A3.1.1 – Review and selection of suitable measurement techniques for biomethane conformity assessment

|  |  |  |
| --- | --- | --- |
| Task3.1 | ActivityA3.1.1 | Reporting date30-03-2024 |
| TitleReview and selection of suitable measurement techniques for biomethane conformity assessment |
| AuthorsAlexander Fateev (DTU), Javis Nwaboh (PTB), Timo Rajamäki (VTT), Lucy Culleton (NPL), Ruben van der Wulp (TFS) and Miguel Ballesteros (GERG)  | Corresponding authorAlexander Fateev (DTU) |
| AbstractThe report reviews measurement techniques and analysers not previously metrologically validated suitable and currently used for biomethane conformity assessment. Several industrial analysers and reference instrumentation have been identified, reviewed, and collected. The Report outcomes are used in the follow up A3.1.2. |
| Key wordsSpectroscopy, gas chromatography, biomethane, analysers, gas sampling |
| NoticeThis work was funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or EURAMET. Neither the European Union nor the granting authority can be held responsible for them.The contents of this report have been obtained using best scientific practices and have been peer-reviewed prior to release. Nevertheless, the material is provided “as is”, without any kind of warranty regarding correctness, completeness, or fitness-for-purpose. |
| AcknowledgementThe project BiometCAP 21NRM04 has received funding from the European Partnership on Metrology, co-financed from the European Union’s Horizon Europe Research and Innovation Programme and by the Participating States. |
| DOI | License | Copyright |

Contents

[1 – Introduction 3](#_Toc162871341)

[2 – Selection of measurement techniques 5](#_Toc162871342)

[2.1 Spectroscopy-based 5](#_Toc162871343)

[2.2 GC-based 6](#_Toc162871344)

[2.3 MS-based 6](#_Toc162871345)

[2.4 Conclusions 7](#_Toc162871346)

[3 – Selection of industrial analysers 7](#_Toc162871347)

[3.1 Analysers for off-line measurements. 7](#_Toc162871348)

[3.2 Analysers for on-line (in field) measurements 7](#_Toc162871349)

[3.3 Conclusions 8](#_Toc162871350)

[Conclusions 9](#_Toc162871351)

[References 9](#_Toc162871352)

# 1 – Introduction

Standards EN16723-1 [1] and EN16723-2 [2] require analysis in a laboratory and therefore require the collection and transport of a gas sample from the point of use with a follow up analysis in the laboratory.

The Table C.1 from [1] gives an overview of the measurement parameters (components) over a lifespan of a biogas plant:



As one can see from the Table C.1 for a “mature” biogas plant there are only few gas components (O2 and H2S) which require continuous measurements (raw 3). The other traces (raw 4) require only a “periodic” sampling/analysis. However, in some cases the periodical sampling can be done more frequently, depending on the feedstock used and gas grid operator requirements for biomethane purity. Thus, for example, a stakeholder in Denmark (biogas plant) has been requested to perform a periodic (every 1-2 months) gas sampling and analysis of the produced biomethane for terpenes.

An example of common practices used in biogas industry in Europe is shown in Table C.2 [1]. The Table C.2 shows also risks associated with impurities for bigas plant and gas grid operators.



To our knowledge and based on the feedback from the stakeholders, the biogas plants and gas grid operators are *continuously* monitoring the following (“must have”) gas components: O2, CO2, H2O (as dew point), odorants (for distribution grids) and H2S. Those impurities are essential for 24/7 biogas plant continuous operation and non-compliance with EN16723 standard emission levels for those will normally lead to a shutoff of the plant from the gas grid and a forced flaring of the produced biomethane which will lead to a lost profit for the plant. Depending on a particular country, the following additional impurities are in focus: NH3 and siloxanes. Both components are of importance for distribution and transmission grids.

