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REVIEW

Need for a protocol for performance evaluation of the gas analyzers used in biomethane conformity assessment

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Abstract

Biomethane may contain trace components that can have adverse effects on gas vehicles performances and on the pipelines when injected in the gas grid. Biomethane quality assurance against specifications is therefore crucial for the integrity of the end-users' appliances. Analytical methods used to assess biomethane conformity assessment must be validated properly and possibly, new methods specifically for biomethane should be developed. This paper provides an overview of the biomethane quality assurance infrastructure and the challenges faced with focus on sampling, analysis methods, reference gas mixtures, and performance evaluation. Currently, requirements for analytical method validation and fit-for-purpose assessments do not exist for biomethane. The industry is in urgent need of a protocol to evaluate the fit-for-purpose of methods in a harmonized manner. Reference gas mixtures to check the accuracy of the instrument and to determine the traceability of the measurement are also urgently required.

Keywords Biomethane · Analyzers · Performance assessment

Introduction

Biomethane can play an essential role in meeting the European Union (EU) 2030 GHG reduction target and achieving net-zero emissions by 2050 [1]. Biomethane, which is mainly composed of methane, is produced either by upgrading biogas or through the gasification of solid biomass followed by methanation. The number of biomethane plants in Europe is in rapid expansion; it has increased from 483 plants in 2018 to 729 units in 2020 [2]. In 2021, the number of biomethane plants increased to 992 i.e., 36 % compared to 2020 [3]. According to the Gas for Climate 2022 report, 32 TWh of biomethane is being produced annually [1]. The European Biogas Association predicted that by 2030, the sector could substantially enlarge its production to 370 TWh and reach 1170 TWh by 2050 [4]. Gas for Climate [1] estimated the sustainable supply potential of biomethane in the EU-27 and UK at 35 billion cubic meters (bcm) in 2030 and 95 bcm by 2050.

Due to the methods of production, biomethane may contain trace components that can have adverse effects on gas vehicle performances and on pipelines when injected in the gas grid. Assessing biomethane quality against specifications is therefore crucial for the integrity of the end-users' appliances.

Specifications for biomethane exist since 2016 as two standards: EN 16723-1 [5] for biomethane injected in the gas grid and EN 16723-2 [6] for direct utilization as a vehicle fuel. However, these standards developed by CEN TC408 will probably be revised in the near future. So far, the test methods proposed in these standards are mostly offline methods developed for other matrices such as natural gas and air. These methods need to be validated properly for biomethane and possibly, new developed methods specifically for biomethane.

Four parameters have maximal limit values in EN 16723-1: total volatile silicon, carbon monoxide (CO), ammonia (NH_3) and amine. Compressor oil and dust impurities have no maximal values; it is instead stated that the biomethane

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shall be free from impurities in amount fractions that renders the biomethane unacceptable for conveyance and use in end-user applications. For chlorinated and fluorinated compounds, the standard EN 16723-1:2016 refers to a technical report prepared by CEN/TC 408, CEN/TR 17238:2018 [7]. This report describes an approach for the assessment of limit values for contaminants that may be found in biomethane to mitigate the potential impact on human health. In addition to these impurities, in EN 16723-2:2017, oxygen (O_2), hydrogen (H_2), and sulfur compounds have requirements in terms of maximal limit values that are not present in EN 16723-1:2016 [5]. EN 16723-2 specifications also contain some physical parameters, such as methane number, hydrocarbon dew point temperature, and water dew point. Biomethane can also contain other impurities which are not yet regulated in EN 16723 standards. Among others, terpenes are often mentioned as potential unwanted contaminants. The concentration of terpenes in the biomethane can be high enough [8] to impact/mask the odorisation of the fuel by compounds such as tetrahydrothiophene (THT) despite terpenes' odor threshold being 1000 times lower than those of THT [9].

A majority of the analytical methods mentioned in EN 16723 standards are based on gas chromatography. However, relatively new techniques based on other analytical principles, such as laser-based spectroscopy, infrared absorption spectroscopy or mass spectrometry, are being developed in recent years to measure biomethane impurities [10]. Moreover, most standardized methods are not yet suitable for online analysis while some newly developed methods can be implemented onsite.

