components associated with corrections and reference standards, contribute to the dispersion.

[ISO/IEC Guide 98-3:2008, 2.2.3]

4.3.3
Standard uncertainty
Uncertainty of the result of a measurement expressed as a standard deviation

[ISO/IEC Guide 98-3:2008, 2.3.1]

4.3.4
Combined standard uncertainty
Standard uncertainty of the results of a measurement when that result is obtained form the values of a number of other quantities, equal to the positive squire root of a sum of terms, the terms being the variances or covariances of these other quantities weighted according to how the measurement result varies with changes in these quantities

[ISO/IEC Guide 98-3:2008, 2.3.4]

4.3.5
Expanded uncertainty
Quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

NOTE 1 The fraction may be reviewed as the coverage probability or level of confidence of the interval.

NOTE 2 To associate a specific level of confidence with the interval defined by the expanded uncertainty requires explicit or implicit assumptions regarding the probability distribution characterized by the measurement result and tis combined standard uncertainty. The level of confidence that may be attributed to this interval can be known only to the extent to which such assumptions may be justified.

NOTE 3 Expanded uncertainty is termed overall uncertainty in Recommendation INC-1 (1980), Paragraph 5. [ISO/IEC Guide 98-3:2008, 2.3.5]

4.3.6
Repeatability (of results of measurements)
Closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement

NOTE 1 These conditions are called repeatability conditions

NOTE 2 Repeatability conditions include:

- The same measurement procedure
- The same observer
- The same measuring instrument, used under the same conditions
- The same location
- Repetition over a short period of time

NOTE 3 Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results. [ISO/IEC Guide 98-3:2008, B.2.15]

4.4 Principle

The pressure of the compressed gas to analyse is drastically reduced by forcing the gas to pass through a nozzle spray with a limited hole diameter (which implies that the temperature of the gas also drops) so as to make the oil condense as droplets and deposit on a coalescing filter. Two filters are connected in series, a main filter and a backup filter. The oil that deposits in the buffer tank is recovered as well. For a typical sampling arrangement, see Figure 1.

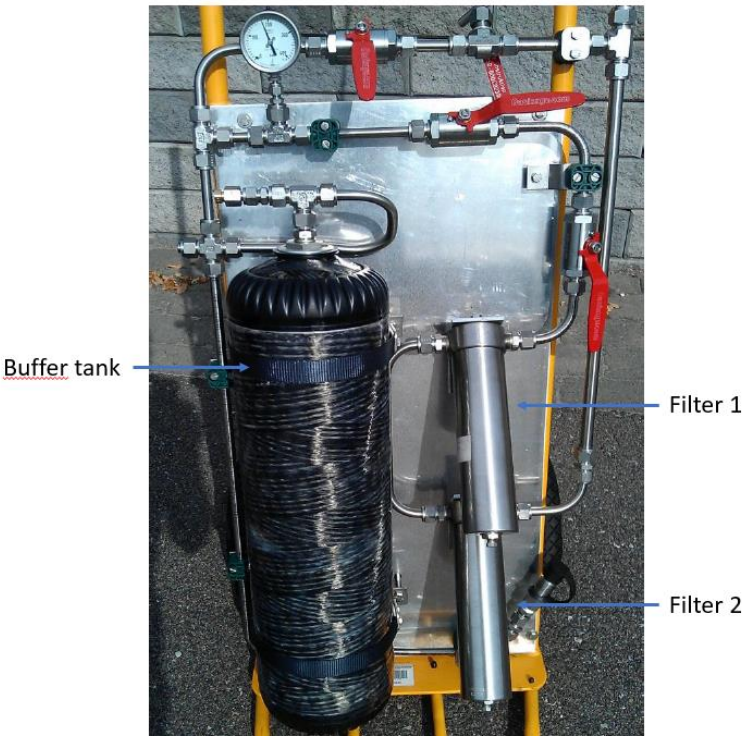


Figure 1: compressor oil sampler

4.5 Chemicals and materials

4.5.1 Compressor oils

For calibration purposes. Samples of all compressor oils used at the station to be tested or any other oils that can be present in the gas to analyse shall be separately collected to be used for preparing the calibration standards. Please note that oil references need to come from the same production batch as the ones actually used at the station.

If not feasible, calibration can be made using equivalent oils.

4.5.2 Dilution solvent

Dichloromethane or hexane, analysis grade, for preparing oil calibration standards. This should be of sufficient purity to ensure that it does not give rise to interferences during the analysis. Use only solvent of recognized analytical grade.

4.5.3 Extraction solvent

Dichloromethane, pentane or other adequate organic solvent. This should be of sufficient purity to ensure that it does not give rise to interferences during the GC/MS analysis. Use only solvent of recognized analytical grade.

4.5.4 Sampling filters

The sampling filters are a high-efficiency coalescing filter made of borosilicate microfibers with fluorocarbon resin binder with more than 99.99% efficiency at 0,01 µm. Flow rate through the sampling filter shall not exceed the manufacturers' recommendation for the test pressure.

4.5.5 Backup filters

This filter is identical to the sampling filter and, in the event of malfunction of the sampling filter, collects any oil, that passes through it.

4.5.6 **Calibration standards, can be prepared by diluting amounts of oil (from 1 mg to 10 mg) in 1 ml of dilution solvent.**

4.6 Apparatus

4.6.1 **Gas chromatography/mass spectrometer (GC/MS), EI mode or gas chromatography/flame ionisation detector (GC/FID)**

4.6.2 **Capillary column, for gas chromatography, fused silica coated with a non-polar bonded phase which performs equivalent to a 5% diphenyl, 95% dimethylpolysiloxane.**

4.6.3 **Ultrasonic bath, with start at ambient temperature. Temperature increase due to sonication can be neglected.**

4.6.4 **Pressurised fluid extraction apparatus. Consisting of extraction cells which can be heated to 150ºC at static pressures up to 10 MPa. The device should be programmable regarding the temperature, duration and number of extraction cycles. The cells must be flushed with the extraction solvent.**

4.6.5 **Filter house, equipped with an inlet for gas (nitrogen, high purity) and an outlet for gas and liquid at the bottom of the filter house.**

4.6.6 **Rotary evaporator, concentration apparatus, that is designed to allow the solvent extract to be reduced from more than 300 ml to 10 - 20 ml.**

4.6.7 **Laboratory glassware**

4.6.7.1 Flat-bottomed flask, capacity 500 ml

4.6.7.2 Measuring cylinder, capacity 500 ml or equivalent large enough to soak a whole filter

4.6.7.3 Beaker, capacity 50 ml

4.7 Sampling

4.7.1 Sampling line

The sampler consists of a NGV1 connection, 1/2” tubing, a manometer, 3 ball valves (oasis engineering ltd), a 12.5 liter composite CNG bottle, and two EU37/25 filter houses (with coalescing filters) connected in series after a spray nozzle of 0.3 mm hole diameter and union tees (see Figure 1).

4.7.2 Sampling

The sampler is connected to the dispenser through the NGV1 connection. A refueling is started and manually stopped (if necessary) when the pressure in the bottle has reached at least 180 bar (which corresponds to between 2.1 to 2.6 m^3 gas sampled). The sampler is then disconnected from the dispenser and brought aside.

NOTE Unless specified otherwise, gas volumes stated in this document refer to standard conditions. If not specified, standard conditions are given in ISO 13443.

The gas sample is released through the chimney by opening a ball valve until the pressure in the bottle reached 180 bar (this pressure has been chosen as it supposedly can be achieved in all stations even the ones working at slightly lower pressures than average). The pressure is read when the temperature in the cylinder has reached equilibrium (the pressure is then stable). The gas is then led through the coalescing filters by opening the two other ball valves. As the gas passes first through the hole of the nozzle, the pressure drops resulting in a temperature drop and the oil is trapped on the filter.

The sampling can then be stopped when the pressure in the bottle reaches 100 bar (approximately equivalent to 1 m3 sampled), 120 bar (approximately equivalent to 0.75 m^3 sampled) or 140 bar (approximately equivalent to 0.5 m^3). These pressures are read when the temperature in the cylinder has reached equilibrium (the pressure is then stable). The correct gas volume is calculated by division with the appropriate compressibility factor, which is calculated by the use of commercial or inhouse software/Excel worksheets based on literature. Input data are pressure, ambient temperature and gas composition. Preferably, the sampler is then refilled with the gas to analyse in the same way to perform several samplings. The filters are removed after one sampling and new filters are installed in the filter houses.

Once all samplings are performed, the gas left in the bottle is released through the chimney.

4.8 Methods to recover the oil from the buffer tank

Oil that eventually has been deposed in the buffer tank is recovered by one of the 2 following methods:

1) After demounting the buffer tank from the sampler, rinse with at least 3 consecutive times with 250 ml pentane. Rinse with nitrogen to remove all solvent

2) Without demounting the buffer tank from the sampler, rinse at least 3 consecutive times with propane. Recover the propane by setting the sampler upside time. Rinse with nitrogen to remove all solvent

4.9 Extraction procedure for coalescing filters

4.9.1 Procedure 1: Ultrasonic extraction – nitrogen flush

Transfer a coalescing filter to a measuring cylinder large enough to soak a whole filter.

Introduce the extraction solvent into the measuring cylinder so the whole filter is soaked.

Perform a 30-minutes (± 5 minutes) long extraction in an ultrasonic bath.

Turn the coalescing filter upside down and perform a 30-minutes (± 5 minutes) long extraction in an ultrasonic bath.

Transfer the extraction solvent into a 500 ml flat-bottomed flask.

Place the filter into a filter house. The solvent remaining on the filter is removed under a flow of pure nitrogen and recovered in a 50 ml beaker. The recovered solvent is added into the 500 ml flat bottomed flask.

Concentrate the solvent extract to reduce the volume from 300-400 ml to 10-20 ml with a rotary evaporator (35 ± 3°C). Note down the final volume. Store the concentrated solvent extract cold until the analysis is carried out.

4.9.2 Procedure 2: Pressurised fluid extraction

The filter is positioned in the extraction cell.

If the filter cannot completely fit in the cell, it can be cut in several pieces. In this case, the cutting devices shall also be rinsed with the extraction solvent to ensure the recovery of oil potentially presents on the cutting device. The solvent used for rinsing the cutting devices shall be added before the evaporation step to the extract obtained after the filter extraction.

The cell is then completed with a neutral matrix, sand, to reduce the void volume in the cell and therefore the solvent consumption (the sand has to be previously extracted under the same experimental conditions as the sample to clean it and remove any potential interferences).

The extraction is then performed using the following conditions:

- Extraction solvent: hexane
- Temperature: 100ºC
- Number of extraction cycles: 2 cycles
- Time for an extraction cycle: 11 minutes
- Pressure: 120 bar
-

The extraction is concentrated under nitrogen at a final volume of 10 ml.

4.10 Analysis

4.10.1 GC/MS 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)). Analyse the concentrated solvent extracts, the calibration standards and the extraction solvent.

Example of a GC/MS chromatogram obtained for a compressor oil and chromatographic conditions is given in Annex A.

4.10.2 GC/FID analysis

The operating conditions of the GC-FID is optimized in accordance with the manufacturer´s instructions. Analyse the concentrated solvent extracts, the calibration standards and the extraction solvents with GC/FID.

Example of gas chromatographic conditions are given in Annex B.

4.11 Calculations

Data from calibration standards is used to calculate a response factor (area/mg oil in 1 ml dichloromethane) for each oil of interest. One (or more) ion(s) specific for the targeted oil should be extracted and used for the quantification. Oil quantities in mg in a sample are calculated as the area of the oil characteristic ion(s) for the sample divided by the response factor divided by the volume of the concentrated solvent extract.

Oil carryover is the sum of the oil recovered on the coalescing filters and the oil recovered in the buffer tank.

The oil recovered on the coalescing filters is expressed in mg/kg according to the following equation:

Oil recovered on the coalescing filter in mg/kg = $m_{oil\ coalescing\ (mg)}$ / $(V_{gas\ coal.(Nm3)} \cdot \rho_{gas\ (kg.Nm-3)})$

The mass fraction oil recovered shall be computed as

$$w_{\mathrm{oil}} = \frac{c_{\mathrm{oil}} V_{\mathrm{sol}}}{V_{\mathrm{gas}} \rho_{\mathrm{gas}}}$$

The mass fraction oil recovered in the buffer tank is expressed in mg/kg according to the following equation:

$$w_{\mathrm{oil}} = \frac{c_{\mathrm{oil}} V_{\mathrm{sol}}}{V_{\mathrm{gas}} \rho_{\mathrm{gas}}}$$

Oil recovered in the buffer tank in mg/kg = $m_{oil\ buffer\ (mg)}$ / $(V_{gas\ buffer\ (Nm3)} \cdot \rho_{gas\ (kg.Nm-3)})$

The density (ρ expressed in kg m^{-3}) shall be determined from an accurate determination of the gas composition (according to ISO 6974 series) and calculation based on composition using ISO 6976. $V_{gas\ coal.}$ is the volume of gas sampled on a coalescing filter, $V_{gas\ buffer}$. is the total volume of gas sampled during one test -minus the volume of gas that has passed through the coalescing filters.

The uncertainty of the mass fraction compressor w_{oil} shall be calculated as follows.

Annex A: Example of a GC/MS chromatogram obtained for a compressor oil

(Mobil Rarus SHC1025)

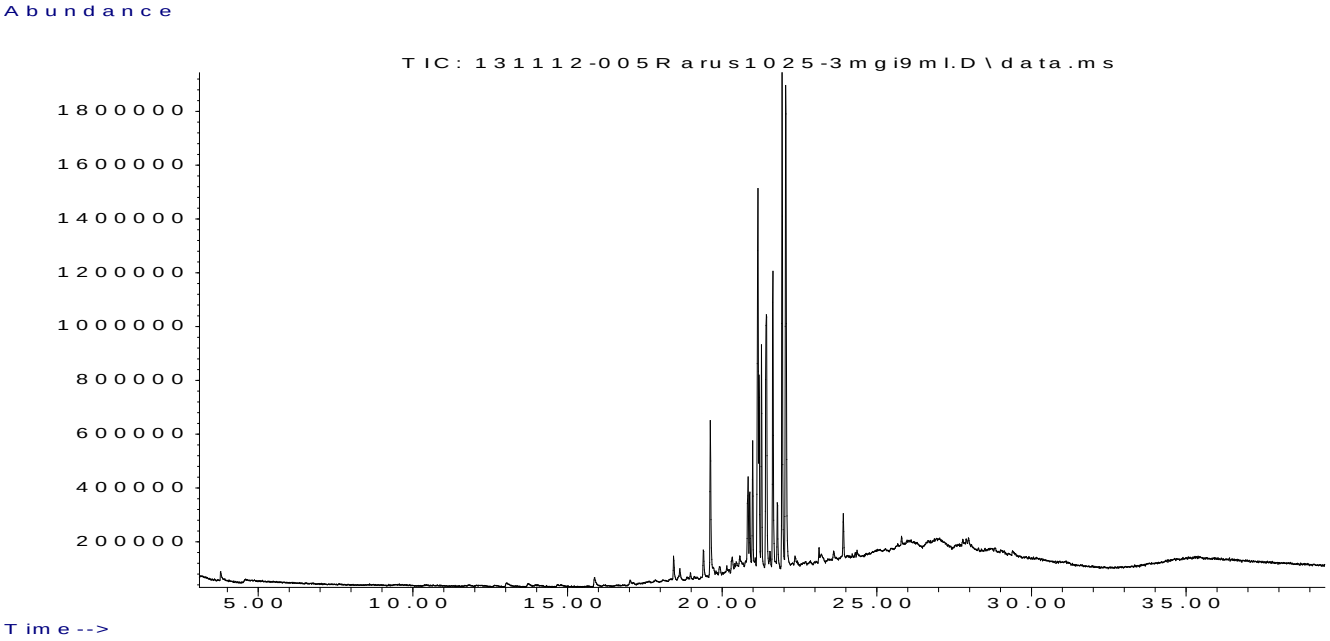


Figure A.1 – chromatogram of a compressor oil with indication of the retention time in minutes

The configuration of the chromatographic system is given in Table A.1.

Table A.1 - Configuration of the chromatographic system

Determination	
Column phase	arylene-stabilized 5% phenyl/95% methyl polydimethylsiloxane (PDMS)
Length	30 m
Internal diameter	250 µm
Film	0,1 µm
Temperature program	35°C (5 min) to 400°C (5 min) at 10°C/min
Carrier gas	Helium

Annex B: Example of a GC/FID chromatogram obtained for a compressor oil

(Mixture of 1/3 v:v of Mobil SHC 1025 oil – 1/3 v:v of Mobil Pegasus 1 and 1/3 v:v of UNIVIS N32 oil)

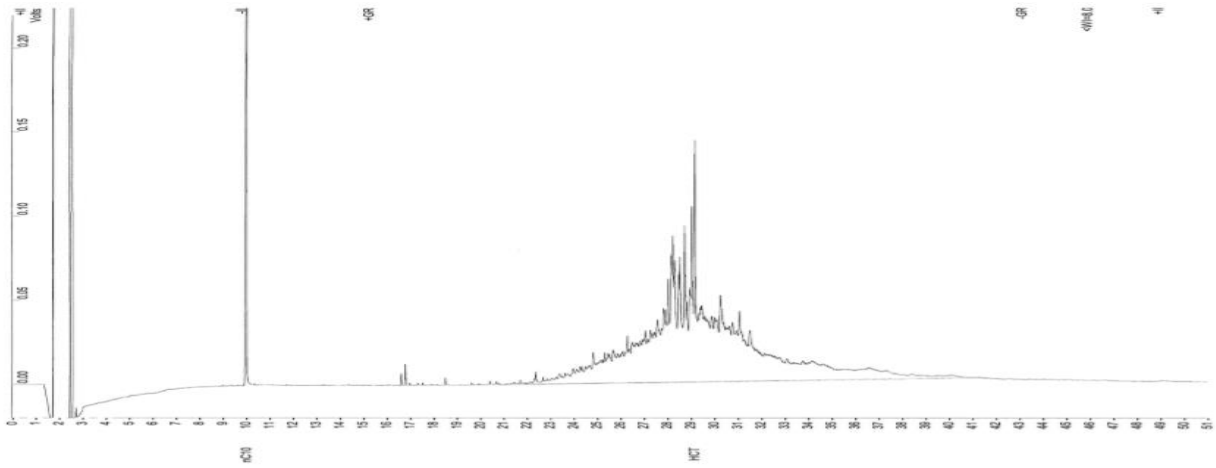


Figure B.1 – chromatogram of a compressor oil with indication of the retention time in minutes (first peak at 10 min corresponds to the hexane solvent)

The configuration of the chromatographic system is given in Table B.1.

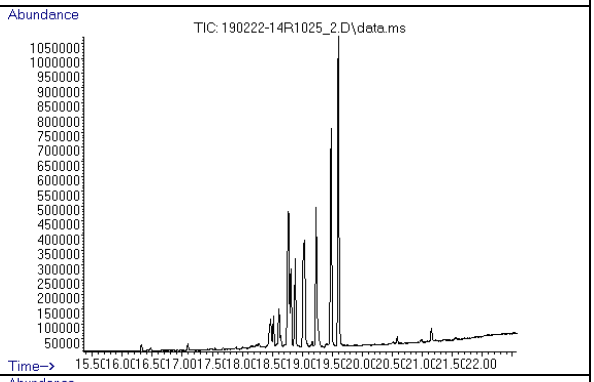
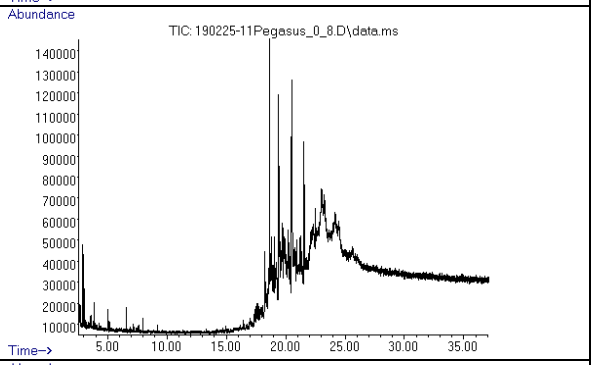
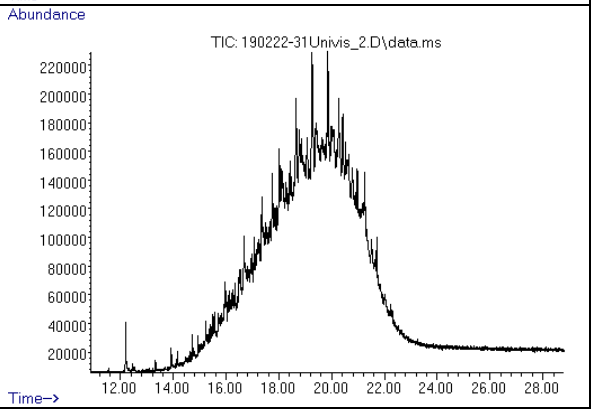
Table B.1 - Configuration of the chromatographic system

Determination	
Column phase	5% phenyl/95% methyl polydimethylsiloxane (PDMS)
Length	30 m
Internal diameter	250 µm
Film	0,25 µm
Temperature program	40°C (5 min) to 300°C (20 min) at 10°C/min
Carrier gas	Helium

Annex C: Different types of oils

Oils are generally composed of many compounds including saturated hydrocarbons that cannot be fully separated from each other with gas chromatography. The GC traces of commonly used compressor oils could be divided into three different profiles: oils exhibiting some well resolved peaks, oils exhibiting globally unresolved peaks with some dominant peaks on top of the hump and oils exhibiting globally unresolved peaks.

