**18SIP03 Si-S/Biogas**

# FINAL PUBLISHABLE REPORT

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| Primary Supporter: Serge Biollaz, Paul Scherrer Institut (PSI) | | |
| Internal Funded Partners:<br>1. VSL, Netherlands<br>2. NPL, United Kingdom | External Funded Partners: | Unfunded Partners:<br>3. PSI, Switzerland |

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# 1 Overview

This project evaluated the industrial biomethane measurement capability for total silicon and total sulphur impurities with traceable primary gas standards (objective 1) and provided training and knowledge transfer on best practice sampling and analysis of biomethane within industry (objective 2). It also promoted the wider uptake of standardisation of biomethane purity requirements (objective 3). Furthermore, the project addressed industry's need for standardised, reliable impurity measurements, thus it improved the overall quality of the framework within the biomethane distribution network. The end-users now understand their measurement capabilities better and can perform better measurements with smaller uncertainties knowing how to avoid potential hidden bias.

# 2 Need

*(*Impurities in biogas can cause extensive damage to the gas infrastructure if the impurity thresholds are not set lower than certain critical thresholds. Therefore, accurate measurement of impurity content is vital and will also help to better support the growing European biogas industry. In response to EC mandate M/475, two EN standards have been published which specify the maximum recommended impurity threshold levels within biomethane (EN 16723-1 and EN 16723-2).

There was a need to increase industry's awareness of these EN standards, in order to prepare for future legislation and facilitate the uptake of standardisation within currently employed ad-hoc gas network-entry agreements (within which local gas distributors and independent gas transporters sign unique contracts with biomethane producers to specify the level of purity testing required). These purity measurements have been performed throughout Europe. However, there was a lack of traceability, so robust validation through a coordinated comparison of measurement capability was required.

Additionally, there was a need to educate the industrial biomethane purity laboratories in best practice sampling and measurement in order to avoid hidden measurement bias, which can lead to incorrect pass / fail criteria being reported for biomethane purity tests due to impurities being adsorbed during sampling and analysis. Specifically, the two most challenging measurements that are prone to these errors within the EN standards are **total silicon and total sulphur contents**, due to their highly adsorptive nature. The project addressed these needs by providing traceable gas standards and organising inter-laboratory comparisons for the evaluation of industrial laboratory measurement capability. The comparisons were performed in conjunction with a workshop and webinar-based training on best practice in sampling and measurement of total silicon and total sulphur in biomethane. The results of the inter-laboratory comparisons, along with the requirements of EN 16723-1 and EN16723-2, were promoted at international events and communicated with related stakeholders to highlight the importance of traceability within the gas quality infrastructure.

# 3 Objectives

The overall aim of the project is to use traceable primary gas standards to evaluate total silicon and total sulphur impurities in biomethane.

The specific objectives are:

1. To evaluate the measurement capability of industrial laboratories performing measurement of total silicon and total sulphur concentration in biomethane with traceable primary gas standards, and to publish the results in an industry publication or an open-access peer-reviewed journal.
2. To disseminate knowledge outputs of EMRP project ENG54 Metrology for biogas in best practice sampling and analysis of total silicon and total sulphur concentration of biomethane to industrial analysis laboratories.
3. To increase the awareness of standards EN 16723-1 and EN 16723-2 within the wider biogas and biomethane industry to support their wider uptake, and to provide input to ISO working group ISO/TC193/SC1/WG25 Biomethane.

# 4 Results

### *4.1 Objective 1: To evaluate the measurement capability of industrial laboratories performing measurement of total silicon and total sulphur concentration in biomethane with traceable primary gas standards, and to publish the results in an industry publication or an open-access peer-reviewed journal.*

This objective has been achieved as follows:

This project organised two inter-laboratory comparisons for the sampling and analysis of total silicon and sulphur-containing components in biomethane. VSL, NPL and PSI prepared protocols for the two inter-laboratory comparisons. The components and their fractions were selected based on the specifications mentioned in EN16723 and relevant information available from the literature and previous EMRP/EMPIR projects. Before it was finalised, the list of components and their fractions were also sent to stakeholders for feedback, and adjustments were made to be sure that the work undertaken will indeed address their needs. A large number of participants were reached (9 for siloxanes and 13 for sulphur-containing components and more expressed interest, but could not join in the end for different reasons) including gas producers, calibration and testing laboratories, instrument manufacturers, NMIs/DIs, research institutes, and other end-users.