Before a method can be implemented for quality assurance and used to make decisions on biomethane quality conformity against the specifications given in a standard, it is critical to demonstrate that the method under consideration has performance capabilities consistent with what the application requires. In other terms, it is necessary to evaluate the method's performance capabilities [11]. To be effective, this process needs to be harmonized i.e., the steps required must be well described, as they would in a validation protocol.

Such protocols already exist for other energy gases. For example, ISO 21087 [12] specifies the validation protocol of analytical methods used for ensuring the quality of the gaseous hydrogen at hydrogen distribution bases and hydrogen refueling stations for road vehicles using proton exchange membrane (PEM) fuel cells. It also gives recommendations on calculating an uncertainty budget for the amount fraction. ISO 10723 [13] specifies a method of determining whether an analytical system for natural gas analysis is fit for purpose. It can be used either to determine a range of gas compositions to which the method can be applied, using a specified calibration gas, or to evaluate the range of errors and uncertainties on the composition and/or property when analyzing gases within a defined range of composition.

A cost-effective, efficient and standardized protocol to evaluate methods for measuring impurity contents in biomethane is currently lacking, hampering the implementation of such methods in laboratories and in the field.

Within the framework of the European Partnership on Metrology (EPM), BiometCAP [14], a new three-year project on biomethane has been granted and started in October 2022. In this project, a protocol will be developed and validated for the sampling, analysis, and performance evaluation of the gas analyzers used for biogas and biomethane conformity assessment. The protocol will be traceably validated and tested on selected industrial gas analyzers. Traceability is defined in the ISO/IEC guide 99 [15] as the property of a measurement result whereby the result can be related to a reference thought a documented unbroken chain of calibrations. The widespread use of this protocol would enable the industry to verify the performance of their measurement equipment and subsequently would enable new industrial products and services for biomethane quality monitoring to be developed and provided.

This paper provides an overview of the biomethane quality assurance infrastructure and the challenges faced with focus on four areas that will be addressed in the EPM BiometCAP project: sampling, analysis methods, reference gas mixtures, and performance evaluation.

Sampling

Standards EN 16723-1 and EN 16723-2 require analysis in a laboratory and therefore require collecting and transporting a gas sample from the point of use. The sample taken must be representative of the gas supplied; no compounds shall be added nor removed from the gas during sampling, transportation, and storage. Depending on the impurities to be analyzed, several types of vessels can be used: cylinders, canisters, adsorbent tubes, impinger bottles, and sampling bags [16]. The choice of vessels and material for the sampling lines depends on many parameters, including the pressure and temperature of the gas at the sampling point, safety aspects, requirements/recommendations in standards, transport regulations, and the suitability of the vessel. Several studies [17–19] have demonstrated that the biggest challenge when sampling biomethane is the risk of losing impurities through adsorption on the wall of the vessels used to collect the gas. These studies showed that concentration, pressure, and the presence of water affect the suitability of a vessel.

The suitability of a vessel can be established by performing stability studies where generally, two parameters are measured: the recovery yield and the storage stability. The recovery yield is defined as the ratio of the measured and the spiked content and expressed as a percentage at the time of the sampling. Storage stability is defined as the change in amount fraction for a given compound as determined at the end of the storage time compared to as determined at the start of the stability test [16]. The use of reference standard mixtures and validated methods is often a pre-requisite to ensure that the results of these tests are accurate. Vessel suitability assessment data can also be found in the calibration gases industry, but the timeline differs; for sampling, stability shall be assessed over some weeks up to a month, whereas for gas calibrants, stability often needs to be demonstrated for over a year. To assist the industry in the selection of appropriate vessels, the results of the stability tests should be readily compiled into a "material compatibility" table. The sampling of natural gas is described in the standard ISO 10715:2022 [20]. The standard has a material compatibility table which is originally from ISO 16664 [21], which contains a table for material compatibility. As natural gas doesn't contain the same impurities as biomethane, this table is only relevant for a few components such as O_2, carbon dioxide (CO_2), CO, alkanes, chlorine (Cl_2), hydrogen chloride (HCl), NH_3, hydrogen sulfide (H_2S), but contains no information for siloxanes, terpenes, halogenated hydrocarbons, and other sulfur compounds than H_2S.