Table C.1 – Description of the different types of oil

Oil Types	
Type 1: GC characteristic: well separated peaks	
Type 2: Globally unresolved peaks with some dominant peaks	
Type 3: Unresolved mixture	

5 Determination of the halogenated VOC content

5.1 Scope

This International Standard describes measurement method(s) for halogenated VOCs in biomethane that meet the requirements of fit-for-purpose measurement methods with known performance and acceptable metrological traceability to support the trade in renewable gases and conformity assessment. and can be implemented by laboratories and industry, also those seeking accreditation on the basis of, e.g., ISO/IEC 17025:2017.

5.2 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 5725-2:2019, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 6142-1:2015, *Gas analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures*

ISO 11352:2012, *Water quality – Estimation of measurement uncertainty based on validation and quality control data*

ISO 14532:2014, *Natural gas — Vocabulary*

ISO/IEC 17025:2017, *General requirements for the competence of testing and calibration laboratories*

EN 16723-1:2016, *Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network – Part 1: Specifications for biomethane for injection in the natural gas network*

EN 16723-2:2017, *Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network – Part 2: Automotive fuels specification*

NFT 90 210, *Water Quality – Protocol for the initial method performance assessment in a laboratory*

5.3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14532 apply.

5.4 Measurement methods

5.4.1 Analysis of sorbent tubes using TD-GC-FID/MS

Halogenated VOCs are analysed by thermal desorption - gas chromatography - flame ionisation detection/mass spectrometry (TD-GC-FID/MS). The analyses were performed after sampling a known volume of gas mixtures containing halogenated hydrocarbons in biomethane onto stainless steel sorbent tubes packed with Tenax TA (weak), Carboxen 1003 (medium), Carbograph 1 (strong) in equal proportions. The tubes were kept in the fridge until the time of the sampling and even after the sampling until the time of the analysis.

The sorbent tubes were desorbed using a Markes TD100 thermal desorber with a two stages desorption; a primary tube desorption followed by a secondary trap desorption. Depending on

the sorbents, different temperatures were used for the primary tube desorption (no inlet split): 275°C for 7 min for the Tenax tubes, 320°C for 7 min for the multi-sorbent tubes (Tenax TA / Carboxen 1003 / Carbograph 1) and 250°C for 7 min for the Chromosorb 106 tubes. In the second stage, a cold trap (-10°C) was heated quickly (1.3°C/s) to 300°C so the compounds were released and reached the gas chromatographic column where they were separated. The outlet split ratio was 6:1. The instrument used for the analyses was an Agilent technologies 6890N coupled with a flame ionization detector and a 5975C inert MSD mass spectrometer (electron impact, EI, mode). The GC column was a BPX5 non-polar capillary column (5% phenyl polysilphenylene-siloxane, 50 m long, 0.32 mm internal diameter, 1 µm film thickness). The initial GC oven temperature was 35°C (hold 4 min). The oven temperature was then raised with three ramp rates: to 100°C at 3°C/min, to 220°C at 8°C/min and finally to 300°C at 15°C/min. The temperature was then held at 300°C for 10 minutes. For detection, one part of the effluent was sent to a flame ionization detector and the other part to the mass spectrometer. Compounds can be quantified using both detectors; the FID or the MS. When quantifying with the MS, two modes can be used; the total ion chromatogram mode which represents the summed intensity across the entire range of masses being detected (m/z 29 to m/z 390) or an extracted-ion chromatogram mode where one m/z value characteristic for one compound are recovered from the entire data set. In this study, data were collected using the total ion chromatogram mode.

5.4.2 Online gas analysis using TD-GC-FID/MS

5.4.2.1 Method 1

Halogenated VOCs are analysed by online sampling of a known volume of gas mixture containing halogenated hydrocarbons in biomethane using thermal desorption - gas chromatography - flame ionisation detection/mass spectrometry (TD-GC-FID/MS). The gas mixture was directly connected to the analytical system. The gas mixture was transferred to a cold trap packed with graphitised carbon at -10°C. The trap was then rapidly heated up to 350°C and the Halogenated VOCs were released into the gas chromatography (GC) column for separation. The column effluent was split at the end of the chromatographic column into two streams for the detection and quantification of individual components, one stream passing through a flame ionisation detector (FID) and the other stream through a mass spectrometer (MS).

The analysis of the sample was performed on a Thermo Scientific Trace Ultra gas chromatograph with two detectors: a flame ionization detector (FID) and a mass spectrometer (MS) Thermo Scientific ISQ operated in the electron impact mode under standard conditions (ionizing electron energy 70 eV, masses scanned from 35 to 350 uma).The column used was a RXi-1MS, 60 m x 0.25 mm ID x 0.25 µm film thickness (Restek).

The column program temperature was from 40°C (hold 10 min) to 150°C at 7.5°C/min, then up to 300°C at 20°C/min (hold 1 min.). Helium was used as a carrier gas at a flow rate of 1 ml/min. The FID detector temperature was set at 300°C. The ion source of the MS was set at 250 °C.

5.4.2.2 Method 2

For the ATD-GC-FID/MS analysis the gas mixture was preconcentrated via online sampling using a Perkin Elmer ATD650 thermal desorber with a two stages desorption; during the first stage the gas mixture from a cylinder was sampled for 5 minutes with a sampling flow of 40 mL min-1 onto a cold trap packed with TTA at -30 ^{o}C. In the second stage, the cold trap is quickly heated (at least 1 ^{o}C s^{-1}) to 225 ^{o}C, so the compounds are released and reach the gas chromatographic column where they are separated. The outlet split was 10 mL min^{-1}. The

instrument used for the analyses is an Agilent technologies 7820A coupled with an FID or MSD detector. The GC column was a Rxi 624Sil MS, 60 m long, 0.25 mm internal diameter, 1.4 µm film thickness. The initial GC oven temperature was 40°C (hold 6 min). The oven temperature was then raised with three ramp rates: to 70°C at 6°C min^{-1}, to 150°C at 20°C min-1 with a hold time of 2 minutes and to 200°C at 5°C min^{-1}. For detection the compounds were quantified using FID or MSD. The range of masses detected with the MSD was m/z 48 to m/z 450 and data were collected using the total ion chromatogram mode.

Annex A: Validation data measurement method – analysis of sorbent tubes using TD-GC-FID/MS

A.1.1 Introduction

The validation of an analytical method allows assessing the method suitability for a particular purpose.

The validation of the method gathers experimental work done to demonstrate that the method works in the end-user´s laboratory. Several parameters are considered as performance characteristics commonly evaluated during method validation: selectivity, limit of detection (LOD) and limit of quantification (LOQ), working range, trueness (bias, recovery), precision (repeatability, intermediate precision and reproducibility) and robustness.

The evaluation of a sufficient number of these parameters allows then to calculate the measurement uncertainty associated with a method for a component to be measured in a specified matrix.

Several documents are available to guide a laboratory through a method validation including the Eurachem guide “The Fitness for purpose of analytical methods” which is used in this study.

In this guide, the following performance characteristics are named:

- Selectivity
- Limit of detection (LOD) and limit of quantification (LOQ)
- Working range
- Analytical sensitivity
- Trueness (bias, recovery)
- Precision (repeatability, intermediate precision and reproducibility)
- Ruggedness (robustness)

The measurement method has been validated using gravimetrically prepared calibration gas mixtures according to ISO 6142-1. The mixtures contained 10 halogenated hydrocarbons in methane at approximately 50 nmol/mol amount fractions (Table A.1).

Table A.1: Physical properties of selected halogenated hydrocarbons

Name	CAS number	Formula	MW (g/mol)	B.P. (°C)
Vinyl chloride	75-01-4	C_2H_3Cl	62.498	-13.65
Ethane, 1,1,2-trichloro-1,2,2-trifluoro (Freon 113)	76-13-1	$C_2Cl_3F_3$	187.376	48
Chloroform	67-66-3	$CHCL_3$	119.4	61

1,2-dichloropropane	78-87-5	$C_3H_6Cl_2$	112.986	97
1,2-dichloroethylene	540-59-0	$C_2H_2Cl_2$	96.943	55
1,1,2-trichloroethane	79-00-5	$C_2H_3Cl_3$	133.404	113.8
Dichloromethane	75-09-2	CH_2CL_2	84.93	39.6
Trichloroethylene	79-01-6	C_2HCl_3	131.388	87.2
Tetrachloroethylene	127-18-4	C_2Cl_4	165.82	121
Chloromethane	74-87-3	CH_3Cl	50.488	-26
Hexane (internal standard)	110-54-3	C_6H1_4	86.1754	69

Sampling of the gas mixture is performed onto stainless steel sorbent tubes packed with different materials. The tubes are kept in the fridge until the time of the sampling and even after the sampling until the time of the analysis.

Three different sorbents were tested:

- Tenax TA
- Multi-bed sorbents: Tenax TA (weak), Carboxen 1003 (medium), Carbograph 1 (strong):
- Train of 2 sorbents (medium/weak): Chromosorb + Tenax TA: used in series

A.1.2 Validation results

A.1.2.1 Selectivity

The selectivity of the method is here two-fold:

The selectivity of a GC- system refers to its capacity to retain targeted components to a significantly greater or lower extent than other components. In other words, the GC-method shall be optimized to avoid coelution of the target compound with another component which also can be present in the sample to analyse (optimization of the temperature program of the column, the flow…).

With the GC-parameters used in this method, the following chromatogram is obtained for a volume of 240 ml gas vinyl chloride, freon 113, chloroform, 1,2-dichloropropane, 1,2-dichloroethylene, 1,1,2-trichloroethane, dichloromethane, trichloroethylene, tetrachloroethylene, chloromethane and hexane (Figure A.1). The separation of the compounds is very good with retention times varying from 5.7 min for vinyl chloride to 24.9 min for tetrachloroethylene (chloromethane could not be seen on Tenax).

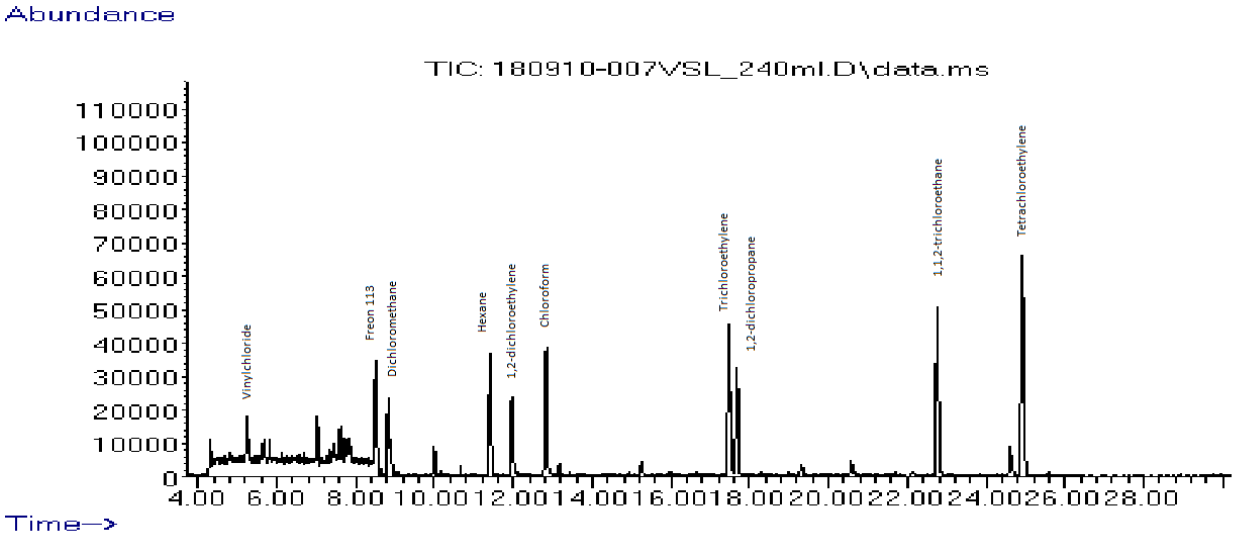
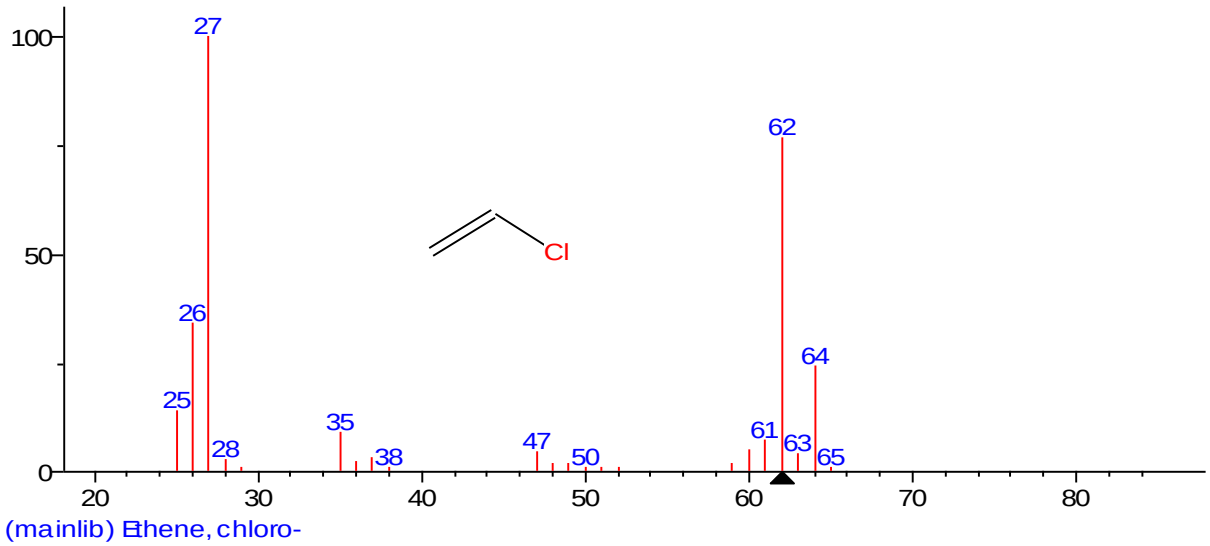
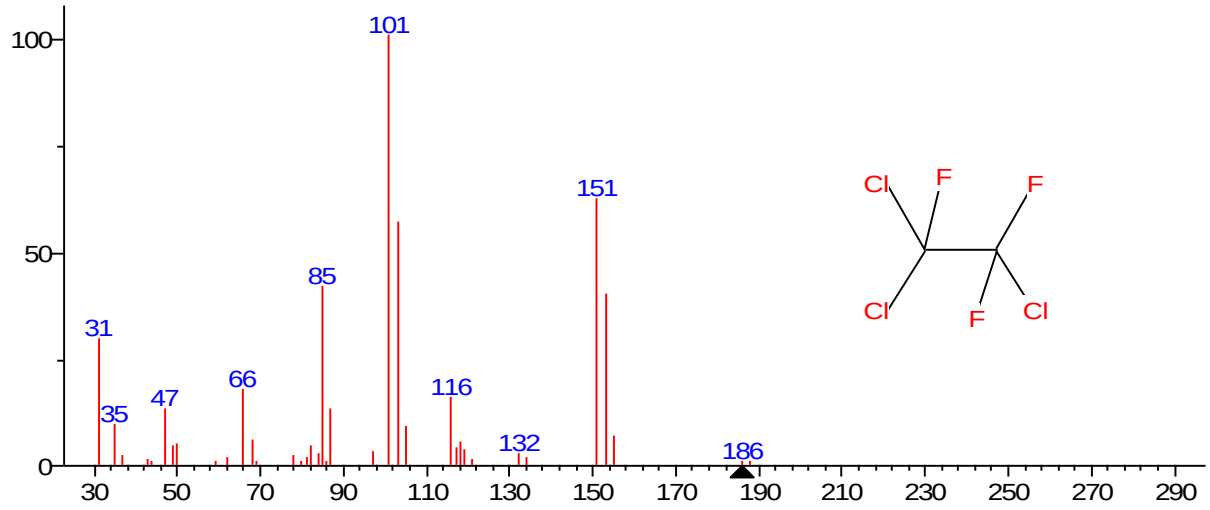


Figure A.1: Chromatogram for the halogenated compounds in methane

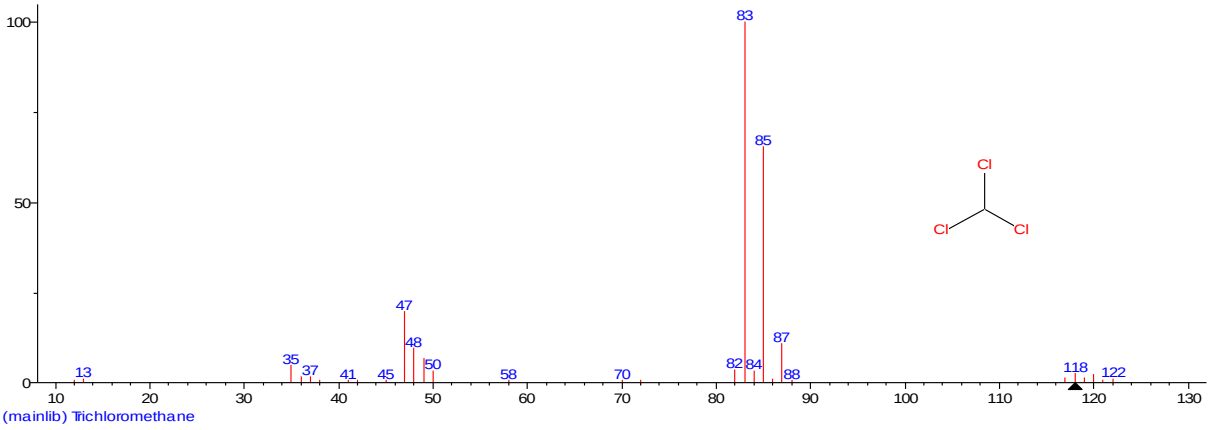
The selectivity of the MS-system is due to the fact that the detector gives structural information (i.e. a mass spectrum for each compound separated by GC), compounds can be identified by comparing their MS to a database of mass spectra or if not present in the database, to pure substances. The pattern of ion fragments will help control if they contain one, two or more chlorine atom as chlorine has two stable and naturally occurring isotopes, chlorine-35 and chrlorine-37, chrlorine-35 being 3 times more abundant. If we find two peaks separated by 2 m/z units and with a ratio of 3:1 in the peak heights, the fragment contains one chlorine (ex: for dichloromethane: m/Z = 49 and m/z = 51). If we find three peaks with gaps of 2 m/z units between them and with heights in the ratio of 9:6:1, the fragment contains 2 chlorine atoms.

On the figure A.2 below are presented the mass spectrum of the targeted compounds. In order: vinyl chloride (ethene, chloro), freon 113, chloroform, 1,2-dichloropropane, 1,2-dichloroethylene, 1,1,2-trichloroethane, dichloromethane, trichloroethylene, tetrachloroethylene, chloromethane and hexane.

