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1 Executive Summary

Introduction

To support the use of green gas, the European Commission issued mandate M/475 to CEN, the European Organisation for Standardisation, concerning the specifications for biogas and biomethane for injection into natural gas grids and for use as transport fuel. This mandate, or authority to carry out a policy, was issued to facilitate the market penetration of biomethane through the development of a European Standard for a quality specification for biomethane, and is for the development of:

- a) A CEN European Standard for a quality specification for biomethane to be used as a fuel for vehicle engines,
- b) Technical Specifications or EN standards for quality specification for biomethane to be injected into natural gas pipelines transporting either High calorific-gas or Low calorific-gas. The specifications and standards shall include a method (such as gas chromatography-mass spectrometry, ¹⁴C-isotope analysis or equivalent) to determine the volume fraction of biogenic methane (or biomethane) in the pipeline.

This project developed the traceable methods and reference materials needed to ensure that measurements of the properties of biogas are robust and reliable.

The Problem

The EU faces an urgent need to reduce its dependency on fossil fuels and has tasked the European Standardisation Organisation CEN to develop a specification for biomethane. The problem is that in order to implement this specification, the current laboratory infrastructure needs to be improved/established, thus it was hampering the widespread use of biomethane and upgraded biogas as substitutes for natural gas.

The Solution

The problem has been solved for a large number of parameters by developing and validating reference methods for the contents of key impurities (e.g., silicon, aromatic hydrocarbons, ammonia, hydrogen cyanide, carbon monoxide, biogenic methane, particulates, and water) and to demonstrate the applicability of direct methods currently in use for natural gas for determining the calorific value, density and heat capacity of biogas and biomethane. We also demonstrated the feasibility of developing a compact spectroscopic analyser for field measurements of, e.g., ammonia, biogenic methane content and carbon monoxide.

Impact

The methods that have been developed will help the laboratories to develop their own methods for the conformity assessment of biomethane. At the same time, some of these methods are being taken up by ISO/TC193/SC1/WG25 "Biomethane" for standardisation. In turn, these developments will lead to the extension of current accreditation programmes so that laboratories can obtain an accreditation for these new services in accordance with ISO/IEC 17025. The regulators, grid owners, and owners of refuelling stations will profit from these methods in that they can formulate their requirements with respect to the implementation of the biomethane specification EN 16723, including the preferred methods. The measurement results generated by the industry will become more reliable and accurate by implementing the methods and by using the services developed for having equipment duly calibrated.

The production of biomethane and biogas can be further optimised, as the improved accuracy of the methods for conformity assessment will enable the gas cleaning part, which is the most expensive part of biomethane production, to be optimised.

The sampling methods developed are essential for trustworthy conformity assessment, and these methods are going to be embedded in the revised standard ISO 10715 to specifically address the sampling of natural gas, biomethane and biogas for impurity contents.

2 Project context, rationale and objectives

Need for the project

As natural gas resources are declining and the EU depends increasingly on imported natural gas, diversification of the European natural gas supply is underway as required by the Renewable Energy Directive 2009/28/EC and EC targets, which specify that 20 % of EC energy consumption should come from renewable sources by 2020, and that biofuels should provide at least 10 % of transport petrol and diesel consumption by the same year. There is now an urgent need to significantly increase the amount of biogas which is injected into natural gas networks.

Biomethane is produced from organic waste, by cleaning biogas, and it is a 100 % renewable energy source. Its properties are similar to those of natural gas, making it suitable for use as a vehicle fuel and in heating applications.

To promote the use of biomethane, as required by the EC Directive concerning the common rules for the internal market in natural gas (2003/55/EC), specifications have been developed for the injection of biomethane into the natural gas transport and distribution grids and for use as transport fuels. Access to the natural gas grids and fuelling stations is essential for the promotion of biomethane. EN 16723-1:2016 contains specifications for gas grid injection, and EN 16723-2:2017 for use as transport fuel. A specification for liquefying biomethane is currently under consideration as new work item in CEN/TC408.

Reliable traceable methods and reference materials are needed for the implementation of the specifications to ensure that measurements of the relevant properties of biogas are robust and reliable. This conformity assessment is a prerequisite for the trade and use of biogas and biomethane.

Prior to this project, there was a lack of traceability and poor comparability between results from different laboratories, and there was a need for new and novel methods for measuring these specifications. Without these, the growth in the use of biogas would be effectively stopped as it would be uneconomic to transport, and the diversification of gas resources and the increased use of renewable fuels could not be met.

Scientific and technical objectives

This project aimed to develop and validate methods for determining key impurities, moisture, particulates, calorific value, and density:

1. Novel traceable methods for the measurement of the contents of key trace-level impurities in biogas and biomethane namely: total silicon and siloxanes, sulphur-containing compounds, aromatic hydrocarbons, halogenated hydrocarbons, ammonia, hydrogen cyanide, hydrogen chloride and carbon monoxide.
2. Robust analytical capabilities for the measurement of the particulate content and water content / dew point of biogas and biomethane.
3. Methods for the measurement of the calorific value, heat capacity, and density of biogas and biomethane.
4. A traceable method for determining the concentration of biomethane in samples of blended biomethane and natural gas. Robust methods for sampling biogas and biomethane in the field, and to enable the biogas industry to perform robust and traceable quality assessment measurements.

The results of this project will enable the National Metrology Institutes (NMIs) to provide services that enable the gas industry to reliably measure key properties of biogas and biomethane. The work undertaken will be discussed with CEN TC408 on biogas and it will support the efforts of this TC and other committees in setting up specifications for biogas and biomethane as well as in developing test methods for key parameters.

3 Research results

3.1 Objective 1: To develop novel traceable methods for the measurement of key trace-level impurities (total silicon and siloxanes, sulphur-containing compounds, aromatic hydrocarbons, and halogenated hydrocarbons, and ammonia, hydrogen cyanide, hydrogen chloride and carbon monoxide) in biogas and biomethane.

3.1.1 Silicon and siloxanes content

Due to the extensive usage of siloxane compounds, their volatility and great affinity to apolar environments, siloxanes are considered as one of the most important impurities in biogas. When biogases containing siloxanes are combusted, they are usually converted into silicon dioxide particles, which are chemically and physically similar to sand, causing significant internal damage to the natural gas grid infrastructure, appliances, and engines. The aim of this task was to develop and validate methods for the analysis of the total silicon content of biogas, supported by the preparation and analysis of high-accuracy reference gas mixtures of siloxanes in cylinders. This aim has been achieved as follows. VSL and NPL prepared a suite of reference gas mixtures of priority siloxanes (e.g., L2 (hexamethyldisiloxane), L3 (octamethyltrisiloxane), D4 (octamethylcyclotetrasiloxane), D5 (decamethylcyclopentasiloxane) in matrices of methane and synthetic biogas (methane, carbon dioxide and nitrogen) using gravimetry. The suite of gravimetrically prepared reference gas mixtures had silicon concentrations in the order of 0.1 mg m^{-3} to 1.0 mg m^{-3} , which when considering the specification EN 16723, this is the most important concentration range.

VSL, NPL, RISE and TUBITAK validated the composition of these mixtures and assessed their stability. To do so, methods were developed using different gas chromatography (GC) techniques. Gas chromatography with a flame ionisation detector (GC-FID) was used by NPL, VSL, RISE and TUBITAK, with mass spectrometry (GC-MS) by NPL, VSL, TUBITAK and RISE, using different configurations and methods. Based on an exchange of gas mixtures between NPL, VSL, TUBITAK and RISE, the composition of the gas mixtures, as well as the calibration of the instruments was compared.

Supplementary to these speciation methods, IMBiH developed a validated MWP-AES (microwave plasma – atomic emission spectrometry) method for the analysis of the total silicon concentration in biogas and biomethane. The MWP-AES method requires a system to transfer gaseous siloxanes into a liquid matrix (to facilitate injection into an MWP-AES) by purging it through adsorptive liquids or by liquid desorption of previously adsorbed siloxanes on solid adsorbents (such as activated carbon, Tenax or silica gel) to be developed. NPL developed an ICP-MS method for the analysis of total silicon concentration in biogas and biomethane.

