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Analysis of natural gas — Biomethane — Determination of VOCs by thermal desorption gas chromatography with flame ionization and/or mass spectrometry detectors

Analyse du gaz naturel — Biométhane — Détermination des COV par chromatographie en phase gazeuse à désorption thermique avec détecteurs à ionisation de flamme et/ou spectrométrie de masse

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Contents

Foreword

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

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

Introduction

This document supports the implementation of specifications for biomethane and biogas when used in the natural gas grids and when used as a transport fuel. Implementation of these specifications require fit-for-purpose test methods with known performance and acceptable metrological traceability to support the trade in renewable gases and conformity assessment.

Depending on the production method, biogas usually contains volatile organic compounds (VOCs) such as terpenes, siloxanes, hydrocarbons, sulfur containing compounds, oxygenated hydrocarbons, halogenated hydrocarbons, ketones, alcohols, and esters. VOCs can also be found in the biomethane even after upgrading.

Analysis of natural gas — Biomethane — Determination of VOCs by thermal desorption gas chromatography with flame ionization and/or mass spectrometry detectors

1 Scope

This document describes a method for sampling and analysis of volatile organic compounds (VOCs), including siloxanes, terpenes, organic sulfur compounds, in natural gas and biomethane matrices, using thermal desorption gas chromatography with flame ionization and/or mass spectrometry detectors (TD-GC-FID/MS).

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*

3 Terms and definitions

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

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

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

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

4 Principle

A measured volume of sample gas is drawn through one sorbent tube where VOCs are retained while highly volatile organic compounds as methane matrix gas pass through. Desorption of the tubes is then carried out by thermal desorption (TD) in which the adsorbed substances are released with heat and then transferred into a gas chromatograph (GC) equipped with a capillary column, a mass spectrometer (MS) and/or a flame ionization detector (FID). MS data of the separated VOC components are compared with a mass spectral library for compound identification. The use of the specific ions in addition to the retention time ensure positive identification of a given VOC. Retention indices can also be used to identify peaks by comparing measured retention indices with tabulated values. Quantification is performed using either the FID and/or the MS detector. The expected quantification limit is (2-5) ng which is equivalent to (20-50) µg/m^3 in the sampled gas assuming a 100 ml gas sample volume.

5 Reagents and materials

5.1 Individual VOCs

For calibration purposes, purity > 99 %. Standard mixtures commercially available.

5.2 Dilution solvent

Dilution solvent of chromatographic quality, for preparing blend solutions for liquid spiking shall be free from compounds of interest and compounds co-eluting with the compound(s) of interest (e.g. in methanol or diethylether).

5.3 Sorbents

Sorbent are preconditioned and kept in a clean atmosphere.

EXAMPLE 2,6-diphenylphenylene oxide polymer.

Tubes compatible with the thermal desorption instrument to be used (6.8.3), typically containing 200 mg sorbent, shall be sealed with for example screw-cap fittings with polytetrafluoroethylene.

The conditioning temperature shall not exceed the maximum rated temperature for the adsorbent resin. The desorption tube shall preferably be conditioned 25 °C higher than the temperature at which it will be desorbed.

6 Apparatus

6.1 Micro-syringe, 5 µl or 10 µl liquid syringe readable to 0,1 µl.

6.2 Gas-tight syringe, 100 ml readable to 5 ml, for indirect sampling.

6.3 Tubings, silicon-free and sulfur-free tubings.

6.4 Volumetric flask, in inert material, e.g. glass, quartz, polytetrafluoroethylene, 50 ml, class A.

6.5 Flowrate controller, volumetric, (50 to 500) ml/min readable to 2 ml/min.

6.6 Precision scale, 1 mg to 20 mg readable to 0,1 mg.

6.7 Sampling system, capable of accurately and precisely drawing natural gas or biomethane flow through the sorbent tubes.

6.8 Gas chromatograph

6.8.1 Detectors, mass spectrometer in electron ionization (EI) mode and/or flame ionization detector.

6.8.2 Capillary column for gas chromatography

EXAMPLE 95 % dimethylpolysiloxane, 5 % diphenyl, 60 m long, 0,32 mm inner diameter and 1 µm film thickness.

6.8.3 Thermal desorption instrument

Preferably two-stage thermal desorption in which the adsorbed substances are first released with heat and then transferred to a cooling trap for focusing. The cooling trap is reheated quickly and the substances are released and transported onto the gas chromatography column for separation.