The material compatibility doesn't only apply to the sampling vessel but also to all the components of the sampling line.

Project BiometCAP intends to review material compatibility using results from stability studies obtained in previous projects such as EMRP JRP ENG54 Biogas [22] and EMPIR 16ENG05 Metrology for biomethane [10] and establish a material compatibility table similar to the one for natural gas in ISO 10715. The definition of the term "suitable" would need to be defined quantitatively, and the conditions using during the tests need to be specified (among others, pressure, concentration, matrix, testing time. For example, the time period of testing is not standardized for stability studies so some studies are performed over months while others may be performed over weeks.

Analysis

Laboratory-based

The analytical methods mentioned in the EN 16723 standards have often been developed for other matrices than biomethane. For total volatile silicon (as Si), the method proposed—EN ISO16017:2000 [23], is based on thermal desorption and gas chromatography (with flame ionization detector, photoionization detector, mass spectrometric or other suitable detector) after active sampling on sorbent tubes. The method is intended to quantify individual compounds in air matrix.

For CO, the method proposed, EN ISO 6974 series [24], is based on gas chromatography and is intended for natural gas matrix. All the methods proposed for NH_3 are for sources emissions (air matrix). The method proposed for amines is intended for air and is based on liquid chromatography (HPLC).

Compressor oil and dust impurities have no maximal values; it is instead stated that the biomethane shall be free from impurities other than amount that renders the biomethane unacceptable for conveyance and use in end-user applications. However, some methods are proposed for these parameters. These standards, ISO 8573-2:2007 [25] and ISO 8573-4:2001 [26], are intended for compressed air and include both the sampling and the analytical procedures. The oil is either collected on coalescing filters followed by weight measurement or on microfiber membrane followed by infrared or gas chromatography (with flame ionization detector) analysis. Particles are measured using different methods such as laser particle counter, condensation nucleus counter, differential mobility scanning mobility particle sizer, or microscope, after sampling on membrane depending on their sizes.

For chlorinated and fluorinated compounds, the standard EN 16723-1:2016 [5] refers to a technical report prepared by CEN/TC 408, CEN/TR 17238:2018 [7] explaining an approach for the assessment of limit values for contaminants that may be found in biomethane to mitigate the potential impact on human health.

For O_2 and H_2, the test method proposed (ISO 6974 series [24]) is the same method proposed for CO in EN 16723-1:2016 [5] (based on gas chromatography and intended for natural gas matrix) with the addition of ISO 6975 [27] for O_2 (gas chromatography with thermal conductivity Detector).

The test methods proposed for sulfur compounds are intended for natural gas. They are based on Wickbold combustion method (ISO 4260 [28]) or Lingener combustion method (ISO 6326-5 [29]) for total sulfur and gas chromatography (ISO 19739 [30]) or potentiometry (ISO 6326-3 [31]) for individual sulfur compounds (such as H_2S or carbonyl sulfide (COS)) or specific groups of sulfur compounds (e.g., thiol sulfur). Standard ISO 6326-1 [32] gives a comparison of standardized methods and provides information for the choice of the method.

The water dew point is proposedly (ISO 6327 [33]) determined with a hygrometer by detecting water vapor condensation occurring on a cooled surface or by checking the stability of the condensation on this surface.

The methods proposed for the hydrocarbon dew point temperature require the knowledge of the composition (obtained by chromatography) in order to calculate this parameter using an appropriate equation of state (ISO 23874 [34]). The use of chilled mirror-type instruments is proposed in ISO/TR 12148:2009 [35].

For the methane number, the method proposed (Annex A of ISO 16726 [36]) is based on a calculation that requires the knowledge of the composition.

New methods have also been developed specifically for biomethane. For example, in a recent article [37], three methods are proposed for the analysis of NH_3 in biogas or biomethane matrices for amount fractions at an upper limit level of 10 mg m^{-3} as specified in EN 16723-1:2016. Three spectroscopic analytical methods, Fourier transform infrared spectroscopy, cavity ring-down spectroscopy, and optical feedback cavity-enhanced absorption spectroscopy, were investigated at three NMIs (NPL, VSL, and RISE, respectively). Based on the results obtained in this study, it was concluded that NMIs can provide the necessary infrastructure to support the measurement of NH_3 impurities as specified in EN 16723.