The evaluation results not only provided metrologically traceable validation of the measurement methods used in industry, by using traceable gas mixtures prepared by VSL and NPL, but also showed interesting scientific insights (see below for details).

**Results of the inter-laboratory comparisons for the sampling and analysis of siloxanes and total silicon in biomethane**

This comparison was organised by NPL with help from VSL and PSI. There were ten laboratories in the comparison.

The gas standards used in the comparison were prepared by NPL gravimetrically, in accordance with ISO 6142-1. These standards contained siloxane components L2 (hexamethyldisiloxane), D4 (Octamethylcyclotetrasiloxane) and D5 (Octamethylcyclotetrasiloxane) in a matrix of synthetic biomethane (methane). The nominal compositions of the Primary Reference Materials (PRMs) were targeted between 50 - 300 nmol $mol^{-1}$ per component, equivalent to approximately 0.1– 1.8 mg $m^{-3}$ mass concentration of silicon per mixture (across L2, D4 and D5 siloxanes). This was chosen to align with the threshold concentrations for total silicon in biomethane as specified in EN 16723-1 and EN 16723-2.

*Z*-scores and $E_n$ number were used to evaluate the results of the comparison and the calculation methods were in accordance with ISO 13528.

The interpretation of the *Z*-scores is the following:

$|Z| \leq 2$ Satisfactory result

$2 < |Z| \leq 3$ Questionable result

$|Z| > 3$ Unsatisfactory result

When using $E_n$-scores for qualification, the following holds:

$|E_n| \leq 1$ Satisfactory result

$|E_n| > 1$ Unsatisfactory result

The following graphs (Figures 1-4) depict the results of the comparison.

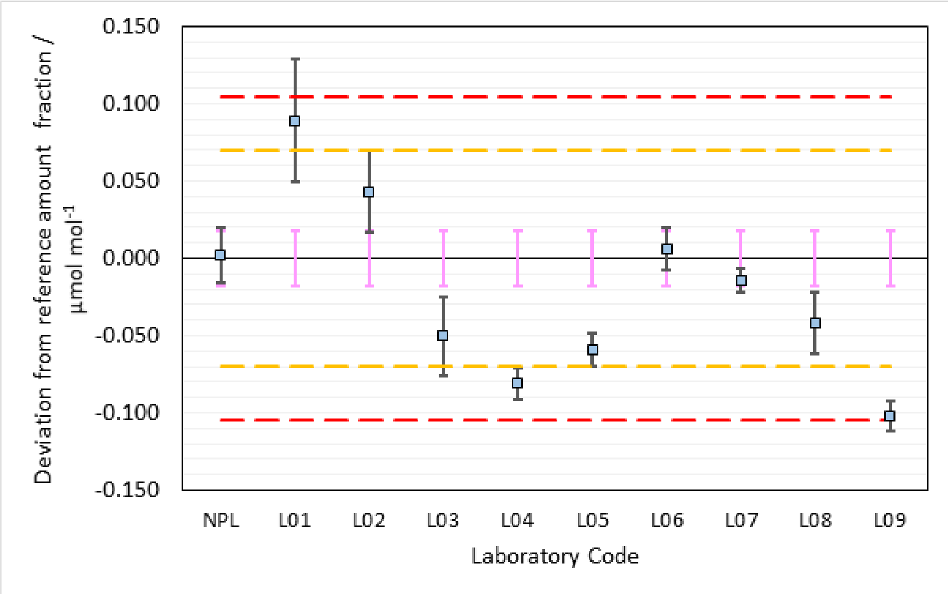


**Figure 1:** Reported amount fractions for L2 siloxane against laboratory code. Pink error bars indicate the expanded uncertainty in the reference values. Black error bars represent the expanded uncertainty reported by participants. Orange dashed lines indicate the z = 2 boundary. Red dashed lines indicate the z = 3 boundary. The same applies for the D4, D5 and total silicon results presented in Figure 2, Figure 3 and Figure 4