The preparation of measurement and transfer standards using the well-known static gravimetric method from ISO 6142-1 presented some problems in that siloxanes are reactive species and substantial losses were recorded initially and over time. The purity analysis of the chemicals was performed in accordance with ISO 19229 and presented few analytical problems. GC-MS (NPL, VSL, RISE) is used for the identification of the impurities and either GC-MS or GC-FID for the quantification. The biggest issue with preparing gas mixtures in cylinders is the initial loss, especially of L2 and L3. These siloxanes appear to be the most reactive ones, and losses of up to 10 % were frequently observed. In view of the losses recorded in the project “Characterisation of Energy Gases” (EMRP JRP ENG01 GAS), this figure was already an improvement, but not satisfactory with respect to a target uncertainty of 5 %.

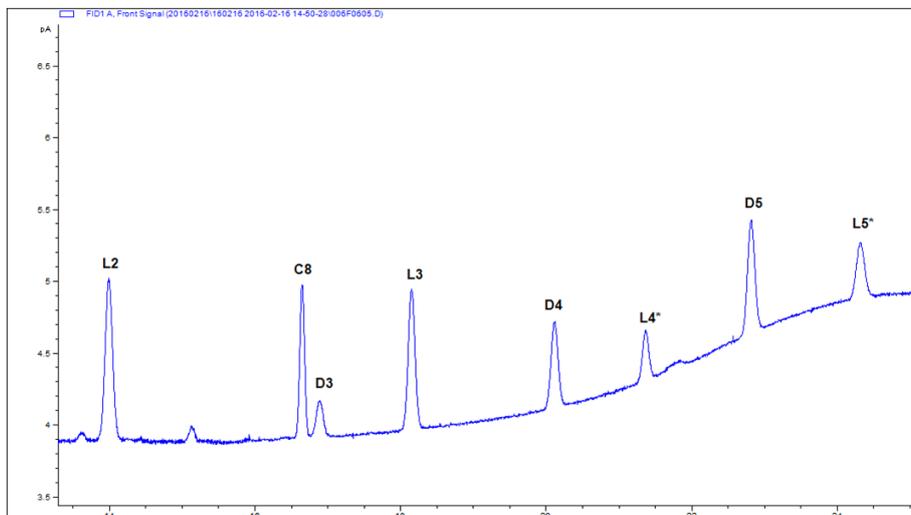


Figure 1: Gas chromatogram of siloxanes. The detector is a flame ionisation detector. C8 denotes *n*-octane, which is used as internal standard

The speciation methods, that quantify the siloxane contents, are all gas chromatography (GC) methods. The separation of the siloxanes is not challenging (see Figure 1), but sampling from cylinders presents some issues in its own right. The heavier siloxanes (e.g., D4 and D5) especially adsorb on metal surfaces such as those from regulators and tubing. Even using passivated regulators and tubing does not completely eliminate the adsorption effects, which is reflected in poorer repeatability and reproducibility figures for the less volatile components. The reproducibility standard deviation was generally between 1 % for the lightest siloxanes and up to 4 % for the heaviest (D5). Methods using an FID usually perform somewhat better than MS-based methods, but FID-based methods are likely to suffer from more interferences when used on real biomethane and biogas, which may also contain numerous other volatile organic hydrocarbons.

To measure the total silicon concentration, a method has been developed based on ICP-AES (Inductively coupled plasma atomic emission spectroscopy) and using an impinger to collect the silicon from the biomethane or biogas sample. Concentrated nitric acid is used as the impinger. The liquid is kept at a temperature of 60 °C and a gas flow of 10 mL/min is used. The derivatisation is done by adding in slight excess an 8 mol/L NaOH solution, followed by adding a hydrogen fluoride (HF) solution. The recovery factor was calculated and ranged from 65 % to 88 %. A comparison with a gravimetrically prepared gas mixture containing siloxanes confirmed the results. A second method for the total silicon concentration was developed using GC-ICP-MS. The GC is used to separate the silicon-containing components from the biomethane or biogas matrix. Then, ICP-MS (Inductively coupled plasma mass spectrometry) is used to quantify the silicon content.

3.1.2 Sulphur content

The aim of this task was to assess the stability of reference gas mixtures containing parts-per-million levels of sulphur-containing compounds in the presence of water, in order to simulate biogas and biomethane. These data are not readily available, yet relevant in relation to sampling methods for biomethane and biogas. The latter may especially contain high levels of moisture.

The maximum levels of sulphur compounds in the specification for biomethane are the same as for natural gas in gas grids and for use as transport fuel. The relevant specification (EN 16726) sets a limit of 20 mg m⁻³ of total sulphur compounds, 5 mg m⁻³ (total) of hydrogen sulphide and carbonyl sulphide and 6 mg m⁻³ of thiols. (At conditions of 20 °C and 1 bar, 5 mg m⁻³ of hydrogen sulphide is equivalent to approximately 3.5 µmol/mol; 6 mg m⁻³ of methanethiol is equivalent to approximately 3.0 µmol/mol).

VSL, NPL, CMI and BFKH gravimetrically prepared the gas mixture, which contained ppm-level sulphur-containing compounds in a matrix of synthetic biogas and various concentrations of water, thus simulating biogas from different sources at various stages of the upgrading process. VSL and NPL targeted the stability of dimethyl disulphide and diethyl sulphide, and CMI and BFKH targeted hydrogen sulphide,

tetrahydrothiophene (odorant) and ethyl methyl sulphide. At the beginning of the study, two mixtures were prepared with the targeted components and respectively 5 ppm and 50 ppm of water in a biomethane matrix.

Analysis of the mixtures for validation and stability testing purposes were performed using the GC-SCD (NPL, VSL), GC-AED (VSL) and/or TD-GC-MS (NPL, BFKH, CMI) methods for sulphur-containing compounds as developed in EMRP JRP ENG01 GAS. The instrument's calibration was performed by a single point calibration in accordance with ISO 12963. The nominal fractions of the freshly prepared calibration gas mixtures of the targeted sulphur compounds was the same as for the mixtures under study.

The gravimetric gas standards without the addition of water were stable within $\pm 2\%$, which is relevant information for the production of transfer standards and certified reference materials for use by the industry. Much greater instability was observed for gravimetric gas standards with 5 ppm and 50 ppm water added. Losses of up to 5% were observed for the more stable compounds (sulphides) in these gas mixtures.

3.1.3 Aromatic hydrocarbons content

The aim of this task was to develop novel reference materials for the measurement of the monocyclic aromatic hydrocarbons (BTEX, *i.e.* benzene, toluene, ethylbenzene, and *ortho*-, *meta*- and *para*-xylenes) in biogas, and to study whether existing methods for the measurement of polycyclic aromatic hydrocarbons (PAHs) in matrices such as workplace air can be applied to the analysis of PAHs in biogas.

BTEX are volatile organic compounds (VOCs) which are widely present in contaminated soil, groundwater and in landfills. Therefore, depending on the origin, various concentrations of BTEX are found in biogas as impurities. Unlike other components which are regulated in the specification EN 16723, maximum levels of BTEX and PAHs are regulated on the basis of health criteria. Furthermore, the work done on these components is pivotal for many other VOCs in biomethane and biogas.

VSL and TUBITAK prepared a suite of 4-5 reference gas mixtures of BTEX in synthetic biogas (a mixture of methane, carbon dioxide and nitrogen). These mixtures contained 1 $\mu\text{mol/mol}$ benzene, 1 $\mu\text{mol/mol}$ toluene, 1 $\mu\text{mol/mol}$ ethyl benzene, 0.5 $\mu\text{mol/mol}$ *ortho*-xylene, 0.25 $\mu\text{mol/mol}$ *meta*-xylene and 0.25 $\mu\text{mol/mol}$ *para*-xylene in a synthetic biogas matrix. The gas mixtures were prepared gravimetrically, and were gravimetrically in accordance with ISO 6142-1 and ISO 19229.