The overall upper impurities levels for biomethane with respect to the on-line biomethane conformity assessment are:

*NH3 ≤ 3 mg/Nm3; O2 ≤ 0.5 moll%; CO2 ≤ 2 mol%; H2S (+OCS) ≤ 5 mg/Nm3; siloxanes ≤ 1 mg/Nm3; mercaptans ≤ 6 mg/Nm3. Water content (as dew point) shall not exceed - 8oC at 70 bar (or 44 ppm at 1 bar).*

The Wobbe index (calorific value) and relative gas density are defined by the major gas components such as CH4 and CxHy in biomethane/natural gas blends and should typically be in between 50.76 to 55.8 MJ/Nm3 and in between 0.555 to 0.7, respectively. If the natural gas is dominated in the grid, the Wobbe index exceed typically 54 MJ/Nm3 value while with a significant biomethane content in the grid, the index falls below 54 MJ/Nm3. Therefore, with temporal variations in biomethane/natural gas ratios it is important to keep the Wobbe index and the gas density in the given legislation limits. The Wobbe Index is essentially calculated with use of CxHy, H2 and CO concentrations. Variations in N2 and CO2 concentrations can influence the biomethane mass balance. Therefore, the analysers used for biomethane conformity assessment need to be 1) insensitive to C1-C6, CO2 and CO variations and 2) provide similar Wobbe Index numbers as installed (calibrated) gas monitoring systems, if the analysers are capable for measurements of those components.

A gas sampling is performed either in gas cylinders or (more frequently) in gas bags. The sample taken must be representative of the gas supplied. This assumes that no compounds are added to or removed from the gas during sampling and transport to the analysis laboratory. However, it is known that adsorption effects in the sampling vessel (cylinder or bags) or sampling line can lead to a loss of the impurities to be analysed. This is considered in detail in the A2.1.2 Report “Review of the requirements for biomethane sample preparation and sampling including dynamical methods (flow through the analysers)”.

This Report is focused on a selection suitable measurement techniques, industrial analysers, and reference instrumentation to be evaluated using the performance assessment protocol developed in WP2.

# 2 – Selection of measurement techniques

There is a vast amount of measurement techniques and methods used for in-situ, on-line or in laboratory measurements of trace gaseous components (and nanoparticles) in various “hot” (e.g. stack gases) and “cold” (e.g. open air or sampled in bags/cylinders) gas matrices.

The modern commercial techniques can commonly be divided into three major groups based on their operational principles:

* Spectroscopy-based (various laser- and broad-band implementations)
* Gas chromatography (GC)-based (with many variations and numerous ad-hoc systems)
* Mass-spectroscopy (MS)-based (hot/cold gas sampling at atmospheric pressure)

There are also various chemically based methods when the sampled gas is flowing through a combination of various capturing devices (impingers) filled by liquids or captured in sorption tubes. Then the analysis of accumulated samples is done in the laboratory typically few days after the sample collection with use of a bench-top analytical equipment. This method is time consuming, however very small amounts of impurities can be measured because of their efficient capture and up-concentration in the liquid or solid phases. The sampling line (before the capturing device) can be washed out with a suitable agent (e.g. acetone) and the solution can further be analysed with use of the same equipment. Those methods are not in the scope of the report.

## 2.1 Spectroscopy-based

Spectroscopy-based techniques use an advantage of non-intrusive gas analysis. They normally are either laser- or a broad-band based light absorption techniques operating typically from UV to NIR and IR spectral ranges. The laser-based techniques use one or few lasers “tuned” into a specific molecule detection and exhibit an excellent detection limit if there are no spectral interferences with other concurrent gas components. The broad-band techniques allow simultaneous measurements of various weakly and strongly light absorbing gas components in a very broad spectral range. Use of various chemometrics methods allow one to make a quantification of the components. The spectroscopy methods rely on temperature, pressure measurements in the measurement volume (gas cell) and fundamental molecular properties such as absorption cross sections or line strength followed by a line-profile modelling. The later are in general pressure and temperature dependent. The absorption cross sections can be measured/tabulated for a specific analyser configuration while the line strengths are typically used from spectral databases such as e.g. HITRAN with a proper choice of the line model. In both cases primary reference materials (PRM), e.g. pre-mixed certificated gas mixtures, can be used for analysers calibration and model validation. There are currently running efforts to master *ab-initio* based quantum mechanical calculations in order to perform line strength calculations (for some molecules) from the first principles and therefore to make the narrow-band laser spectroscopy as a primary standard.