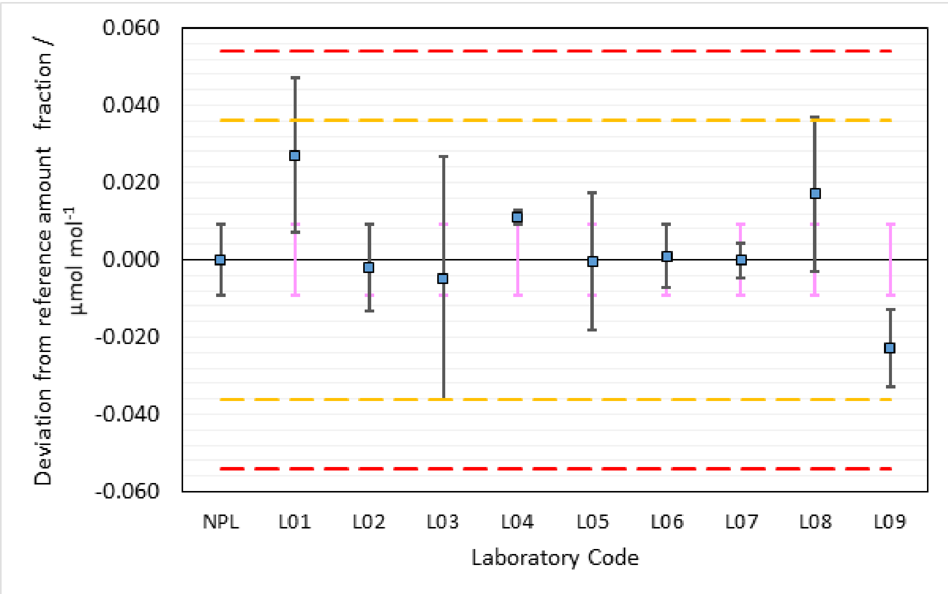


**Figure 2:** Reported amount fractions for D4 siloxane against laboratory code

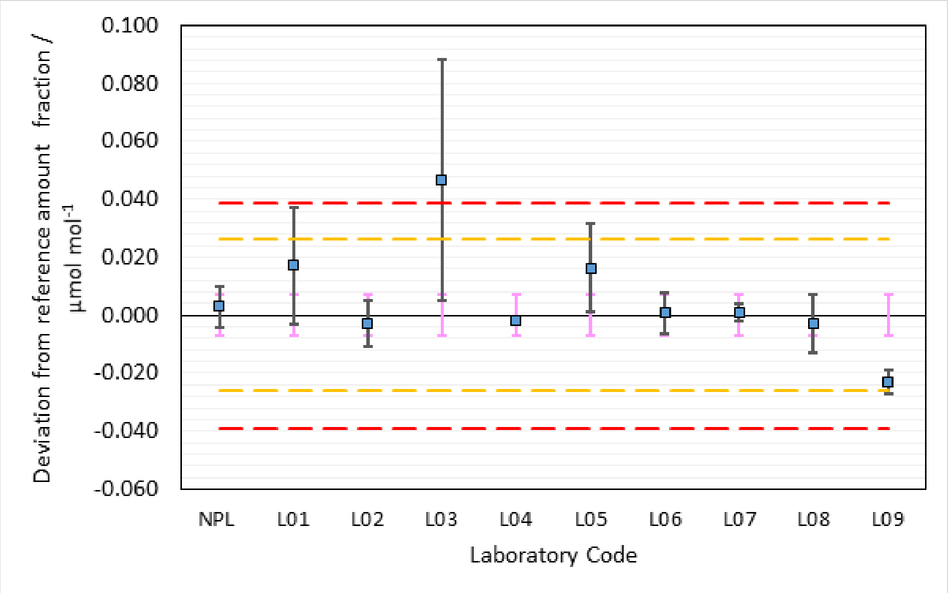


**Figure 3:** Reported amount fractions for D5 siloxane against laboratory code

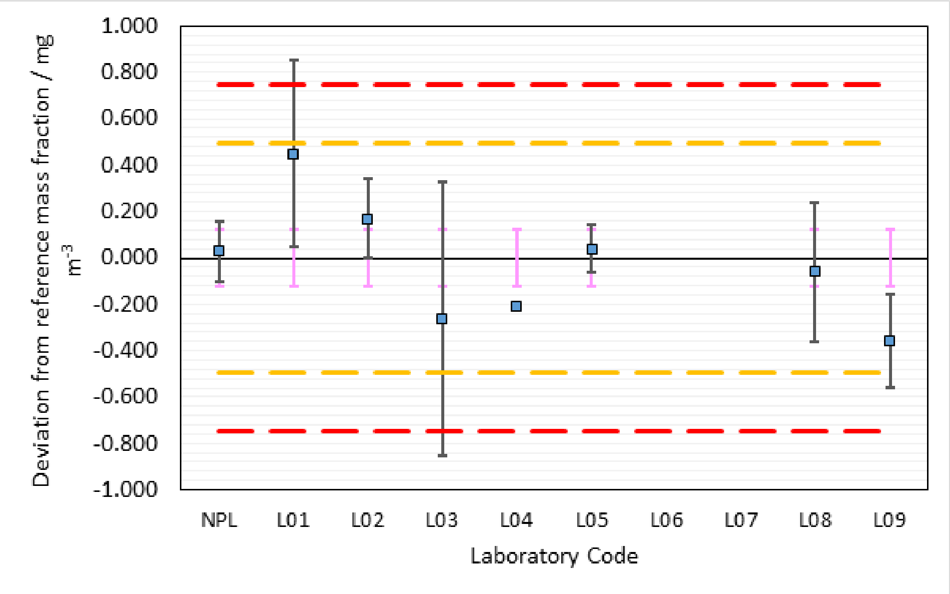


**Figure 4:** Reported amount fractions for total silicon against laboratory code

This comparison provided an insight into the performance of ten laboratories for the measurement of total silicon and siloxanes in biomethane at amount fractions of between 83 - 222 nmol mol$^{-1,}$ (approximately 1.55 mg m$^{-3}$ total silicon per mixture). Ten different analytical methods were used, including GC-MS, TD-GC-MS, GC-IMS, GC-FID, ATD-GC-FID, GC-ICP-MS and GC-AED. The reported uncertainties ranged between 0.2 % – 57 % relative.

The largest deviations were seen in the **L2 siloxane** results, where 7 out of 10 laboratories achieved satisfactory *Z*-scores and 3 out of 10 achieved satisfactory $E_n$ numbers. The cause of one of the questionable *Z*-scores was identified to be due to systematic error in the measurement procedure, whereas the reasons for the other two require further investigation following stability trial results, indicating stability was not a root cause. The more volatile nature of L2 renders it prone to issues with sampling via sorption tubes, which was proposed as a potential cause for some of the questionable results following discussions with participants. For the labs that achieved satisfactory scores for both criteria, the associated L2 results were all within 23 % of the reference values. This figure increases to 46 % when considering all L2 results.