RISE, VSL, TUBITAK, NPL, REG(INERIS) and CMI developed and validated traceable GC analysis methods for measuring BTEX in biogas by comparing them against primary reference gas mixtures. Two variants will be developed, one for direct measurement in the gaseous phase (GC-FID (VSL, NPL, CMI), GC-TOF-MS (TUBITAK)) and a second for adsorption tubes (TD-GC-FID (RISE, VSL, REG(INERIS)), TD-GC-MS (RISE, REG(INERIS))). A typical chromatogram is shown in Figure 2. The only analytical challenge is the well-known issue of separating *para*- and *meta*-xylene, which can be achieved by selecting an appropriate column.

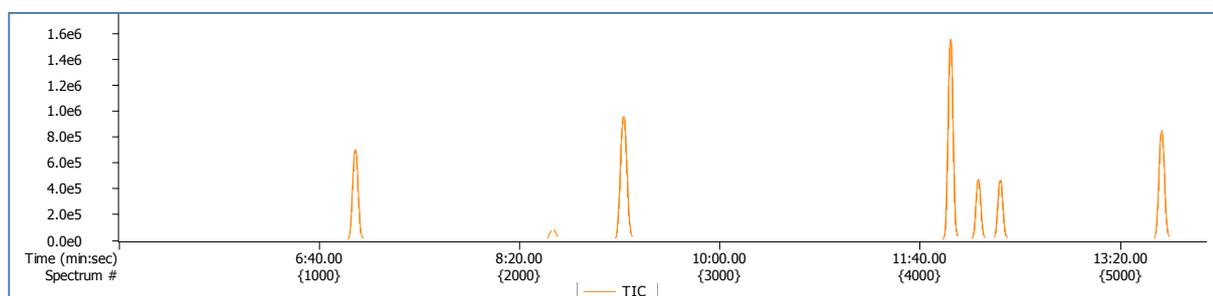


Figure 2 – A representative chromatogram of BTEX compounds (in order of retention time: benzene, toluene-d8, toluene, ethyl benzene, *para*-xylene, *meta*-xylene, *ortho*-xylene)

Calibration can be performed using reference gas mixtures. During this study, it has been observed that the adsorption of xylenes occurred in the standard regulator (not treated to minimise adsorption) and it was necessary to warm the regulator during sampling in order to partly avoid these adsorption effects as shown in Figure 3. It was also suspected that the low flow through the transfer line (from the reference gas mixture bottle to the sorbent tube) was contributing to the adsorption of xylenes so the use of a split was tested to increase the flow but no significant improvement was observed.

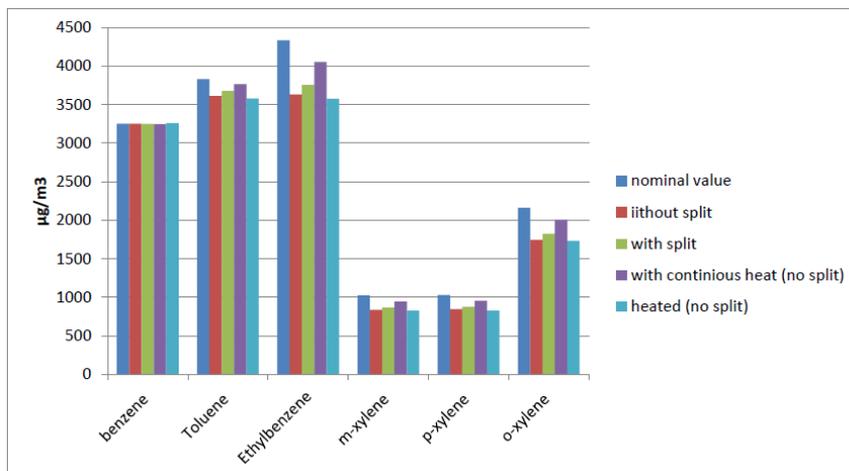


Figure 3 – Effects of using higher flow rates and heating in the analysis of BTEX

Two types of GC-FID and GC-MS methods have been developed for BTEX in biomethane and biogas. The first type directly quantifies the mole fraction of these components, whereas the second uses a sample pre-concentration trap (SPT) before the sample is injected into the GC. The latter types of method have greater sensitivity, often at the expense of a somewhat poorer repeatability and reproducibility. The relative expanded uncertainty achieved at 1 range from 2 % (benzene) to 4 % (o-xylene), was not very much different from the performance for these components in air quality measurements. The project also demonstrated that the stability of measurement and transfer standards of BTEX in biomethane and biogas is also similar to those in nitrogen or air.

A GC-TOF-MS method for the measurement of PAHs from thermal desorption tubes was developed by TUBITAK. Tenax TA thermal desorption tubes were used for method development (see Figure 4). PAHs in solutions were spiked into the Tenax TA tubes using a syringe. A Perkin-Elmer Turbo Matrix ATD thermal desorption instrument and a LECO HRT TOF-MS were used for MS applications. A method for GC-MS was developed to measure naphthalene, benz(a)anthracene and benzo(a)pyrene compounds. A typical chromatogram of the three PAHs selected is shown in Figure 5. Analytical challenges can arise with real biogas and biomethane, containing many more PAHs, which may co-elute.