Common laser-based techniques are OFCEAS and various CRDS, QCL and TDLS variants, while common broad-band techniques are based on use UV, FTIR or NDIR spectroscopy tools. There are numerous small/large instrument producers for both techniques, e.g. AP2E, Process Insight (Tiger Optics), NEO or SICK (laser-based) and TFS, Agilent, MKS or Gasmet (UV/FTIR/NDIR-based).

Despite analysers already available on the market, there is a continuous development of new methods and techniques. In the ENG54 “Metrology for Biogas” (2014-2017) project [3], an on-line FTIR-based system for siloxanes together with HCN/HCl and NH3 measurements with use of CRDS and OFCEAS techniques, respectively, were developed.

PTB (project partner) has recently been developing an optical gas standard (OGS) for ammonia measurements within the BiometCAP project which will be applied for low-level NH3 measurements in biomethane. The OGS system will be employed in WP3 for performance evaluation using the performance assessment protocol from WP2.

In general, there is no “one-fits-all” solution, and a combination of several techniques is frequently required. Thus, for example, in the ENG05 “Metrology for Biomethane” (2017-2020) project [4], OFCEAS and UV/Vis techniques for NH3 measurements have been suggested.

It should be noted that, apart from the analyser itself, practical implementations also require a sampling interface (probe and gas sampling line) which physically connects the gas sampling (intake) point and the analyser. The sampling interface is a part of a full analyser configuration, and a special consideration should be done for the interface optimisation in regard to impurities retainment in the gas phase.

## 2.2 GC-based

Gas chromatography is the most popular measurement technique for low-level impurities measurements, not only related to biomethane applications. The basis of a typical GC-system is a column and an analyser. Majority of the advanced GC-based techniques are only used and suitable for laboratory use for operation, maintenance, and costs reasons. There are however so-called micro-GC systems (mGC) those are a still quite advanced, compact, transportable and can be used for both on-site and in laboratory measurements of various major and minor (trace) gas components. The majority of the GC-based systems market is occupied by Agilent.

In the ENG05 “Metrology for Biomethane” (2017-2020) [4], several target biomethane impurities have been considered and several GC-realizations have been developed and used:

* GS-IMS (electron mobility; siloxanes measurements),
* GC-BID (barrier ionization: VOC’s measurements)
* Ion chromatography (HCl/HF measurements)
* mGC-TCD (terpenes)
* TD-GC-MS (thermal desorption-GC-MS: amines measurements)
* GC-MS and GC-FID (compressor oil measurements)

That project was a follow up on to the previous ENG54 “Metrology for Biogas” (2014-2017) project [3] aimed to develop and validate methods for determining key impurities (total silicon and siloxanes, sulphur-containing compounds, aromatic hydrocarbons, halogenated hydrocarbons, ammonia, hydrogen cyanide, hydrogen chloride and carbon monoxide), moisture, particulates, calorific value, and density. Ion mobility spectroscopy was also used for HCl measurements.

All GC-based systems require an obligatory and periodical calibration with use of PRM’s, ideally in the same matrix as a typical biomethane is. For current project, two commercialized techniques are considered: mGC-TCD and a new GC-IMS one, because of their abilities to be used both in the laboratory and in the field.

## 2.3 MS-based

Mass-spectroscopy is a well-known and established stand-alone measurement technique typically used for low-pressure applications (e.g. in microelectronics, fundamental science etc.). Nowadays it is possible to use the MS for gas sampling from sources at atmospheric pressure which opens wide application possibilities. There are several producers such as e.g. TFS, Hidden or Pfeiffer offering such systems. Thus, for example, OmniStar mass spectrometer (Pfeiffer) can perform (hot) gas sampling and analysis at atmospheric pressure with low detection limits (below 1 ppm). MS Prima PRO (TFS) can perform fast on-line monitoring of Wobbe Index although is not capable of low-level impurities measurements (detection limit above 10 ppm). HIDEN’s MS QIC-line offers high pressure gas sampling (up to 2 bar or with special inlet configurations up to 30 bar) and real time measurements with up to 5 ppb detection levels for some components. While the MS Prima Pro (TFS) is quite heavy (240 kg), the MS OmniStar (Pfeiffer) and MS QGA 2.0 (HIDEN, up to 0.1 ppm detection limit) are in 30-35 kg weight range and can easily be used for laboratory and in field work.