The results for **D4 siloxane** were the most consistent, with all participant laboratories achieving satisfactory Z-scores and 7 out of 10 achieving satisfactory $E_n$ numbers. For the labs that achieved satisfactory scores for both criteria, the associated D4 results were all within 15 % of the reference values. This figure increases to 24 % when considering all D4 results.

For **D5 siloxane**, 9 out of 10 laboratories achieved satisfactory Z-scores and 8 out of 10 achieved satisfactory $E_n$ numbers. For the labs that achieved satisfactory scores for both criteria, the associated D5 results were all within 20 % of the reference values. This figure increases to 57 % when considering all D5 results.

For **total silicon**, 8 out of 8 laboratories achieved satisfactory *Z*-scores and 7 out of 8 achieved satisfactory $E_n$ numbers. For the labs that achieved satisfactory scores for both criteria, the associated total silicon results were all within 29 % of the reference values. This figure remains at 29 % when considering all total silicon results.

The results demonstrate that the measurement of siloxanes and total silicon was achieved successfully by the majority of the participants, with some challenges identified, particularly for L2 siloxane. As siloxanes have a tendency to adsorb onto surfaces, this may be a cause of some of the issues seen if materials were not appropriately passivated during calibration, sampling and analysis. Typically, the effect of adsorption is more prevalent for heavier siloxanes such as D4 and D5, rather than L2.

