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# Analysis of natural gas — Biomethane — Determination of terpenes' content by micro gas chromatography

*Analyse du gaz naturel — Biométhane — Détermination de la teneur en terpènes par micro-chromatographie en phase gazeuse*



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# Foreword

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

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

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

Terpenes can occur naturally in biogas and remain as trace components after treatment in the biomethane produced. Terpenes are odoriferous compounds that have the potential to mask the smell of the odorant added to the biomethane before injection into the natural gas grid. For safety reasons it is necessary to monitor these impurities.

This document describes a method to perform the analysis of five terpenes in biomethane. The method includes both on-line and offline measurement techniques based on chromatography and can be of interest to fuel specifications for biomethane.

This document contributes to the standardization of the determination of terpenes in biomethane. The document relates to good housekeeping in supply of biomethane into the natural gas grid.

# Analysis of natural gas — Biomethane — Determination of terpenes' content by micro gas chromatography

## 1 Scope

This document specifies a micro gas chromatography method for the on-line or offline determination of the content of five terpenes in biomethane, namely:

— alpha-pinene,

— beta-pinene,

— para-cymene,

— limonene,

— 3-carene.

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

The method is applicable to the determination of individual amount fractions of the five terpenes from 1 µmol/mol up to and including 10 µmol/mol. With minor modifications it can also be used for terpene amount fractions above 10 µmol/mol.



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

ISO 10715, *Natural gas — Gas sampling*

ISO 14532, *Natural gas — Vocabulary*

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

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

## 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 terminology databases for use in standardization at the following addresses:

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

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

**3.1**
**terpene**
product mainly consisting of terpenic hydrocarbons obtained as a by-product of an essential oil by distillation, concentration or other separation techniques

[SOURCE: ISO 9235:2021, 3.31, modified — The EXAMPLE was deleted.]

# 4 Principles of analysis

## 4.1 General considerations

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

## 4.2 Sample handling and injection

### 4.2.1 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 can be helpful, but they shall only contain material proposed in ISO 10715 and shall not cause adsorption of terpenes.



### 4.2.2 Sampling of biomethane into vessels



Sampling shall be performed in accordance with ISO 10715.

Use appropriate materials or passivation that reduce terpenes adsorption to a level that will not cause analytical bias (e.g. passivated stainless steel). The length of sampling lines should be minimized where possible to minimise adsorption.

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

NOTE An example of the evacuated cylinder technique is described in ISO 10715.

### 4.2.3 Sample injection

Special attention shall be given to prevent condensation of heavier components when handling the sample contained in the sample cylinder. ISO 16664 shall be followed for the handling of calibration gases and gas mixtures.

When on-line biomethane analysis is performed on site the following can help to minimize the danger of condensation:

— external heating of the sample gas at or before the reducer;

— using more than one reducer to drop the pressure in stages.

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.

# 5 Materials

## 5.1 Terpenes calibration standards

Calibration gas mixtures can be prepared by appropriate methods (see ISO 6142-1 and the ISO 6145 series) from nominally pure terpenes in a methane matrix. If nominally pure terpenes are used, their purity shall be analysed based on ISO 19229.

Calibration gas mixtures with the relevant terpenes (namely: alpha-pinene, beta-pinene, para-cymene, limonene and 3-carene), prepared in a methane matrix with amount fractions ranging from 1 µmol/mol to 10 µmol/mol, and relative expanded measurement uncertainties below 5 % shall be used for the calibration of the analyser.

For higher amount fractions, a set of gas standards shall be used covering the desired amount fractions.

## 5.2 Micro gas chromatograph (µGC-TCD)

A micro gas chromatograph equipped with a module containing pneumatics, injector, column, and thermal conductivity detector (TCD) is used for the analysis. The detector should be capable of detecting limonene at the amount fraction of 0,5 µmol/mol with a signal to noise ratio 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) stationary phase is an example of column proven to be suitable for terpene analysis in biomethane.



# 6 Analysis



## 6.1 Analytical conditions

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

## 6.2 Collection of samples

Sample the biomethane with a suitably cleaned and prepared cylinder using one of the methods described in ISO 10715. Sampling into a 500 mL cylinder at 1,5 bar absolute[1)] is suitable. The size of the sample should be sufficient to carry out at least 20 analyses. Analyse the biomethane sample as soon as possible after sampling.

For online analysis, gas 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. A fast loop shall be installed in order to provide a representative sample gas composition to the analyser. Guidelines given in ISO 10715 shall be followed.

## 6.3 Quantification method

The sample gas shall be analysed and the amount fraction and uncertainty for individual terpenes in the sample gas be determined in accordance with ISO 6143. 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 five 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.

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

## 7 Performance characteristics

Before the method described in this document is used, the performance characteristics shall be determined. This determination should include, as a minimum, the estimation of measurement uncertainty for 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.

NOTE 1 Within laboratory validation has demonstrated that a repeatability less than 5 % and a reproducibility less than 10 % can be achieved. For this document, no interlaboratory evaluation of this method has taken place.

Furthermore, the limits of detection and quantification shall be determined for each terpene. The limits of quantification shall be below 1 µmol/mol.

The measurement uncertainty associated with the result shall be evaluated.

NOTE 2 Within-laboratory validation has demonstrated expanded uncertainties less than 13 % for amount fractions above 2 µmol/mol (coverage factor $k$ = 2 and 95 % confidence level).

NOTE 3 For further guidance, refer to the ISO/IEC Guide 98-3[1], to the Eurachem/ CITAC Guide on Measurement uncertainty[5] and the Eurachem Guide on method validation[6].



## 8 Test report

The test report shall include at least the following information:



a) reference to this document and the analytical method used;

b) purpose of the measurements;

c) description of the stream and the sampling point location;

d) cylinder identification (for spot sampling);

e) date and time of the sampling (at the beginning and at the end of the sampling);

f) sampling conditions (temperature, relative humidity, flow rate, duration);

g) quantification limits of the analytical method;

h) amount fractions of identified terpenes;

i) expanded uncertainty of the reported results (coverage factor $k$ = 2 and 95 % confidence level);

j) comments, including any deviation from specified procedure, and/or problems concerning the sample;

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