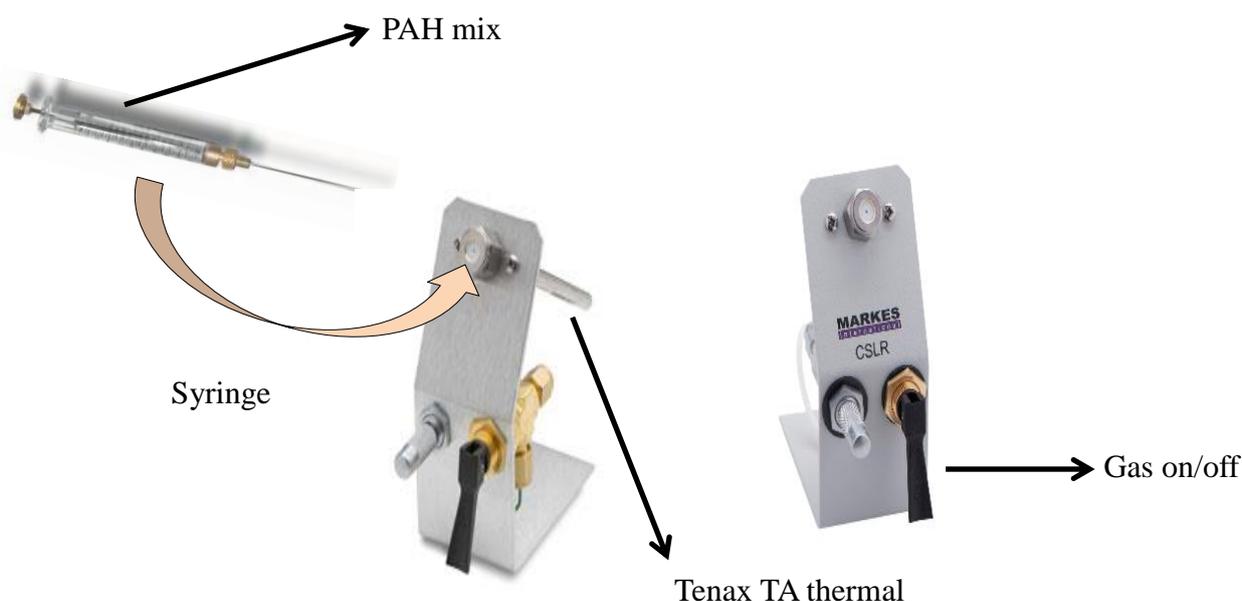


Figure 4 -- Spiking onto a thermal desorption tube by CSLR

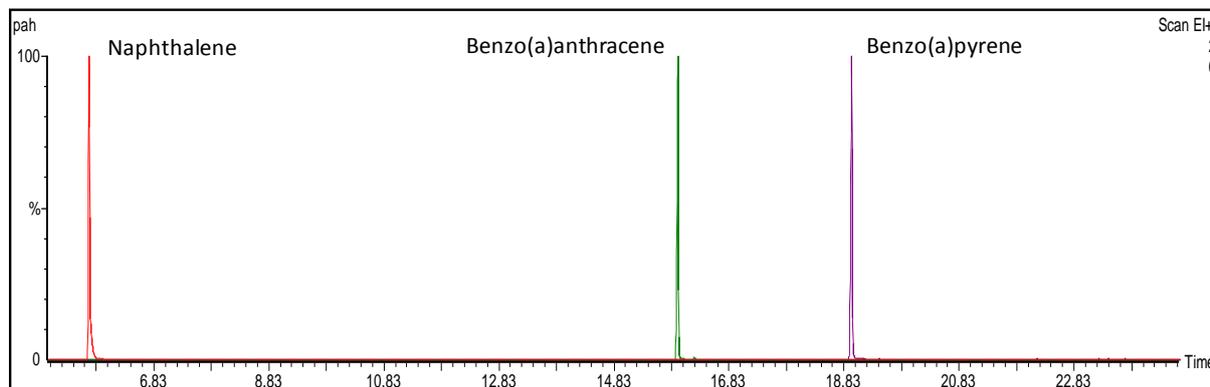


Figure 5 – A representative chromatogram of PAHs

3.1.4 Halogenated hydrocarbons content

The aim of this task was to develop methods for the analysis of trace levels of halogenated hydrocarbons in biogas. The measurement of these compounds is important as, for example, the presence of halogenated hydrocarbons in biogas may result in the production of hydrogen chloride and hydrogen fluoride on combustion, which are extremely corrosive to processing equipment and appliances. Also, unfavourable conditions of combustion (incomplete combustion at low temperature), in the presence of catalytic amounts of copper, may cause the halogenated hydrocarbons to be transformed into dioxins and furans. In the specification for biomethane EN 16723, halogenated hydrocarbons are currently included under 'chlorides' and 'fluorides'.

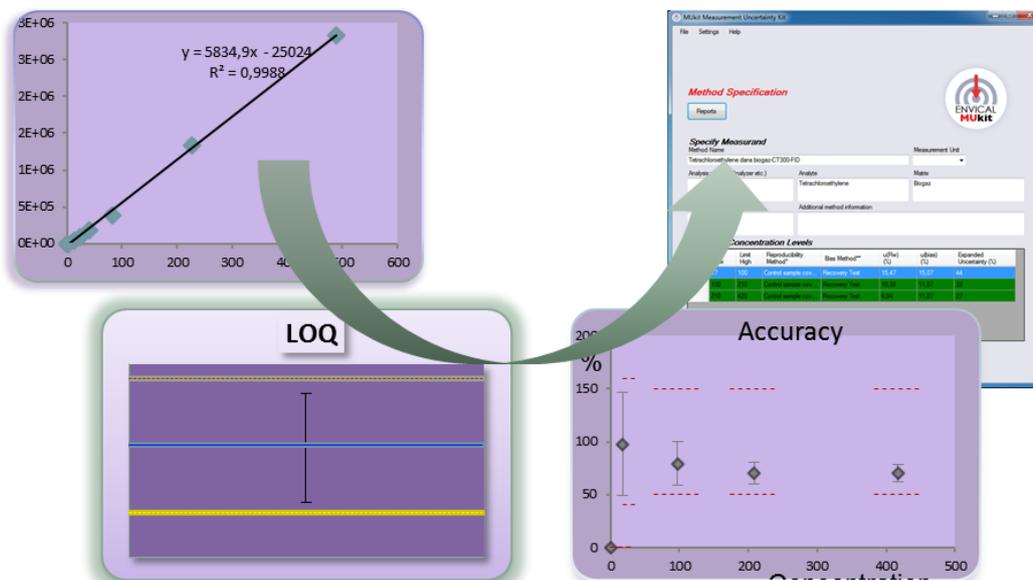
A review was undertaken by RISE, VSL and REG(INERIS) in order to identify relevant halogenated hydrocarbons based on criteria such as their occurrence in biogases, existing or innovative analytical methods for their measurement, and their availability in reference gas mixtures. The diversity of halogenated VOCs in biomethane and biogas is large. Overall, relevant halogenated VOCs cover the boiling point, ranging from -82 °C (trifluoro methane) to more than 300 °C (hexachlorobenzene). Therefore, the determination of all species in a single analysis is almost impossible in routine analysis.

Based on the survey, 5 halogenated VOCs were selected for the preparation of reference gas mixtures and method development: dichlorodifluoromethane, dichloromethane, tetrachloroethylene, m-dichlorobenzene, trichloro-trifluoroethane. Dichlorodifluoromethane was removed from the list as commercial analytical standards were no longer available due to concern about its damaging impact to the ozone layer. These regulations present an additional difficulty, as many of the more prevalent halogenated VOCs are banned substances.

A method based on thermal desorption- gas chromatography with flame ionization/ mass spectrometry detection was then developed. Three different sorbents were tested for the sampling:

- Tenax TA (weak strength)
- Carbotrap B (graphitised carbon black) (very weak strength)
- Multisorbent: Carbotrap 300 (packed with Carbopack C very weak strength, Carbopack B medium strength, Carbosieve SIII very strong strength)

The results showed that none of the sorbents tested were fully suitable for the halogenated VOCs selected. Large discrepancies in recoveries were observed in some cases and/or large biases were obtained when analysing the reference gas mixtures. The method needs to be further developed in upcoming research projects.



Due to the poor performance of the analytical method developed, it was not possible to evaluate the stability of the gravimetrically prepared reference gas mixtures.

3.1.5 Ammonia content

The European standard EN 16723 sets an upper limit for ammonia within biogas of 0.1 mg/m³. If ammonia is present at a high amount fraction, it poses a risk to health, and can lead to corrosion of infrastructure and contribute towards NO_x emissions when combusted.

In response to this measurement need, three traceable analytical methods and reference standards for the analysis of trace (ppb) amount fractions of ammonia in biogas were developed. The measurement techniques investigated were CRDS (Cavity Ring-Down Spectroscopy) by VSL, OFCEAS (Optical Feedback Cavity Enhanced Absorption Spectroscopy) by RISE, NDIR (Non-Dispersive Infrared) and FTIR (Fourier Transform Infrared) by NPL.

The most notable result of the study was that traditional techniques for measuring ammonia in nitrogen (such as CRDS and NDIR) are not always suitable for ammonia in biogas due to spectral interferences caused by the biogas or biomethane matrix (Figure 6). Refinement of existing methods were required in order to produce accurate results for biogas, which included an additional step for matrix subtraction.

The study also revealed the importance of applying an appropriate sampling procedure for ammonia measurement, as adsorbance of ammonia on untreated surfaces and certain particulate filters significantly increased the measurement stabilisation time as observed via OFCEAS (Figure 7). Application of proper conditioning for the entire sample path was found to reduce the measurement stabilisation time sufficiently to perform a measurement within 5 minutes (VSL's CRDS technique).

The presence of water was found to cause a decrease in the measured ammonia concentration when introduced to the mixture by RISE (Figure 8), causing a negative effect on the conditioning of the system.

The study was able to quantify a limit of detection of 0.2 µmol/mol (0.14 mg/m³) via VSL's CRDS technique for ammonia in biogas.

Stability measurements were performed by FTIR, indicating static mixtures of 10 ppm ammonia in biogas are stable to within 10 % over a two year period at the *k* = 2 uncertainty level (Figure 9).

