# Publishable Summary for 16ENG05 Biomethane
# Metrology for biomethane

## Overview

The overall objective of this project was to develop standardised test methods for the parameters (mostly impurities) to be monitored when injecting biomethane into the natural gas grid and when using it as a vehicle fuel. A further objective was to develop or improve the measurement standards for these parameters, in order to enable SI-traceable calibration and measurement results. This project closely liaised with the biogas producing and upgrading industry, regulators and biomethane testing laboratories to ensure that the developed test methods are robust and efficient and can readily be implemented. The objectives were largely met, and novel and improved measurement standards were developed. Nine test methods were developed, validated and offered to ISO/TC193/SC1/WG25 “Biomethane” for further processing as international standards.

## Need

As European natural gas resources are declining, the EU is depending increasingly on imported natural gas. Consequently, diversification of the European natural gas supply has become necessary and this continues to be implemented as required by the second Renewable Energy Directive, which states that by 2030 renewable energy should account for 32 % of the total energy consumption. For biomethane, this implied that it should have access to existing transmission and distribution systems, such as the natural gas grids and refuelling stations. A specification for biomethane (EN 16723) quality was issued, requiring the conformity assessment of the fuel quality for a number of additional parameters, mostly impurities.

To assess conformity with these specifications this project aimed to develop robust and accurate standardised test methods, for *e.g.* the content of total silicon and siloxanes, halogenated volatile organic compounds (VOCs), hydrogen chloride (HCl), hydrogen fluoride (HF), ammonia, compressor oil and amines in biomethane, as well as the supporting measurement standards. Furthermore, the industry also urgently required a similar infrastructure for terpenes, which can interfere with natural gas odorisation. Finally, for legal and taxation purposes, a standardised test method was needed for determining the fraction of biogenic methane in blends of biomethane and natural gas.

At the outset of the project, the test methods cited in EN 16723 were neither harmonised nor validated, lacked aspects of metrological traceability, and were usually not dedicated to biomethane. Thus, they hampered the energy transition from natural gas to biomethane. Regulators, grids and refuelling station owners, and testing laboratories urgently required harmonised and validated test methods to enable the transportation of biomethane using existing infrastructure as well as clear financial transactions without disputes. To implement the specification, fit-for-purpose measurement methods, supported by metrologically traceable measurement standards were required so that laboratories can produce reliable and traceable measurement results.

## Objectives

The overall objective of this project was to develop novel and robust standardised test methods for the parameters mentioned in the specification for biomethane (EN 16723), terpenes content and biogenic methane content, and to develop or improve the necessary measurement standards and high-accuracy reference methods.

The specific objectives of the project were:

1. To improve the long-term stability (2-3 years for static standards) of the measurement standards and the performance of related calibration methods that are used in the measurement of the contents of VOC impurities in biomethane (*i.e.* the target relative expanded uncertainties are 3 % for total silicon and siloxanes, 3 % for halogenated VOCs, < 4 % for terpenes, and 5 % for amines).

2. To improve the long term stability (2-3 years for static standards) and the performance (i.e., by eliminating biases in the instruments' readings caused by biomethane, for dynamic standards based on ISO 6145 methods) of the measurement standards and the related calibration methods that are used in the measurement of the contents of corrosive impurities and compressor oil in biomethane (i.e. the target relative expanded uncertainties are 3 % for ammonia, 3 % for HCl, 10 % for HF, 10 % for compressor oil).

3. To develop and validate novel test methods, based on existing calibration methods, for the regular conformity assessment of biomethane during which the content of total silicon and siloxanes, total fluorine and chlorine, ammonia, terpenes, compressor oil, amines, and biogenic methane (based on determining the $^{14}CH_4$ content in biomethane and blends of biogas and natural gas) are measured.

4. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (accredited laboratories, instrument manufacturers), standards developing organisations (CEN, ISO) and end users (energy sector, automotive industry).

**Progress beyond the state of the art**
Measurement standards and related harmonised high-accuracy reference methods for the contents of HF, amines, compressor oil and terpenes did not exist for biomethane at the outset of the project. In addition, some of the measurement standards for the contents of impurities in biomethane developed in ENG54 "Metrology for biogas" needed improvement to be fit for purpose: total silicon and siloxanes, halogenated VOCs, ammonia, and HCl.

At the outset of the project, the preparation of dynamic gas mixtures resulted in a large uncertainty in the development of the measurement standards for ammonia and HCl. The improvements in dynamic gas mixture preparation improved the state-of-the-art in two ways: a lower expanded uncertainty for the dilution of gas mixtures (target down to 1 % - 3 %) and an extension to matrices relevant for the trade in renewable gas (e.g. biomethane).