A further study would be recommended to ascertain whether the differences observed are due to calibration, sampling or the measurement method, as this would give an insight into how to inform best practice. An example of how this could be investigated would be as follows:

1. Use of the same sampling and analysis method, testing different calibration techniques.
2. Use of the same calibration and analysis method, testing different sampling techniques.
3. Use of the same calibration and sampling techniques, testing different analysis methods.

Future goals for the measurement of siloxanes and total silicon in biomethane would be to expand on the list of siloxanes tested and also investigate the influence of interferences expected within real biogas and biomethane samples (i.e. by having participants measure a sample containing other impurities that may cause interferences, such as e.g. terpenes and water). Such a test would be more representative of the challenges encountered within real-world measurements, and provide further insight into best practice for siloxanes and total silicon measurement.

### Results of the inter-laboratory comparisons for the sampling and analysis of sulphur-containing compounds and total sulphur in biomethane

This comparison was organised by VSL with help from NPL and PSI. There were 13 laboratories in the comparison.

The gas mixtures used in the comparison were prepared by VSL in accordance with ISO 6142-1 (gravimetric method) in high-pressure passivated cylinders. The nominal composition of the mixtures used in this comparison is shown in Table 1.

**Table 1:** Nominal ranges of amount fractions

| Component | Chemical formula | Mixture nominal amount fractions *x (mol/mol)* |
|---|---|---|
| Hydrogen sulphide | $H_2S$ | Between (1.0 – 10.0) · $10^{-6}$ |
| Carbonyl sulphide | $COS$ | Between (1.0 – 10.0) · $10^{-6}$ |
| Methyl mercaptan | $CH_3SH$ | Between (1.0 – 10.0) · $10^{-6}$ |
| Ethyl mercaptan | $C_2H_5SH$ | Between (1.0 – 10.0) · $10^{-6}$ |
| Tetrahydrothiophene (THT) | $C_4H_8S$ | Between (1.0 – 10.0) · $10^{-6}$ |
| Dimethyl sulphide (DMS) | $CH_3SCH_3$ | Between (1.0 – 10.0) · $10^{-6}$ |
| Diethyl sulphide (DES) | $(C_2H_5)_2S$ | Between (1.0 – 10.0) · $10^{-6}$ |
| Methane | $CH_4$ | Balance |

The results of the participant were evaluated by means of $Z$-scores and $E_n$-scores using methods from ISO13528. The interpretations of $Z$-scores and $E_n$-scores are the same as mentioned in the siloxane comparison.

The results of the comparison were summarised in the Figure 5. Please note that not all laboratories were able to measure all of the compounds presented in the mixtures. Therefore, in the figure some laboratories were missing from the results for some compounds.