A number of test methods have been developed specifically for biomethane during the EMRP project ENG54 Metrology for biogas and the EMPIR project Metrology for biomethane.

- Determination of amine content with Gas Chromatography with Flame Ionization and/or Mass Spectrometry detectors (TD-GC-MS/FID).
- Determination of NH_3 with diode laser, tunable diode laser absorption spectroscopy, cavity enhanced absorption spectroscopy or ultraviolet visible spectroscopy.
- Determination of the oil content with gas chromatography with mass spectrometry using a specially developed sampler.
- Determination of the halogenated hydrocarbons content with TD-GC-MS/FID.
- Determination of HCl and hydrogen fluoride by ion chromatography.
- Determination of siloxane content by gas chromatography ion mobility spectrometry.
- Determination of the total silicon content with ICP/MWP (Inductively Coupled Plasma)/(Microwave plasma).
- Determination of siloxane content with TD-GC-MS/FID.

New work items proposals were subsequently developed for some of these methods. These are handled by ISO/TC 193/SC 1/WG 25 “Biomethane” and at different levels of standardization, the first to be published being ISO/TS 2610:2022 [38] for the determination of amine content. The status of the method standardization is summarized in Table 1. When no methods are being standardized, information on progresses or advancements made during different projects are mentioned.

Industrial analyzers

Commercial analyzers using various measurement principles are available for measuring some of the components in biogas and biomethane. Most of these analyzers focused on methane measurement and on the measurement of the main impurities such as CO_2, H_2S, H_2O, NH_3, and O_2 but analyzers for the measurement of impurities such as siloxanes are available. AP2E has developed a gas analyzer to monitor methane (CH_4), CO_2, H_2S and O_2 [39]. The measurement technique used by the AP2E analyzer is called Optical Feedback Cavity Enhanced Spectroscopy (OFCEAS). The technique relies on direct intensity measurement. The optical cavity serves to trap the light so that it passes through the sample gas multiple times as it is reflected by the cavity mirrors. The resulting effective path length is typically several kilometers. ABB has also developed an analyzer for trace H_2S, H_2O, CO_2, and O_2 analysis [40] in biomethane. The measurements are done on process gas chromatographs coupled with different detection principles such as thermal conductivity, flame ionization, flame photometric, and discharge ionization. Protea has developed a gas analyzer for the real-time monitoring of siloxanes using Fourier Transform Infrared Spectroscopy (FTIR) [41]. The FTIR technique also allows for the measurement of the main gas components such as CH_4, CO_2, and NH_3. Although absorption features of the siloxane groups are similar, small changes in response due to the underlying vibrational frequency difference of the molecules are used for the detection; G.A.S. developed a siloxane analyzer [42] based on gas chromatography-ion mobility spectrometry (GC-IMS) using nitrogen or air as a carrier gas; QUALVISTA [43] proposed different analyzers including the Qualvista Biogas Monitor which uses the Non-Dispersive Infrared (NDIR) method for siloxane measurement and the Qualvista Compact Biogas Monitor for H_2S, O_2, CO_2, CH_4 based on the electrochemical principle and NDIR measurement technology. Cambridge-Sensotec developed gas analyzers using either IR or electrochemical sensors to measure CH_4, CO_2, CO, H_2O, O_2, and H_2S [44]. To ensure that the measurement provided by these analyzers are reliable, their analytical performances must be evaluated in a traceable and standardized manner via controlled laboratory and field tests.

Reference gas mixtures

Calibration of the analytical instruments has two objectives: to check the instrument´s accuracy and to determine the traceability of the measurement. A reference gas mixture, a mixture of gaseous components, is used as a comparative reference in the calibration of gas analyzers or gas detectors and as a means of establishing a known response to a certified chemical component concentration.