This project delivered dedicated standardised test methods for the parameters in EN 16723, as well as for terpenes and biogenic methane content, and disseminated these in the form of NWIPs (New Work Item Proposals) to ISO/TC193/SC1/WG25 "Biomethane". These methods provide valuable input to relevant normalisation organisations that are considering replacing the currently cited methods in EN 16723, which are not dedicated to biomethane, lack metrological traceability, and have not been demonstrated to be fit-for-purpose. The NWIPs will be supported by the results of the validation and performance evaluation, enabling the standardisation committee to assess the suitability of the methods. The method development used the high-accuracy analytical methods developed in ENG54 "Metrology for biogas" and in this project as their basis and the specificity of the methods was improved, so that the standardised test methods will generate SI-traceable results with known uncertainty.

**Results**
1. *To improve the long-term stability (2-3 years for static standards) of the measurement standards and the performance of related calibration methods that are used in the measurement of the contents of VOC impurities in biomethane (i.e. the target relative expanded uncertainties are 3 % for total silicon and siloxanes, 3 % for halogenated VOCs, < 4 % for terpenes, and 5 % for amines).*

This project delivered measurement standards and related high-accuracy reference methods for the contents of siloxanes, halogenated VOCs, terpenes and amines in biomethane.

The lifetime of the measurement standards of halogenated VOCs has increased from 6 months to 2 years, with an expanded uncertainty of 6 % - 18 %, depending on the component. The supporting analytical methods have an uncertainty between 3 % and 10 % at 50 nmol $mol^{-1}$.

For terpenes, methods have been setup with an uncertainty of 4 % - 8 %, including one suitable for field use.

The stability over an 18 month period of the measurement standards for siloxanes has been demonstrated within a 3 % - 10 % expanded uncertainty at the levels of the biomethane specification. The analytical method has also been improved with a relative expanded uncertainty between 2 % and 14 %.

Standards for amines have been realised by spiking sorption tubes. An analytical method has also been developed using gas chromatography, but its optimisation turned out to be complicated. The measurement uncertainty is dominated by the reproducibility of the results and varies between 10 % and 60 %, depending on the component.

Overall, this objective was met. The targeted expanded uncertainty was not always achieved, but the project outcomes are nevertheless fit-for-purpose and an important step forward.

2. *To improve the long term stability (2-3 years for static standards) and the performance (i.e., by eliminating biases in the instruments' readings caused by biomethane, for dynamic standards based on ISO 6145 methods) of the measurement standards and the related calibration methods that are used in the measurement of the contents of corrosive impurities and compressor oil in biomethane (i.e. the target relative expanded uncertainties are 3 % for ammonia, 3 % for HCl, 10 % for HF, 10 % for compressor oil).*

The project delivered measurement standards and calibration methods for the content of ammonia, HCl, HF and compressor oil in biomethane. The successful work on hydrogen fluoride is the first of its kind worldwide.

For ammonia at the level of the biomethane specification, static standards have been developed with an expanded uncertainty of 1.7 % with 18 months stability demonstrated.

A dynamic measurement standard for ammonia, hydrogen chloride and hydrogen fluoride based on permeation was built and validated. The expanded uncertainty for ammonia is 1.6 %, for hydrogen chloride 1.4 % and for hydrogen fluoride 6 %. Also, analytical spectroscopic methods were developed with an uncertainty of 3 %, 5 % and 7 % respectively. A dilution system was built to generate calibration gas mixtures with different compositions of the matrix. The expanded uncertainty of the matrix gas composition was between 1 % - 2 %.

The peak broadening coefficient for hydrogen chloride in methane has been determined with an expanded uncertainty of 1.4 %. This coefficient was used in the development of a spectrometer for hydrogen chloride in methane. It operates with an expanded uncertainty of 5 %.

A dynamic measurement standard for ammonia, hydrogen chloride and hydrogen fluoride based on evaporation of a solution was built and validated. The expanded uncertainty for ammonia is 2.3 %, for hydrogen chloride 3 % - 5 % and for hydrogen fluoride 5 % - 7 %.

For compressor oil content, measurement standards have been developed by diluting compressor oil with a solvent. Different analytical techniques were developed based on infrared spectroscopy and gas chromatography; the expanded uncertainty ranged from 10 % to 30 %, including effects from sampling. The expanded uncertainty of the analytical methods was 10 %, which is in agreement with the objective.