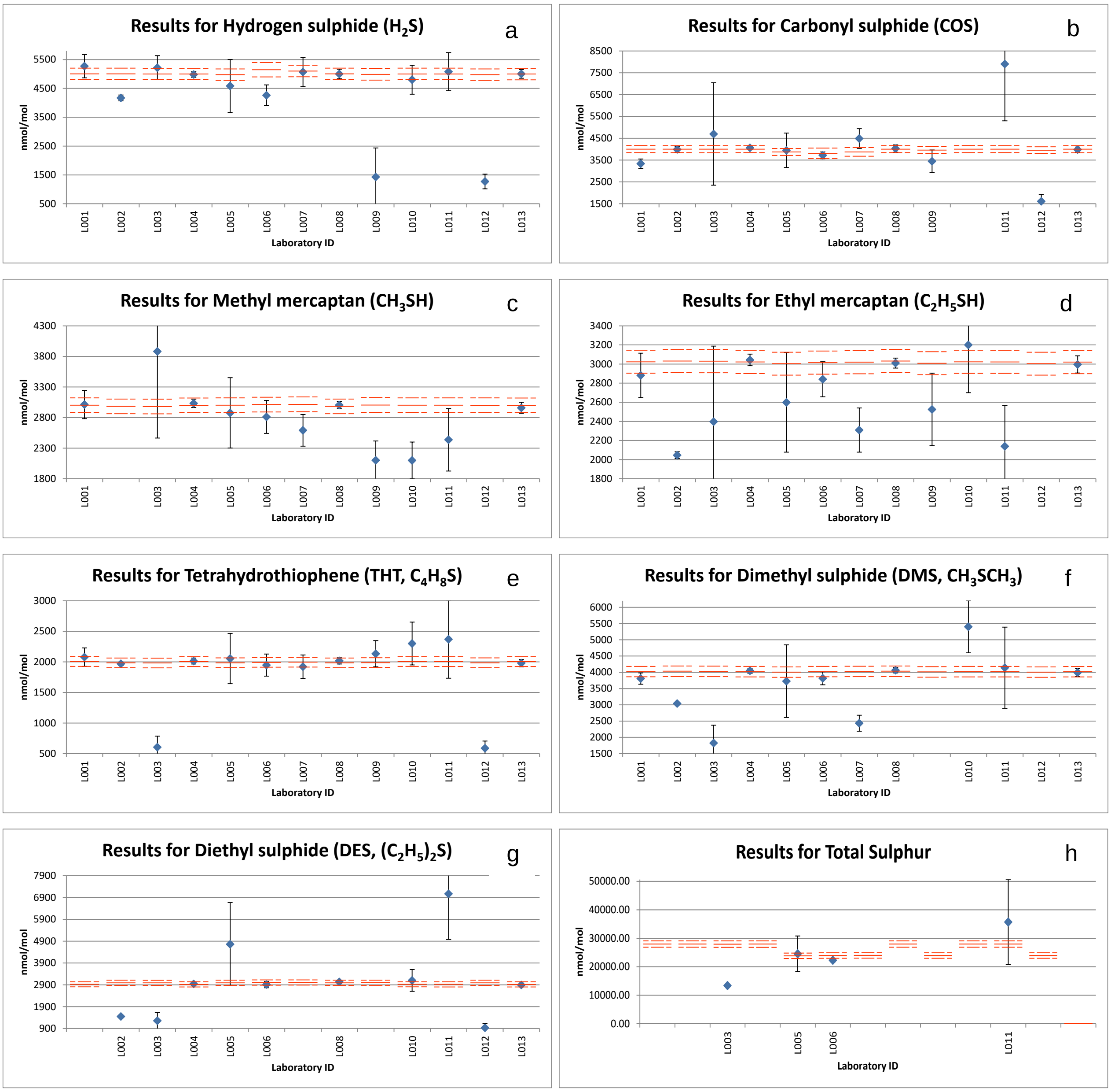


**Figure 5.** The results of the comparison on sulphur-containing compounds and total sulphur: a) Hydrogen sulphide, b) Carbonyl sulphide, c) Methyl mercaptan, d) Ethyl mercaptan, e) Tetrahydrothiophene, f) Dimethyl sulphide, g) Diethyl sulphide, and h) Total sulphur

Generally, the comparison demonstrates good comparability of results. The laboratories showing satisfactory performance in this comparison indicates the required performance for both the analysis of sulphur content (and sulphur species) in biomethane in accordance with EN 16723, as well as for the odorisation using, *e.g.*, tetrahydrothiophene or ethyl mercaptan.

To summarise, with great collaborations between the partners, this project achieved this objective by successfully organising two inter-laboratory comparisons, which provides industry with an improved understanding of their measurement capabilities and on how to perform accurate measurements for siloxanes and sulphur-containing components. These were the two very challenging ones due to their highly adsorptive nature. Two reports on the inter-laboratory comparisons for sampling and analysis of total silicon and total sulphur content in biomethane have been produced. The findings of the industrial laboratory comparisons were presented to the participants and disseminated at webinars, a workshop and a conference. The results are also being included in a paper which was uploaded on the project website and will be submitted to a suitable open-access peer-reviewed journal.

### 4.2 Objective 2: To disseminate knowledge outputs of EMRP project ENG54 Metrology for biogas in best practice sampling and analysis of total silicon and total sulphur concentration of biomethane to industrial analysis laboratories.

