A2.1.1 - Requirements for the performance assessment protocol that will be developed for the measurement systems that are used for biomethane conformity assessment

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Title

Requirements for the performance assessment protocol that will be developed for the measurement systems that are used for biomethane conformity assessment

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Abstract

Reliable and traceable purity measurements can only be obtained with equipment of known performance, from which the validation parameters have been traceably evaluated. Despite similar approaches existing for other green fuels, a suitable biomethane evaluation protocol does not yet exist.

In this report, we performed a review of the requirements for the performance assessment protocol, specifically, the technologies and associated existing standardised methods, the existing general and specific standardised protocols and the relevant validation parameters. This information will be used to draft a comprehensive protocol for the validation and performance evaluation of the analytical instruments and methods that are used in the conformity assessment of biomethane.

Key words

Biomethane conformity assessment, biomethane, protocol, performance assessment

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1 – Introduction

Biomethane is already used widely within Europe as a means to sustainably displace fossil fuels. Biomethane quality monitoring is essential to prevent damage to the existing natural gas infrastructure and to end user appliances. Damages can be caused by harmful impurities in biomethane which need to be kept below limit thresholds (as specified in EN 16723 for gas grids [EN 16723 1 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, 2016] and vehicles [EN 16723 2 Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network Part 2: Automotive fuel specifications, 2017]).

Reliable and traceable purity measurements can only be obtained with equipment of known performance, from which the validation parameters have been traceably evaluated. Despite similar approaches existing for other green fuels, e.g. hydrogen, a suitable biomethane evaluation protocol does not yet exist.

A performance assessment protocol detailing how to evaluate the instruments that are used to measure key impurities in biomethane will be develop as part of the BiometCAP project. The protocol will be applicable to the different techniques used for biomethane conformity assessment including laser-based and optical techniques, analysers equipped with GC systems, and mass spectrometry-related systems. The protocol will cover best practice in sample preparation and sampling to ensure the accuracy of the results. The protocol will take existing generic guidance on method validation into account.

In this report, we performed a review of the requirements for the performance assessment protocol, specifically, the technologies and associated existing standardised methods, the existing general and specific standardised protocols and the relevant validation parameters.

2 – Validation parameters and their definitions

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

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 [1], “The compendium of analytical nomenclature (IUPAC) [2] – orange book” and “The Compendium of Chemical Terminology (IUPAC) – gold book” [3]. In this document, we chose to use the terms and definitions from the VIM and the Gold book.

The EURACHEM guide “The fitness for Purpose of Analytical Methods” 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. Selectivity is sometimes replaced by specificity (mostly in the pharmaceutical industry), and ruggedness by robustness. Trueness and precision are two components of the accuracy. Working range is sometimes replaced by measuring interval, measurement range or range. These terms are not always fully interchangeable. In ISO/IEC 17025:2018 [4], linearity and repeatability or reproducibility are also included as performance characteristics. Other performance characteristics are sometimes mentioned [5] such as applicability, calibration and recovery but we have not detailed in the sections below.

2.1- Selectivity

Selectivity [1] is a property of a measuring system, used with a specified measurement procedure, whereby it provides measured quantity values for one or more measurands such that the values of each measurand are independent of other measurands or other quantities in the phenomenon, body or substance being investigated. It relates to "the extent to which the method can be used to determine particular analytes in mixtures or matrices without interferences from other components of similar behaviour" [6].

It is crucial to establish that the measured property is only due to the analyte and not to something chemically or physically similar or arising as a coincidence thus causing a bias in the measurement result [7].

The selectivity of a method is usually investigated by studying its ability to measure the analyte of interest in samples to which specific interferences have been deliberately introduced. Where it is unclear whether or not interferences are already present, the selectivity of the method can be investigated by studying its ability to measure the analyte compared to other independent methods.

2.2 - Limit of detection and limit of quantification

The limit of detection (LOD) [1] is the measured quantity value, obtained by a given measurement procedure, for which the probability of falsely claiming the absence of a component in a material is β, given a probability α of falsely claiming its presence. 0.05 is generally used for both α and β. The aim when determining the LOD is typically to establish the lowest concentration of the analyte present in a sample that can be detected with a specified level of confidence.

According to UIPAC [3], the limit of detection is derived from the smallest measure that can be detected with reasonable certainty for a given analytical procedure.

The **limit of quantification** (LOQ) is not defined in [1], [7] or [3]. But the definition of UIPAC can be adapted. The limit of quantification is derived from the smallest measure that can be quantified with reasonable certainty for a given analytical procedure.

2.3 – Working range

The **working range** is called measuring interval in [1] and is defined as a set of values of quantities of the same kind that can be measured by a given measuring instrument or measuring system with specified instrumental measurement uncertainty, under defined conditions.