Overall, this objective was met. The performance of the developed and improved measurement standards meets the targets set at the beginning of the project. For the first time, an SI-traceable measurement standard for hydrogen fluoride content was realised.

3. *To develop and validate novel test methods, based on existing calibration methods, for the regular conformity assessment of biomethane during which the content of total silicon and siloxanes, total fluorine and chlorine, ammonia, terpenes, compressor oil, amines, and biogenic methane (based on determining the $^{14}CH_4$ content in biomethane and blends of biogas and natural gas) are measured.*

Altogether nine methods have been proposed for the regular conformity assessment of biomethane and evidence of their validation is provided below.

An instrumental method for measuring the total concentration of silicon in biomethane was developed. A liquid impinger was used to trap the silicon-containing species. Metrological traceability was achieved by calibration with an aqueous silicon solution.

For siloxanes, a method based on gas chromatography with ion mobility spectrometry has been developed and validated. The instrument was calibrated using static gas standards containing the relevant siloxanes.

For hydrogen fluoride and hydrogen chloride, a method based on ion-exchange chromatography has been developed and validated.

A method for measuring the amount fractions of volatile organic hydrocarbons has been developed using gas chromatography with a barrier ionisation detector. Also methods with other detectors have been developed and evaluated. Calibration was performed with either static gas standards or adsorption tubes.

For ammonia, spectroscopic methods using Optical Feedback Cavity-Enhanced Absorption Spectroscopy and UV/vis spectroscopy have been proposed. A multipoint calibration was required using dynamic or static gas standards to obtain results with metrological traceability.

For terpenes, a method using a micro-gas chromatograph has been developed. This method can be used in the field. Static gas standards can be used for the calibration of the instrument.

For compressor oil concentration, a sampling and analysis method has been developed using gas chromatography. The instrument can be calibrated by standards prepared as dilutions of compressor oil.

For amines concentration, a gas chromatography method involving thermal desorption has been developed. Calibration was performed by using spiked adsorption tubes.

For biogenic methane content, a radiocarbon method has been validated. The method involved converting the biomethane (or mixtures of biomethane with natural gas) (or mixtures of biomethane with natural gas) into carbon dioxide, which can then be analysed for its radiocarbon content. The method was well-aligned with similar methods for other materials.

Overall, this objective was met. In total, nine methods have been proposed and validated which are capable of providing metrologically traceable measurement results for the conformity assessment of biomethane.

4. *To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (accredited laboratories, instrument manufacturers), standards developing organisations (CEN, ISO) and end users (energy sector, automotive industry).*

This project delivered dedicated test methods for the parameters described in EN 16723, and for the terpene and biogenic methane content. These methods have been disseminated, in the form of nine NWIPs, to the working group of ISO/TC193/SC1/WG25 "Biomethane". The project provided input to the activities of other committees, such as the CCQM Gas Analysis Working Group (GAWG), CEN/TC408, Euramet/Metchem SC-GAS, BSI PTI 15, DIN NA 062-25-73 AA and various other national working groups and mirror committees. The consortium developed services for end users. These services include: a) calibration gas mixtures/ standards; b) measurement services; c) direct characterisation in the field for biogas and biomethane assessment; d) measurement and calibration facilities; e) proficiency testing; f) consultation and g) training. The consortium was represented in various standardisation committees, and input was given to a large number of meetings. A stakeholder committee was formed with 35 stakeholders, and a strong interaction with stakeholders was built. The project website was established, and the project logo was designed and extensively used as a hallmark. A large number of presentations have been made at conferences. Two international workshops were organised (22-23 January 2019; 8-9 September 2020) on "conformity assessment for biomethane" which were open to the public. The goals of the workshops were achieved, and the outputs were directly fed into standardisation bodies. Furthermore, 7 scientific peer-reviewed publications have been drafted, of which two submitted and one published. 2 industrial trade papers have been published. In addition to contributing to the development of documentary standards, a good practice guide has been issued as an extra project deliverable to fast track route to promote the uptake of the project outcomes. The good practice guide is available on the project website: http://empir.npl.co.uk/biomethane/.

Overall, this objective was met. There has been a good collaboration with stakeholders and the membership of ISO/TC193/SC1/WG25. The first step towards transforming the methods into ISO standards is underway at the time of writing.

**Impact**

This project generated impact for all of the parties involved in the renewable gas supply chain, e.g., biogas and biomethane producers, biogas upgraders, natural gas grid operators and refuelling station owners, as well as laboratories, equipment manufacturers and regulators. Impact has been achieved through various forms of dissemination (see the results of objective 4 above for details). This will result in the uptake of the improved sampling and testing methods for the key parameters mentioned in the specification for biomethane and upgraded biogas EN 16723.