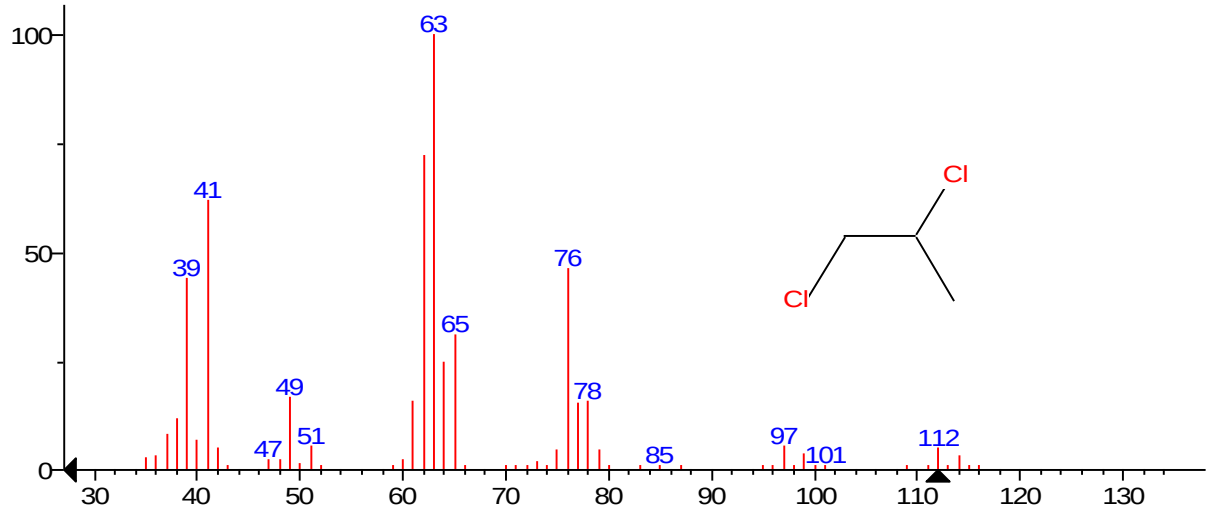




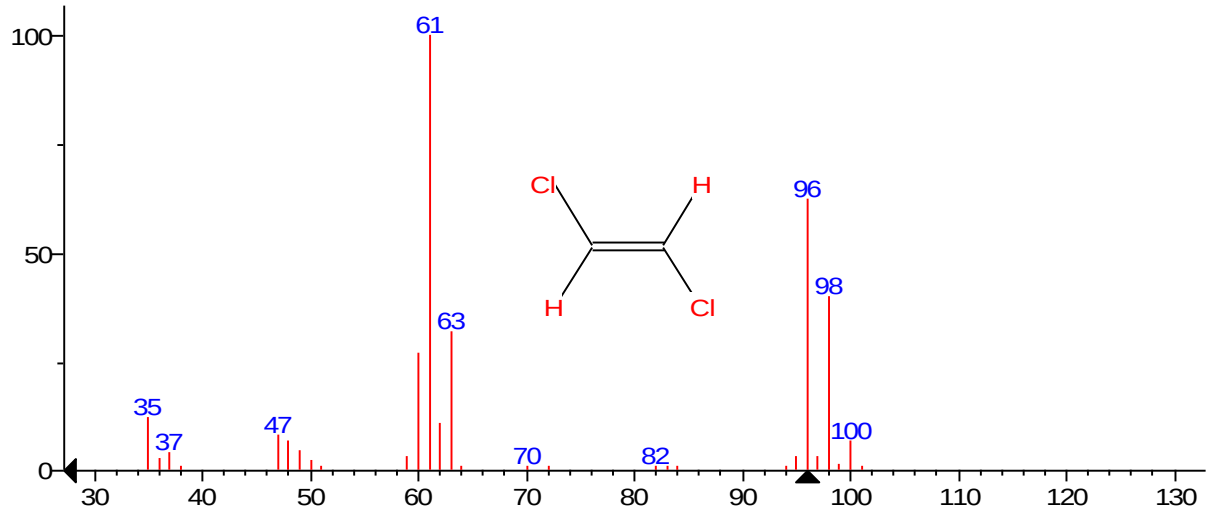
(replib) Ethane, 1,1,2-trichloro-1,2,2-trifluoro-



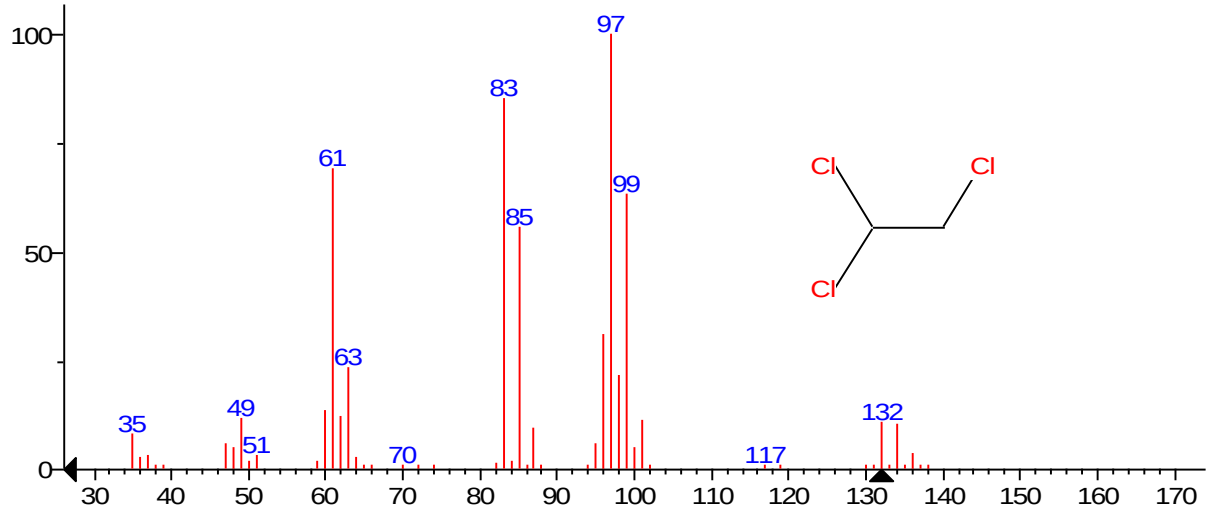
(mainlib) Trichloromethane



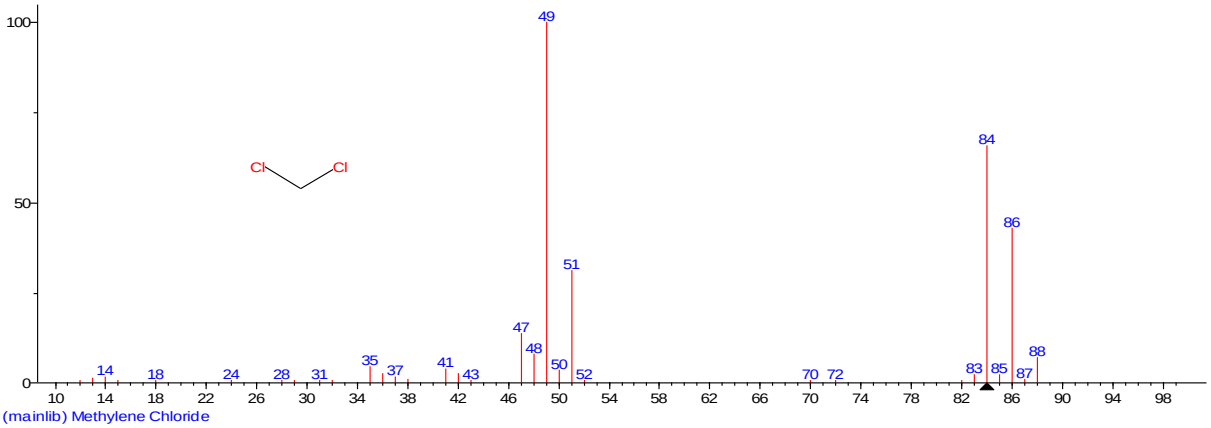
(replib) Propane, 1,2-dichloro-



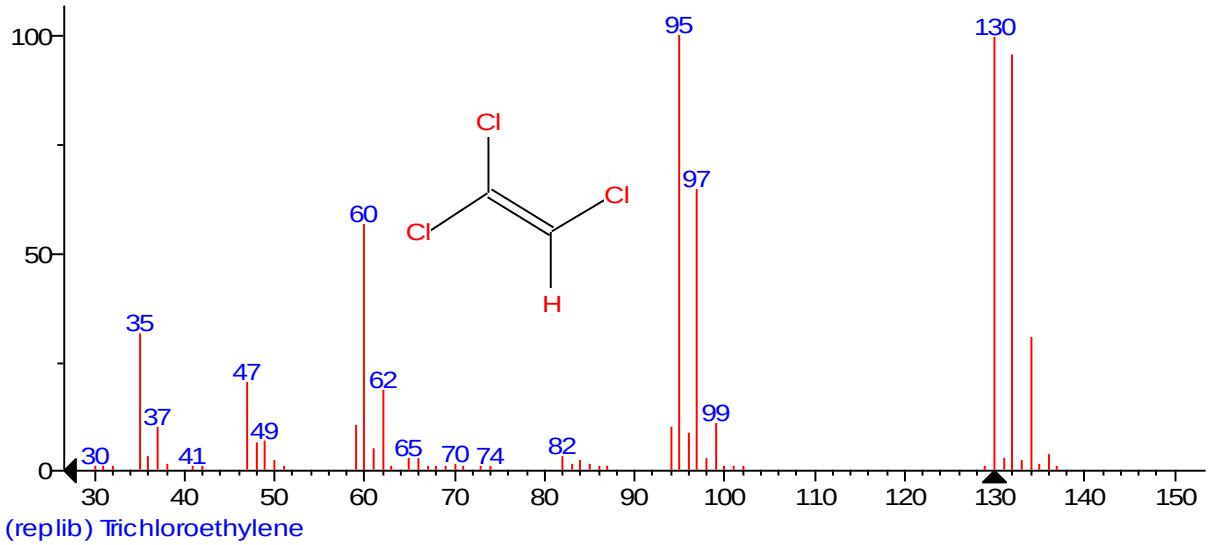
(mainlib) Ethene, 1,2-dichloro-, (E)-

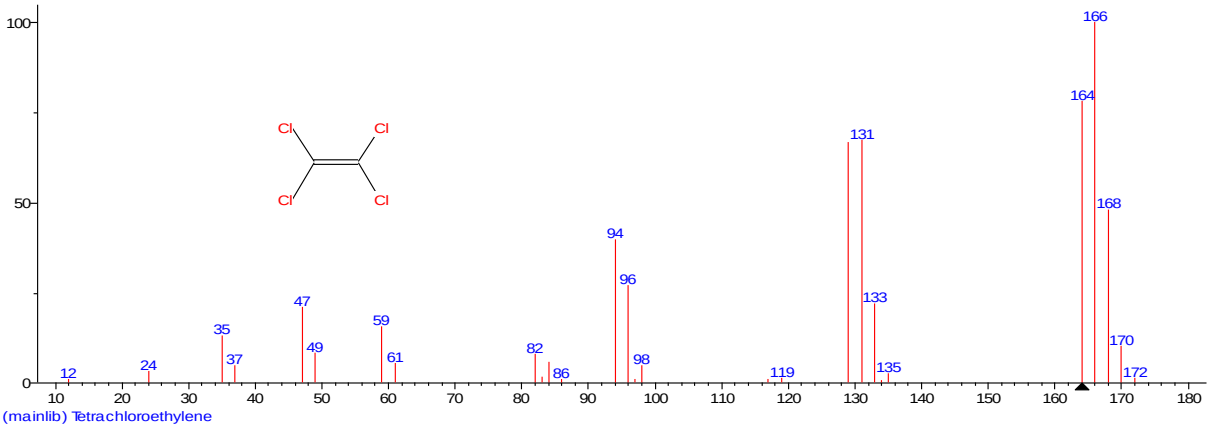


(replib) Ethane, 1,1,2-trichloro-



(mainlib) Methylene Chloride





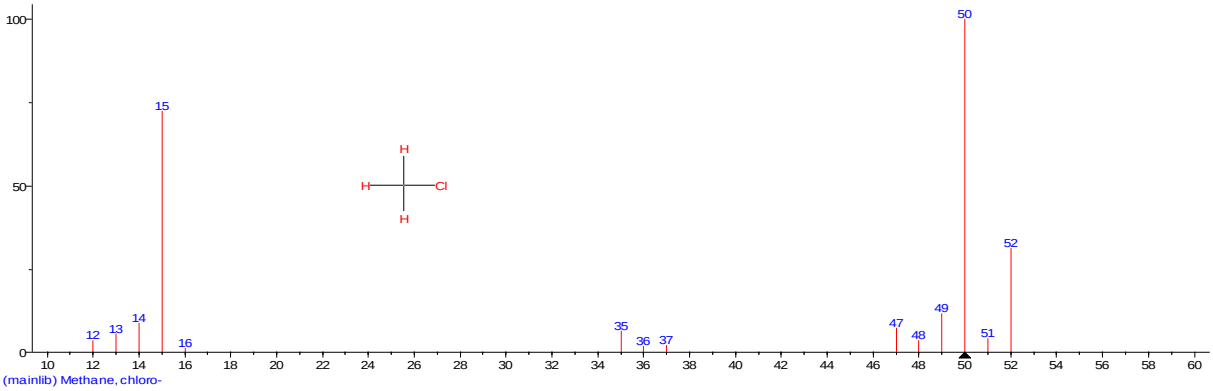


Figure A.2: Mass spectra for halogenated compounds (from top to bottom: vinyl chloride, freon 113, chloroform, 1,2-dichloropropane, 1,2-dichloroethylene, 1,1,2-trichloroethane, dichloromethane, trichloroethylene, tetrachloroethylene, chloromethane, hexane

From the mass spectra above, the following ions chosen as characteristic for each compound are presented in table A.2.

Table A.2: ions selected for quantification and identification of the targeted halogenated compounds

Name	Specific ions for identification (in bold, ions used for quantification)
Vinyl chloride	**62**-64
Freon 113	**101**-103-151-153
Chloroform	**83**-85-87 (ratio 9:6:1)
1,2-dichloropropane	**63**-76-111
1,2-dichloroethylene	**61**-96-98
1,1,2-trichloroethane	**97**-99-83-61
Dichloromethane	**84**-86-88 (ratio 9:6:1)
Trichloroethylene	**130**-132-95
Tetrachloroethylene	164-**166**-168
Chloromethane	**50**-52
Hexane	**146**-148-150 (ratio 9:6:1)

A.1.2.2 Limit of detection and limit of quantification

For the determination of the limit of detection (LOD) and the limit of quantification (LOQ), the method based on Signal-to-Noise (S/N) was used.

The determination of the S/N ratio is performed by comparing measured signals from sample with known low concentrations of analyte with those of blank samples and by establishing the minimum concentration at which the analyte can be reliably quantified. A typical S/N for LOD is 3:1 and for LOQ 10:1.

The LOD and LOQ were calculated using solutions of the targeted compounds in diethylether injected on Tenax TA tubes (corresponding to 2.35 ng/tube respective 4.7 ng/tube for each compound).

The chromatograms obtained for two targeted compounds (chloroform and tetrachloroethylene) are presented in the following figures.

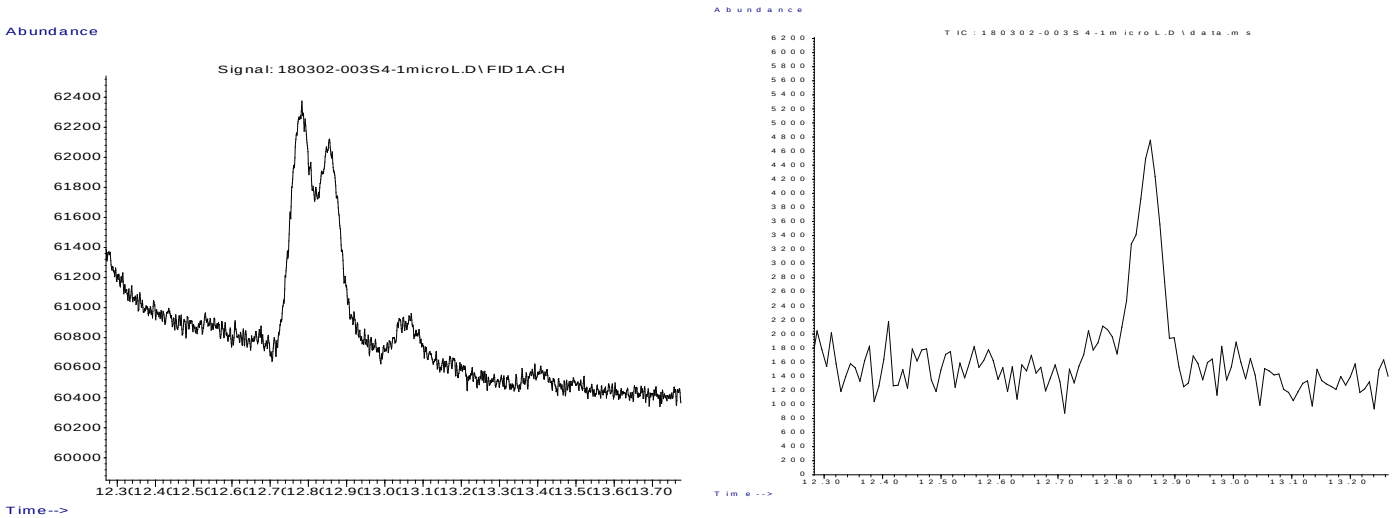


Figure A.3: Chloroform (4.7 ng, left: FID, right: MS TIC)

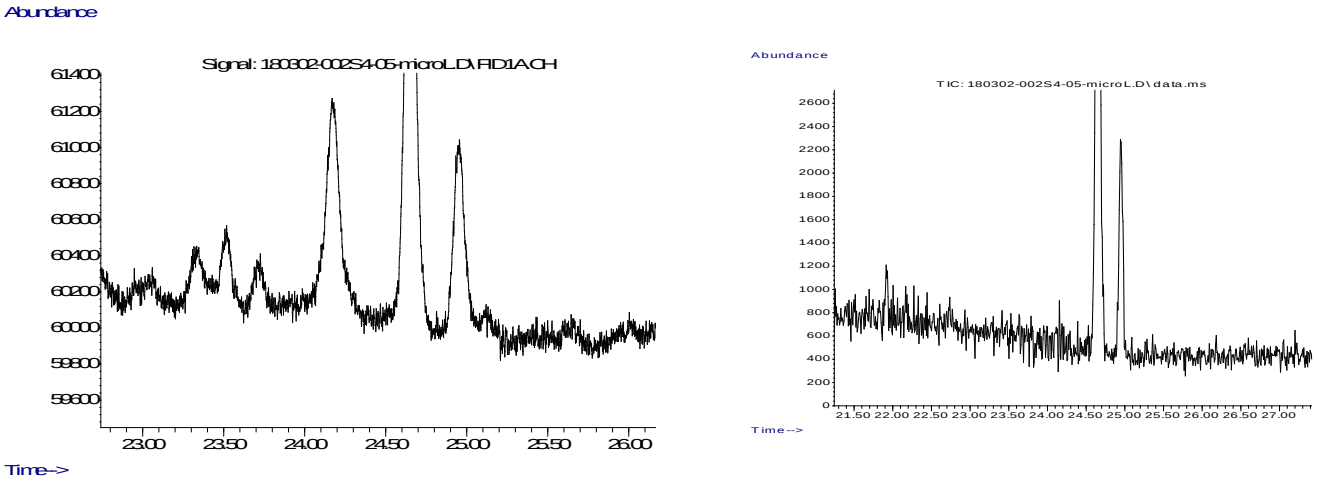


Figure A.4: Tetrachloroethylene (2.35 ng, left: FID, right: MS TIC)

The results are summarized on the following tables:

Table A.3: LOD in ng/tube for halogenated compounds on Tenax TA

ng/tube	FID	MS TIC	MS extracted ion
Chloroform	10	8	7
Tetrachloroethylene	6	4	12

If 100 ml of biomethane is sampled on the tube, there results can be expressed in nmol/mol:

Table A.4: LOD in nmol/mol for halogenated compounds on Tenax TA

nmol/mol	FID	MS TIC	MS extracted ion
Chloroform	9	4	3
Tetrachloroethylene	6	2	4

A.1.2.3 Working range

The linearity of the newly developed method was assessed by injecting some µl (0.5, 1 or 2) of solutions containing the targeted compounds so the tubes contain 2.35, 4.7, 9.4, 23.5, 47, 94 respectively 235 ng of each compound. This data was treated by plotting a linear regression and evaluation of the correlation coefficients (R-squared) undertaken.

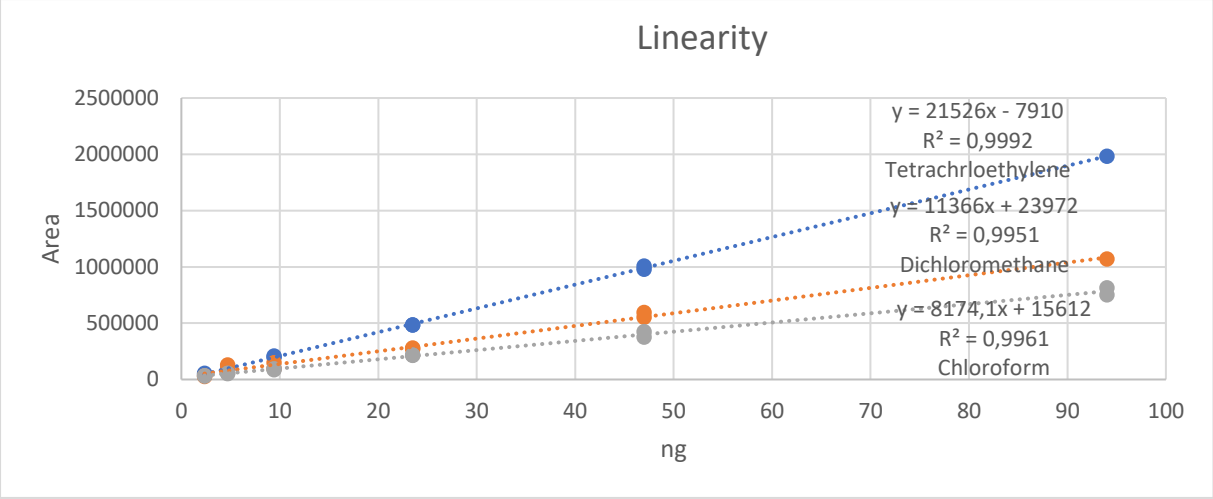


Figure A.5: Plot of linearity for tested halogenated compounds at 2.35, 4.7, 9.4, 23.5, 47, 94, 235 ng

As can be seen in Figure A.5, all correlation coefficients are close to a value of 1.00, indicating that the equation for the linear regression describes/fits the data closely. This in turn indicates that the method has potentially a linear working range of 5 to 250 ng/tube for halogenated compounds.