In [7], the working range is the interval over which the method provides results with an acceptable uncertainty. The lower end of the working range is bounded by the limit of quantification LOQ. The upper end of the working range is defined by concentrations at which significant anomalies in the analytical sensitivity are observed.

In IUPAC [6], the range of measurement is defined as the range of concentration between the measurement threshold and the maximum usable indication. IUPAC distinguishes the linear range (concentration range over which the intensity of the signal obtained is directly proportional to the concentration of the species producing the signal) and the dynamic range (the ratio between the maximum usable indication and the minimum usable indication). In the dynamic range, the response may be non-linear, especially at higher concentrations.

2.4 – Sensitivity

Sensitivity [7] is the change in instrument response which corresponds to a change in the measured quantity (for example an analyte concentration), i.e., the gradient of the response curve.

In UIPAC [3], the sensitivity is defined as the slope of the calibration curve. If the curve is in fact a 'curve', rather than a straight line, then of course sensitivity will be a function of analyte concentration or amount. If sensitivity is to be a unique performance characteristic, it must depend only on the chemical measurement process, not upon scale factors.

According to EURACHEM, the sensitivity is not a particularly important performance characteristic but as two useful applications i.e., when the theoretical sensitivity is known and in spectrophotometric measuring systems.

2.5 – Trueness and precision

Trueness [1] is the closeness of agreement between the average of an infinite number of replicates measured quantity values and a reference quantity value. Since it is not possible to take an infinite number of measurements, trueness cannot be measured. A practical assessment of the trueness can however be made [7]. This assessment is normally expressed quantitatively in terms of 'bias'.

Precision [1] is the closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions. Measurement precision is related to random measurement error and is a measure of how close results are to one another.

2.6 – Accuracy

Measurement **repeatability** [7] (when a measurement is performed by a single analyst using the same equipment over a short timescale) and measurement **reproducibility** (variability in results between laboratories) represents the two extreme measures of precision which can be obtained. In between, there is the **intermediate (measurement) precision** (different analysts, extended timescale, different pieces of equipment etc.).

Accuracy [1] is the closeness of agreement between a measured quantity and a true quantity value of a measurand. Measurement accuracy describes how close a single measurement result is to the true quantity value and therefore includes the effect of both precision and trueness.

2.7 – Ruggedness, robustness

Ruggedness [7] (**robustness**) of an analytical procedure is a measure of its capacity to remain unaffected by small, but deliberate variations in method parameters. Ruggedness provides an indication of the method's reliability during normal usage.

2.8 – Measurement uncertainty

Measurement uncertainty [1] is a non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used. Measurement uncertainty provides a quantitative indication of the quality of a measurement result.

3- Relevant standardised protocols

3.1- ISO 17025

ISO 17025 [8] "General requirements for the competence of testing and calibration laboratories", contains the specific section 7.2 on method validation. The standard states in clause 7.2.1.5 that "The laboratory shall verify that it can properly perform methods before introducing them by ensuring that it can achieve the required performance...". Key requirements for validation of methods within ISO 17025 are:

- Validation can include sampling, handling and transportation of calibration items
- Validation can include evaluation of bias, precision, systematic effects, robustness, and measurement uncertainty, comparison against other validated methods and interlaboratory comparisons

- The effects of any changes to validated methods should be determined, and a new validation performed of original validation has been affected.
- The performance characteristics shall be relevant to the end user needs (including parameters such as range, accuracy, uncertainty, limit of detection, selectivity. Linearity, repeatability, robustness, cross-sensitivity and bias)

ISO 17025 also contains information on sampling plans and records. Key requirements are:

- The laboratory shall use a defined sampling method and sampling plan, which is to be available at the site where it is used.
- The sampling method should describe sample and site selection, the sampling plan and any sample preparation that is required.
- Records of sampling should include the method; date and time of sampling; unique identification data for the sample; identification of staff involved; equipment; environmental and transport conditions; sampling location (e.g. via a diagram); any deviations from the sampling method and sampling plan.

3.2 - ISO 21087

ISO 21087 [9] specifies analytical methods used for ensuring the quality of gaseous hydrogen at hydrogen distribution bases and hydrogen fueling stations for road vehicles using proton exchange membrane fuel cells. Section 6 specifies requirements for analytical method validation for hydrogen applications. The structure of ISO 21087 is provided in Figure 1.