7 Preparation

7.1 Field tube blanks

Determine levels of VOCs on unspiked, conditioned tubes.

7.2 Solutions for liquid spiking

7.2.1 General

Prepare solutions for liquid spiking for each family of VOCs to be determined.

For example, for siloxanes, the following compounds can be selected:

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

Other VOCs of interest include terpenes such as D-Limonene, α-pinene, β-pinene, 3-carene, p-cymene, ketones such as 2-butanone, 2-pentanone, 3-pentanone, furans such as 2-methylfuran, 3-methylfuran, 2-ethylfuran, alkanes such as octane, nonane, decane, undecane, organic sulfur compounds such as 1-propanethiol, dimethylsulfide, dimethyldisulfide.

7.2.2 Solution containing approximately 0,2 mg/ml of each component

Accurately weigh approximately 10 mg of each of the selected compounds into a 50 ml volumetric flask, starting by the least volatile compound. Make up to 50 ml with dilution solvent, seal the volumetric flask and invert it to thoroughly mix the solution.

7.2.3 Solution containing approximately 0,04 mg/ml of each component

Introduce 25 ml of dilution solvent into a 50 ml volumetric flask. Add 10 ml of the solution described in 7.2.2. Make up to 50 ml with dilution solvent, seal the volumetric flask and invert it to thoroughly mix the solution.

7.2.4 Solution containing approximately 0,01 mg/ml of each component

Introduce 25 ml of dilution solvent into a 50 ml volumetric flask. Add 2,5 ml of the solution described in 7.2.2. Make up to 50 ml with dilution solvent, seal the volumetric flask and invert it to thoroughly mix the solution.

7.2.5 Standard tubes loaded with liquid spiking

Inject aliquots of solutions for liquid spiking onto clean sorbent tubes. For each solution, perform at least two injections, typically 1 µl on the first tube and 2 µl on the second tube. Purge the tubes under a flow of inert gas to eliminate most of the dilution solvent from the tube. The purity of the inert carrier gas (e.g. He, Ar, N_2) used to purge sorbent tubes for at least one minute during standard introduction is of great importance, as any contaminants contained in the gas are enriched on the sorbent together with the substances to be analysed. An appropriate flow rate for the inert carrier gas is in the range of 50 ml/min to 200 ml/min.

8 Sampling

Multiple sorbents, suitable for thermal desorption, are commercially available. They range in strength from very retentive sorbents required to retain low boiling point VOCs (<50 °C) to very weak sorbents suitable for quantitative sampling and release of VOC with boiling point over 250 °C. A list of sorbents is given in ISO 16000-6:2021, Annex D. Collection of an accurately known volume of natural gas/biomethane is critical to the accuracy of the results.

The use of a field tube blank (7.1), a conditioned tube with seals transported to field sites and then returned to the laboratory for analysis, is recommended. Use recommended conditioning parameters for various individual sorbents (see 5.3).

Prior to sampling, ensure that the flowrate controller has been calibrated over a range including the rate to be used for sampling (typically 50 ml/min to 500 ml/min), with a test tube. The flow must be stable for at least four minutes.

To avoid risks of adsorption of analytes in the sampling line, which would lead to underestimation of their concentration, use short tubing and non-adsorptive or passivated materials for tubing.

Remove the seals of the tubes just prior to initiation of the sampling.

Operate the sampling for the desired time (typically 1 min to 4 min) and record the following parameters on an appropriate data sheet:

- sampling location,
- sample name,
- date and time,
- flowrate (if applicable),
- sampling time, (if applicable),
- volume,
- tube number,
- temperature and pressure,
- any other relevant information.

Remove the tube and seal it.

At least two replicates should be taken for one site.

Sampling may also be performed via an appropriate inert polymeric sampling bag (see ISO 10715 and Reference [3]). In that case, sampling on sorbent tubes shall be conducted shortly (preferably within 30 min) after the filling of the bag to avoid loss by adsorption on the walls on the bag. Collection of an accurately known volume of natural gas/biomethane from the bag may be done using a gas-tight syringe. [4]

9 Sample handling

Avoid contamination of the sorbent tube with the compound(s) of interest. Be careful in the storage and handling of the tubes throughout the entire sampling and analysis process to minimize this risk. The tubes should be analysed as soon as possible and preferably within two weeks after collection. They shall be tightly sealed using caps and stored in a low emission container at ambient room temperature or under refrigerated conditions (4 °C or below). Make sure that the gas to analyse does not come in contact with silicon containing materials (such as tubings or greases).