*Impact on industrial and other user communities*

This project has fostered the implementation of the specifications for biomethane for injection into the natural gas grid (EN 16723-1) and for use as transport fuel (EN 16723-2). The proposed candidate-standard test methods for the conformity assessment of biomethane have been disseminated to end users, enabling laboratories to implement these in their organisations and to obtain a laboratory accreditation by meeting the requirements of ISO/IEC 17025. By implication, laboratories are able to provide metrologically traceable measurement results, with a known uncertainty, for the trade in biomethane - thus facilitating the conformity assessment of biomethane. Implementing the developed infrastructure contributes to mitigating the risks of false acceptance and false rejection of biomethane, thus building trust and confidence in this source of renewable energy.

The project's outputs enable NMIs, DIs, and industrial parties to deliver calibrations, certified reference materials and proficiency testing, thereby ensuring that equipment can be calibrated with SI-traceability. Based on the same outputs, these organisations can implement appropriate quality control measures, disseminate metrological traceability to their customers, and perform method validation and performance evaluations with the required rigour.

By facilitating the implementation of EN 16723, the project's outputs enable the owners of gas grids and refuelling stations to better guarantee the quality of the gas they sell to industrial customers and other end-users. The developed methods for terpenes enable these organisations to control and mitigate the health and safety risks associated with the masking of the odour of natural gas and biomethane in gas grids. Likewise, the standards and methods enable the effects of compressor-oil carryover at refuelling stations to be mitigated, thus building further confidence in biomethane as transport fuel. To carry out these activities at a European level will smooth the implementation and raise awareness of the relevant standards, thus making the use of biomethane in European gas networks more efficient.

*Impact on the metrology and scientific communities*

This project created impact on the metrology and scientific communities by completing the suite of measurement standards for impurities (siloxanes, hydrogenated VOCs, ammonia, hydrogen chloride, hydrogen fluoride, amines, compressor oil) in biomethane and components affecting odorants (terpenes). The work on hydrogen fluoride was pivotal, not only for biomethane (especially from gasification processes), but it also contributed to the development of an infrastructure for this component in emission monitoring. So far, metrological traceability of measurement results in this area has been lacking.

The work on a variety of spectroscopic analysis techniques for hydrogen chloride and hydrogen fluoride laid a solid foundation to foster further development of gas analysers for these components that are field-deployable and can be used for continuous monitoring. The deployable dynamic gas standard can already be used for validating methods currently in use, both onsite as well as in laboratories.

The project outputs enable these communities to deliver the appropriate services to laboratories, biogas producers, and instrument manufacturers to support their business by providing fit-for-purpose support to their activities in this area. The outputs enable the verification and validation of instruments and methods, including those currently in use because they are in EN 16723.

*Impact on relevant standards*

The project delivered nine NWIPs which are necessary for extending the portfolio of international standards supporting natural gas, biogas and biomethane characterisation and quality assessment. The nine NWIPs extend the current methods for natural gas properties by providing methods for assessing supplementary parameters relevant for biomethane. These NWIPs have been submitted to the ISO/TC193/SC1/WG25 Biomethane Working Group. WG25 discussed the proposals in October 2020 in preparation for creating projects within ISO. Once these are completed, it will lead to new international standards.

CEN/TC408, responsible for the biomethane specification EN 16723 can update, under its mandate M/475, the currently referenced methods with new methods that are dedicated to biomethane. The project's outputs enable ISO/TC 158 to further develop its documentary standards, for example the ISO 6145 series for use with energy gases. Currently these standards are mainly focussed on applications where the gas matrix does not fluctuate in composition, such as in air quality.

The outputs from the project provide valuable information to other committees, such as JCGM WG1 (GUM) in the form of examples of how the uncertainty of the gas composition can be evaluated. The GAWG of the CCQM and EURAMET/Metchem SC-GAS have seen that methods currently only contemplated in environmental gas analysis can also be successfully employed in the energy area. National mirror committees on biomethane, such as NEN 310 408, BSI PTI 15, and DIN NA 062-25-73 AA can take up the developed methods to disseminate these to their membership.

*Longer-term economic, social and environmental impacts*

The improvement in the metrological traceability, comparability and thus reliability of the measurement results enables biogas/biomethane production and upgrading plants to run more efficiently, especially with regard to the costly gas cleaning and upgrading facilities. With the more accurate measurement methods, they can better mitigate the risk of producing off-specification biomethane, ensuring that the specifications in EN 16723 are reliably met. At the same time, these methods prevent raw biogas from being upgraded much further than necessary. This reduces the production costs of biomethane and upgraded biogas making it more competitive with fossil natural gas. Metrologically traceable, reliable and accurate measurements allow us to reduce the deterioration of end-user appliances, industrial gas-fired plants and facilities, and gas distribution networks, thus avoiding additional operational costs and protecting the market and the consumer.

