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Analysis of natural gas — Biomethane — Determination of amines content

Analyse du gaz naturel — Biométhane — Détermination de la teneur en amine

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

~~International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2~~

~~The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.~~

~~In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of document:~~

- ~~an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;~~
- ~~an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.~~

~~An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.~~

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

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

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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 was developed in response to biomethane specifications such as EN 16723 (all parts)[7]. In other regions, other specifications can apply for biomethane.

In the process of biogas upgrading into biomethane, alkanolamines are used for removing of sulphur-containing components and carbon dioxide. Due to this reason, trace level of these components can be present in biomethane. This method is suited for the detection of these components as well as the determination of their concentration. To inject biomethane into natural gas grids and to use it as an automotive fuel, it needs to meet specifications. For amines the maximum limit value in biomethane is set as 10 mg/m³ is set in EN 16723 (all parts)[7]. Other specifications can state other thresholds.

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Analysis of natural gas — Biomethane — Determination of amines content

1 Scope

This document specifies the determination of the concentration of alkanolamines in biomethane. The measurement method ~~involve Thermal Desorption Gas Chromatography~~involves thermal desorption gas chromatography with ~~Flame Ionization~~flame ionization and/or ~~Mass Spectrometry~~mass spectrometry detectors (TD-GC-MS/FID). The described method is specifically developed for the analysis of five amine compounds, namely:

— ~~Monoethanolamine~~monoethanolamine (MEA~~)~~);

— ~~Diglycolamine~~diglycolamine (DGA~~)~~);

— ~~Diethanolamine~~diethanolamine (DEA~~)~~);

— *N*-methyldiethanolamine (MDEA~~)~~);

— ~~Piperazine~~piperazine (PZ~~)~~).

Information about the compounds is given in Annex A.

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.

~~<std>ISO 10715, *Natural gas — Sampling guidelines*</std>~~

~~<std>ISO 13443, *Natural gas — Standard reference conditions*</std>~~

~~<std>ISO 14532, *Natural gas — Vocabulary*</std>~~

~~<std>~~ISO 10715, *Natural gas — Sampling guidelines*

ISO 14532, *Natural gas — Vocabulary*

ISO 16000-6, *Indoor air — Part 6: Determination of organic compounds (VVOC, VOC, SVOC) in indoor and test chamber air by active sampling on sorbent tubes, thermal desorption and gas chromatography using MS or MS FID*~~</std>~~

~~<std>~~ISO 19229, *Gas analysis — Purity analysis and the treatment of purity data*~~</std>~~

~~<std>ISO/TR 27912:2016, *Carbon dioxide capture — Carbon dioxide capture systems, technologies and processes*</std>~~

~~<std>ISO/TS 16550:2014, *Nanotechnologies — Determination of silver nanoparticles potency by release of muramic acid from Staphylococcus aureus*</std>~~

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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 https://www.electropedia.org/

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]

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

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

4 Reference conditions

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

Other reference conditions may be chosen if the context in which the measurements are performed, or the results to be used, dictate to do so.

5 Principle

A known volume of biomethane is actively sampled on a sorbent 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.

6 Reagents and equipment

~~6.1~~ 6.1 Calibration standards.

~~6.1.1~~ 6.1.1 Amine standards

~~Pure~~, pure amine components shall be used, and their purity shall be assessed in accordance with ISO 19229. Amines (except DGA) should be at least 99 % purity grade. For DGA, purity should be at least 98 %.

~~6.1.2~~ 6.1.2 Reference standard

N-~~Octane~~octane of at least 99 % purity grade.

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~~6.2~~ 6.2 Dilution solvent

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

~~6.3~~ 6.3 Sorbent tubes

~~Sorbent tubes shall be,~~ equipped with a suitable sorbent. It is also recommended to use stainless steel tubes with proper coating treatment (amines are photosensitive).

EXAMPLE Tenax TA®[1] based polymer (2,6-diphelylene oxide polymer).

~~6.4~~ 6.4 Gas chromatograph (GC~~)~~

~~Gas chromatograph shall be),~~ equipped with a flame ionization detector (FID) and/or a mass spectrometer (MS). Moreover, the GC shall be equipped with a thermal desorption system associated to a cryogenic trap.