Table 1 Summary of available standardized methods for biomethane measurement parameters

Parameter	Existing standardized methods relevant to non-biomethane applications	New standardized methods in development relevant to biomethane applications
Total silicon	EN ISO16017:2000	ISO/FDIS 2613-1 Analysis of natural gas—Silicon content of biomethane—Part 1: determination of total silicon by atomic emission spectroscopy (AES) ISO/DIS 2613-2 Analysis of natural gas—Biomethane—Part 2: determination of siloxane content by gas chromatography ion mobility spectrometry
Hydrogen fraction	ISO 6974 series	ISO 6974 standards are under revision by ISO/TC 193/SC 1/WG17 (ongoing discussions to include biogas and biomethane matrices)
Hydrocarbon dew point	ISO 23874, ISO/TR 12148:2009	None
Oxygen fraction	ISO 6974 series, ISO 6975	ISO 6974 standards are under revision by ISO/TC 193/SC 1/WG17 (ongoing discussions to include biogas and biomethane matrices)
Sulfur concentration	ISO 4260, ISO 6326-5, ISO 19739, ISO 6326-3, ISO 6326-1	Method based on GC-SCD was developed during EMRP project ENG01 Characterization of energy gases but the method is not being standardized
Compressor oil content	ISO 8573-2:2007, ISO 8573-4:2001	Determination of the oil content with Gas Chromatography with mass spectrometry using a specially developed sampler
Dust impurities	ISO 8573-4:2001	None
Amines content	VDI 2467 Blatt 2:1991–08	ISO/TS 2610:2022 Analysis of natural gas—biomethane—determination of amines content
Water dew point	ISO 6327	Calculation methods for the enhancement factor has been extended to gas compositions relevant to biogas within the EMPIR project ENG54 Metrology for Biogas
Chloride concentration	CEN/TR 17238:2018	Determination of the halogenated VOC content with TD-GC-MS/FID Determination of HCl and HF by ion chromatography
Fluoride concentration	CEN/TR 17238:2018	Determination of the halogenated VOC content with TD-GC-MS/FID Determination of HCl and HF by ion chromatography
Carbon monoxide fraction	EN ISO 6974 series	ISO 6974 standards are under revision by ISO/TC 193/SC 1/WG17 (ongoing discussions to include biogas and biomethane matrices)
Ammonia concentration	NEN 2826:1999 or VDI 3496 Blatt 1:1982–04 NF X43–303:2011	ISO/DIS 2612 Analysis of natural gas—biomethane—determination of NH_3 content by Tunable Diode Laser Absorption Spectroscopy
Terpenes	EN ISO16017:2000	ISO/DIS analysis of natural gas—biomethane—determination of terpenes' content by micro gas chromatography
Methane number	ISO 16726	None

"ENG54 Metrology for Biogas" and "16ENG05 Metrology for Biomethane" projects developed the foundation for the necessary infrastructure for establishing metrological traceability for the content of trace-level impurities in biogas and biomethane. This included reference standards for total silicon, terpenes, hydrogen chloride, NH_3, total sulfur, halogenated volatile organic compounds (VOCs), H_2, nitrogen, oxygen, and CO as single component/species mixtures. Uncertainties ranged from 1 to 20%, which are considered fit for purpose for most applications. Despite these advances, several limiting barriers remain for their widespread exploitation by industry.

Static reference standards are not currently available for HCl, HF, and amines however, dynamic gas standards were developed for HCl and HF during 16ENG05 Metrology for Biomethane [10]. Standards containing the full EN 16723 impurity range have yet to be developed and multiple standards must be used to evaluate analyzers performances. Finally, gas matrix effects and cross-interferences of biomethane impurities must be studied as different impurities are often present simultaneously in real biomethane. The newly started EPM project 21NRM04 BiometCAP will improve the accessibility of traceability by developing and validating missing standards.

A cost-effective static transfer standard containing multiple EN 16723 specified impurities with a target stability of 1 year and a $\leq 10\%$ expanded uncertainty for all impurities (improving on the previous 1 % to 20 %) will be developed. Novel dynamic transfer standards capable of producing multi-point calibrations of custom blends of at least nine impurities at EN 16723 threshold values will be prepared, including portable options.

These standards will facilitate improved access to traceability for instrument developers and laboratories performing verification, validation and quality control as required by e.g., ISO/IEC 17025.

Performance evaluation

As shown in the previous sections, a relatively large panel of analytical methods can be implemented for each parameter to be analyzed in the EN 16723 standards. However, for all these analytical methods, results must be demonstrably reliable. This can be achieved via a performance evaluation protocol that supports the validation of an analytical method and the assessment of its suitability for a particular purpose.