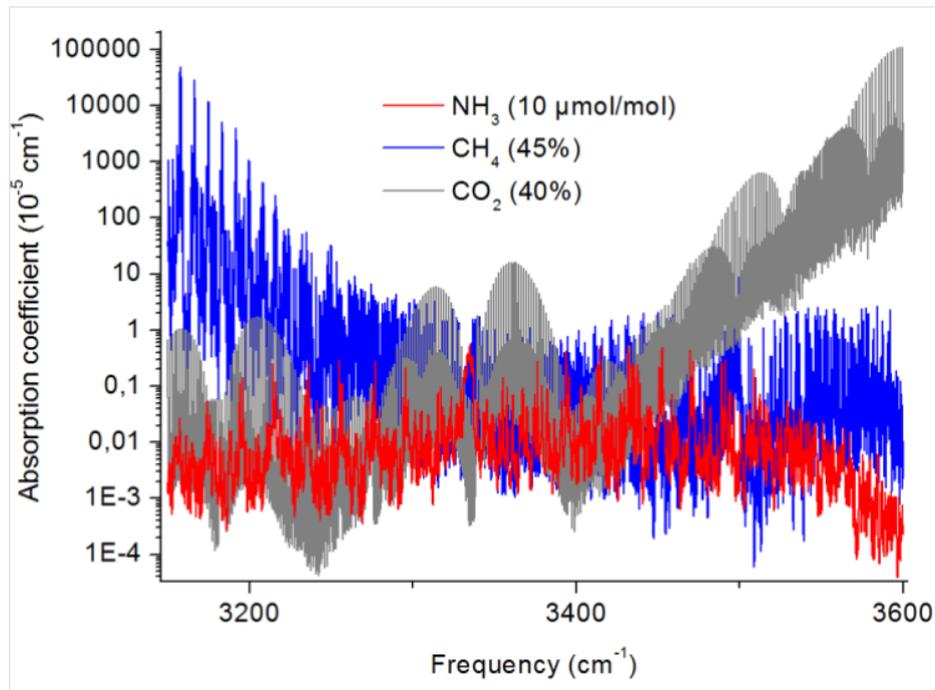


Figure 6 -- Spectral interferences due to methane and carbon dioxide characterised with CRDS for a 10 ammonia in biogas mixture

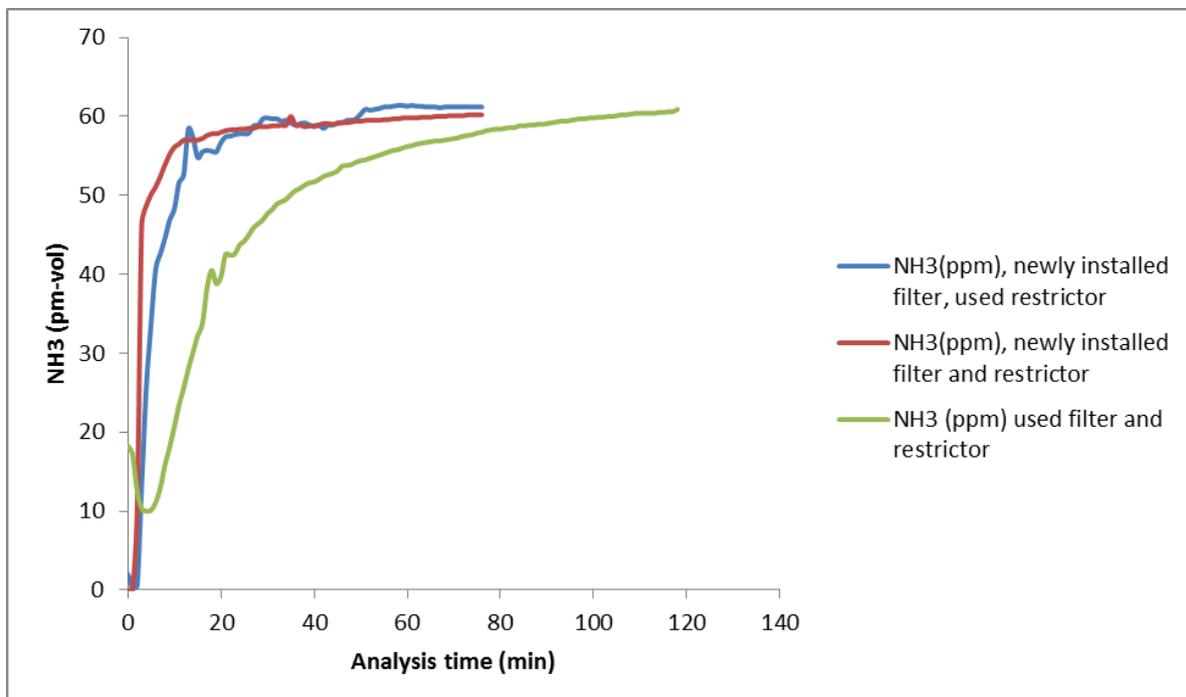


Figure 7 – The effect of stainless steel particle filter condition when analysing biomethane for the determination of ammonia concentration

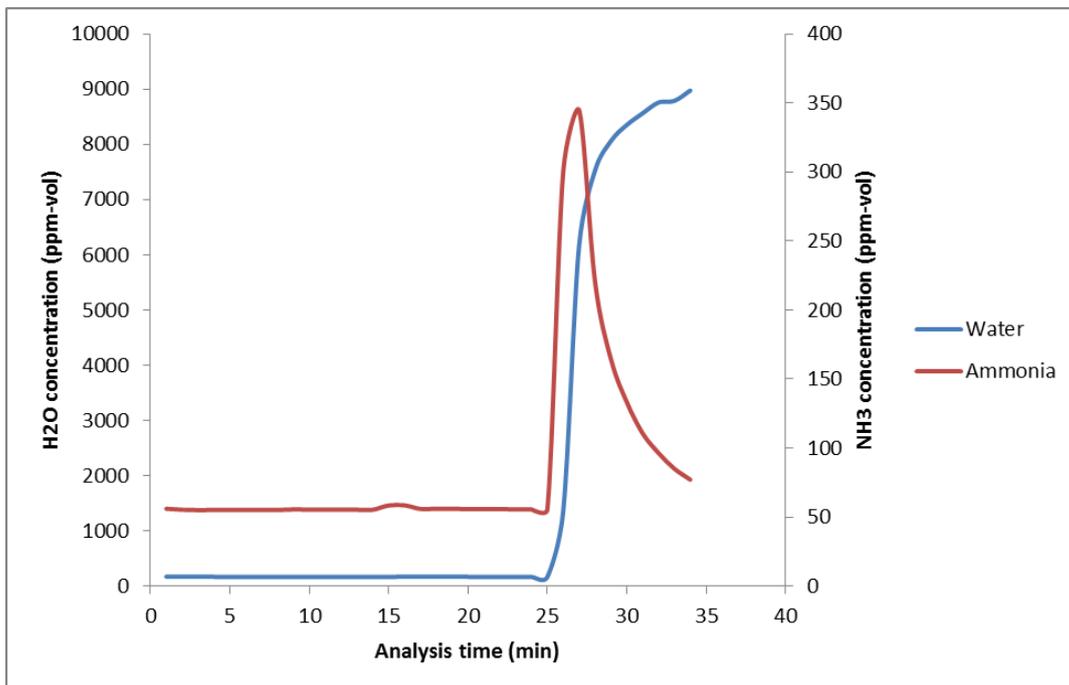


Figure 8 -- Deconditioning of an OFCEAS instrument when water is introduced into the instrument