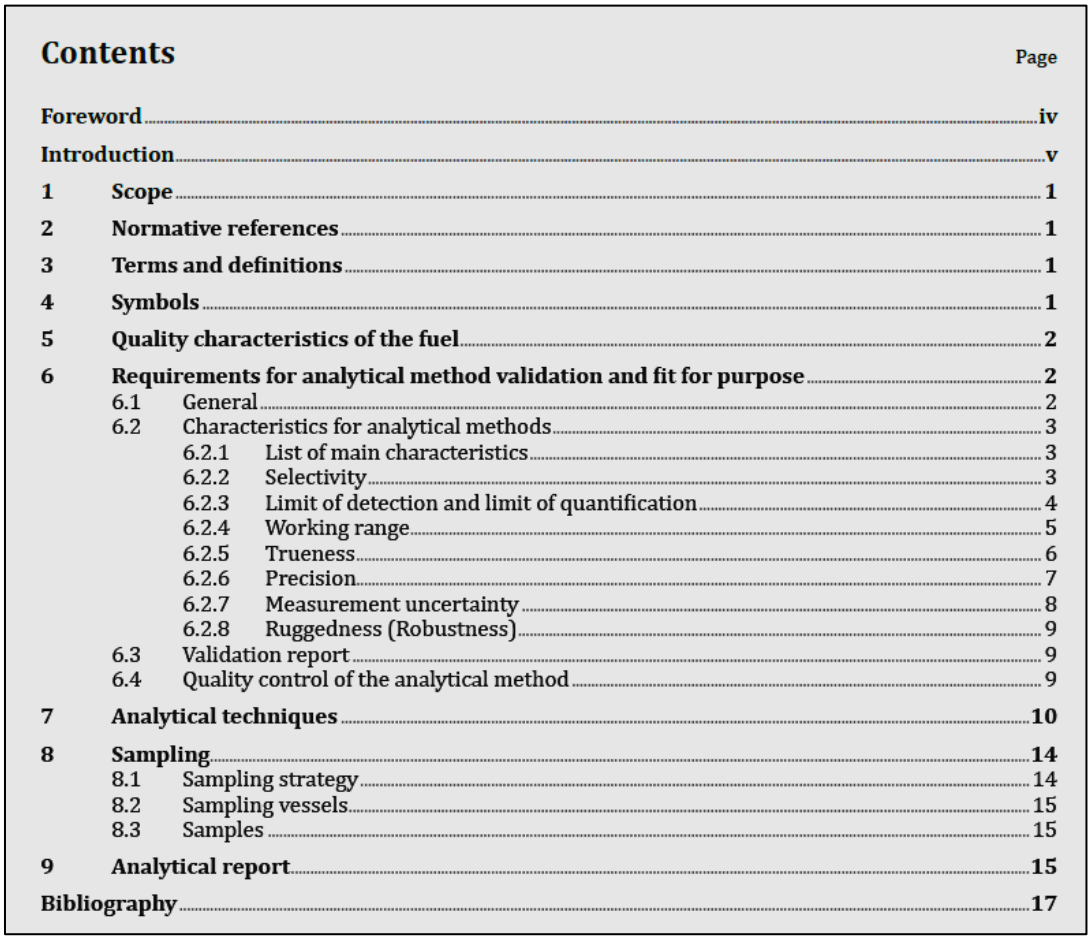

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Figure 1: Structure of ISO 21087:2019

The standard specifies the following method characteristics: selectivity, LOD, LOQ, working range, trueness, precision, measurement uncertainty and ruggedness. For each characteristic, two sub-clauses are provided; “Definition and calculation” and “Fit for purpose for H_2 analysis”.

The **validation report** section suggests the following sections to be included: “title”, “planning”, “performance characteristics” and “summary.

Within the **quality control** section it states that reference standards (referred to as “known samples”) are to be used as part of the quality control process, it states “In practice, these known samples should be measured with every batch of samples as part of the quality control process.”

Within the **analytical techniques** section, a table is provided, listing the analytical methods suitable for measurement of impurities in hydrogen. It specifies that “Each laboratory shall verify the performance of the method against the fitness for purpose acceptance criteria of this document before introducing them.” It provides a statement saying that the table provided “reflects the existing state of the art analytical techniques but others can be applied if fully validated according to the previous protocol.”

The **sampling** section contains references to collection strategies from ISO 19880-1 [10], in which a table is provided containing the following parameter headers:

- Method
- Sampling time
- Site-specific parameters for hydrogen refuelling stations (such as if fuelling override was used and the sink type)
- Sample-cylinder volume
- Reference sample pressure

The relevant equivalent standard to reference for biomethane applications is ISO 10715, which contains extensive guidance for natural gas and biomethane.

A.2 Components and ranges of composition

This document may be used to sample all the components that are listed in EN 16726[4] and EN 16723-1[5] and EN 16723-2[6].