Validation parameters are used to establish documented evidence proving that a method meets the requirements for the intended analytical applications. According to IUPAC [45], performance characteristics are defined as quantifiable terms, which may indicate the extent of the quality of the processes.

The list of method performance characteristics, their definitions, and how to assess those vary slightly depending on the source. For instance, the vocabulary is defined in different documents such as in the "International vocabulary of metrology" VIM3 [46], "The compendium of analytical nomenclature (IUPAC) [45] —orange book" and "The Compendium of Chemical Terminology (IUPAC)—gold book" [47].

The Eurachem guide "The Fitness for Purpose of Analytical Methods" [11] details eight method performance characteristics: Selectivity, limit of detection and limit of quantification, working range, analytical sensitivity, trueness, precision, measurement uncertainty, and ruggedness. Strictly, measurement uncertainty is not a performance characteristic, but a property of the results obtained using a measurement procedure. Different guides such as the Eurachem guide describe how to evaluate these performance characteristics. However, this guide is general, and no specific protocol exists for validating instruments used in the biomethane industry to help determine if methods are suitable for the analysis of biomethane.

Such a protocol for performance evaluation exists for hydrogen. ISO 21087 [12] specifies the validation protocol of analytical methods used to ensure the gaseous hydrogen quality at hydrogen distribution bases and hydrogen refueling stations for road vehicles using proton exchange membrane (PEM) fuel cells. It also gives recommendations on calculating an uncertainty budget for the amount fraction. For each of the seven performance characteristics, the standard gives a definition, calculation method, and quantitative criteria to assess the fitness for purpose of H_2 analysis. For example, for the measurement uncertainty, the relative combined uncertainty for that concentration shall be below 10 % of the concentration except for the amount fraction equal to or below 10 nmol/mol, for which a combined standard measurement uncertainty not higher than 50 % of the amount fraction could be accepted.

Another protocol exists in the form of ISO 10723:2012 [13], which describes performance evaluation of analytical systems intended for the analysis of natural gas. The standard covers determination of errors and uncertainties in measured composition over given ranges. The scope of the document states that 'the analytical system is intended to be applied to gases having compositions which vary over ranges normally found in gas transmission and distribution systems', however, the components stated within the standard are specific to natural gas only and do not cover all the relevant components found within biomethane.

Conclusion

Biomethane production contributes to an efficient circular economy by recycling organic waste, to produce valuable renewable gas and biofertilizers. The number of biomethane plants is in rapid expansion in Europe. To avoid hamper this trend, ensuring the quality of biomethane is critical for the end-users and society. Previous metrology projects have paved the way for the development of the European quality infrastructure for the biomethane conformity assessment. A relatively large panel of analytical methods is now available for each parameter to be analyzed in the EN 16723 standards, and new methods and/or industrial analyzers are commercially available. Before any method can be used to make decisions on biomethane quality conformity against the specifications given in a standard, the user must demonstrate that the method under consideration has performance capabilities consistent with the application's requirement. Currently, requirements for analytical method validation and fit-for-purpose assessments do not exist for biomethane. The industry is now in urgent need of a protocol to evaluate the fit-for-purpose of methods in a harmonized manner. This also requires reference gas mixtures to check the accuracy of the instrument and to determine the traceability of the measurement, specifically static transfer standards containing multiple EN 16723 specified impurities for cost-effectivity and study of cross-interferences. Moreover, for offline methods, the reliability of the measurement is intrinsically linked to the representativity and reliability of the sampling. The choice of vessels for the sampling has been shown to be one of the most critical parameters due to the risks of loss of impurities by adsorption through the wall of the vessel. This choice and handling depend on many parameters, including the pressure and temperature of the gas at the sampling point, safety aspects, requirements/recommendations in standards, transport regulations, and material compatibility for vessels and sampling lines. The newly started EPM project 21NRM04 BiometCAP will tackle the challenges underlined in this paper.

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Declarations

Conflict of interest The authors declare no competing interests.