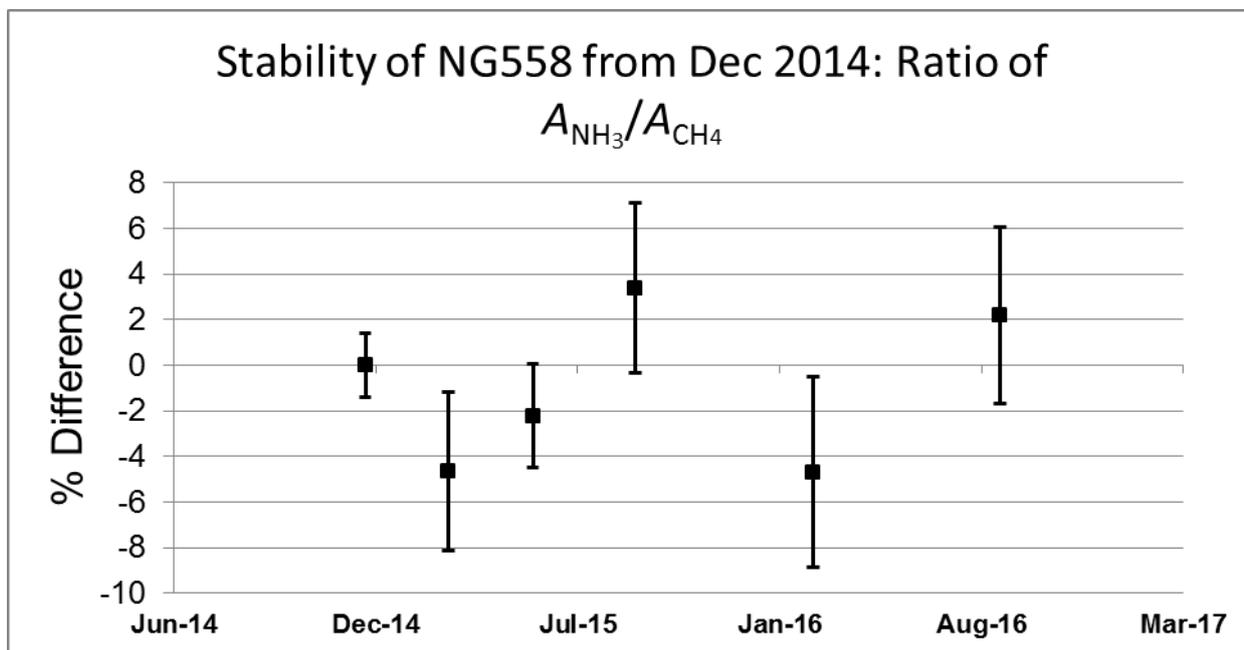


Figure 9 -- Stability of a static reference standard of 10 ppm ammonia in biogas as measured by FTIR spectroscopy, taking the ratio of the baseline corrected absorbances A_{NH_3}/A_{CH_4} . Error bars are $k = 2$

3.1.6 Hydrogen cyanide content

Hydrogen cyanide (HCN) is a very toxic gas (exposure limit value of 10 $\mu\text{mol/mol}$ for 15 min exposure) with a bitter almond odour. HCN can be present at low levels as a contaminant in landfill gas. The content can be further reduced using suitable gas scrubbing techniques, hence the presence of HCN in biogas is not normally considered a risk. However, very limited data is available due to, among others, a lack of suitable measurement methods and standards. HCN is not regulated in the biomethane specification, but there is an

upper limit in the Netherlands of 10 $\mu\text{mol/mol}$ with a relative expanded uncertainty of 20 %. The aim of this task was to develop a method for the analysis of trace levels of hydrogen cyanide (HCN) in biogas.

There are a wide variety of methods for measuring the HCN content in various matrices. In biogas, HCN can be analysed by colorimetric measurement. According to a report of the RIVM (Rijksinstituut voor Volksgezondheid en Milieu, the Netherlands) low levels of HCN are difficult to measure in biogas.

Currently no national metrology institute provides reference gas standards for HCN. A permeation system for the dynamic preparation of calibration gas mixtures for HCN was set up (Figure 10) by VSL. The permeation tube was kept at a temperature of 30 °C. The permeation tube was manually weighed over time to calculate the mass flow rate. The permeation tube (VICI Metronics) was certified to have a permeation rate of 238 ng min^{-1} at 30 °C. The tube was however used beyond the 1-year expiry date of the certificate. No mass loss was observed for the permeation tube during the weighing period, which may have been caused by take up of moisture from the laboratory air. The use of a permeation set up with an automatic magnetic suspension balance for weighing the permeation tube is expected to solve the problem in the near future.

VSL used their CRDS spectrometer to detect the HCN generated from the permeation system. HCN could be readily detected, notwithstanding the problems with recording the mass loss of the permeation tube. For the selected wavelength range, the spectral interference of several biogas matrices was determined. It was found that the interference of all biogas matrices under test was relatively small (comparable to the case of ammonia in biogas and thus much smaller than for HCl in biogas). With respect to sampling, the response of the system to HCN is faster than to both HCl and NH_3 as HCN adsorbs less to the materials used in the gas lines and measurement cell (mainly SilcoNert 2000 coated stainless steel).

The provisional limit of detection, based on the line strength, for HCN in biogas is around 10 nmol/mol . Once the issues with the permeation system have been solved, the limit of detection will be determined, after validating the line strength parameters. It is expected that the relative expanded uncertainty of the mole fraction HCN will be in the order of 5 %, considering that this level of performance is achievable for NH_3 .

As for HCl, the use of a magnetic suspension balance instead of manual weighing is anticipated to improve the reliability of the dynamic generation (reduce the influence of moisture, no large temperature changes etc).

3.1.7 Hydrogen chloride content

The aim of this task was to develop an analysis method for the measurement of trace levels of hydrogen chloride (HCl) in biogas. When biogas is used for energy production, even trace levels of HCl as an impurity can cause corrosion in vehicle and combustion engines. The industry has set different criteria on the total amount of halogens for different engines, ranging from a few ppm to thousands of ppm. Accurate quantification for HCl at amount fractions of 10 $\mu\text{mol/mol}$ and below is problematic due to the high reactivity of the compound.

VSL set up the system for the dynamic generation of HCl in synthetic biogas using permeation. NPL prepared and validated reference standards of 10 $\mu\text{mol/mol}$ HCl in synthetic biogas by comparing the compositions calculated from the preparation data with the measured compositions. NPL developed and validated the dynamic dilution system for the HCl reference standards developed in D2.3.3 by comparing the compositions calculated from the preparation data with the measured compositions.

HCP and VSL will design and simulate, using appropriate software, a tuneable mid-IR laser module with an intracavity optical parametric oscillation (IC-OPO) laser configuration for HCl sensing at $\lambda=3.4\text{--}3.8 \mu\text{m}$. HCP and VSL used the laser module to develop a tuneable mid-IR laser module with improved wavelength stability ($\leq 0.01 \text{ nm}$) and output power (target $\geq 50 \text{ mW}$). HCP and VSL manufactured and characterised the integrated biogas sensing subsystem with respect to the decay and cell response times and will integrate it with the mid-IR laser module. NPL and VSL validated the methods for the analysis of HCl down to 10 nmol/mol by IMS. The measured compositions will be compared with the compositions calculated from the preparation data. Compositions suitable for validation will be selected to investigate matrix effects, the limit of detection, and to enable the measurement uncertainty of the preparation and measurement methods to be calculated.

The measurement of the mole fraction HCl in biomethane and biogas has turned out to be more difficult than anticipated. The approach chosen was very similar to that of HCN. The results for HCl in nitrogen have proved to be very useful and satisfying. With the same permeation system as used for HCN (Figure 10), the

line strength parameters for HCl were confirmed (Figure 11). This confirmation is important for metrologically traceable measurement of the mole fraction.