Figure 2: Statement from ISO 10715:2022 annex A.2 regarding applicability for biomethane

3.3 - Other relevant guidelines

Other protocols exist globally, including:

- ASTM E2857-22 “Standard Guide for Validating Analytical Methods” [11] describes procedures for the validation of chemical and spectrochemical analytical methods of analysis that are used by a metals, ores, and related materials analysis laboratory.
- “Guidelines for the validation and verification of quantitative and qualitative test methods” [12] issued by the National Association of Testing Authorities, Australia.
- “Guidelines for Standard Method Performance Requirements”, AOAC Official Methods of Analysis (2019) [13]
- ISO 10723 [14] 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.

Summary: ISO 17025, ISO 21087, ISO 10723, and ISO 10715 contain relevant information that make them suitable to use as a reference to inform the development of the performance evaluation protocol for biomethane conformity assessment applications.

4 – Analytical methods

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 for biomethane impurities in recent years [15]. Moreover, most standardized methods are not yet suitable for on-line analysis while some newly developed methods can be implemented onsite. 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 main impurities such as CO_2, H_2S, H_2O, NH_3, and O_2 but even analyzers for the measurement of impurities such as siloxanes are available.

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 [16], 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 carbon monoxide, the method proposed, EN ISO 6974 series [17], is based on gas chromatography and is intended for natural gas matrix. All the methods proposed for ammonia 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 does not render 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 [18] and ISO 8573-4:2001 [19], 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 infra-red 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 [20] refers to a technical report prepared by CEN/TC 408, CEN/TR 17238:2018 [21] 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 oxygen and hydrogen, the test method proposed (ISO 6974 series [17]) is the same method proposed for carbon monoxide in EN 16723-1:2016 [20] (based on gas chromatography and intended for natural gas matrix) with the addition of ISO 6975 [22] for oxygen (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 [23]) or Lingener combustion method (ISO 6326-5 [24]) for total sulfur and gas chromatography (ISO 19739 [25]) or potentiometry (ISO 6326-3 [26]) for individual sulfur compounds (such as hydrogen sulfide, H_2S or carbonyl sulfide, COS) or specific groups of sulfur compounds (e.g., thiol sulfur). Standard ISO 6326-1 [27] gives a comparison of standardized methods and provides information for the choice of the method.
The water dew point is proposedly (ISO 6327 [28]) 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 [29]). The use of chilled mirror-type instruments is proposed in ISO/TR 12148:2009 [30].
For the methane number, the method proposed (Annex A of ISO 16726 [31]) 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 [32], three methods are proposed for the analysis of ammonia 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 [33], [34]:

- Determination of amine content with Gas Chromatography with Flame Ionization and/or Mass Spectrometry detectors (TD-GC-MS/FID)
- Determination of ammonia with diode laser, tuneable 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 VOC content with TD-GC-MS/FID
- Determination of HCl and HF 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 **[35]**. These are handled by ISO/TC 193/SC 1/WG 25 "Biomethane" and at different levels of standardization, among which the technical specification ISO/TS 2610:2022 **[36]** for the determination of amine content has been published in 2022. The status of the method standardization is summarized in table 1.

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 ISO/CD 2620 Analysis of natural gas — Biomethane — Determination of VOCs by thermal desorption gas chromatography with flame ionization and/or mass spectrometry detectors
Hydrogen fraction	ISO 6974 series	
Hydrocarbon dew point	ISO 23874, ISO/TR 12148:2009	
Oxygen fraction	ISO 6974 series, ISO 6975	
Sulphur concentration	ISO 4260, ISO 6326-5, ISO 19739, ISO 6326-3, ISO 6326-1	For organic sulfur compounds: ISO/CD 2620 Analysis of natural gas — Biomethane — Determination of VOCs by thermal desorption gas chromatography with flame ionization and/or mass spectrometry detectors
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		
Amines content		ISO/TS 2610:2022 Analysis of natural gas — Biomethane — Determination of amines content
Water dew point	ISO 6327	
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	
Ammonia concentration		ISO/DIS 2612 Analysis of natural gas — Biomethane — Determination of ammonia

		content by Tuneable Diode Laser Absorption Spectroscopy
Terpenes		ISO/DIS 2614 Analysis of natural gas — Biomethane — Determination of terpenes' content by micro gas chromatography ISO/CD 2620 Analysis of natural gas — Biomethane — Determination of VOCs by thermal desorption gas chromatography with flame ionization and/or mass spectrometry detectors
Methane number	ISO 16726	

Conclusion

Due to the lack of a specific validated protocol, currently, gas analysers for biogas and biomethane applications cannot be reliably evaluated for performance. The project BiometCAP intends to develop and validate such a protocol. The first step is a number of reviews which are performed as different activities in WP2. The report A2.1.1 reviews the requirements for the performance assessment protocol, specifically, the technologies and associated existing standardised methods, the existing general and specific standardised protocols and the relevant validation parameters. The information will later on be used to draft the protocol.

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