References

1. Gf Climate (2022) Biomethane production potentials in the EU, A gas for climate report, 07 2022. https://gasforclimate2050.eu/wp-content/uploads/2022/10/Guidehouse_GfC_report_design_final_v3.pdf. Accessed 01 Dec 2022
2. EBA (2022) European biogas map, European Biogas Association. https://www.europeanbiogas.eu/wp-content/uploads/2020/06/GIE_EBA_BIO_2020_A0_FULL_FINAL.pdf. Accessed 01 Dec 2022
3. Gf Climate (2022) New report provides unique overview on latest developments in biomethane and hydrogen markets. https://gasforclimate2050.eu/news-item/new-report-provides-unique-overview-on-latest-developments-in-biomethane-and-hydrogen-markets-showing-a-clear-acceleration-of-supply-and-demand/. Accessed 01 Dec 2022
4. European Gas Association (2022) News: The 'European Biomethane Map 2020' shows a 51% increase of biomethane plants in Europe in two years. https://www.europeanbiogas.eu/the-european-biomethane-map-2020-shows-a-51-increase-of-biomethane-plants-in-europe-in-two-years/. Accessed 01 Dec 2022
5. ISO 16723-1:2016 (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, European Committee for Standardization, Brussels, Belgium
6. 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, European Committee for Standardization, Brussels, Belgium
7. CEN/TR 17238 (2018) Proposed limit values for contaminants in biomethane based on health assessment criteria, European Committee for Standardization, Brussels, Belgium
8. Arrhenius K, Holmqvist A, Carlsson M, Engelbrektsson J, Jansson A, Rosell L, Yaghooby H, Fischer A (2017) Terpenes in biogas plants digesting food wastes—study to gain insight into the role of terpenes. Energiforsk AB, Report 2017:350
9. Polman EA, Top B, Gerritsen B, Rekers A (2015) Development of existing and new measurement technologies for determination of the gas composition, EDGaR, GT15-0029, 2015
10. 16ENG05 Metrology for biomethane, EURAMET, 2017–2020
11. Eurachem (1998) The fitness for purpose of analytical methods, Teddington
12. ISO 21087 (2019) Gas analysis—analytical methods for hydrogen fuel—proton exchange, International Standardization Organization, Geneva, Switzerland
13. ISO 10723 (2012) Natural gas—performance evaluation for analytical systems, International Standardization Organization, Geneva, Switzerland
14. Euramet (2022) Protocol for SI-traceable validation of methods for biomethane conformity assessment. https://www.euramet.org/research-innovation/search-research-projects/details/project/protocol-for-si-traceable-validation-of-methods-for-biomethane-conformity-assessment. Accessed 02 Dec 2022
15. ISO/IEC Guide 99 (2007) International vocabulary of metrology—basic and general concepts and associated terms (VIM), International Standardization Organization, Geneva, Switzerland
16. Arrhenius K, Brown AS, van der Veen AMH (2016) Suitability of different containers for the sampling and storage of biogas and biomethane for the determination of trace-level impurities. Anal Chim Acta 22–32:902
17. Arrhenius K, Yaghooby H, Rosell L, Büker O, Culleton L, Bartlett S, Murugan A, Brewer P, Li J, van der Veen AMH, de Krom I, Lestremau F, Beranek J (2017) Suitability of vessels and adsorbents for the short-term storage of biogas/biomethane for the determination of impurities—siloxanes, sulfur compounds, halogenated hydrocarbons, BTEX. Biomass Bioenergy 127:105
18. Arrhenius K, Francini L, Büker O (2022) Sampling methods for renewable gases and related gases: challenges and current limitations. Anal Bioanal Chem. https://doi.org/10.1007/s00216-022-03949-0
19. Lecharlier A, Carrier H, Le Hecho I (2022) Characterization of biogas and biomethane trace compounds: a critical review of advances in in situ sampling and preconcentration techniques. Anal Chimica Acta 340174:1229. https://doi.org/10.1016/j.aca.2022.340174. (**Epub 2022 jul 18 PMID: 36156213**)
20. ISO 10715 (2022) Natural gas–gas sampling, International Standardization Organization, Geneva, Switzerland