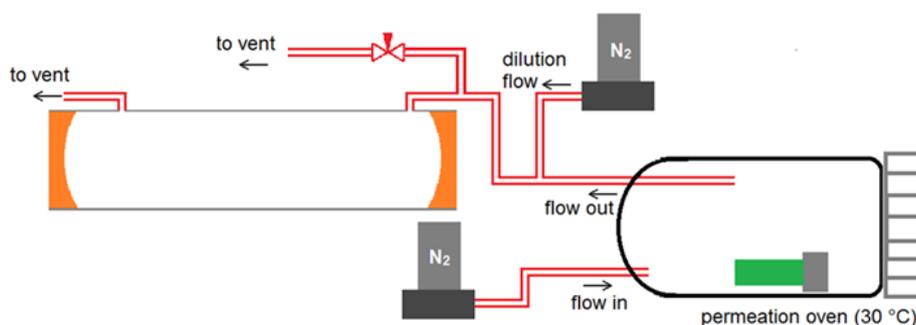


Figure 10 – The permeation and dilution system used for preparing calibration gas mixtures with HCN and HCl

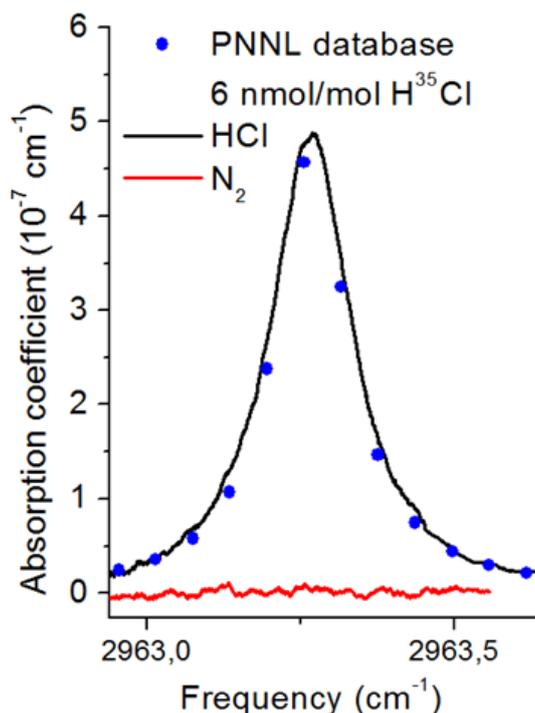


Figure 11 -- Predicted (PNNL) and observed absorption peak for HCl at 6 nmol/mol in nitrogen

The interferences of the biomethane and biogas matrices are much larger for HCl than for NH₃ and HCN. Further work is required, for example at low pressure in the measurement cell, to reduce the interferences and to see whether measurements can be performed with acceptable accuracy.

NPL studied the adsorption behaviour of HCl in passivated gas cylinders (Figure 12). Two kinds of experiments were conducted: blow-down (venting off the gas mixture and topping up the gas mixture with the balance gas) and decanting the gas mixture into an evacuated cylinder. These experiments show an increase in the mole fraction HCl at low pressures. Prepared reference gas mixtures are stable for at least 6 months.

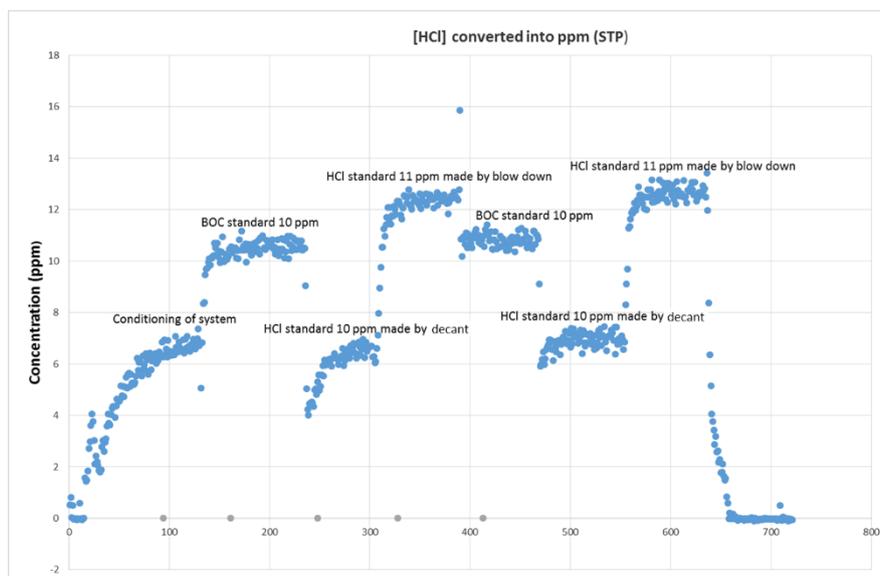


Figure 12 – Adsorption effects of hydrogen chloride in passivated gas cylinders

3.1.8 Carbon monoxide content

The aim of this task was to develop measurement methods and standards for the determination of the CO content in biogas. According to the specification for biomethane and upgraded biogas, a maximum mole fraction of 0.1 % (1000 ppm) CO is permitted for injection of biomethane into the natural gas grid. Carbon monoxide is a very poisonous gas and exposure to CO can easily lead to [tachycardia](#), dizziness, nausea and death. The specification suggests using ISO 6974 as the method for analysing carbon monoxide.

Two approaches were followed, one based on laser spectroscopy, the other on gas chromatography. The former approach has been used to investigate the possibility of analysing carbon monoxide in biogas and biomethane by means of spectroscopic techniques. The price of a field gas chromatograph is an obstacle for regularly measuring the biogas composition. Spectroscopy may provide a financially attractive alternative when used in a field instrument for a number of relevant components in biogas.

An interband cascade laser (ICL) spectrometer has been developed by PTB, based on the direct tuneable diode laser absorption spectroscopy (dTDLAS) principle and it has been equipped with a single pass gas cell, for CO measurements in biogas (Figure 13). The relative uncertainty of CO amount fraction results delivered by the system at the 1000 $\mu\text{mol/mol}$ range is estimated to be in the 1.4 % range ($k = 1$). The system's minimum detectable CO amount fraction is about 1.6 $\mu\text{mol/mol}$. The linearity of the system was confirmed (Figure 14, Figure 15).

A simple infrared laser spectrometer has been developed based on direct absorption by VSL. The system has been tested for CO (mole fraction 10-400 $\mu\text{mol/mol}$) in biogas of various compositions (15 % - 44 % CO_2 , 5 % - 25 % N_2 and 41 % - 70 % CH_4). Spectral interference by the biogas matrix was shown to be very small for all tested compositions. The combination of a relatively high upper limit for CO of 0.1 % in biomethane as set in EN 16723-1:2016 and the low interference by the biogas matrix components opens up possibilities to measure CO in biogas with even simpler and hence cheaper devices based on infrared (e.g. using IR LEDs).

RISE and VSL have developed a method, using a gas chromatograph with a thermal conductivity detector, to analyse CO in biogas in accordance with ISO 6974. This documentary standard is cited by the specification (EN 16723). The target detection limit with this method is 100 ppm. The analysis method used here has the potential for further development in order to detect lower quantities of carbon monoxide if so required. The sampling is performed in gas sampling bags which are connected to the instrument via a gas pump and a sample loop. The gas pump is used to draw gas samples from the bag into the sample loop. The expanded uncertainty for the method of 3 % rel., has been calculated using the software MUKit Measurement Uncertainty kit. The method involving static gas mixtures in cylinders (VSL) provided an expanded uncertainty of 0.2 % at the threshold level for carbon monoxide.