10 Procedure

10.1 Desorption and analysis

Tune in the mass spectrometer in accordance with the manufacturer's instructions.

Record the mass spectra in full scan (typically 32 amu to 450 amu (absolute mass units)). Selected ion extraction may be performed afterwards for the identification.

For example, a list of diagnostic ions for some VOCs are given in Table 1.

Table 1 — Diagnostic masses of VOCs

	Diagnostic ion 1 m/z	Diagnostic ion 2 m/z
Silanol, trimethyl-	75	45
Disiloxane, hexamethyl	147	73
Trisiloxane, octamethyl	221	73
Tetrasiloxane, decamethyl	207	73
Pentasiloxane, dodecamethyl	281	73
Cyclotrisiloxane, hexamethyl	207	96
Cyclotetrasiloxane, octamethyl	281	73
Cyclopentasiloxane, decamethyl	73	267
Cyclohexasiloxane, dodecamethyl	73	341
D-limonene	68	93
α-pinene	93	136
β-pinene	93	136
3-carene	93	136
p-cymene	119	134
2-butanone	72	43
2-pentanone	86	43
3-pentanone	86	57
2-methylfuran	82	53
3-methylfuran	82	53
Ethylfuran	96	81
Octane	114	57
Nonane	128	57
Decane	142	57
Undecane	156	57
1-Propanethiol	76	47
Dimethylsulfide	62	47
Dimethyldisulfide	94	79

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

- desorption temperature: 250 °C to 300 °C depending on the sorbent material,
- desorption time: 5 min to 10 min,
- carrier gas: helium,

- desorption flowrate: 30 ml/min to 60 ml/min,
- split ratios: split ratios between the sample tube and secondary trap and between the secondary trap and the column should be selected dependent on expected concentration.

10.2 Quantification

Chromatographic peaks shall be integrated using automated methods using software provided by the instrument manufacturer. The analyst shall review the automated integration and make adjustments and manually integrate the peaks, if necessary.

For MS, quantifier and qualifier mass ions extracted from the TIC signal shall be used. The choice of quantifier and qualifier ions for each compound shall be documented and available in the laboratory and shall be reported if requested. Where possible, quantifier and qualifier ions shall be selected that are not present in neighbouring peaks and that are major fragments of the compound in question. Selected ion monitoring (SIM) can also be used for targeted compounds.

For quantification with FID, the retention time of a GC peak cannot, on its own, be used as confirmation of compound identity. Identification is preferentially performed using MS. Confirmation of the identification is obtained if the peak retention time also corresponds to that of the respective standard on FID.

10.3 Calculations

Use the data from the solutions for liquid spiking (7.2) to calculate a response factor (area/nanogram injected) for each component of interest.

Calculate the analyte quantities on a sample tube, in nanograms, as the area of the analyte's peak divided by the response factor. If the mass spectrometer is used for quantification, the same characteristic ion shall be chosen for the analyte in the sample and in standard produced by liquid spiking.

Use Formula (1) to calculate the concentration of each VOC in the sampled natural gas or biomethane, c_m, expressed in µg/m³ at 25 °C and 101,325 kPa.

$$c_m = \frac{m_s - m_{sb}}{V} \cdot \frac{101{,}325}{p} \cdot \frac{T}{25} \qquad (1)$$

where

m_s is the mass of a VOC present in the actual sample, expressed in ng;

m_{sb} is the mass of a VOC present in the field tube blank, expressed in ng;

V is the volume of sample taken, expressed in l;

p is the actual pressure of the gas sampled, expressed in kPa;

T is the actual temperature of the gas sampled, expressed in °C.

If the sample concentration is higher than the calibration range, add a calibration point to verify linearity. Use preferably the FID signal as FID has a linear range for 6 or 7 orders of magnitude (10^6 to 10^7).

For siloxane and sulfur, the data can then be used to calculate total element concentration. For example, the total siloxanes content is calculated as the sum of the individual siloxanes each corrected by the fractional amount of silicon present in a particular siloxane. The method only determines sulfur content in organic sulfur components. Other sulfur components such as hydrogen sulfide, carbonyl sulfide and carbon disulfide shall be determined with another method and added to the organic sulfur content to obtain the total sulfur content.