## 2.4 Conclusions

There is a wide range of the measurement techniques and analysers for major and minor gas component measurements in biomethane. It is clear, that industrial analysers usage can be divided into two categories: 1) for use in a laboratory and 2) for use in a field (continuous or time-by-time measurements).

As for 1) a wide range of bench-top advanced systems are available. The systems are mostly GC-based and there are many variations with a wide choice of the detector, e.g. GC-MS, GC-BID or GC-IMS. The GC systems offers an excellent sensitivity and a wide range of detectable components. A mGC realization is an attractive choice because it can be used in both laboratory and in field measurements.

As for 2) there are commonly two measurement techniques, mostly used: industrial-grade GC’s (e.g. MEMS-based GC-TCD) used for Wobbe Index, gas calorific value and some impurities measurements and spectroscopy-based (OFCEAS and NIR/FTIR analysers) for measurements of selected impurities. As it was discussed in the Introduction, the subset of the measurable gas components defined by the EN16723 standard, on-site practical requirements and particular country legislations forms a subset of typical impurities (listed in the Introduction) important for 24/7 biomethane quality assessment.

For the following work in the WP 2 and 3, it is therefore suggested to use GC-, laser/FITR (i.e. spectroscopy-based) and MS-based measurement techniques for biomethane conformity assessment using industrial analysers and reference instrumentation. Those three techniques are suitable for impurities measurements mentioned above and can be deployed in a variety of laboratory and in the field applications.

# 3 – Selection of industrial analysers

The list of key impurities important for 24/7 biomethane conformity assessment includes following gas components:

*NH3 ≤ 3 mg/Nm3; O2 ≤ 0.5 moll%; CO2 ≤ 2 mol%; H2S (+OCS) ≤ 5 mg/Nm3; siloxanes ≤ 1 mg/Nm3; mercaptans ≤ 6 mg/Nm3. Water content (as dew point) shall not exceed - 8oC at 70 bar (or 44 ppm at 1 bar).*

Based on outcomes of the Section 2 and the feedback received from the stakeholders, following analysers have been selected.

## 3.1 Analysers for off-line measurements.

Selected reference instrumentation:

* OGS NH3: OFCEAS -based NH3 analyser (available from PTB, project partner)
* GC-IMS-SILOX: siloxanes analyser from Gas Dortmund (available from NPL, project partner)

The OGS at PTB within the BiometCAP project is a transportable analyser and can be used in filed measurements. SILOX is a new GC-IMS analyser produced by Gas Dortmund company for siloxanes measurements (detection range 0.03- 5 mg/Nm3). It operates at ambient pressure. Weight 15.5 kg. IP20, Operation temperature: 0-40oC

## 3.2 Analysers for on-line (in field) measurements

Selected industrial analysers:

* mGC Agilent 990: micro-GC from Agilent (available from DTU, project partner)
* MAX-iR: new FTIR analyser from TFS (available from TFS, project partner);
* ProCEAS: laser analyser for NH3 from AP2E (available from VTT, project partner)
* OmniStar: MS analyser (available from DTU, project partner)

mGC Agilent 990 (Agilent):

One of industrial GC-TCD analysers, widely used for 24/7 Wobbe Index and gas composition measurements (incl. N2, CO2, O2, THT, COS and H2S) on gas grids, is EnCal 3000 (Elster/Honeywell) which is built with use of MEMS (mTCD) and capillary column technology. Inlet pressures 3-5 bar. Weight: below 30 kg. IP66 rating. Operation temperature: from -20 to +55oC. Unfortunately, we have not been able to get this GC either for laboratory or field tests. Therefore, it was decided to use a micro-GC system available at DTU (tabletop which is identical to the mobile version for on-site measurements).

The mGC Agilent 990 has two columns: Molsieve 5Å and PoraPLOT Q. The fist column is used for permanent gases such as N2, O2, CH4, CO etc, while the second on is used for C1-C6 hydrocarbons, halocarbons, H2S, CO2, SO2 etc. Typical detection limit for PLOT columns is 2 ppm that should be sufficient for major impurities such as N2, CO2, O2 and H2S. Weight < 25 kg, Operation temperature: 0-50oC.