To verify the working range and linearity, we measured calibration standards 2-3 times at 7 concentrations evenly spaced across the linear range. We then calculated and plotted residuals (difference between observed y value and calculated y value predicted by the straight line for each x value. The results are shown in Figure A.6 for Tetrachloroethylene with a FID detector.

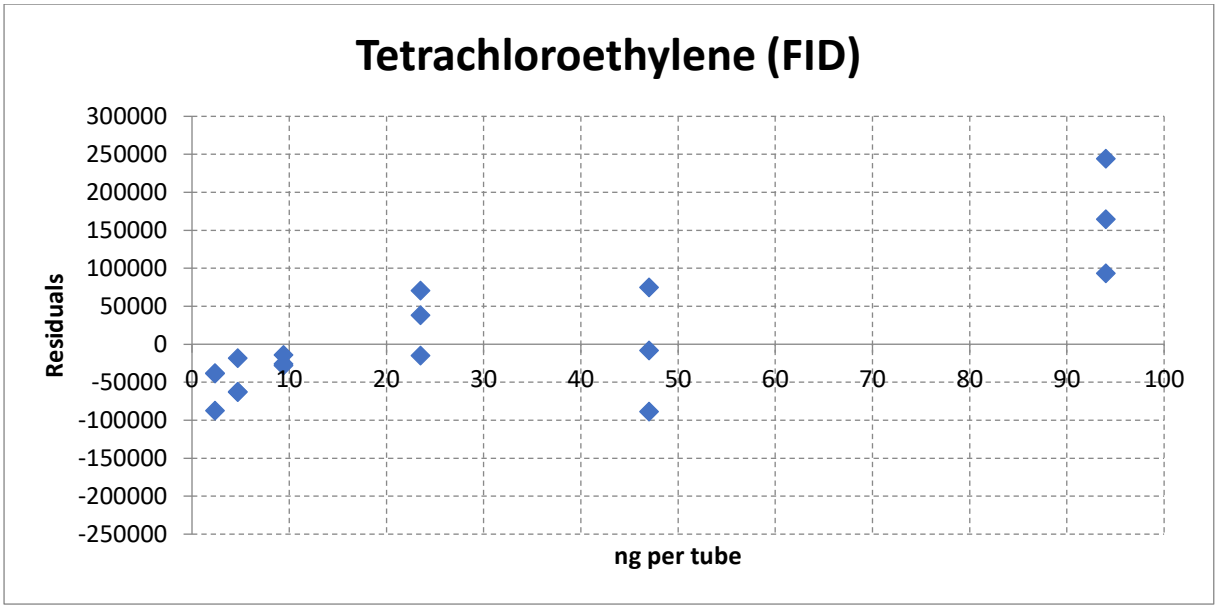


Figure A.6: Residuals for tetrachloroethylene (FID) for 2.35, 4.7, 9.4, 23.5, 47, 94, 235 ng per tube

The distribution of residuals is random, confirming the linearity (and working range).

A.1.2.4 Precision

The precision of the method was assessed using replicate measurements at a number of concentrations across the range of interest. The intermediate precision (different analysts, same equipment, same laboratory, two weeks' timescale) was then estimated. In Table A.5, the estimated intermediate precision is given some targeted compounds.

Table A.5: Estimation of the intermediate precisions for halogenated (some outsiders from the 14 measurements are removed)

$S_{Rw}/\sqrt{2}$ (%)	FID	MS TIC	MS extracted ion
Dichloromethane	3.7 (n=10)	3.3 (n=10)	3.3 (n=10)
Chloroform	2.7 (n=13)	2.3 (n=13)	1.7 (n=13)
Tetrachloroethylene	1.7 (n=12)	1.8 (n=13)	2.0 (n=10)

The intermediate precision is around 2% rel. for most compounds with all three quantification methods (FID, MS TIC or MS extracted ion) except for dichloromethane (around 3% rel.). This is probably due to the fact that dichloromethane eluates within the tail of the solvent leading to a higher background under the dichloromethane´s peak mostly in FID.

A.1.2.5 Trueness

The trueness of the method was calculated using a certified reference gas mixture containing 10 halogenated hydrocarbons at around 50 nmol/mol each.

Table A.6: Bias on Tenax and on Tenax TA/ Carboxen 1003/ Carbograph 1

	Certified concentration (nmol/mol)	Tenax	Rel.stdev %	Tenax TA/ Carboxen 1003 /Carbograph 1	Rel.stdev %
Chloromethane	51.303	-	-	46.8	9.2
Vinyl chloride	50.0879	22.7	16.5	46.6	1.4
Ethane, 1,1,2-trichloro-1,2,2-trifluoro	47.681	20.3	12.0	46.3	1.7
Dichloromethane	50.046	42.8	4.0	52.1	3.3
12-dichloroethylene	51.728	43.7	6.1	49.9	3.4
Chloroform	51.964	50.6	1.3	50.8	2.1
Trichloroethylene	52.757	45.4	4.6	50.6	2.8
12-dichloropropane	52.61	51.4	2.2	49.7	1.5
112-trichloroethane	69.51	67.4	2.7	67.8	3.7
Tetrachloroethylene	52.422	53.5	1.8	52.0	1.8

A.1.2.6 Ruggedness (robustness)

The flow and the pressure across the tube during sampling are most certainly the variables which could have a significant effect on method performance.

If the pressure is too high during sampling, the tubes may be damaged.

The effect of the flow was tested using a home-made gas mixture containing the targeted compounds at 150 to 400 nmol/mol. Five different flows were tested on Tenax TA tubes. Three flow rates, 67 ml/min, 100 ml/min and 200 ml/min, were in the traditionally accepted ranges (up to 250 ml/min) and two flow rates were above, 400 ml/min and 1200 ml/min. The results are presented on figure A.7.

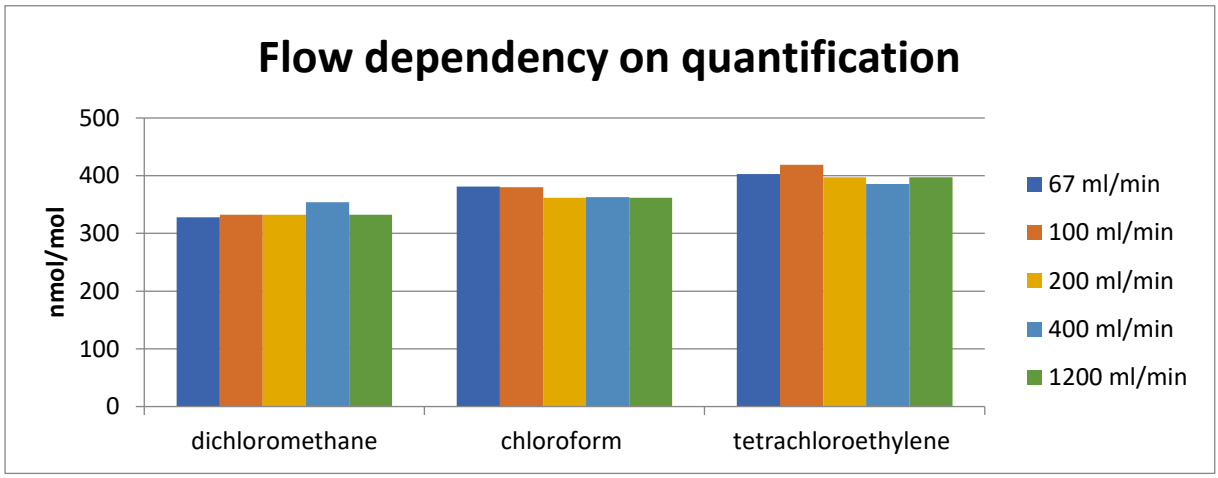


Figure A.7: Quantification of targeted halogenated compounds when sampling at 5 different flow rates

Even at higher flow rates than traditionally recommended, no effects were observed on the results. This may be because of the low volume of gas sampled on the tubes, 100 ml.

A.1.3 Measurement uncertainties

The expanded uncertainty has been calculated using the software MUKit Measurement Uncertainty kit. This software is based on Nordtest report 537, www.nordtest.info where uncertainty is estimated using quality control and validation data.

The repeatability has been overestimated when using the program as the repeability in the program is calculated for single measurement.

An example is given for chloroform on Tenax TA/Carboxen 1003 / Carbograph 1:

RISE MEASUREMENT UNCERTAINTY ESTIMATION

Step	Action	Halogenated hydrocabons -	2019-02-18
1	Specify Measurand	Analyte measured: Chloroform TCC Concentration range: 2 - 200 nmol/mol Matrix: hydrogen or other gases that do not adsorb on the sorbent Analysis method: TD-GC/MS-FID Sample preparation: sampled 100 ml on the tube	
2	Quantify within-laboratory reproducibility, $u(R_w)$ A: Control sample B: Possible steps not covered by control sample	**A: Control samples:** Matrix: Hydrogen or other gases Number of control samples: 9 Average concentration: 51,100000 nmol/mol Standard deviation, s_{Rw} : 0,89 % **B: Routine replicate samples :** Number of routine replicate samples: 9 Number of parallell measurements: 2 Concentration range: 30,485269 - 43,270786 nmol/mol Standard deviation estimate from range, s_r : 1,57 % $u(R_w) = \sqrt{{s_{Rw}}^2 + {s_r}^2}$ = 1,81 %	
3	Quantify method and laboratory bias, $u(bias)$	**Method and laboratory bias from certified reference material:** Different certified reference materials count, N : 1	
		i: 1 Certified concetration, $c_{ref\,i}$: 51,964 nmol/mol Standard uncertainty of certified concentration, $u(c_{ref_i})$: 2,00 % Measured concentration, c_i: 50,8 nmol/mol Standard deviation of measured concentration, s_{bias}: 2,10 % Number of Measurements, n_i: 9 $bias_i = \frac{c_i - c_{ref_i}}{c_{ref_i}} \cdot 100\%$: -2,24 % Period of measurements: - Matrix: Additional information:	
		$u(bias) = \sqrt{{bias_1}^2 + \left(\frac{s_{bias_1}}{\sqrt{n_1}}\right)^2 + u\left(c_{ref_1}\right)^2}$ = 3,08 %	
4	Convert components to standard uncertainty	$u(R_w)$ = 1,81 % $u(bias)$ = 3,08 %	
5	Calculate combined standard uncertainty, u_c	$u_c = \sqrt{u(Rw)^2 + u(bias)^2}$ = 3,57 %	
6	Calculate expanded uncertainty, U	$U = 2 \cdot u_c$ = 8 %	

The results for the other compounds are presented in the following table (results for the compounds for which a certified reference material was available):

Table A.7: measurement uncertainties on Tenax and Tenax TA/Carboxen 1003 / Carbograph 1

	Tenax			Tenax TA/Carboxen 1003 / Carbograph 1:		
	$U(R_w)$ (%)	u(bias) (%)	U (%)	$U(R_w)$ (%)	u(bias) (%)	U (%)
Chloroform	4.20	3.33	11	1.81	3.08	8
Dichloromethane	5.45	14.66	32	4.47	4.54	13
Tetrachloroethylene	3.64	2.90	10	2.88	2.26	8

A.1.4 Suitability of sorbent materials for halogenated hydrocarbons

The suitability of sorbents for halogenated have been assessed by measuring the recovery yield and the storage stability for each compound. The recovery yield is defined as the ratio of the measured and the spiked content and expressed as a percentage. To evaluate the different

sorbents, the following criteria were adopted: recoveries above 90% were considered as very good; recoveries between 85 to 90% were considered as good; recoveries from 50 to 84% were considered as low and finally, for recoveries below 50%, the sorbent material was considered as not suitable for the targeted compound.

The storage stability is defined as the change in content for a given compound as determined at the end of the storage time compared to that at the start of the stability test. Storage periods of two weeks were evaluated since this is the period typically required to complete the collection, transport and analysis of hydrogen samples. To evaluate the different sorbents, the following criteria were selected: the storage stability was considered as very stable in the cases where the D14 concentration was found to be less (or more) than 10% lower than the initial concentration (D0); the storage stability was considered to be relatively stable in the cases where D14 (or D10 in some tests) was found to be less than 25% lower than the D0 concentration; the storage stability was considered as not stable in the cases where the D14 concentration (or D10 in some tests) was found to be more than 26% lower than the initial concentration (D0). The results are presented in Table A.8.

Table A.8: Evaluation of the suitability of sorbent materials for halogenated hydrocarbons

	BP (°)	Chromosorb 106		TCC		Tenax TA	
		Recovery yield	Storage stability	Recovery yield	Storage stability	Recovery yield	Storage stability
Chloromethane	-26	Not suitable	n.d.	Low	Relatively Stable	Not suitable	n.d.
Vinyl chloride	-14	Not suitable*	Very stable	Not suitable*	Unstable	Low	Very Stable
Freon 113 (trichloroethane)	47	Very good	Very stable	Very good	Relatively Stable	Not suitable	Very Stable
Dichloromethane	40	Very good	Very stable	Very good	Unstable	Good	Very Stable
12-Dichloroethylene	55	Very good	Very stable	Very good	Relatively Stable	Good	Very Stable
Chloroform	61	Low	Very stable	Low	Unstable	Low	Very Stable
Trichloroethylene	87	Good	Unstable	Very good	Very Stable	Very good	Very Stable
1,2-Dichloropropane	97	Very good	Very stable	Very good	Relatively Stable	Very good	Very Stable
1,1,2-Trichloroethane	114	Good	Very stable	Very good	Relatively Stable	Very good	Very Stable
tetrachloroethylene	121	Very good	Very stable	Very good	Relatively Stable	Very good	Very Stable

Among the targeted compounds, chloromethane was the only compound for which none of the sorbent materials tested were found to be suitable. This is due to the very low boiling point of this compound. Vinyl chloride was found to be unstable as it gave rise to high variations when analysing replicates.

Annex B: Validation data measurement method – online gas analysis using TD-GC-FID/MS – method 1

B.1 Introduction

The characterization of the method was carried out by applying:

- the requirements of the NF T 90-210 standard for the characterization of the calibration curve, the validation of the limit of quantification, the determination of the accuracy at various levels of HC concentrations;

- the requirements of the EN ISO 11352 standard for the evaluation of uncertainties at various levels of halogenated VOC concentrations.

The study was performed using a certified reference gas mixture supplied by VSL (code APEX1170589) containing the 10 targeted compounds + n-hexane (used as internal standard) in a mixture of methane, carbon dioxide and nitrogen. The concentrations are expressed in mol/mol.

Table B.1: nominal concentrations of BTEX in the reference gas mixture

Compounds	Nomimal value (mol/mol)
methyl chloride (chloromethane)	50E-09
vinyl chloride	50E-09
trichloro trifluoroethane (Freon 113)	50E-09
methylene chloride (DCM)	50E-09
dichloroethylene-1.2 cis	50E-09
n hexane	50E-09
chloroform (trichloromethane)	50E-09
trichloroethylene	50E-09
dichloropropane-1.2	50E-09
trichloroethane-1.1.2	70E-09
ethylene tetrachloride (tetrachloroethylene)	50E-09

B2 Calibration curve

6 different levels of concentration are prepared by trapping different quantities (volume) of the reference mixture prepared by VSL at controlled flow rates and time.

The calibration is performed using these 6 levels at various concentrations. Studied compounds of the reference mixture are directly injected into the analytical system for analysis by GC/FID

or GC/MS. The calibration ranges from about 10 ng/tube to about 400 ng/tube (depending on compounds).

B.3 Sampling method of the HC

Following a test of several sorbents (data not shown), "Air toxics" tubes were selected as the most suitable to trap efficiently the selected compounds. "Air toxics" tubes (acquired from Antelia, France) are composed of Carbotrap B 20/40 mesh and Carboxen 1000 60/80 mesh and have been cited in EPA TO-17 (Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes).

The sampling is performed by using the VSL reference gas mixture at controlled flow rates (50 ml/min) with variable lengths of time onto Air Toxic tubes. The tubes are connected directly to the flow regulator mounted on the gas bottle. A mass flow meter is connected after the tubes to control the flow.

This sampling method is used for the evaluation of the accuracy and of the uncertainties at different levels of concentrations of compounds in biomethane.

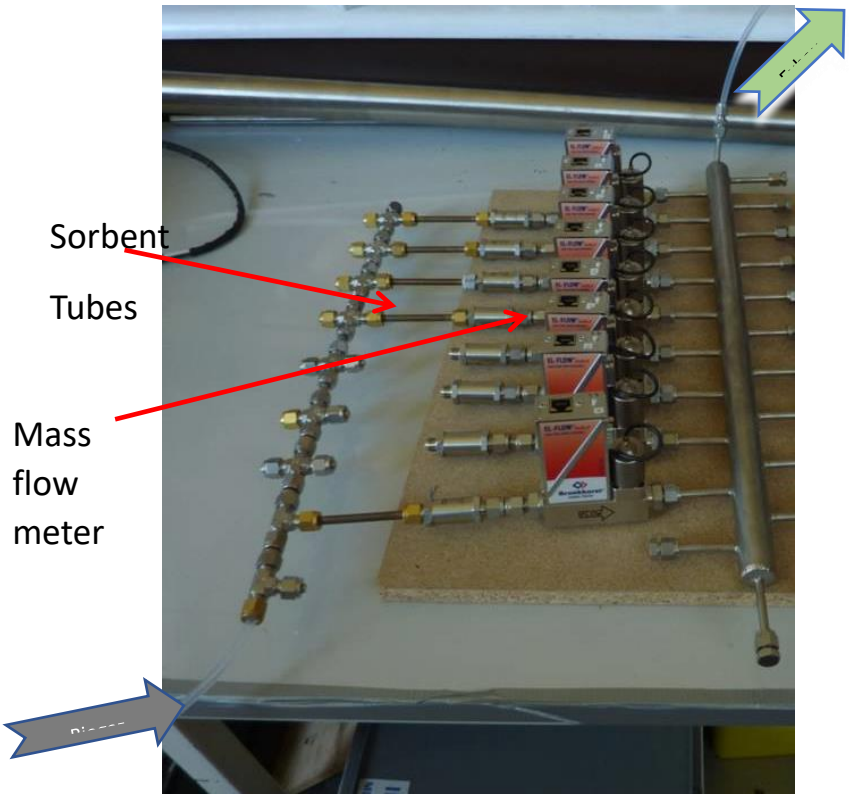


Figure B.1: Sampling system with sorbent tubes for the gas mixture

B.4 Validation results

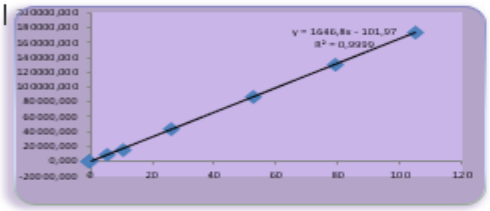
B.4.1 Linear range

The characterization of the calibration curve for the HC is performed using 6 levels of concentration from, depending on compounds, about 5 ng/tube to about 20 ng/tube for the lowest level to about 100 to 400 ng/tube for the highest levels. Each calibration is performed 5 times in conditions of intermediate precision (same person, different day). Weighed linear regression in 1/x is used as the calibration model. The linear range is verified according to the

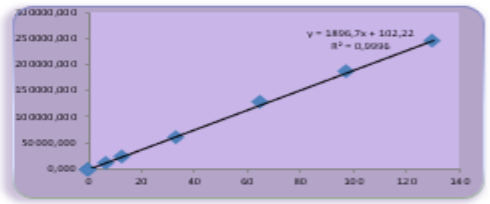
French standard NF T 90-210 requirements, with a correlation coefficient over 0.9988 for FID detection and over 0.998 for MS detection, for this concentration range. Calibration curves could not be performed for methyl chloride and vinyl chloride in FID detection due to the interference provided by methane.

