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Analysis of natural gas — Biomethane — Determination of ammonia content by tuneable diode laser absorption spectroscopy

Analyse du gaz naturel — Biométhane — Détermination de la teneur en ammoniac par spectroscopie d'absorption laser à diode accordable

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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

Ammonia is a common trace impurity found in biomethane. It is a product from the anaerobic digestion of biomass, formed from the breakdown of amino acids during the production of biogas. As an impurity in biogas and biomethane, ammonia is corrosive when it dissolves in the presence of water, damaging process equipment and leads to an increase in anti-knock processes in combustion engines when used as a fuel for vehicles. Ammonia is detrimental to the environment and as an air pollutant forms particulates which are damaging to public health. Additionally, when present in the combustion of biomethane, ammonia can lead to the formation of nitrogen oxides (NO_x), which are regulated pollutants as they are toxic and affect air quality. Therefore, the presence of ammonia in biogas and biomethane is undesirable to gas distributers and their customers.

Measuring ammonia content in mixtures of methane at the trace level (i.e. mg m^{-3}) is technically difficult due to the adsorptive nature (i.e. "stickiness") of ammonia. Particularly spectral NH_3 measurements can be severely hampered by spectral interferences from the matrix gas components, which further increases the complexity of these measurements. Measurements in biogas or biomethane are also dangerous due to the potentially explosive nature of methane, when mixed with an oxidizer like ambient air.

This method supports the implementation of specifications for biomethane and biogas such as EN 16723-1[8] and EN 16723-2[9] when used in the natural gas grids and when using it as a transportation fuel. Implementation of these specifications require fit-for-purpose measurement methods with known performance and acceptable metrological traceability to support the trade of renewable gases as well as conformity assessment. Currently, methods are referenced in standards such as EN 16723-1 which have not been validated for use with biomethane and biogas. This document describes measurement methods that meet these requirements and can be implemented by laboratories and industry, also those seeking accreditation on the basis of, e.g. ISO/IEC 17025.

The methods described are based on commercially available spectroscopic analysers, specific to the measurement of ammonia. They have been shown to perform at an acceptable level when quantifying the ammonia content of biomethane at the 10 mg m^{-3} level, as specified in, e.g. EN 16723-1.

Analysis of natural gas — Biomethane — Determination of ammonia content by tuneable diode laser absorption spectroscopy

WARNING — The use of this document can involve hazardous materials, operations and equipment. This document does not aim to address all of the safety problems associated with the materials specified. It is the responsibility of the user of this document to establish appropriate safety and health practices and to determine the applicability of any other restrictions prior to use.

1 Scope

This document describes several test methods for measuring the ammonia amount fraction 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 are comprised of readily available commercial spectroscopic analysers that are specific to ammonia. These NH_3 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 and above the 10 mg m^{-3} (14 µmol mol^{-1}) level and applies to analysis within absolute pressure ranges of 1 bar – 2 bar, temperatures of 0 °C – 40 °C and relative humidity <90 %.

References are also made to additional standards that are applied either to natural gas analysis or air quality measurements. In this document the matrix gas is always methane or biomethane and the measurand is the amount fraction NH_3.

NOTE 1 bar = 0,1 MPa =10^5 Pa; 1 MPa = 1 N/mm^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 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

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

ISO 7504, *Gas analysis — Vocabulary*

ISO 9169, *Air quality — Definition and determination of performance characteristics of an automatic measuring system*

ISO 10715, *Natural gas — Gas sampling*

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

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

ISO 14532, *Natural gas — Vocabulary*

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

IEC 61207-7, *Expression of performance of gas analyzers — Part 7: Tuneable semiconductor laser gas analyzers*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 6143, ISO 7504, ISO 9169, ISO 10715, ISO 10723, ISO 14532, IEC 61207-7 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
diode laser
semiconductor laser which is formed from a p-n junction and powered by injected electric current

[SOURCE: IEC 61207-7:2013, 3.2]

3.2
ultraviolet-visible spectroscopy
UV/vis
spectroscopy of radiation that consists of electromagnetic radiation with wavelengths in the ultraviolet and/or visible regions

[SOURCE: ISO/TS 80004-6:2021, 5.6, modified — The second term was originally "UV-Vis spectroscopy".]

3.3
span gas
gas or gas mixture used to adjust and check the *span point* (3.4) on the response line of the measuring system

Note 1 to entry: This amount fraction is often chosen around 70 % to 90 % of full scale.