Implementation of the novel methods contributes substantially to the safer transmission and distribution of biomethane in gas networks, thus expanding the number of potential consumers. They will help to maintain the quality of the gas, the integrity of the transmission, distribution and measurement infrastructure, and keep the safety risks associated with the use of biomethane and upgraded biogas in industrial and domestic appliances, as well as in gas-fuelled vehicles, within the limits accepted for natural gas.

The accurate measurement of trace-level toxic impurities will secure a proper health and safety threshold set by regulations. The methodologies developed in this project can readily be extended to other impurities, which may be relevant when other feedstocks are contemplated for the production of biomethane and upgraded biogas. The cycle needed to develop dedicated methods is appreciably shortened by taking advantage of the lessons learnt in this project.

Overall, the implementation and use of the project’s outcome fosters the increased use of biomethane and upgraded biogas, not only as an energy resource, but also as a feedstock for industries which currently rely on natural gas. It helps to reduce Europe's dependence on natural gas imports, to decarbonise the gas grids, to meet the goals of the 2016 Paris Agreement on climate change, and eventually to help the EU’s Renewable Energy target to be met.

**List of publications**


1. K. Arrhenius, A. Fischer, O. Büker, H. Adrien, A.E. Masri, F. Lestremau, T. Robinson, Analytical methods for the determination of oil carryover from CNG/biomethane refueling stations recovered in a solvent, *RSC Advances, Royal Society of Chemistry (RSC),* **2020***, 10*, 11907-11917, https://doi.org/10.1039/D0RA01399D

2. J. Nwaboh, O. Werhahn, V. Ebert. Laser detection of HCl in biomethane for combustion engines, 2020. Physikalisch-Technische Bundesanstalt (PTB). DOI: https://doi.org/10.7795/810.20200319

3. L. Cuccia, B. Sanz, D.B Castro, J. Li, A.M.H. van der Veen, E.A. di Meane, S. Moreno, L.P. Culleton, D. Vorin, C. Senné, F. Bougueroua, L. Pyrée, Y. Courtois, C. Tastard, Development of standardized methods for the analysis of amines, terpenes and ammonia in biomethane, 19th International Congress of Metrology (CIM2019), EDP Sciences, 2019, https://doi.org/10.1051/metrology/201906001

4. J. Li, S. Persijn, I. de Krom, H. Meuzelaar, A.M.H. van der Veen, Metrology for biomethane conformity assessment: measure trace gas impurities in biomethane, 19th International Congress of Metrology (CIM2019), EDP Sciences, 2019 https://doi.org/10.1051/metrology/201906002

5. A.M.H. van der Veen (ed), Test methods for the conformity assessment of biomethane, http://empir.npl.co.uk/biomethane/wp-content/uploads/sites/28/2020/11/EMPIR-16ENG05-D11_Methods_for_biomethane_characterisation.pdf

6. J. Nwaboh Anyangwe, H. Meuzelaar, J. Liu, S. Persijn, J. Li, A.M.H. van der Veen A.M.H., N. Chatellier, A. Papin, Z. Qu, O. Werhahn, V. Ebert, “Accurate analysis of HCl in biomethane using laser absorption spectroscopy and ion-exchange chromatography”, Analyst, DOI https://doi.org/10.1039/d0an01955k


This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

| Project start date and duration: | | 01 June 2017, 40 months |
|---|---|---|
| Coordinator: Dr. Jianrong Li, VSL<br>Project website address: http://empir.npl.co.uk/biomethane/ | Tel: +31 15 2691573 | E-mail: jli@vsl.nl |
| Internal Funded Partners:<br>1. VSL, Netherlands<br>2. IMBiH, Bosnia and Herzegovina<br>3. NPL, United Kingdom<br>4. PTB, Germany<br>5. RISE, Sweden<br>6. VTT, Finland | External Funded Partners:<br>7. ENGIE, France (withdrawn from 31 December 2017)<br>8. INERIS, France<br>9. ISSI, Italy<br>10. NEN, Netherlands<br>11. RUG, Netherlands<br>12. WAL, United Kingdom<br>13. GRTgaz, France (joined from 1 January 2018) | Unfunded Partners: |
| RMG: - | | |