Table B.2: Low and high concentration of the linear range

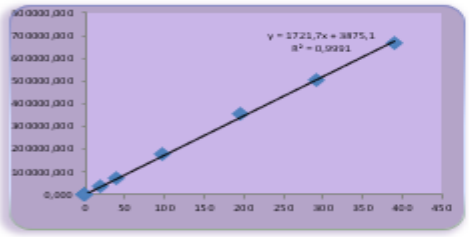
Compound	Low level (ng/tube)		High level (ng/tube)	
	FID	MS	FID	MS
methyl chloride	-	5,3	105	105
vinyl chloride	-	6,5	130	130
trichloro trifluoroethane (FREON)	19,1	19,1	382	382
methylene chloride (DCM)	8.8	8.8	117	117
n hexane	9	9	180	180
dichloroethylene-1.2 cis	10,1	10,1	202	202
chloroform	12,4	12,4	249	249
trichloroethylene	13,7	13,7	274	274
dichloropropane-1.2	11,8	11,8	235	235
trichloroethane-1.1.2	13,9	13,9	278	278
ethylene tetrachloride	17,2	17,2	344	344



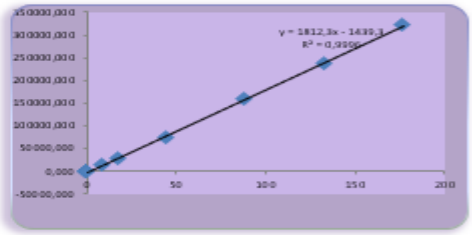
Calibration curve for methyle chloride



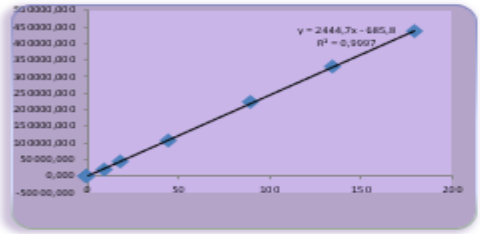
Calibration curve for methyle chloride



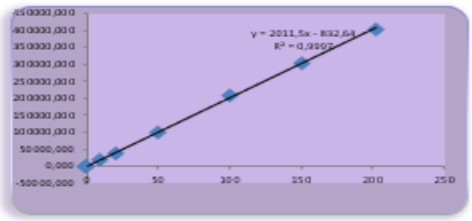
Calibration curve for trichlorotrifluoroethane



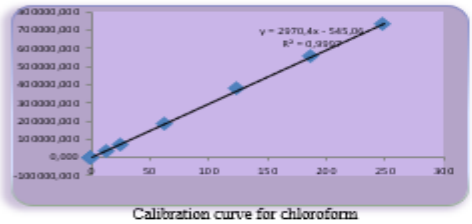
Calibration curve for methylene chloride



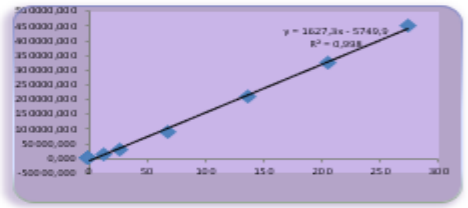
Calibration curve for hexan



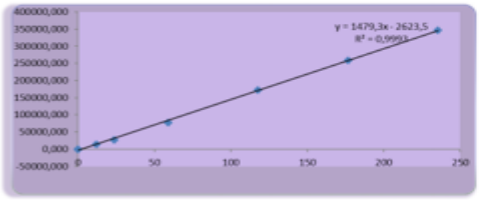
Calibration curve for dichloroethylene-1.2-cis



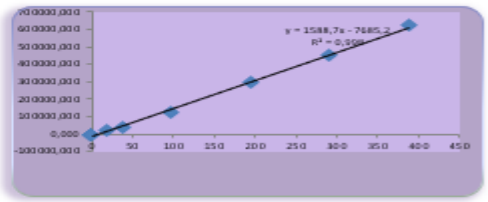
Calibration curve for chloroform



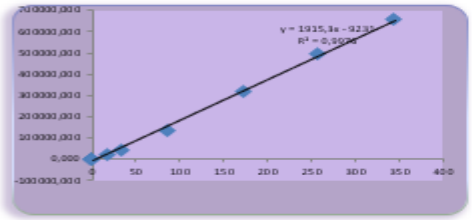
Calibration curve for trichloroethylene



Calibration curve for dichloropropane-1.2

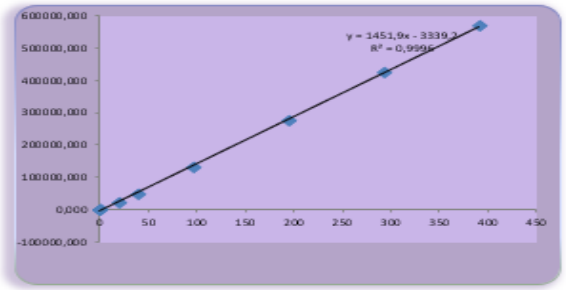


Calibration curve for trichloroethane1.1.2

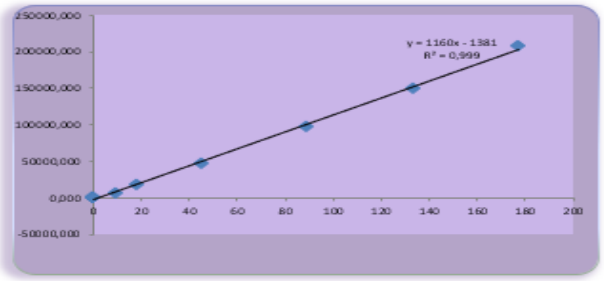


Calibration curve for tetrachloroethylen

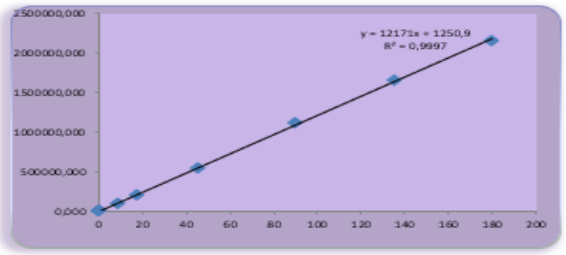
Figure B.2: Calibration curves for HC (MS)



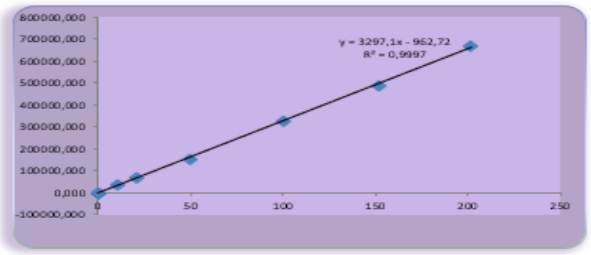
Calibration curve for trichlorotrifluoroethane



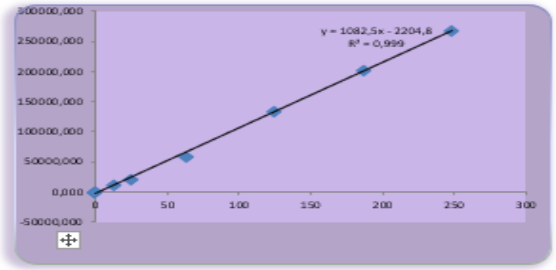
Calibration curve for dichloromethane



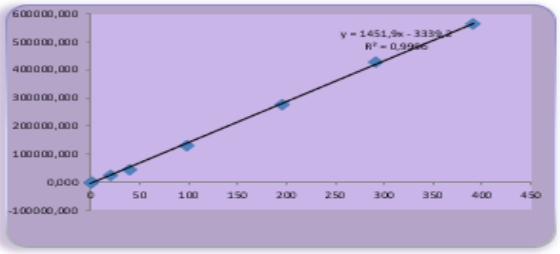
Calibration curve for hexane



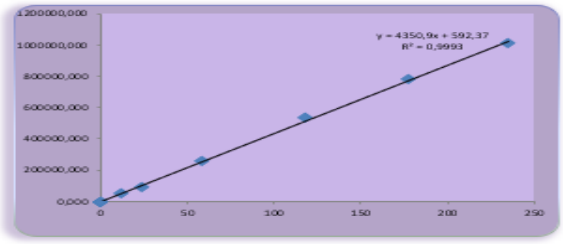
Calibration curve for dichloroethylene-1.2-cis



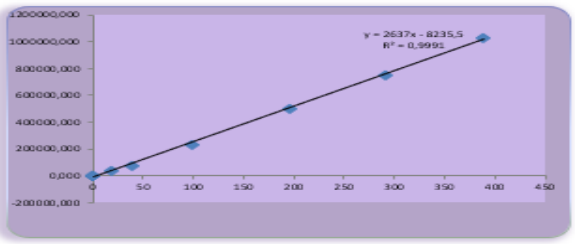
Calibration curve for chloroform



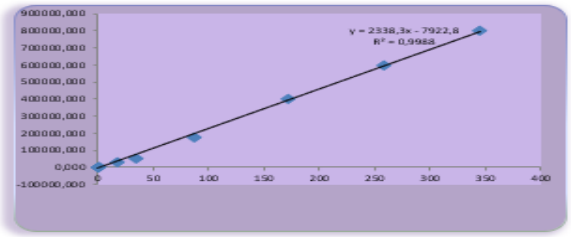
Calibration curve for trichloroethylen



Calibration curve for dichloropropane-1.2



Calibration curve for trichloroethane-1.1.2



Calibration curve for tetrachloroethylene

Figure B.3: Calibration curves for HC (FID)

B.4.2 Limit of Quantification (LOQ)

LOQs are determined according to the NFT 90-210, a French standard based on the ISO 5725 accuracy measurements methodology. LOQs are evaluated within conditions of repeatability with duplicates for the extraction (two tubes spiked at the same level of concentration), and interday precision by performing 6 series of duplicate extraction on 6 different days. This methodology analyzes trueness and precision of the results for each HC at a concentration close to the supposed limit of quantification. This test ensures that accuracy (trueness and precision) does not exceed ± 60% of the supposed LOQ. The experiments for the determination of the LOQ were performed by spiking an appropriate volume of the VSL reference mixture onto the sorbent tubes.

Table B.3: validated Limits of Quantification according to NF T 90-210 Standard and the detector used

Compounds	LOQs (ng/tube) validated according to NF T 90-210 Standard	
	FID	MS
methyl chloride (chloromethane)	-	10
vinyl chloride	-	6,5
trichloro trifluoroethane (Freon 113)	19,1	19,1
methylene chloride (DCM)	17,6	17,6
dichloroethylene-1.2 cis	10,1	10,1
chloroform (trichloromethane)	24,8	12,4
trichloroethylene	27,4	27,4
dichloropropane-1.2	11,8	11,8
trichloroethane-1.1.2	27,8	27,8
ethylene tetrachloride (tetrachloroethylene)	34,4	34,4

B.4.3 Accuracy

Accuracy of the analytical method is evaluated according to the French NF T 90-210 Standard. Tests are performed at 3 levels of concentration within conditions of repeatability with duplicates for the sampling and extraction (two tubes spiked at the same level of concentration) and interday precision by performing 6 series of extraction in duplicates on 5 different days.

The sampling of the reference gas mixture is performed at controlled flow rates (50 ml/min) with variable exposure time onto AirToxic tubes.

This methodology analyzes trueness and precision of the results for each HC at the studied concentration. This test ensures that accuracy (trueness and precision) does not exceed ± 40% of the spiked concentration for intermediate concentrations and ± 30% of the spiked concentration for the highest concentration.

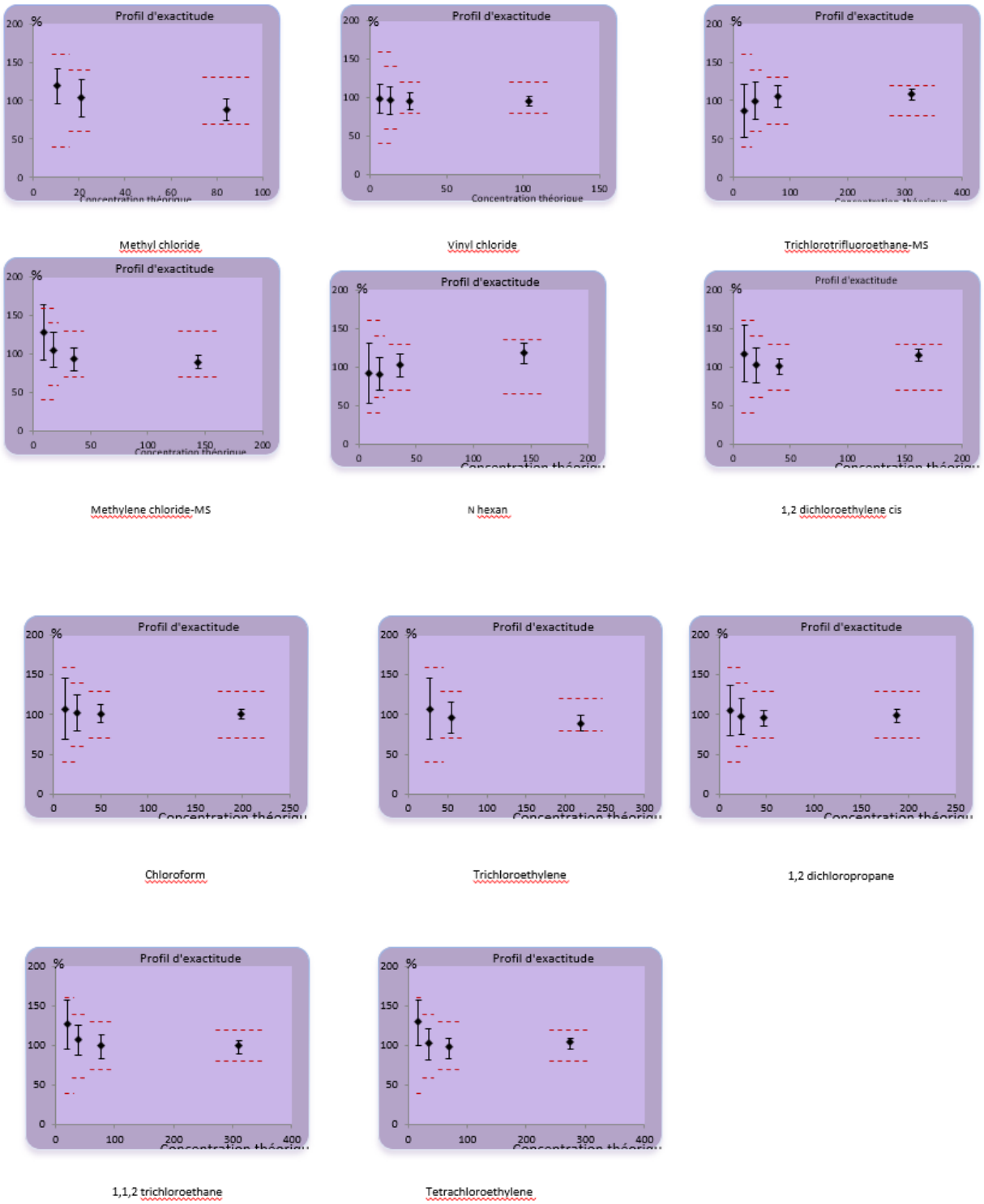


Figure B.4: Accuracy profiles at LOQ and other levels of concentration (MS)

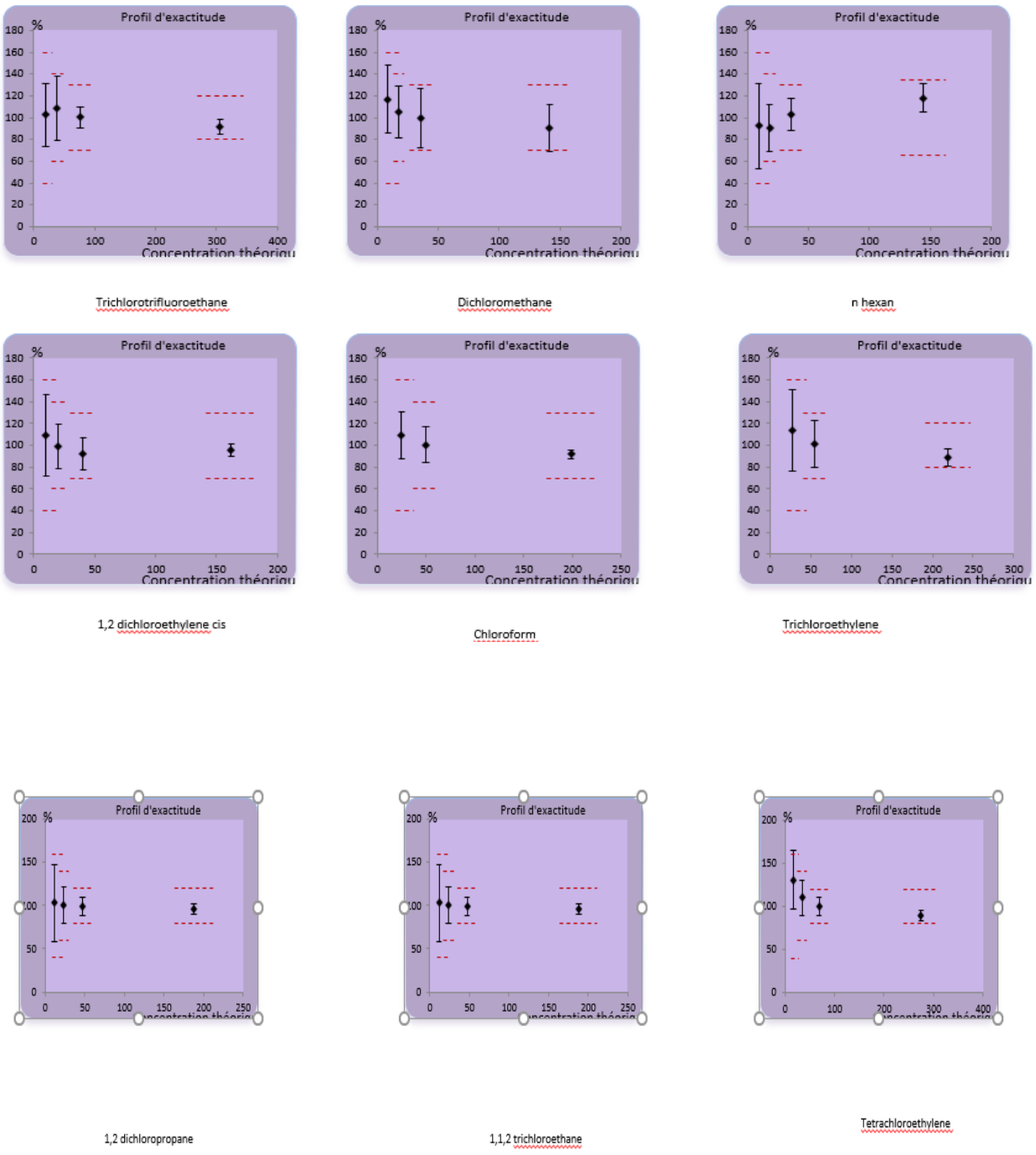


Figure B.5: Accuracy profiles at LOQ and other levels of concentration (FID)

B.5 Measurement uncertainty

The expanded uncertainties have been calculated according to the requirements of ISO 11352 Standard using the software MUKit Measurement Uncertainty kit. Considering that the measurement uncertainty may vary depending on the concentration range, the uncertainty is estimated separately for 4 concentration ranges within the linear concentration range. The determination of uncertainty is based on validation and quality control which represent the within-laboratory reproducibility of the method and the laboratory bias. In this standard, the expanded measurement uncertainty is quantified as the interval comprising the value on the measurand with a probability of about 95%.

Table B.4: Summary table of the expanded uncertainties (*k*=2) obtained at the various tested levels

Compound	Detector	LOQ*	≈20 % of the highest level	≈80 % of the highest level
methyl chloride	MS	60	42	40
	FID	-	-	-
vinyl chloride	MS	60	29	24
	FID	-	-	-
trichloro trifluoroethane (FREON)	MS	139	79	55
	FID	80	53	65
methylene chloride (DCM)	MS	51	22	15
	FID	109	90	79
dichloroethylene-1.2 cis	MS	78	21	47
	FID	112	56	42
chloroform	MS	56	41	46
	FID	90	66	46
trichloroethylene	MS	47	32	50
	FID	114	72	39
dichloropropane-1.2	MS	105	49	60
	FID	69	52	41
trichloroethane-1.1.2	MS	98	72	69
	FID	94	62	47
ethylene tetrachloride	MS	70	50	64
	FID	103	66	35

Annex C: Validation data measurement method – online gas analysis using TD-GC-FID/MS – method 2

The ATD-GC can be used in FID and MSD mode. The measurement method has been validated using gravimetrically prepared calibration gas mixtures according to ISO 6142-1. The mixtures contained 10 halogenated hydrocarbons in methane at approximately 750 and 50 nmol/mol amount fractions (Table C.1).

Table C.1: Physical properties of selected halogenated hydrocarbons

Name	CAS number	Formula	MW (g/mol)	B.P. (°C)
Vinyl chloride	75-01-4	C_2H_3Cl	62.498	-13.65
Ethane, 1,1,2-trichloro-1,2,2-trifluoro (Freon 113)	76-13-1	$C_2Cl_3F_3$	187.376	48
Chloroform	67-66-3	$CHCL_3$	119.4	61
1,2-dichloropropane	78-87-5	$C_3H_6Cl_2$	112.986	97
1,2-dichloroethylene	540-59-0	$C_2H_2Cl_2$	96.943	55
1,1,2-trichloroethane	79-00-5	$C_2H_3Cl_3$	133.404	113.8
Dichloromethane	75-09-2	CH_2CL_2	84.93	39.6
Trichloroethylene	79-01-6	C_2HCl_3	131.388	87.2
Tetrachloroethylene	127-18-4	C_2Cl_4	165.82	121
Chloromethane	74-87-3	CH_3Cl	50.488	-26
Hexane (internal standard)	110-54-3	C_6H1_4	86.1754	69

All halogenated VOCs could be detected using ATD-GC in MSD mode (Figure C.1). In the FID mode chloromethane and vinyl chloride could not be detected (Figure C.2).