This objective has been achieved as follows:

When the project had just started in June 2019, an informal workshop, combined with the project kick-off meeting, was organised by VSL with help from NPL and PSI. The project was introduced to the participants. Feedback from the participants were collected by the consortium. A flyer was prepared and distributed by VSL at the GAS2019 conference held in June 2019 where the project was introduced to the conference participants. During a European Energy Gases workshop held in January 2020, VSL prepared a project flyer which was presented by NPL to the workshop participants. From time to time, the project's outputs were provided to the EMN on Energy Gases by VSL and NPL. To enlarge the impact of the project and the contacting community, the partners (VSL, NPL and PSI) have also done other social networking activities. With input from all partners, the stakeholder committee was established which consists of around 40 members. A project website (http://empir.npl.co.uk/si-s-biogas/) was created at the beginning by NPL with help from VSL.

NPL and VSL prepared training materials on best practice sampling and on the analysis of siloxanes, total silicon, sulphur-containing components, and total sulphur contents in biogas and/or biomethane. These training materials were used in the online webinars and workshops organised by the project. In total, there were 5 online webinars organised by the consortium, focused on best practice sampling and analysis of total silicon and total sulphur content in biogas and/or biomethane. Towards the end of the project, a project final workshop was hosted online by the partners, during which presentations from the consortium and stakeholders were organised. Knowledge transfer and exchange were clearly recognised. Feedback was collected by all partners from the participants of the 5 webinars and the project final workshop. For each webinar and the workshop, there were 25-40 participants from different parts of the world. These participants were from gas producers, calibration and testing laboratories, instrument manufacturers, NMIs/DIs, research institutes, and other end-users.

A paper containing results from the inter-laboratory comparisons was written, which was led by NPL with inputs from VSL and PSI. The draft manuscript was uploaded to the open-access project website hosted by NPL. A final version will be submitted to a selected open-access peer-reviewed journal shortly after the project ended. Two comparison reports were shared with the participants of the comparisons as well as with the audiences of the webinars and the final project workshop. A lecture presentation was given by NPL at the European Conference on Fuel and Energy Research and its Applications, held in September 2021. Two abstracts were submitted by VSL and NPL to the GAS2021 conference which was postponed to 2022 due to the COVID-19 pandemic. These two abstracts have been accepted as two lectures, which will be given at the GAS2022 conference in May 2022 (after the project officially ended).

The great collaboration between partners and the collaborative approach used in the project, certainly produced added value beyond that achievable by individual partners. Especially considering the organisation of the online webinars and workshop, large diversity of participants was reached thanks for each partner's efforts and good contacts with them.

### 4.3 Objective 3: To increase the awareness of standards EN 16723-1 and EN 16723-2 within the wider biogas and biomethane industry to support their wider uptake, and to provide input to ISO working group ISO/TC193/SC1/WG25 Biomethane.

This objective has been achieved as follows:

The partners attended several ISO/TC193/SC1/WG25 “Biomethane” (NPL and VSL) and Dutch national NEN NC310408 “Biomethane” (VSL) meetings where the project outputs were presented. Test methods used in the inter-laboratory comparisons have been summarised by NPL and VSL and delivered to these Working Groups, feedback was received. This feedback along with the results of the inter-laboratory comparisons will lead to a realistic overview of industrial capabilities.

The standards EN 16723-1 and EN 16723-2 were introduced and referred to in the conference presentation(s), at the webinars, workshops, and in a written paper. This will support wider uptake by the biogas and biomethane industry.

# 5 Impact

The project organised two inter-laboratory comparisons, a series of training webinars and workshops for the sampling and analysis of total silicon and sulphur-containing components in biomethane. Flyers and presentations promoting the project's activities were disseminated at conferences and other events. A paper containing results from the inter-laboratory comparisons was drafted, uploaded to the open-access project website and will be submitted to an open access peer-reviewed journal. Project outputs were provided to standardisation bodies (such as the ISO/TC193/SC1/WG25 "Biomethane" and the Dutch national NEN NC310408 "Biomethane") and to the EMN on Energy Gases. A stakeholder committee was established which consists of around 40 members.