MAX-iR FTIR analyser (TFS):

MAX-iR is a new FTIR-based rack analyser line developed by the project partner – TFS. The analyser contains a 10 m pathlength gas cell together with a TE-cooled MCT detector which allows measurements major and trace gases. The analyser has been optimized for measurements in CH4 matrices. Typical impurities: NH3, CO, HF, CO2, siloxanes etc. should be possible to measure. The analyser has in-built spectral database for more than 200 organic/non-organic components. The analyser is capable for Wobbe Index calculations based on measured C1-C5, CO2 and CO concentrations. Weight 34 kg. Operation temperature: 20-30oC. The analyser will be investigated in the Wp2 and 3.

ProCEAS NH3 trace analyser (A2PE):

This is a NH3 analyser based on OFCEAS technique (measurement range: from 0 to 100 ppm). The gas is sampled through a heated line and analysed at low pressures (0.1 bar) in a multi-pass (few km) gas cell. Weight: 20 kg. Operation temperature: 15-35oC.

The NH3 measurements in presence of CH4 at high concentrations (90 mol% <) can however be inaccurate because strong spectral interferences between NH3 and CH4 lines. This will further be investigated in the Wp2 and 3.

OmniStar GSD 320 MS spectrometer (Pfeiffer):

A benchtop mass spectrometer, corrosive gas version with heated sampling line. Faraday Cup and c-SEM detectors (below 1 ppm detection); 1-100 or 1-200 amu mass range versions are available. Atmospheric pressure gas inlet. Weight: 35 kg. IP30 rating, Operation temperature:12-35oC.

The OmniStar GSD 320 is quite similar to QGA 2.0 MS (HIDEN) which has similar mass range (1-200/1-300 amu) and similar detectors (dual Faraday/CEM). Weight around 30 kg. The QFA 2.0 has detection range from 0.1 to 100% which should be quite similar to OmniStar’s one. The OmniStar was capable of Xe isotopes detection in 129-136 amu range (136Xe in air is 7.8 ppb). The performance of the OmniStar in CH4 matrices will be further investigated in the Wp2 and 3.

## 3.3 Conclusions

As one can see, the majority of analysers are intended for use in indoors measurements, although most of the selected analysers can tolerate temperatures from about +12oC and up. That temperature (apart from the ATEX-requirements) can be achieved in most rain-protected and ventilated areas at biogas production sites, even around all year time. The GC EnCal 3000 is the most robust analyser and can be operated in most outdoor environments. The spectroscopy analysers (ProCEAS and MAX-iR) are mostly stringent to ambient temperature requirements and therefore their performance must be evaluated with respect to possible ambient temperature variations. This should be accounted in the Protocol development in the WP2. High CH4 concentration in the biomethane can influence analyser performance. Therefore, all selected analysers and instrumentation should be investigated in respect of their response in CH4 matrices.

# Conclusions

Various measurement techniques for biomethane conformity assessment have been analysed. Three measurement techniques such as GC-, laser/FITR (i.e. spectroscopy-based) and MS-based have been selected. Upon on those and with support from the project stakeholders, four analysers and three reference instrumentations have been identified for further work. The selected analysers and reference instrumentation should cover the subset and respective concentration ranges of the impurities given.

# References

|  |  |
| --- | --- |
| [1]  | *EN16723-1:2016 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,* Bruxelles, Belgium: European Commite on Standardisation, 2016.  |
| [2]  | *EN16723-2:2017 Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network, part 2: Automotive fuels specification,* Bruxelles, Belgium: European Commite on Standardisation, 2017.  |
| [3]  | *Metrology for biogas, European metrology research programme ENG54,* EURAMET, www.euramet.org/research-innovation . [Accessed 05 07 2021]., 2014-2017.  |
| [4]  | *Metrology for biomethane - European Metrology Programme for Innovation and Research, EMPIR ENG05,* EURAMET, www.euramet.org/research-innovation/search-research-projects/details/project/metrology-for-biomethane/. [Accessed 20 10 2021], 2017-2020.  |