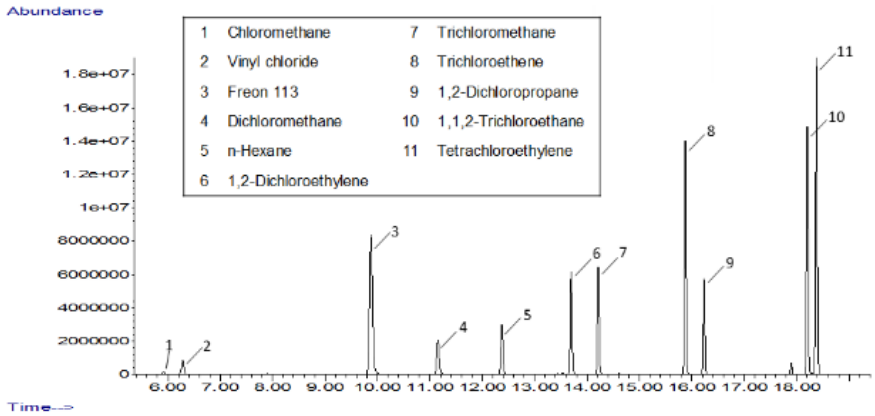


Figure C.1: ATD-GC-MSD chromatogram

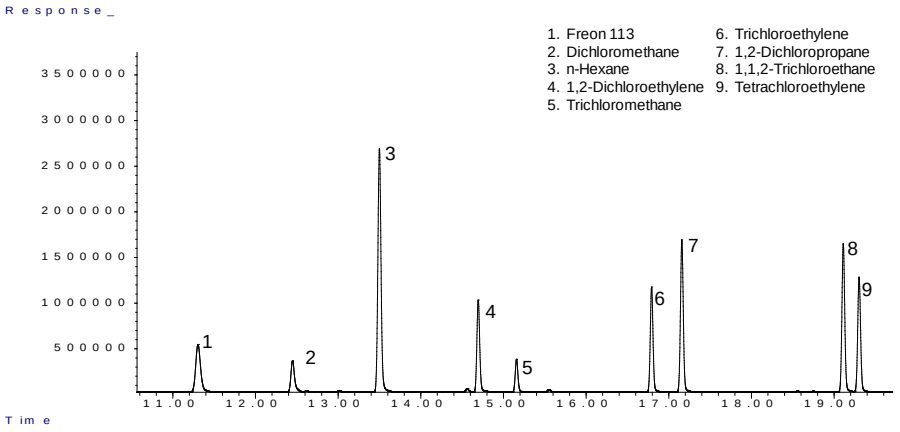


Figure C.2: ATD-GC-FID chromatogram

To compare the two detection methods the repeatability (s(r)) and reproducibility (s(R)) was determined based on the measurements performed. Using the FID mode the first 3 measurements were used, approximately 44, 91 and 136 day's after preparation, and in MSD mode all 4 measurements were used, approximately 323, 502, 586 and 615 days after preparation. The relative response factors were determined against the internal standard n-hexane and using statistical ANOVA calculations, according to ISO 5725-2, s(r) and s(R) were calculated (Table C.2).

Table C.2: Repeatability (s(r)) and reproducibility (s(R)) from the analysis of the halogenated VOCs in methane at approximately 750 ppb and 50 ppb.

ATD-GC-MSD	VSL370601 (750 ppb)		VSL261150 (750 ppb)		VSL170579 (50 ppb)		VSL370590 (50 ppb)	
	s(r) (%)	s(R) (%)	s(r) (%)	s(R) (%)	s(r) (%)	s(R) (%)	s(r) (%)	s(R) (%)
Chloromethane	2.4	9	2.4	9	2.2	12	8	10
Vinyl chloride	2.1	16	2.0	15	8	14	7	15
Freon 113	1.7	9	1.8	8	1.1	9	2.5	13
Dichloromethane	1.9	16	2.0	16	1.5	16	3.5	16
Cis-1,2-Dichloroethylene	1.6	6	1.8	6	1.5	9	3.3	9
Trichloromethane	1.5	12	1.8	11	1.2	13	2.4	15
Trichloroethene	1.6	9	1.8	10	1.5	8	3.1	8
1,2-Dichloropropane	1.5	16	1.8	8	1.6	6	3.1	6
1,1,2-Trichloroethane	1.5	11	1.6	12	1.4	8	3.5	9
Tetrachloroethylene	1.6	17	1.8	18	1.7	15	3.5	13
ATD-GC-FID	VSL261150 (750 ppb)		VSL370601 (750 ppb)		VSL170579 (50 ppb)		VSL370590 (50 ppb)	
	s(r) (%)	s(R) (%)	s(r) (%)	s(R) (%)	s(r) (%)	s(R) (%)	s(r) (%)	s(R) (%)
Freon 113	1.9	2.5	1.3	1.7	1.5	9	1.6	4
Dichloromethane	1.8	2.2	1.0	1.8	0.9	10	1.8	10
Cis-1,2-Dichloroethylene	1.9	1.9	1.0	1.4	1.5	2.8	3.5	4
Trichloromethane	1.8	1.8	1.0	1.0	1.5	5	1.7	4
Trichloroethene	1.9	1.9	1.0	1.4	1.6	3.6	3.1	3.1
1,2-Dichloropropane	1.8	1.8	1.0	1.7	1.6	1.6	1.8	3.0

1,1,2-Trichloroethane	2.0	2.0	1.0	1.8	2.5	7	4	4
Tetrachloroethylene	1.8	1.8	1.0	2.1	1.9	5	1.1	1.2

The s(r) values are comparable when using the ATD-GC in FID or MSD mode. Overall a s(r) of ≤ 2 % has been obtained using both FID and MSD, except for chloromethane and vinyl chloride. The s(R) values for the MSD measurements are between 6 % and 18 %, which is very high compared to the s(R) values of the FID measurements. For the 750 ppb gas mixtures the s(R) values are the same or a bid higher than the s(r) values ranging from 1.0 % to 2.5 %. For the 50 ppb gas mixtures the s(R) values increased to values between 1.6 % and 10 %. Especially compounds containing non or only a few C-H bonds have a higher value for s(R) when using FID. furthermore, the s(R) values of the 50 ppb gas mixtures differ quite a lot between the two different cylinders, which makes it clear these measurements are much more challenging than analysis of the 750 ppb gas mixtures. In general, the s(r) values obtained with MSD and FID are comparable, however the s(R) values are higher when using the ATD-GC in MDS mode.

6 Determination of HCl and HF in biomethane by Ion Chromatography

6.1 Scope

This document specifies a method for the determination of the concentration hydrochloric acid (HCl) and hydrofluoric acid (HF) in biomethane, after absorption on an alkali-impregnated quartz fiber filter or in a sorbent trap, by ion chromatography (IC) with conductimetric detection.

The method is applicable to biomethane in levels:

- for HCl: 0.07 mg/m^3 to 34.3 mg/m^3;
- for HF: 0.07 mg/m^3 to 17.5 mg/m^3.

6.2 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 6974-1:2012 *Natural gas - Determination of composition and associated uncertainty by gas chromatography - Part 1: General guidelines and calculation of composition*

ISO 6974-2:2012 *Natural gas - Determination of composition and associated uncertainty by gas chromatography - Part 2: Uncertainty calculations*

ISO 6974-3:2018 *Natural gas - Determination of composition and associated uncertainty by gas chromatography - Part 3: Precision and bias*

ISO 6976:2016 *Natural gas - Calculation of calorific values, density, relative density and Wobbe indices from composition*

ISO 14532, *Natural gas -- Vocabulary*

ISO 11352:2012, *Water quality — Estimation of measurement uncertainty based on validation and quality control data*

EN 1911:2010, *Stationary source emissions — Determination of mass concentration of gaseous chlorides expressed as HCl - Standard reference method*

OSHA ID-174SG Hydrogen Chloride in workplace Atmospheres

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 10304-1:2007, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate*

6.3 Terms and definitions

For the purposes of this document, the terms and definitions in ISO 14532 and the following apply.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

6.3.1

analyte
element, ion or substance to be determined by an analytical method
[SOURCE: EN 16687:2015, 4.1.11]

6.3.2

limit of quantification
LOQ
lowest value of an analyte (determinant) that can be determined with an acceptable level of accuracy and precision, generally determined as three times the limit of detection of the method
[SOURCE: EN 16687:2015, 4.1.14]

6.3.3

laboratory sample
sample intended for laboratory inspection or testing
[SOURCE: EN ISO 11074:2015, 4.3.7]

6.4 Symbols and abbreviations

6.4.1 Symbols

Symbol	Description
$C_{(x)}$	Concentration of gaseous hydrogen chlorides or hydrogen fluorides in biomethane in µg/m3
$C_{(x-)}$	Concentration in ions chlorides or fluorides in µg/L
$M_{(x-)}$	Molar mass of ions chlorides or fluorides
$M_{(x)}$	Molar mass of hydrogen chloride or hydrogen fluoride
$M_{(x)}$	Mass of gaseous chlorides or fluorides collected in µg
Vs	Volume of extract solution in liters (L)
V_{gas}	Volume of the gas sampled
q_V	Volume flow rate of the gas during sampling
p	Pressure at reference conditions
p_{gas}	Pressure at sampling conditions
t	Sampling time
T_0	Temperature at reference conditions

T_{gas}	Temperature at sampling conditions
Z	Compressibility factor

6.4.2 Abbreviations

CD	Coulometric detector
HCl	Hydrogen chloride
HF	Hydrogen fluoride
KOH	Potassium hydroxide
SI	International System of Units

6.5 Principle

Gaseous hydrochloric acid (HCl) and hydrofluoric acid (HF) contained in biomethane are trapped on an alkali-impregnated quartz fiber filter. Inorganic halides are eluted by an aqueous extraction with a sonification step.

NOTE Where "biomethane" is written, it is implied that it also covers biogas.

The analysis of chlorides and fluorides in the extracts is performed by ion chromatography with a conductimetric detector (CD).

When using CDs, it is essential that the eluents show a sufficiently low conductivity. For this reason, CDs are usually combined with a suppressor device (cation exchanger), which will reduce the conductivity of the eluent and transform the sample species into their respective acids.

6.6 Reagents and consumables

Use only reagents of recognized analytical grade. Weigh the reagents with a relative expanded uncertainty of ± 1 % (k = 2) of the nominal mass, unless stated otherwise.

6.6.1 Water, complying with grade 1 in accordance with EN ISO 3696.

6.6.2 Sodium carbonate solution, Na_2CO_3 50 g L^{-1}

6.6.3 Sodium bicarbonate solution, NaHCO3 0.0024 M

6.6.4 Chloride and fluoride stock standard solutions,

ρ = 1 000 +/- 10 mg L^{-1} each.

Single anion and mixed anion stock solutions with adequate and required specification are commercially available. These solutions are stable for several months.

6.6.5 Chloride and fluoride standard solutions,

6.6.5.1 General

Depending on the concentrations expected, prepare single or mixed standard solutions of chloride and fluoride concentrations from the stock standard solution (6.4).
Store the standard solutions in polyethene bottles.

6.6.5.2 Example for a chloride and fluoride mixed standard solution, ρ= 10 mg L^{-1} each.

Pipette using a volumetric pipette 1,0 mL of each of the stock standard solutions (6.4) into a 100 mL volumetric flask and fill the flask up to the volume with water (6.1).
These solutions shall be stored in the dark at 2 °C to 8 °C in polyethene bottles and shall be used until one week after preparation.

6.6.6 Chloride and fluoride calibration solutions

Depending on the concentrations expected in the sample, use the standard solution (6.5.2) to prepare e.g. 5 to 10 calibration solutions distributed as evenly as possible over the expected working range.

EXAMPLE For example, proceed as follows for the range 0,05 mg L^{-1} to 0,5 mg L^{-1}:
Pipette, into a series of 20 mLmL volumetric flasks, the following volumes: 100 µL, 200 µL, 300 µL, 400 µL, 500 µL, 600 µL, 700 µL, 800 µL, 900 µL or 1 000 µL of the standard solution (6.5.2) and dilute to volume with water (6.1).

The concentrations of the anions in these calibration solutions are: 0,05 mg L^{-1}, 0,1 mg L^{-1}, 0,15 mg L^{-1}, 0,2 mg L^{-1}, 0,25 mg L^{-1}, 0,3 mg L^{-1}, 0,35 mg L^{-1}, 0,4 mg L^{-1}, 0,45 mg L^{-1} or 0,5 mg L^{-1}, respectively.

Prepare the calibration solutions on the day of use.

6.6.7 Blank

Fill a volumetric flask (e.g. 100 mL flask) with water (6.1).

6.6.8 Eluents

Degas all water used for eluent preparation. In order to minimize the growth of bacteria or algae, prepare
eluents freshly after 3 days.

The choice of eluent (for example, Potassium hydroxide, KOH) depends on the chosen column, seek advice from the column supplier. The chosen combination of separator column and eluent shall meet the resolution requirements stated in 7.2.

6.6.9 Quartz filters

Quartz fiber filters of a 37 mm diameter in a sampling cassette.

6.6.10 Syringe filters

Nylon syringe filter with diameter of 0.45 µm.

6.6.11 Sorbent tubes

Activated Silica Gel cartridges

6.7 Apparatus

Usual laboratory apparatus, and, in particular:

6.7.1 Ion chromatography system

In general, it consists of the following components (see Figure 1).

6.7.1.1 *Eluent reservoir, and degassing unit*

6.7.1.2 *Metal-free HPLC Pump*

6.7.1.3 *Precolumn, if necessary*

6.7.1.4 *Separator column, with the specified separating performance (6.7.2)*

6.7.1.5 *Conductivity detector (CD)*

6.7.1.6 *Recording device (e.g. a computer with software for data acquisition and evaluation)*

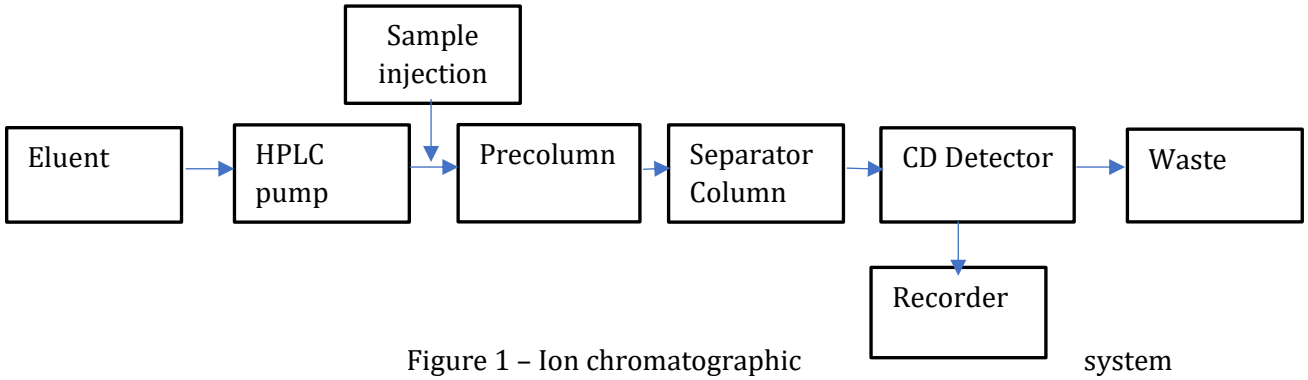


Figure 1 – Ion chromatographic system

6.7.2 Quality requirements for the separator column

In chromatograms of samples and standard solutions, the peak resolution, R, between the anion of interest and its nearest peak, shall not fall below 1,3.

Separation conditions shall be such that possible interfering anions will not interfere with the anion of interest.

6.8 Sampling and sample pre-treatment

6.8.1 General

Gaseous chlorides and fluorides can be sampled simultaneously. Two different methods can be used for the sampling, one based on quartz filter and the other on cartridges/sorbent tubes. For evaluating performances of the methods, a dynamic generation as indicated in Annex B can be used.

6.8.2 Sampling equipment

6.8.2.1 *Filter eg Whatman (QMA: 1851-037)1*

A quartz fiber filter is impregnated by deposit of 500 µL of a carbonate solution prepared at 50 g Na_2CO_3 per liter. After impregnation, dry the filter in a ventilated oven at the temperature of about 50 °C at least 1 h.

Two alkali-impregnated quartz fiber filters are required. Place a first filter at the bottom of the sampling cassette and a second filter on the top of the sampling cassette.

[1] Whatman (QMA: 1851-037) is an example of a suitable product available commercially. These examples are given for the convenience of users of this document and do not constitute an endorsement by CEN of these products.

6.8.2.2 Cartridges

Use activated silica gel sorbent tubes, eg commercially available such as ORBO-53 (Supelco)[2]. The cartridges are divided in two section by glass fiber filter. The first part collects the HCl and HF and the second part is a backup section that eventually collects the amount of acids that have not been collected in the first part.

6.8.2.3 Pump

Use a leak-free pump capable of sampling gas at a set flow rate, for quartz filter sampling a pump with flow between 1 to 3 L/min and for cartridges sampling, a pump with flow between 0.1 to 1L/min

6.8.3 Sampling

Filter-based method

The sampling is performed with controlled volume flow rates set at 1L/min during 30 min onto the alkali-impregnated quartz fiber filters.

The two filters are positioned in succession in the holder with the second filter used as a control to verify if HCl or HF would break through the first filter.

Cartridge-based method

In the sorbent tube the sampling is performed with a controlled flow volume set at most 0.5 L/min for 20 min or less if the sample contain high concentration of HCl or HF. The tube is divided in two sections, the second section to check if not all HCl or HF have been adsorbed in the first one.

For both methods, the volume flow rate shall be measured using a calibrated flow meter. The calibration shall take any effects from biomethane into consideration. The volume flow rate, temperature, pressure and sampling time shall be recorded. The volume gas is calculated as

$$V_{gas} = q_V \cdot t \cdot \frac{Z(T_0, p_0)}{Z(T_{gas}, p_{gas})} \quad (1)$$

The compressibility factors $Z(T_0, p_0)$ and $Z(T_{gas}, p_{gas})$ shall be calculated in accordance with ISO 6976. If the composition of the biomethane is not known, it shall be measured in accordance with ISO 6974. For the purpose of this document, the measurement uncertainty associated with the compressibility factors may be ignored.

NOTE Unless specified otherwise, gas volumes stated in this document refer to standard conditions. If not specified, standard conditions are given in ISO 13443.

6.8.4 Sample pre-treatment

Filter-based method

[2] ORBO-53 (Supelco) is an example of a suitable product available commercially. These examples are given for the convenience of users of this document and do not constitute an endorsement by CEN of these products.

Open the cassette taking care not to lose any particles deposited on the walls and not to pollute the impregnated filters.

Place each filter used for sampling, laboratory and field blanks separately on the bottom of beakers or bottles. Place 20 mL of water on each filter. If necessary, this volume of water can be adapted to obtain an extract more concentrated.

Ultrasonic the vessels for 5 minutes in a bath at room temperature.
Extract must be filtered at 0.45 µm with a nylon syringe filter before injection for the analysis.

Cartridges-based method
Remove the tubes from the sampling line taking care not to break the glass.

Cut the first end of the trap, remove the glass wool and put it in the first vial. Remove the sorbent material from the tube and add it in the first polyethylene vial with10 ml of solution of 0.003 M CO_3^{--}/ 0.0024 M HCO_3^- . Boil the vial for 10 min in pure water, cool down and dilute with water in a graduate flask. Treat the back section in the same way.

6.9 Procedure

6.9.1 General

This analytical method is described in EN ISO 10304-1. Therefore, the following is only a reminder of the procedure.

Set up the ion chromatographic system (7.1) according to the instrument manufacturer's instructions. An example of a suitable analytical condition is provided in Annex A.

Run the eluent, wait for a stable baseline and ensure that the system is free of chloride and fluoride by injecting water.

Perform the calibration as described in 9.2. Measure the samples, calibration (6.6) and blank solution (6.7) as described in 9.3.

6.9.2 Calibration

Prepare the calibration solutions as described in 6.6.

Inject the calibration solutions (see 6.6) including a blank to cover the expected concentration range of the samples, while remaining within the linear response range of the apparatus. Identify the peaks for anions by comparing the retention times with those of the calibration solutions (6.6). Deviation of retention times shall not exceed ± 10 % within a batch.

Using linear or quadratic regression, establish the equation of the reference straight line or curve.
Adjust the established calibration function, if necessary (e.g. measure standard solutions of different anion concentrations in the lower and upper third of the working range).

6.9.3 Measurement

After establishing the calibration function, inject the sample into the chromatograph and measure the peaks as described above (9.2).

Note 1 The use of a precolumn is recommended not only for the analyses of aqueous extract loaded with the matrices made of filter with carbonates but also to protect the analytical separator column.

If the concentration of the analyte exceeds the calibration range, dilute the sample or establish a separate calibration function for a higher working range and re-analyse it.

If the concentration of the analyte falls short of the calibration range, establish a separate calibration function for the lower working range, and re-analyse it, if necessary.

If matrix interferences are expected, use the method of standard addition to confirm the results (verify the peaks by comparing the retention time of the spiked sample with those of the original sample).

Measure the blank solution (6.7) in the same way as the sample.

6.10 Calculation

Calculate the concentration, $C_{(x-)}$, in micrograms per liter, or milligrams per liter, of the ion chlorides and of the ions fluorides in the extract solution using the peak areas or peak heights according to the calibration function used (9.2).

Take into account all dilution steps.

The gaseous chlorides (HCl) and fluorides (HF) mass in the filters are calculated using the following formula:

$$M_{(x)} = C_{(x-)} \times Vs \times M_{(x)} / M_{(x-)}$$

where
$M_{(x)}$ is the quantity of gaseous chlorides or fluorides collected in µg;
$C_{(x-)}$ is the concentration in ions chlorides or fluorides in µg/L;
Vs is the volume of extract solution (see 8.4), in liters (L);
$M_{(x-)}$ is the molar mass of ions chlorides or fluorides;
$M_{(x)}$ is the molar mass of hydrogen chloride or hydrogen fluoride.