Through the results outlined in the Results section above, the following impact has been (or will be) generated:

The high-level impact of the project was achieved by improving the framework that underpins the growing biomethane industry, thus furthering the diversification of the European energy supply, reducing reliance on fossil fuels and increasing the proportion of renewable energy used in Europe. Moreover, this was made possible through the enhanced industry awareness of the EN standards that specify maximum recommended limit levels of impurities of biomethane for injection into the gas grid and use in vehicle fuel (EN 16723-1 and EN16723-2, respectively). The enhanced visibility of these EN standards will provide both large- and small-scale businesses with the know-how they need to prepare for future legislation and grid entry agreements with gas distributors.

The inter-laboratory comparisons using accurate and SI-traceable gas mixtures, paired with the dissemination of knowledge in best practice in the sampling and analysis of impurities in biomethane will provide industry with confidence in their capability for measuring these compounds in biogas and biomethane. It will also provide industry with an improved understanding of how to perform accurate measurements and on how to avoid hidden quantification bias which can lead to false negatives in pass / fail tests (*e.g.* impurities are adsorbed during sampling). This will directly impact the quality of the biomethane that is injected into the gas grid and used as a vehicle fuel. Reducing the damage caused by impurities will improve the long-term integrity of the associated gas infrastructure in both industrial and home settings.

PSI as primary supporter is directly benefitting from this project via participating in the comparisons, the uptake, exploitation and use of research outputs as well as the dedicated support of VSL and NPL. Not only that, PSI is gaining a better understanding of, and confidence in, their capability for measuring these compounds in biogas and biomethane, this has also endorsed their progress in multiple projects where clean biogas and knowledge of siloxanes and sulphur compounds are required. It also reduced the risk of using unqualified gas in the biogas cleaning systems that PSI is involved in. Accurate and traceable gas standards and knowledge on siloxanes and sulphur has also indirectly stimulated development and validation of cheap and reliable gas sensors for usage in sensitive downstream processes and advanced gas cleaning systems.

The training and inter-laboratory comparisons created direct impact on the European biogas industry by allowing biogas producers, operators of landfill and wastewater sites, gas distribution networks and testing laboratories to perform accurate and traceable measurements of total silicon and total sulphur in biogas and biomethane using metrologically validated methods that comply with purity quality standards. The wider promotion of standards EN 16723-1 and EN 16723-2 within the gas industry allows grid operators to improve the level of the impurity thresholds they set within network entry agreements and it drives legislation for improving the quality framework within the industry. The gas end-users will benefit from the increased accuracy in analytical results for harmful impurity levels which, if reported incorrectly, could cause damage to the gas infrastructure.

The project's output has been shared with the ISO/TC193/SC1/WG25 Biomethane working group to help the WG to have a more realistic overview of industrial capabilities which is helpful for revising relevant ISO standards or developing new ones. Furthermore, the metrology community is benefitting from calibration and measurement services, training and other joint services provided by the partners. In order to stimulate innovation in the production and upgrading of biogas to biomethane which meet industry's specifications, traceable gas standards and calibration services are needed. The project has engaged directly with industry by organising various activities (such as the inter-laboratory comparisons, knowledge transfer, training etc.) so the metrological community can obtain an insight into the actual measurement needs of industry, which will allow tailored calibration services to be developed.

Further expansion of the biogas/ biomethane industry in Europe is foreseen. The use of biogas (in the form of biomethane) for injection into the natural gas grid and for use as a vehicle fuel will reduce dependency on the import of natural gas, liquefied natural gas (LNG), liquefied petroleum gas (LPG) and other oil and petroleum products into Europe, and improve the energy self-sufficiency of the continent. It will also provide a carbon-offset due to biogas being a carbon neutral fuel. Its use in road vehicles will provide decreased pollution levels compared to fossil fuel alternatives such as petroleum oil. Biogas use will also offset environmental damage caused by the extraction of fossil fuels. Decarbonisation of the world energy supply is at the forefront of global research efforts, with Europe leading its promotion and the utilisation of renewable energy. The project contributed to facilitating a reduction in carbon emissions and to promoting energy sustainability.

The use of biogas (as biomethane) in the existing natural gas infrastructure is promoted by EC Directives (2003/55/EC & 2009/73/EC) and will help meet target of the EC Renewable Energy Directive (REDII/2018/2001), which specify that at least 32 % renewables in the final energy consumption in the EU by 2030.

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