If an FID is used, the selectivity of the method regarding amines shall be established (see ISO 6974-1~~[1]~~.). As biomethane composition regarding trace compounds (e.g., terpenes) is related to the nature of the inputs, the method shall be tested towards a real biomethane sample, and adapt it if necessary to avoid coelution of components.

~~6.5~~ 6.5 Capillary column

~~A,~~ GC capillary column suited for the separation of ethanolamines shall be selected.

~~EXAMPLES~~EXAMPLES:

Volatile amines, 30 m, 0,32 mm ID, 5 µm;

Rtx-5 Amine, 30 m, 0,25 mm ID, 0,50 µm.

~~6.6~~ 6.6 Thermal desorption (TD) system.

The apparatus is 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 -30 °C to -100 °C (a cryogenic-free system may be used when working at ~~–~~30 C).

— A direct connection to the GC (6.4).

[1] Tenax® is a registered trademark of Buchem BV, Apeldoorn, the Netherlands. This information is given for the convenience of users and does not constitute an endorsement by ISO for the product named.

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~~6.7~~ 6.7 Precision syringes

~~Precision syringes,~~ intended for tubes spiking shall be readable to 0,1 ~~µL~~µl or better resolution. The capacity shall be in agreement with the volume to be deposited on the sorbent. Conditioning of the sorbent tubes.

6.8 Conditioning of sorbent tubes.

Commercial sorbent tubes (6.3) can contain many impurities that shall be removed before any sampling. Thus, tubes shall be conditioned at high temperature under inert flow gas before usage. Conditioning shall be performed at 300 °C for at least 120 min under inert gas flow rate of approx. 50 ml min^{-1} in order to remove any potential impurities present on the sorbent. Other conditions can apply – consult the documentation of the sorbent tubes or the literature.

7 Sampling

With respect to biomethane sampling, ~~the~~ guidance of ISO- 10715 shall be followed. Sampling using thermal desorption tubes ~~is~~shall be as described in ISO 16000-6. These guidances shall be followed in the absence of a dedicated sampling method for biomethane. Flow rate measurements shall be performed using devices that have been calibrated with methane or biomethane. Furthermore, the sampling method proposed in this document is adapted for a dry biomethane.

The sorbent tubes shall be conditioned prior to sampling (~~see Clause 0~~6.8). Breakthrough volume of amines on the sorbent tubes shall be studied to obtain the total sample capacity of the sorbent tubes and to adapt to proper sampling volume. A sufficient volume of gas shall be sampled and trapped on the sorbent tubes to ensure that based on the analysis results an assessment can be made that the total amines concentration meets the applicable specification. A sufficient number (at least three) of tubes shall be sampled to enable replicate analysis.

Attention shall be paid to the possibility of amines in the form of aerosols, sampling technique shall be adapted.

8 Preparation of the calibration tubes

8.1 Prior to any sample analysis, a calibration of the instrument for the five amines shall be performed. Prepare calibration standards in the form of sorbent tubes spiked with known masses of the relevant amines. The sorbent tubes shall be conditioned beforehand (see Clause 7). After preparing the liquid calibration solutions containing the five amines at different concentrations (one solution per calibration point), a proper volume (usually below 100 µL) of solution should be directly deposited on the conditioned sorbent tube (preliminary conditioned).

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

8.2.1 Prepare a concentrated liquid mixture containing desired amounts of MEA, DEA, DGA, MDEA, PZ (6.1.1) and ~~n~~*N*-octane (6.1.2) with mass/volume concentration.

8.2.2 Dilute this mixture with high-purity methanol (6.2) to obtain desired low concentrations of amines as end-mixture.

8.2.3 Spike the end-mixture onto conditioned sorbent tubes (~~9.2.4~~6.3) with known volume and calculated mass.

8.2.4 Flush the spiked sorbent tubes with nitrogen for a duration of at least 20 min to remove most of the methanol. Then the measurement standards for amine components are ready to be used.

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