In function of the sampling conditions, the hydrogen chloride or hydrogen fluoride concentrations in biomethane are calculated using the following formula:

$$C_{(x)} = M_{(x)} / V_{gas} / 1000$$

where
$C_{(x)}$ is the concentration of gaseous hydrogen chlorides or hydrogen fluorides in biomethane in µg/m³;
V_{gas} is the sampling volume (see 8.3), in liters (L).

In the evaluation of measurement uncertainty, the following factors should be taken into account:

- Repeatability
- Reproducibility
- Recovery
- Sampling

6.11 Expression of results

The results shall be reported using SI Unit (e.g. µg/L or µg/m³).

In general, values shall not be expressed to a degree of accuracy greater than three significant figures. The rounding of values will depend on the statistics of the quality control procedures mentioned earlier, and the requirements of the analysis.
The measurement uncertainty reported for the results should reflect the results from quality control measurements and incorporate the deviation between the individual readings for the sample in question.

6.12 Performance characteristics

6.12.1 Calibration check

For demonstration of calibration traceability, a calibration verification solution with certified concentration and known measurement uncertainty shall be used. Additionally, this solution or a calibration solution may be used for drift control during the measurement cycle. The accepted deviation shall be in the limit of the laboratory quality control policy.

6.12.2 Performance data

The performance characteristics have been determined in a validation study. The results of this study are given in Annex A.

6.13 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

8) The date, time and location of sampling
9) The value, expanded uncertainty, and coverage factor used
10) The reference conditions used
11) A reference to this document

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

Annex A: Characteristic of the method

A.1 Analytical conditions

As an example, the analysis of the samples was performed on a Thermo Scientific chromatograph with conductimetric detector (model ICS 5000+).

The analytical conditions were:

- Precolumn and Column: AG19 et AS19 4 mm/250 mm (Thermo Scientific);
- Flow: 1 mL/min ;
- Eluant: KOH ;
- Temperature of the column: 30°C ;
- Injection volume: 25 µl ;
- Elution mode : gradient of eluent concentration ;

Time (min)	Events	mM KOH
-7	Stabilization	10

0	Start acquisition	10
10		10
1001		45
17		45
1701	End	10

- Detection: conductimetric ;
- Temperature of the conductimetric cell: 35°C ;
- Electrochemical suppression ;
- Suppressor ASRS - 4mm (Thermo Scientific);
- Suppression current: 112 mA ;
- Retention time: 5 min for F^- and 8.02 min for Cl^-.

A.2 Validation data

The method has been validated according to the NF T 90-210 standard.

The calibration ranges has been defined from:
- for HCl: 2 µg Cl^-/filter to 1000 µg Cl^-/filter equivalent to 0.07 mg/m³ to 34.3 mg/m³ ;
- for HF: 2 µg F^-/filter to 500 µg F^-/filter equivalent to 0.07 mg/m³ to 17.5 mg/m³.

The expanded uncertainties have been calculated according to the requirements of ISO 11352.

Table 1: Uncertainties obtained at the various tested levels for the filter-based method

Compound	0.49 mg/m3	0.98 mg/m3	6.13 mg/m3	23.3 mg/m3
HCl	37%	14%	37%	10%

Compound	0.71 mg/m3	3.83 mg/m3	15.3 mg/m3
HF	35 %	40 %	13 %

Table 2 Uncertainties obtained at various tested levels for the cartridges-based method with sorbent tubes using dynamic gas generator as reference

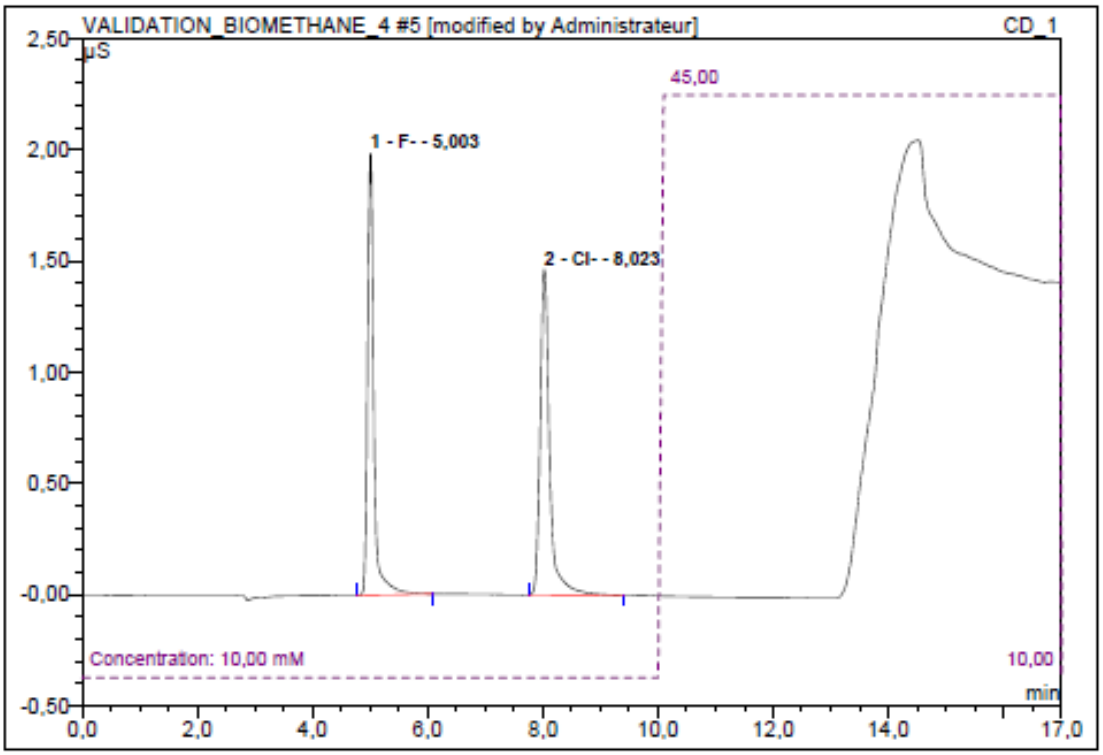
compound	5.09 mg/m³	10 mg/m³	15.17 mg/m³
HCl	12.3 %	17.4%	30.9%

compound	10.34 mg/m³	11.05 mg/m³
HF	48.8%	48.3%

As an example, an obtained chromatogram as showed in Figure A.1 with the chromatographic separation for chlorides and fluorides in a standard solution prepared at 0.5 mg F-/L and 1mg Cl-/L.

5 Etalon 1Cl/0.5F

Sample Name:	Etalon 1Cl/0.5F	*Injection Volume:*	25,0
Vial Number:	6	*Channel:*	CD_1
Sample Type:	standard	*Wavelength:*	n.a.
Control Program:	Gradient2_EG_AS19_F_Cl	*Bandwidth:*	n.a.
Quantif. Method:	anions	*Dilution Factor:*	1,0000
Recording Time:	20/11/2019 19:11	*Sample Weight:*	1,0000
Run Time (min):	17,01	*Sample Amount:*	1,0000



No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount mg/l	Type
1	5,00	F-	1,987	0,251	47,31	0,477	BMB*
2	8,02	Cl-	1,463	0,279	52,69	0,954	BMB*
Total:			3,451	0,530	100,00	1,430	

Figure A.1 — Example of IC chromatogram for a standard at 0.5 mg F^-/L and 1mg Cl^-/L

Annex B: Dynamic generation of HCl and HF

In gaseous form, HCl and HF are reactive chemicals that easily stick to sampling system surfaces. To estimate uncertainty caused by this effect on the analysis, dynamic generation method for HCl and/or HF containing reference gas is useable.

It is possible to apply liquid evaporative method to dynamically generate reference gas mixtures with an accurately know concentration of HCl and/or HF, at relevant concentration levels. In this method, liquid solution with a known concentration of HCl and/or HF is mixed into carrier gas, e.g. methane or biomethane, using an evaporative generator.

Volumetric flow of liquid and gas streams in the generator are determined. Knowing the concentration of HCl and/or HF in the liquid solution, they are used to calculate concentration of the HCl and/or HF in generated reference gas flow.

Sampling and analysis of the reference gas flow is made as described in 8 and 9. From the results, the difference in calculated and analysed results is determined. This value gives an estimate of uncertainty of the method.

7 Determination of siloxane content by Gas Chromatography Ion Mobility Spectrometry

7.1 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 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	$C_6H_{18}Si_2O$	0,1	10,0
octamethyltrisiloxane	L3	$C_8H_{24}Si_3O_2$	0,1	10,0
decamethyltetrasiloxane	L4	$C_{10}H_{30}Si_4O_3$	0,1	10,0
dodecamethylpentasiloxane	L5	$C_{12}H_{36}Si_5O_4$	0,1	10,0
hexamethylcyclotrisiloxane	D3	$C_{12}H_{18}O_3Si_3$	0,1	10,0
octamethylcyclotetrasiloxane	D4	$C_8H_{24}O_4Si_4$	0,1	10,0
octamethylcyclotetrasiloxane	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 Although one or more components in a sample may not be present at detectable levels, the method is still applicable.

7.2 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 — Determination of composition of calibration gas mixtures — Comparison methods*

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

ISO 6145, *Gas analysis — Preparation of calibration gas mixtures using dynamic methods*

ISO 6974-1, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 1: General guidelines and calculation of composition*

ISO 6974-2, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 2: Uncertainty calculations*

ISO 7504, *Gas analysis — Vocabulary*

ISO 10715, *Natural gas — Sampling guidelines*

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

ISO 14532, *Natural gas — Vocabulary*

ISO/IEC guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

7.3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 7504, ISO/IEC guide 98-3:2008, ISO 14532 and the following apply.

7.3.1
gas chromatography
GC

analytical method used to separate and determine the components of complex mixtures based on partitioning between a gas phase and a stationary phase

[SOURCE: ISO 11504:2012]

7.3.2
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

7.4 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, which applies a defined electric field and a flow of inert nitrogen drift gas that 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.

7.5 Materials

7.5.1 Calibration gases

Calibration gases containing siloxanes of appropriate concentrations for calibration in a methane matrix. Calibration gases should 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 certified standard cylinders for each concentration needed;

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

7.5.2 Diluent gas

Pressurised cylinder of pure methane or ≥99,999 % 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.

7.5.3 Carrier & drift gas

Pressurised nitrogen of at least 10 bar pressure and ≥99,999 % purity grade.

7.6 Apparatus

7.6.1 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. Column stationary phase in combination with the ion mobility spectrometer must able to separate the siloxane compounds to be analysed.

An example schematic is provided in annex A.

7.6.2 Pressure regulator

To supply carrier and drift gas flow rates from source cylinders to the analyser; as specified by manufacturer.

7.6.3 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.

7.7 Sampling

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 could lead to bias in the measurements and should 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.

7.7.1 Safety precautions

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

7.7.2 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 may have 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).

7.7.3 Construction materials

Use appropriate materials or passivation that reduce siloxane adsorption to a level that will not cause analytical bias. The general considerations of ISO 10715 should always be followed.

7.7.4 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 must not cause adsorption of siloxanes.

7.7.5 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 Annex F of ISO 10715:1997.

7.7.6 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.

NOTE One principle for the connection of a calibration gas cylinder in direct sampling is shown in ISO 10715:1997, Annex A.

7.7.7 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.

7.7.8 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.

7.7.9 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.

7.7.10 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 may cause problems related to diffusion of humidity from the environmental air.

7.8 Calibration

7.8.1 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.

7.8.2 Calibration using multiple gas reference standards

Use a series of reference standards to calibrate the instrument over the desired range of interest. The calibration should be in accordance with ISO 10723.

7.8.3 Calibration using dynamic dilution system

Use a reference standard and methane diluent gas to calibrate the instrument over the desired range of interest. The calibration should be in accordance with ISO 6145.

7.9 Procedure

7.9.1 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.

7.9.2 Analysis

Establish calibration, check the analyser system operating parameters are suitable for performing analysis, and set the sample flowrate.

Perform quantitative analysis and determine the mass concentration and uncertainty budget of siloxanes in the sample gas in accordance with ISO 6143. Example method parameters are provided in annex A.

7.10 Expression of results

Refer to ISO 6974-1.

7.10.1 Uncertainty

Refer to ISO 6974-2.

7.10.2 Test report

The test report shall include the following information:

a) identification of the sample, including

— time and date of sampling (if available),

— sample point (location) (if available), and

— identification number for the cylinder (or vessel) used for the sample;

b) information on the gas chromatographic method used, including

— a reference to the appropriate part(s) of documented methods, and

— any significant deviations from the referenced method;

c) analytical information, including

— result of the analysis, expressed as a mass concentration or mole fraction,

— the expanded uncertainty of the analytical value (stating the coverage factor, *k*, used to expand the uncertainty; k will usually be 2),

— date of the analysis, and

— information about any corrections made for contamination by air or other gases, if appropriate;

d) laboratory information, including:

— date of issuance of the report,

— name and address of the laboratory, and

— signature of the authorized signatory.

Annex A: Example of application

A.2 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 (300MBq - 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 (Nitrogen 6.0 used for study)
Sample Loop volume	1 mL
Method run time	60 minutes
Analytes measured	L2, L3, L4, L5, D3, D4, D5, D6, (+ total Si, total SiO_2, total siloxanes)

An example schematic of a GC-IMS analytical set up for siloxanes analysis is provided in Figure A.1.

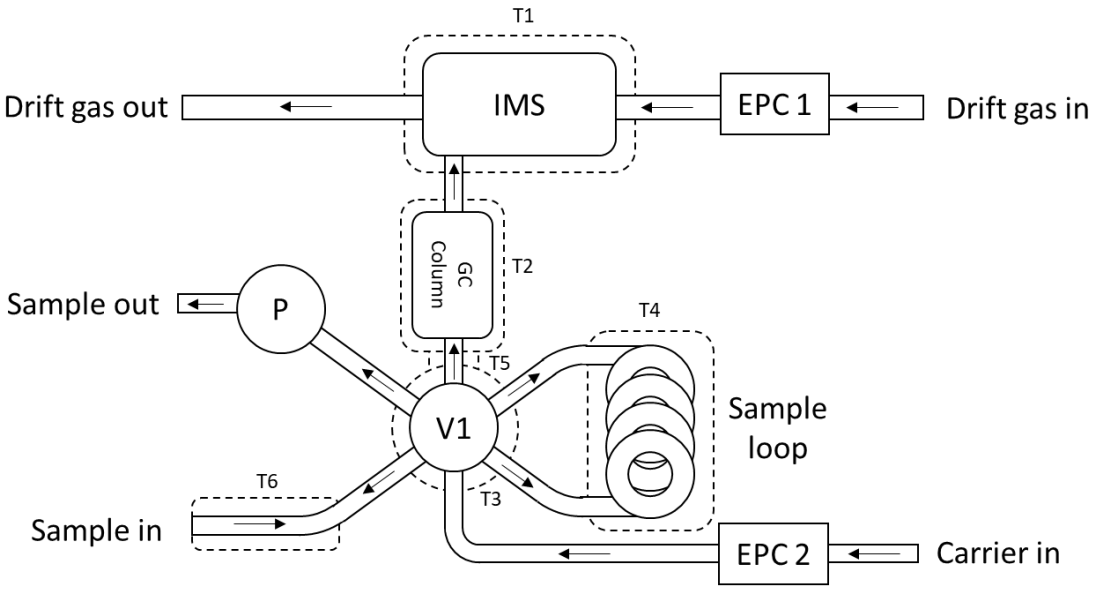


Figure A.1 – Example GC-IMS schematic

8 Determination of the total silicon content

8.1 Scope

This document is applicable to the measurement of the total silicon content in gaseous matrices such as biomethane, biogas and landfill gas. Silicon is present in a gas phase contained predominantly in siloxane compounds, trimethylsilane and trimethylsilanol. The analytical form of the silicon measured in liquid phase after conducted sampling and derivatization procedure is soluble hexafluorosilicate anion stable in slightly acidified media. Total silicon is expressed as a mass of silicon in the volume of the analysed gas.

This document is applicable to all stated gas matrices with silicon concentrations up to 5 mg/m^3, and it is prevalently intended for the biomethane matrices containing 0,1 to 0,5 mg/m^3. It can be used for higher concentration but then the absorption efficiency of the bubblers/impingers should be checked before the results can be regarded as valid. The detection limit of the method is estimated as 0,05 mg/m^3 based on a sample volume of 0,020 m^3. All compounds present in the gas phase are volatile at the absorption and derivatization temperature and gaseous siloxanes are trapped in absorbance media and derivatized into analytical silicon specie are measured by this method. The concentration of the silicon is measured in diluted derivatization media using atomic emission spectrometer upon atomisation/ionisation in microwave or inductively coupled plasma.

NOTE: When using appropriate dilution factors, the method can also be applied for concentrations above 5 mg/m^3.

8.2 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 3696:1987, *Water for analytical laboratory use — Specification and test method*

ISO 5725-1:1994 + Cor1:1998, IDT *Accuracy (trueness and precision) of measurement methods and results— Part 1: General principles and definitions*

ISO 5725-2:1994 + Cor1:2002, IDT *Accuracy (trueness and precision) of measurement methods and results— Part 2: basic method for the determination of repeatability and reproducibility of standard measurement method*

ISO 14532, *Natural gas – Vocabulary*

ISO 10715, *Natural gas — Sampling guidelines*

8.3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14532 and the following apply.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

8.3.1
Landfill gas

Landfill gas is a complex mix of different gases created by the action of microorganisms within a landfill. Landfill gas is approximately forty to sixty percent methane, with the remainder being mostly carbon dioxide. Trace amounts of other volatile organic compounds (VOCs) comprise the remainder (<1%). These trace gases include a large array of species, mainly simple hydrocarbons.

[SOURCE: Hans-Jürgen Ehrig, Hans-Joachim Schneider and Volkmar Gossow "Waste, 7. Deposition" in Ullmann's Encyclopaedia of Industrial Chemistry, 2011, Wiley-VCH, Weinheim]

8.3.2
Siloxanes

Siloxanes are functional groups where two silicon atoms are connected via an oxygen atom. Depending on the substrate used to produce biogas and the process used for purification, biomethane can contain siloxanes. During combustion, siloxanes can be oxidized to silicon dioxide, an abrasive compound harmful for mechanical moving parts in e.g. engines and turbines.

[SOURCE: Biomethane - Status and Factors Affecting Market Development and Trade, IEA Bioenergy ISBN 978-1-910154-10-6]

8.4 Principle

Methane matrix gas sample containing siloxane compounds is passed through liquid absorbent (nitric acid) in serially connected gas bubblers/impingers to collect the silicon-containing compounds. After sampling of adequate gas volume, content of sampling vessels (gas bubblers) is subjected to derivatisation by adding hydroxide solutions and hydrofluoric acid in order to obtain silicon in analytical from, hexafluorosilicate anion.

Derivatized sample is analysed for silicon content using ICP/MWP atomic emission spectrometer at selected characteristic silicon emission wavelengths by means of weighted linear line calibration generated from standard silicon solutions.

8.5 Reagents and labware

To carry out the method, the following reagents are required to be of a recognized analytical grade and only ISO 3696 grade 1 water. If it is visually determined that the reagents have changed their appearance (colour, consistency, turbidity) they should be discarded.

8.5.1 Absorber media

8.5.1.1 Nitric acid (HNO_3); ρ_{20} = 1,41 g/cm3; 65% HNO_3 (mass fraction)

8.5.2 Derivatization media

8.5.2.1 Sodium or potassium hydroxide pellets for the preparation of 8-10M hydroxide solution

Accurately weigh appropriate amount of sodium or potassium hydroxide pellets and dissolve in appropriate amount of reagent water (5.3). As an example for 100 mL of 10M sodium hydroxide solutions, weigh 40 g of sodium hydroxide pellets and dissolve in water.

WARNING: Reaction of dissolving sodium hydroxide in water is highly exothermic! Heat will be released and care should be taken when handling the reaction. Add pellets slowly to the water and cool the dissolution vessel until the dissolution is complete.

8.5.2.2 Hydrofluoric acid (HF); ρ_{20} = 1,16 g/cm^3; 48% HF (mass fraction).

WARNING: Hydrofluoric acid is a very toxic acid and penetrates the skin and tissues deeply if not treated immediately. Injury occurs in two stages: firstly, by hydration that induces tissue necrosis; and secondly, by penetration of fluoride ions deep into the tissue and thereby reacting with calcium. Boric acid and/or other complexing reagents and appropriate treatment agents should be administered immediately. Consult appropriate safety literature for determining the proper protective eyewear, clothing and gloves to use when handling hydrofluoric acid. Always have appropriate treatment materials readily available prior to working with this acid.

8.5.3 **Water,** complying with grade 1 of ISO 3696

8.5.4 Pure siloxane compounds:

Linear siloxanes	**Cyclic siloxanes**
Hexamethyldisiloxane - L2; H_6Si_2O	Hexamethylcyclotrisiloxane - D3; $H_6Si_3O_3$
Octamethyltrisiloxane - L3; $H_8Si_3O_2$	Octamethylcyclotetrasiloxane - D4; $H_8Si_4O_4$
Decamethyltetrasiloxane - L4; $H_{10}Si_4O_3$	Decamethylcyclopentasiloxane - D5; $H_{10}Si_5O_5$
Dodecamethylpentasiloxane - L5; $H_{12}Si_5O_4$	Dodecamethylcyclohexasiloxane - D6; $H_{12}Si_6O_6$

Note: Use at least one representative of chain and one representative of cyclic siloxane compounds for the purpose of performing initial and regular quality control of the method validity.