[SOURCE: ISO 12039:2019, 3.15]

3.4
span point
value of the output quantity (measured signal) of the automatic measuring system for the purpose of calibration, adjustment, etc. that represents a correct measured value generated by reference material

[SOURCE: ISO 13199:2012, 3.14]

3.5
performance characteristic
one of the quantities assigned to the analytical instrument in order to define its performance

[SOURCE: ISO 13199:2012, 3.9, modified — The phrase "to equipment" has been replaced by "to the analytical instrument" and the Note 1 to entry has been deleted.]

3.6
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

[SOURCE: ISO 9169:2006, 2.2.4]

3.7
interference
negative or positive effect upon the response of the measuring system, due to a component of the sample that is not the measurand

[SOURCE: ISO 13199:2012, 3.4]

3.8
interfering substance
substance present in the sample under investigation, other than the analyte, that affects the response

[SOURCE: ISO 9169:2006, 2.1.12, modified — "air mass" was replaced by "sample", "measurand" was replaced by "analyte" and the term "interferent" was removed.]

3.9
measurement system
complete set of measurement instrumentation and associated equipment used for the determination of a specified measurand

[SOURCE: ISO 11771:2010, 2.4]

4 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 ISO 10715:2022, Clause 4. Ensure that cylinder pressure regulators are in serviceable condition and that they are constructed of materials recommended by the producer of the calibration gas.

5 Principle

A biomethane sample or calibration mixture is introduced into a measurement system which comprises a gas delivery/vent system and a spectroscopic NH_3 analyser.

As biomethane may have non-negligible absorption, for example, in the infrared region of the spectrum, it shall be confirmed that a particular analyser/technical configuration does not suffer from unacceptable interference in the measurement range.

The spectroscopic analyser is specific to NH_3 detection and is characterised by certified calibration materials specified to meet the requirements of relevant standards, e.g. EN 16723-1 [8].

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

The amount fraction of NH_3 in the sample is determined from a calibration function, e.g. as specified in ISO 6143.

6 Apparatus

6.1 NH_3 analyser

The analyser shall be an NH_3 specific instrument based on the detection and quantification of NH_3 by absorption spectroscopy. The analyser shall be suitable for measuring trace amounts of NH_3 in a methane matrix. See Annex A for example analyser performance characteristics.

6.2 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 6.5.4) becomes faulty. The design shall include consideration of the construction materials (see 8.2).

6.3 Temperature sensor

Temperature sensor that is capable of measuring sample gas temperature to ±1 °C. This item is typically present within commercial analysers.

6.4 Pressure sensor

Pressure sensor that is capable of measuring sample gas pressure to ±1 kPa. This item is typically present within commercial analysers.

6.5 Calibration equipment

6.5.1 General

Two methods for multipoint calibration of NH_3 analysers are:

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

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

The methods require the following equipment.

6.5.2 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 gas cylinders are to be obtained for the correct cylinder fitting size required for the regulator.

6.5.3 Flow controller

The flow controller can be any device (valve) capable of adjusting and regulating the flowrate of the calibration gas mixture. If the dilution method is used, a second device is required for the methane. In this case, the flow controller can be a part of the dilution device.

6.5.4 Flow meter

A calibrated flow meter that is capable of measuring and monitoring the calibration gas mixture flowrate. If the dilution method is used, the flow meter may be a part of the dilution device.

6.5.5 Dilution device

The dilution device can be any device capable of diluting with methane a parent NH_3 gas mixture to a required concentration levels.

The dilution device shall be designed to provide thorough mixing of the parent NH_3 gas mixture and methane.

The dilution device shall be capable of providing the required flowrate of the generated calibration gas mixtures.

Uncertainty of the dilution factor shall be known and taken into account in the uncertainty budget.

Dilution device shall be calibrated according to ISO 6145-1.

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

6.5.6 Output manifold

The output manifold should be of sufficient diameter to ensure the pressure drop at the analyser connection is minimized. This can be ensured by using the same diameter connections as the analyser input connection. The system shall have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

7 Reagents and materials

7.1 Methane

A pressurized cylinder of pure (99,99 cmol/mol or greater) methane certified to contain less than the LOD of the measurement system of NH_3 shall be used. Methane is used as the zero-point gas and diluent gas in the case of calibration by dynamic dilution.

7.2 Calibration gases

Use pressurized cylinders containing calibration gas mixtures with amount fractions of NH_3 in methane corresponding to the instrument operating range, that is, 10 %, 20 %, 40 % and 80 % of full-scale range. The amount fraction values shall be traceable to a 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 in the range between 20 % and 60 % of the full-scale range should be used in parallel to check for bias in the calibration curve.