21. ISO 16664:2018 (2018) Gas analysis—handling of calibration gases and gas, International Standardization Organization, Geneva, Switzerland
22. EMPIR ENG54 Metrology for Biogas, EURAMET, 2014–2017
23. EN ISO 16017-1 (2000) Indoor, ambient and workplace air—sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography–Part 1: pumped sampling, International Organization for Standardization, Geneva, Switzerland
24. ISO 6974-series Natural gas—determination of composition and associated uncertainty by gas chromatography, International Organization of Standardization, Geneva, Switzerland
25. ISO 8573-2 (2001) Compressed air—Part 2: test methods for oil aerosol content, International Organization for Standardization, Geneva, Switzerland
26. ISO8573-4 (2001) Compressed air—Part 4: test methods for solid particle content, International Organization for Standardization, Geneva, Switzerland
27. EN ISO 6975 (2005) Natural gas–extended analysis—gas chromatographic method, International Organization for Standardization, Geneva, Switzerland
28. ISO 4260 (1987) Petroleum products and hydrocarbons–determination of sulfur content—Wickbold combustion method, International Organization for Standardization, Geneva, Switzerland
29. EN ISO 6326-5 (1989) Natural gas—determination of sulfur compounds—Part 5: Lingener combustion method, International Organization for Standardization, Geneva, Switzerland
30. EN ISO19739 (2004) Natural gas—determination of sulfur compounds using gas chromatography, International Organization for Standardization, Geneva, Switzerland
31. EN ISO 6326-3 (1998) Determination of sulfur compounds in natural gas—Part 3: determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry, International Organization for Standardization, Geneva, Switzerland
32. EN ISO 6326-1 (2007) Natural gas—determination of sulfur compounds—Part 1: general introduction, International Organization for Standardization, Geneva, Switzerland
33. ISO 6327 (2008) Gas analysis—Determination of the water dew point of natural gas—cooled surface condensation hygrometers, International Organization for Standardization, Geneva, Switzerland
34. ISO 23874 (2006) Natural gas—gas chromatographic requirements for hydrocarbon dewpoint calculation, International Organization for Standardization, Geneva, Switzerland
35. ISO/TR 12148 (2009) Natural gas—calibration of chilled mirror type instruments for hydrocarbon dewpoint (liquid formation), International Organization for Standardization, Geneva, Switzerland
36. EN 16726 (2016) Gas infrastructure—quality of gas—group H, European Committee on Standardization, Brussels, Belgium
37. Culleton L, Amico Di Meane E, Ward MK, Ferracci V, Persijn S, Holmqvist A, Arrhenius K, Murugan A, Brewer PJ (2022) Characterization of Fourier transform infrared, cavity ring-down spectroscopy, and optical feedback cavity-enhanced absorption spectroscopy instruments for the analysis of ammonia in biogas and biomethane. Anal Chem 15207–15214:94
38. ISO/TS 2610 (2022) Analysis of natural gas—biomethane—determination of amines content, International Standardization Organization, Geneva, Switzerland
39. Proceas the new generation of biogas analysers. https://www.ap2e.com/en/application-notes/biogas-analyzers/. Accessed 06 Dec 2022
40. Gas analyzers for LNG processing, biogas and biomethane upgrades. https://new.abb.com/products/measurement-products/measurement-analytics/industrial-gas/lng-and-biomethane. Accessed 05 Dec 2022
41. The complete gas analysis solution provider for industry and research (2022) The complete gas analysis solution provider for industry and research. https://protea.ltd.uk/siloxanes.html. Accessed 06 Dec 2022
42. GC-IMS-SILOX (2022) gas-dortmund.de. Accessed 06 Dec 2022
43. Accurate and robust siloxane monitoring for the biogas industry. https://qualvista.com/. Accessed 06 Dec 2022
44. Rapidox 5100 Portable Multigas Analyser (2022) https://www.cambridge-sensotec.co.uk/products/rapidox-5100-gas-analyser/. Accessed 06 Dec 2022
45. Inczedy J, Lengyel T, Ure A (1998) IUPAC Compendium on analytical nomenclature, definitive rules 1997. Blackwell Science
46. Barwick V, Prichard E (2011) Terminology in analytical measurement—introduction to VIM3. Eurachem
47. McNaught D, Wilkinson A (1997) IUPAC Compendium of chemical terminology, 2nd edn. Blackwell Scientific Publications, Oxford