8.5.5 **pH colour-fixed indicator strips,** pH range from 0-14

8.5.6 Calibration solutions:

Note: the following procedure for the preparation of standard and calibration solutions of silicon is adjusted to the lower range of silicon concentration in gas sample. If higher concentrations of silicon it is to be analysed, adjust the concentrations of the working standard and calibration solutions accordingly.

Note: When determining silicon in aqueous samples, only plastic, PTFE or quartz labware should be used from time of sample collection to completion of analysis.

8.5.6.1 Certified ICP-Si stock standard solution, (water, traces HF) 10000 µg/ml ±0,5% or better

Note: Certified Si standard solutions of other concentration can also be used. Adjust the procedure for preparing standard solution accordingly.

Note: If Si stock standard solution is prepared in-house gravimetrically from salt containing silicon, apply required statistical procedure for obtaining accurate concentration accompanied with uncertainty value.

8.5.6.2 Si standard solution

$\rho(Si) \approx 100$ mg/kg

Weigh empty 50 ml plastic volumetric flask using analytical balance (6.3). Add around 10 ml of 2% nitric acid. Accurately pipette 0,5 ml of stock solution (5.6.1) and add it to the plastic

volumetric flask. Dilute with 2 % nitric acid to volume. Weigh full plastic volumetric flask and calculate the concentration of silicon.

Store the solution in plastic volumetric flask or similar vessel of silicon free material properly stoppered at room temperature or refrigerated (~5°C). The solution is stable for at least 2 weeks if stored properly.

8.5.6.3 Si calibration solutions

Gravimetrically prepare a minimum of five calibration solutions in accordance with expected silicon concentration in the collected sample.

As an example proceed as follows for the range from 10 µg Si/kg to 200 µg Si/kg:

Weigh empty 100 ml (or 200ml) plastic volumetric flasks

Pipette 10 µl; 20 µl; 50µl; 75 µl; 100µl; 150µl; and 200µl; respectively of silicon standard solution (5.6.2) into 100 ml one-mark plastic volumetric flask that was empty-weighted and prefilled with around 10-20 ml of 2% nitric acid. Dilute with 2 % nitric acid to volume. Weigh full plastic volumetric flask and calculate the concentration of silicon.

The calibration solutions contain 10 µg Si/kg; 20 µg Si/kg; 50 µg Si/kg; 75 µg Si/kg; 100 µg Si/kg; 150 µg Si/kg and 200 µg Si/kg respectively.

8.5.6.4 Solution for wavelength calibration control, usually provided by the manufacturer of the equipment

Prior to daily calibration of the instrument for the analysis of silicon, perform wavelength check using solution containing assorted elements covering the wavelength range of the instrumentation used provided by the manufacturer. This solution is usually provided as concentrate that needs to be diluted prior to the analysis in accordance with the manufacturer's instructions. Wavelength calibration control test result shows if the optical settings of the instrument are appropriate, and if the readings of the emission lines for each individual element correspond to the instrumental settings when selecting the analytical wavelengths for the analyte of interest.

8.5.7 Quality control

8.5.7.1 Blanks

Three types of blanks are used during the analysis. The calibration blank is used in establishing the analytical curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure and a rinse blank is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids as used for the standards; in this case it is 2% nitric acid. The calibration blank should be stored in a plastic container as samples.

The laboratory reagent blank should contain all the reagents in the same volumes as used in the processing of the samples. The must be carried through the same entire preparation scheme as

the samples including sample derivatisation. This type of blank should be prepared at least every time new reagents are used.

The rinse blank is prepared by acidifying reagent water to the same concentrations of nitric acid as used in the calibration blank and stored in a convenient manner.

8.5.7.2 Instrument performance check i.e. wavelength calibration control sample (see 8.5.6.4)

8.5.7.3 Calibration Control Sample (CC)

A calibration control sample is required for initial and periodic verification of calibration standards or stock standard solutions in order to verify instrument performance. The CC must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. It can be either ready standard solution obtained from a different supplier, or at least from a different lot, or it can be prepared gravimetrically using pure $(NH_4)_2SiF_6$ salt. The concentration of the silicon in the CC solution should be near to expected concentration of silicon in the sample or at the middle of calibration range. A fresh solution should be prepared prior to the analysis and stored in plastic container as samples.

8.5.7.4 Derivatization control sample (DC)

A derivatisation control sample is required for initial and periodic verification of the completeness of the derivatization process. For this purpose pure siloxane compounds are used. For example, L2 and D4 siloxanes represent linear and cyclic siloxanes found in biomethane matrices. Other siloxanes can be used as well. The DC is prepared by accurately pipetting appropriate amount of siloxane with previously calculated mas of silicon contained, and adding this amount to the aliquot of nitric acid thus simulating the absorbance procedure. The solution of siloxane(s) is then subjected to derivatisation by adding appropriate amount of hydroxide solution and hydrofluoric sample. The DC should be store in a plastic container as sample. Concentration of the silicon in DC must be within the calibration range and can be adjusted by dilution if needed.

8.5.7.5 Reference gas mixture (methane) with certified silicon content (optional) in the range 0,1 to 0,5 mg/m^3

8.6 Apparatus

8.6.1 Sampling and derivatization equipment

A schematic diagram of the equipment for the sampling of gas is given in Figure 1. The apparatus consists of a gas flow meter and an impinger train containing absorbent (conc. nitric acid) to capture gaseous siloxanes. Thermometer is required if the laboratory has no controlled ambient temperature within 3°C. If gas flow meter used is not equipped with the embedded software providing data for normalization of standard conditions of 273,15 K and 101,325 kPa, barometer is also required to measure atmospheric pressure during collection of the gas.

All tubing, gaskets and seals used to for passing of the sample gas, as well as the impingers and derivatization vessels and stirring rod have to be made of plastic polymer silicon free.

8.6.1.1 *Gas flow meter with temperature sensor, calibrated with methane, range: 0-20 ml/L with the software readout of normalized values for the volume of gas*

8.6.1.2 *Gas cylinder with gas pressure regulator*

8.6.1.3 *Digital or manual automatic pipettes, adjustable volume 1-5 mL, and 20 – 200 µL with silicon free tips*

8.6.1.4 *Plastic gas bubblers/impingers with tubing, 20-50 mL capacity with stoppers, silicon free*

8.6.1.5 *Plastic vessels for the derivatisation, 200 mL capacity with stoppers, heat durable*

8.6.1.6 *Stirring rod, plastic, silicon free*

8.6.1.7 *Laboratory fume hood with constant ventilation EX design*

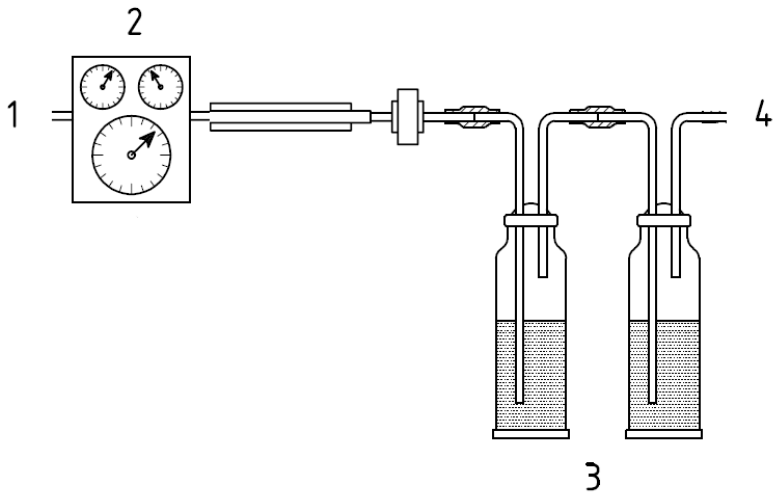
8.6.2 **Microwave plasma (MWP)/ Inductively coupled plasma (ICP) emission spectrometer** capable of measuring silicon emission lines (250,590 nm; 251,432 nm; 251,611 nm (the most sensitive line); 288,158 nm) with a minimum optical resolution 0,05 nm.

8.6.3 Analytical balance accurate to 0,01 mg.

8.7 Sampling

Sampling shall be conducted in accordance with ISO 10715.

The sampling procedure refers to the sampling from pressurized gas cylinder equipped with gas pressure regulator displaying the pressure inside cylinder as well as the outlet pressure. Gas regulator is airtight connected to the gas flow meter with plastic silicon free tubing ensuring quantitative measurement of gas flow and volume released. Gas flow meter is connected with the same type of plastic silicon free tubing with serially connected gas 2 to 3 bubblers/impingers (see 6.1.4) containing absorbent media – concentrated nitric acid (see 5.1).



Legend

1 pressurised gas cylinder with pressure regulator attached

2 gas flow controller with temperature sensor

3 gas bubbler/impingers containing absorbent

4 exhaust of the excess gas

It is necessary to ensure that the opening of the tube through which the gas is being introduced in the bubblers is immersed in the absorbent. Adjust the volume of the absorbent accordingly. If 50 mL gas bubblers are used, this volume should not be smaller than 7,5 ml. In order to ensure quantitative sampling, bubblers are equipped with stoppers (rubber or some similar adhesive elastic material) airtight with PFTE tape. The whole sampling setting consisting of serially connected bubblers and gas flow meter should be placed in fume hood, especially the exhaust on the las bubbler in line, releasing the excess gas.

Sampling flow should be kept constant at approximately 10 ml/min and the normalized total volume of gas passed read from the flow meter after the sampling was finalized. Adjust the gas volume sampled in accordance with the expected level of silicon in the sample. In order to ensure as quantitative sampling as possible, keep the gas flow low and constant for the whole sampling time. In order to ensure reasonable duration of the sampling, the total volume should be in the range of 2-20 litres (dm^3) of gas.

Absorbing liquid from both gas bubblers shall be quantitatively transferred to plastic silicon free derivatization vessel.

8.8 Derivatisation

Absorbent media from the bubblers after the sampling is quantitatively transferred to derivatisation vessel (see 6.1.5). Derivatisation vessels must be accurately weighed empty with corresponding stoppers.

Add 8-10M sodium or potassium hydroxide solution (see 5.2.1) dropwise until slightly basic pH is reached. Calculate the volume of hydroxide solution needed to neutralize the nitric acid in absorbent and add couple of drops in excess. After basic pH of the solution is reached, immediately add appropriate volume of concentrated hydrofluoric acid (see 5.2.2) dropwise until acidic pH value of around 3,5 is reached. After acidic pH of the solution is reached add water (see 5.3) to dilute the sample matrix (usually on third of the total volume). Total volume depends on the volume of absorbent used. It should be taken into account prior sampling that derivatization vessels are of required volume.

Use pH indicator strips (see 5.5) to check the pH of the solution throughout the derivatisation procedure by placing one drop of the homogenized solution on the strip using plastic stirring rod.

Accurately weigh derivatized sample by subtracting the mass of the solution with the vessel with the mass of empty vessel recorded. Samples can be subjected to further dilution if needed to obtain concentration within calibration range.

Note: The same procedure is applied when reference gas mixture (see 5.7.5) is used as control sample. Calculate the expected mass of silicon collected and check the recovery by reading the sample as unknown.

8.9 Analytical procedure

The data processing unit of the ICP/MWP spectrometer is used to establish a measuring programme in which the intensities of the silicon emission lines 250,590 nm, 251,611 nm (most sensitive line) and 288,158 nm are measured in the same sample simultaneously or within very short timeframe. After ignition allow ISP/MWP torch at least 15 minutes to stabilize before use.

Aspirate the rinse blank solution (see 5.7.1.3) through the system for at least 20 minutes prior analysis to minimise carry over interferences from the tubing.

Calibrate the optical detection system by performing wavelength control check (see 5.6.4). If the check passes continue with the analysis. If the check is not satisfactory, perform the same procedure again until desired result is obtained.

Upon selection of the silicon emission lines to be measured, optimize the nebulizer pressure and viewing position for the particular analysis. This check should be performed prior to every calibration and analysis since it strongly depends on the plasma stability, ionic strength and density of the sample, total dissolved solids and other matrix characteristics.

8.9.1 Calibration line

Prepare calibration sequence by entering calculated concentrations of calibration standards by means of instrument software. After the sample introduction system has been appropriately flushed with rinse blank, aspirate calibration solutions including calibration blank (see 5.7.1.1) in ascending order of concentration. Record emission intensities for each selected wavelength against concentration. Plot linear weighted calibration curve. Squared correlation coefficient of the curve should be $r^2 > 0{,}995$.

Note: follow the manufacturer's instructions when selecting instrument method parameters. The number of readings of the standard solutions should be a minimum of seven to allow monitoring of the stability of readings under repeatability conditions.

8.9.2 Analysis of unknown and QC samples

Prepare the analysis sequence for unknown samples and QC samples in the following order: calibration blank, laboratory reagent blank, unknown sample(s), derivatisation control sample (DC), calibration blank, calibration control sample (CC), rinse blank solution.

After each measuring series, but at least after 5 to 10 measurements, re-analyse the calibration blank and calibration control sample to check whether the calibration curve is still valid.

If the silicon content in the unknown sample solutions exceeds the range of validity of the calibration curve, dilute the measuring solution accordingly with calibration blank (2% NHO_3).

Note: Follow the manufacturer's instructions when selecting instrument method parameters. The number of readings of the unknown and QC sample solutions should be a minimum of seven to allow monitoring of the stability of readings under repeatability conditions.

8.10 Calculation

Establish the calibration function by linear regression using the data obtained from the measurement of the calibration solutions.

Calculate the mass concentration of silicon ρ(Si) expressed in mg/kg in the liquid derivatized sample including any dilutions prior to readings.

$$\rho(Si) = \rho_x(Si)\ x\ D$$

where:

$\rho(Si)$ mass concentration of silicon in liquid sample expressed in mg/kg

$\rho_x(Si)$ mass concentration of silicon in liquid sample expressed in mg/kg read from the calibration curve

D dilution factor (non-dimensional number)

Calculate the mass concentration of silicon $\rho_g(Si)$ in gas sample expressed in mg/m^3 of sample gas.

$$\rho_g(Si) = \frac{\rho(Si)x\ m_x}{Vx}\ x\ 10^3$$

where:

$\rho_g(Si)$ mass concentration of silicon in gas sample expressed in mg/m^3

m_x mass of the liquid derivatized sample in derivatization vessel expressed in kg

V_x volume of sample gas collected expressed in dm^3 (normalized to STD)

10^3 conversion factor to cubic meters of gas

8.11 Expression of results

The values shall be rounded to the nearest 0,01 mg/m^3.

8.12 Precision of the method

A weighted standard deviation of readings under intra-laboratory reproducibility conditions (different concentrations, time shift) was taken as a measure of the precision of the method. For calculation purposes, emission line data for the selected concentration range were used. The calculated weighted deviation is expressed in percentages, where the mean intensity signal on the calibration curves is used as the mean of the readings.

The calculated data refers to approximately 2.5% RSD as a measure of intra-laboratory precision of the method.

8.13 Test report

The test report shall contain the following information:

a) a reference to this document;
b) complete identification of the gas sample(s);
c) expression of the results, according to clause 11;
d) any deviations of the procedure and all the circumstances which may have affected the results.

9 Determination of terpenes content by micro gas chromatography

9.1 Scope

This document specifies a micro gas chromatographic method for the on-line or offline monitoring of 5 terpenes in biomethane, namely:

- alpha-pinene
- beta-pinene
- para-cymene
- limonene
- 3-carene.

The described method was specifically developed for these five compounds. Information about the compounds are given in Annex A.

The method described is applicable to the determination of individual concentrations of the five terpenes from 1 ppm mol up to 10 ppm mol.

9.2 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.

EN 16723-1, *Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network — Part 1: Specifications for biomethane for injection in the natural gas network*

ISO 14532, *Natural gas — Vocabulary*

ISO 10715, *Natural gas — Sampling guidelines*

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

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

ISO 16664, *Gas analysis — Handling of calibration gases and gas mixtures — Guidelines*

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

9.3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14532 and the following apply.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

9.3.1

terpenes

products mainly consisting of terpenic hydrocarbons obtained as by-products of an **essential oil** (2.11) by distillation, concentration or other separation techniques

ISO 9235:2013(en), 2.30

9.3.2

gas chromatography

analytical method that is used to separate and determine the components of complex mixtures based on partitioning between a gas phase and a stationary phase

[SOURCE: ISO 11504:2012]

9.4 Principles of analysis

9.4.1 General considerations

The five terpenes to be determined in a biomethane sample are physically separated by means of gas chromatography (GC) and measured by comparison with calibration data obtained under the same set of conditions. Therefore, the components within the calibration gas(es) and within the gas sample shall be analysed with the same measuring system under the same set of conditions.

9.4.2 Sample handling and injection

The biomethane sample is contained within a cylinder that is attached to the chromatograph gas sampling valve or is continuously sampled from a pipeline and flows through the chromatograph gas sampling valve, which is used to inject a representative sample into the chromatograph.

Sampling shall be performed in accordance with ISO 10715.

Special attention shall be given to prevent condensation of heavier components when the sample pressure is reduced of both the sample cylinder as well as when using calibration gas mixtures compressed in cylinders. ISO 16664 shall be followed for the handling of calibration gases and gas mixtures.

9.5 Materials

9.5.1 Terpenes measurement standards

Pure terpene components should be used, and their purity should be analysed based on ISO 19229:2019.

Calibration gas mixtures with the relevant terpenes (namely: alpha-pinene, beta-pinene, para-cymene, limonene and 3-carene), prepared in methane matrix with amount fractions ranging from 5 to 10 ppm mol, and presenting associates measurement uncertainties below 5% should be used for the calibration of the analyser.

9.5.2 Micro Gas chromatograph (µGC-TCD)

Micro Gas chromatograph equipped with a module containing pneumatics, injector, column, and thermal conductivity detector (TCD). The detector should be capable of detecting an injection of at least 0,5 ppm mol limonene with a signal to noise ration of at least 3 to 1. A suitable µGC capillary column is selected for separation of analytes in the sample. A nonpolar micro column containing a 100% dimethylpolysiloxane (PDMS) phase is an example of column proven to be suitable for terpene analysis in biomethane.

9.6 Analysis

9.6.1 Analytical conditions

Select injection time, columns and injector temperature as well as column pressure in order to achieve a good resolution in minimal time.

9.6.2 Analysis of samples

When the biomethane is sampled into a cylinder and gas samples are then taken from the cylinder and injected into the analyser, it is recommended that 20 analyses be carried out. Analyse the biomethane sample as soon as possible from sampling.

9.6.3 Quantification method

Terpenes are quantified using their individual response factors. Response factors are determined by calibrating the analytical system with gaseous standards. When the analysis function of the analyser has been verified to be first order with a zero intercept over the range of concentration of interest, a calibration curve is prepared using a single concentration selected at the top of the linear range.

Analyse each of the reference gases. It is recommended that a minimum of 20 analyses be performed for each reference gas so as to ensure that the mean response of the 5 last injections and their standard uncertainties are determined with a precision that is fit for purpose. Determine the mean response of the analyser to each component.

Perform quantitative analysis and determine the mass concentration and uncertainty budget of individual terpenes in the sample gas in accordance with ISO 6143.

9.7 Performance characteristics

Before this method is used, its performance characteristics should be determined in accordance with ISO/IEC Guide 98-3. This determination should include, as a minimum, the estimation of uncertainty components from the following steps:

- Sampling (see ISO 10715)
- Calibration
- Analysis

The accuracy and repeatability of the measuring method are important factors, which shall be determined in order to evaluate the results and the suitability of the method for the intended purpose. The performance characteristics of the used method should be:

- Repeatability: <5%
- Reproducibility: <10%
- Uncertainty budget: <10%

9.8 Test report

The test report shall include at least the following information:

k) Reference to this International Standard and the analytical method used;
l) Purpose of the measurements;
m) Precisions about the process method used to upgrade biogas into biomethane;
n) Description of the stream and the sampling point location;
o) Cylinder identification (for spot sampling)
p) Time and date of the sampling (at the beginning and at the end of the sampling);
q) Sampling conditions (temperature, relative humidity, flow rate, duration);
r) Full description of the sampling procedure;
s) Full description of the analytical procedure;
t) Detection and quantification limits of the analytical method;
u) Concentrations of identified terpenes, provided with CAS numbers, including calculation and calibration principles used;
v) Uncertainty of the reported results;
w) Comments, including any deviation from specified procedure, and/or problems concerning the sample;
x) Date of analysis, name of laboratory and signature of analyst.

Annex A: Characteristics of the terpenes to be quantified

Table A.2

Name	CAS Number
α-pinene ($C_{10}H_{16}$)	7785-26-4
β-pinene ($C_{10}H_{16}$)	18172-67-3
3-carene ($C_{10}H_{16}$)	13466-78-9
D-limonene ($C_{10}H_{14}$)	5989-27-5
ρ-cymene ($C_{10}H_{16}$)	99-87-6