Span gas which is an NH_3 in methane calibration gas mixture meeting the requirements of relevant standards, e.g. EN 16723-1.

The requirements of ISO 16664 shall be followed for the handling of calibration gas mixtures.

7.3 Inert gas

A dry inert gas, for example, pure (99,99 cmol/mol or greater) nitrogen of water dewpoint below -70 °C, 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.

8 Sampling

8.1 General

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.

8.2 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 NH_3 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. Passivation of stainless steel using proprietary techniques is available to inhibit adsorption as

demonstrated by research[10]. Results of investigations into coating suitability are available as part of research project outputs, such as EMRP ENG54 "Metrology for biogas"[11] and EMPIR 16ENG05 "Metrology for biomethane"[12]. The general considerations of ISO 10715 should always be followed.

8.3 Cleanliness

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. Ambient air and humidity are to be thoroughly 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 or response time of the measurement system from the presence of a particle filter shall also be investigated, if installed.

8.4 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 NH_3 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.

8.5 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.

8.6 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 amount fraction levels, always flush the transfer lines and the valves with dry N_2 or CH_4 in order to avoid memory effects.

8.7 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 in the sample or calibration gas mixture and materials used in the measurement system

8.8 Leak 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.

9 Calibration

9.1 Calibration procedures

The instrument can be calibrated over the desired range of interest using either multiple calibration gas mixtures in the cylinders or one calibration gas mixture in the cylinder together with dilution device and methane as diluent gas. The calibration should be in accordance with ISO 6143.

9.2 Frequency of calibration

9.2.1 Multipoint calibration

Perform a multipoint calibration when:

a) the analyser is first used;

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 point calibrations are performed.

Evaluate the calibration data in accordance with ISO 6143.

9.2.2 Zero and span point calibration

Perform zero and span point calibrations before and after each sampling period. If the analyser is used continuously, calibrations should be performed before the end of the time period out of which the measurement system drift exceeds the acceptable limit.

10 Interferences

10.1 Interfering absorbers

Other gas components that show spectral absorption nearby or in the same spectral window as NH_3 can overlap with the NH_3 absorption spectrum 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 substances on the analyser. If any interfering substance identified is listed in relevant standards, for example, EN 16723-1[8], the measurement system response to that component shall also be characterised in the same manner as NH_3.

10.2 Matrix gas

The analyser response for NH_3 can change significantly between different matrix gas compositions. Measurement systems using high spectral resolution detection methods, for example, laser spectroscopic analysers, are particularly susceptible. Therefore, the calibration matrix gas shall match the sample gas matrix.

10.3 Secondary level spectroscopic effects: Gas temperature, gas pressure, spatial homogeneity

Instrumentation working with high spectral resolution, for example, laser-based devices, may show considerable susceptibility to secondary spectroscopic deviations:

a) matrix gas effects can depend strongly on gas temperature and gas pressure;

b) the calibration function can depend on gas temperature with coefficients of up to several %/K;

c) the absorption signal is integrated over the entire light path and hence is sensitive to spatial inhomogeneities in gas pressure and in gas temperature (e.g. caused by excessive flow) in particular in large volume or long gas cells, hence care should be taken that these inhomogeneities are smaller than 0,5 K and 0,2 kPa. This consideration is of relevance for cases where modification is performed to the device.

10.4 Humidity and carbon dioxide

Humidity and CO_2 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 respectively with or without CO_2 background .

11 Measurement procedure

Determine the performance characteristics in accordance with ISO 9169.

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

Perform quantitative analysis and determine the amount fraction and uncertainty budget of NH_3 in the sample gas in accordance with ISO 6143. The reproducibility of the method shall also be determined in order to contribute towards the uncertainty budget of the measurement, by following suitable guidelines, e.g. Reference [13].

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.

12 Expression of results

12.1 Quantities and units

To meet the requirements of relevant standards, for example, EN 16723-1, the content of NH_3 in biomethane shall be expressed in units of mass concentration (mg m^{-3}). However, NH_3 content in the calibration gas mixtures used is expressed in units of amount fraction (µmol mol^{-1}). The compositional data shall therefore, be converted from amount fraction to mass concentration according to ISO 14912. When the results are expressed in terms of mass concentration, respective reference pressure and temperature values shall be specified.

12.2 Uncertainty

The uncertainty of the measurement shall be evaluated and reported. The first step shall identify the individual sources of random and systematic errors in the method. These are then estimated and/or determined experimentally and combined in an uncertainty budget. Correlations between individual sources should be investigated and taken into account in accordance with the relevant mathematical model. Finally, the combined uncertainty is multiplied by an appropriate coverage factor to produce an