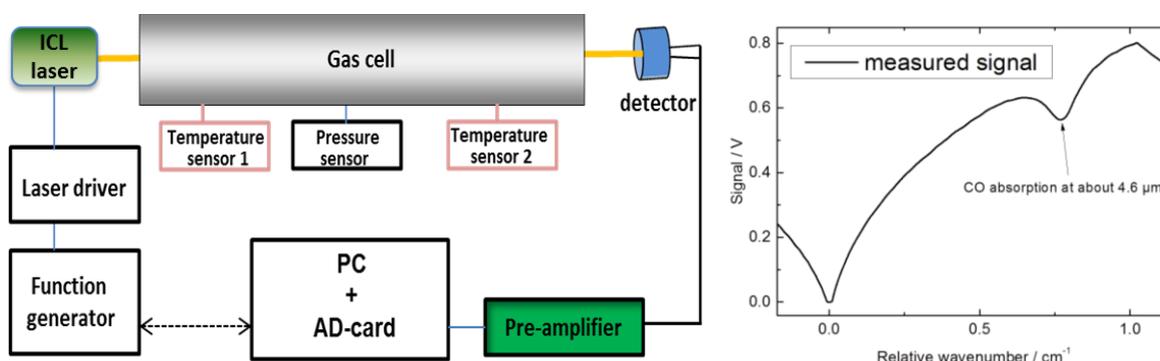


Figure 13 -- Schematic of a direct absorption spectrometer setup, based on direct tunable diode laser absorption spectroscopy (dTDLAS), for CO in biogas. ICL: Interband Cascade Laser. Gas cell: single pass. Right: Typical dTDLAS signal measured with the setup

HCP have developed a compact instrument for the analysis of biogas based on photoacoustic spectroscopy (PAS) and including highly tuneable / high-resolution optical parametric oscillator (OPO) lasers, electronics, photo-acoustic gas cell, condenser microphone and software to probe various gases in the [2.7-3.7]μm and [4~4.7]μm MIR bands.

The performance of this sensitive detector were evaluated both at HCP and in the laboratories of our VSL (NL) and VTT/MIKES (FIN) partners and they were benchmarked against EU recommendations for Biogas sensing. The investigations revolved around key laser parameters (radiant power, wavelength stability, tunability and spectral resolution), as well as the limit of detection and sensitivity characterising the photoacoustic gas cell and overall instrument's performances. The gases used in this endeavour were specific to the biogas industry itself, and thus focused on detecting methane and its isotopes, thus providing a means to ascertain its biogenic origin, as well as for the detection of several inorganic impurities whose presence in too high levels is known to be detrimental to the safe use of biogas as a fuel.

The ability of the [2.7-3.7]μm laser module to deliver at least 50 mW radiant power was hence successfully checked with a power measured at twice the recommended value. The laser stability was measured at 100 MHz over 1 hour, or 3 times better than the target. The sensitivity was also within specified range for the detection of HCl mixtures and evaluated at $1.9 \times 10^{-7} \text{ cm}^{-1}$. Our laser's 100 GHz tuneability and 20 MHz spectral resolution allowed us to detect the presence of isotopologues of CH₄ in pure methane, a key step in the traceability of bio-methane. That same laser module was also successfully tested for the detection of NH₃ in biogas mixtures (CH₄, CO₂, N₂), thus probing the "multi-gas capability" of our instrument. To cater, finally, to the other important MIR band for biogas sensing, our [4~4.7]μm laser OPO was applied to the detection of CO, with a limit of detection evaluated at 5 ppm, i.e., two times better than the detection limit suggested for that highly toxic gas. In summary, the development of a compact and affordable multi-gas detector, with specifications suitable for biogas applications and gas sensing in general has been successful.

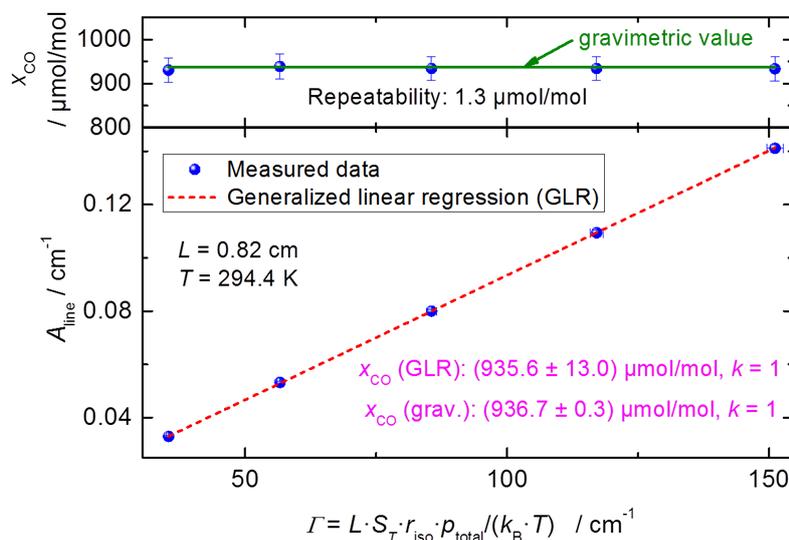


Figure 14 -- Linearity assessment of the TDLAS shown in Figure 12 using a suite of calibration gas mixtures of carbon monoxide in nitrogen

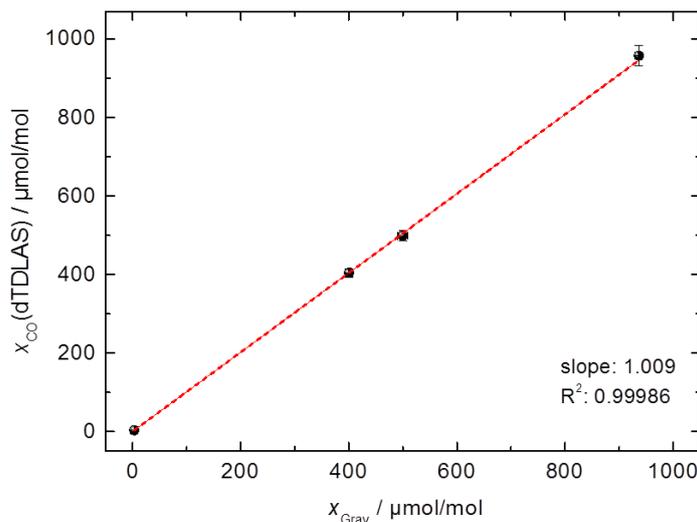


Figure 15-- Linearity assessment of the dTDLAS spectrometer shown in Figure 13 using a suite of calibration gas mixtures (3 μmol/mol - 1000 μmol/mol –CO in N₂/air/biogas)

3.2 Objective 2: To develop robust analytical capabilities for the measurement of the particulate content and water content / dew point of biogas and biomethane.

3.2.1 Water content

The aim of the task was the experimental investigation of the enhancement factor of water vapour in biogas up to 6 MPa and the development of an analytical function for the calculation of the enhancement factor. The water content of biogas plays an important role in the design of biogas processes. Enhancement factors are needed for the calculation of the water mixture fraction in gas mixtures, here biogas, from measured dew point temperatures, considering non-ideal behaviour and influences of mixture and pressure.

Three different experimental setups were used to determine the enhancement factor of water vapour in biogas. PTB’s experimental setup uses a commercial two-pressure generator (MBW G1 HX) for the

generation of the moistened nitrogen stream with known water content. This stream is mixed with the biogas mixture which is dynamically prepared using mass flow meters and controllers. The frost point and the respective dew point temperature is measured by a chilled mirror hygrometer (MBW 373 LHX). Three different gas mixtures were studied at pressures up to 0.5 MPa: CH₄ (48.5 %), N₂ (3 %) and CO₂ (48.5 %), and CH₄ (77 %), N₂ (3 %) and CO₂ (20 %), and CH₄ (92.5 %), N₂ (2.5 %) and CO₂ (5 %)

In the system developed at VTT MIKES, a known water vapour mole fraction in biogas is obtained by feeding water with a calibrated syringe pump through an evaporator into a dry biogas stream and measuring the mass flow rate of the dry biogas. The dew-point temperature of the biogas-water vapour mixture is determined with a CCDI method. In this method, gas flows through a temperature controlled heat exchanger coil before entering a capacitive humidity sensor. When cooling the coil step by step the dew point is detected with the humidity sensor and the corresponding dew-point temperature is determined from the coil temperature. Using a gas pressurising unit and gas drier unit, the system is arranged as a closed gas flow loop minimising the gas consumption in experiments.

At VSL the tests were performed using three different carrier gases from Air Products Netherlands: pure methane, CH₄ (92 %), N₂ (5 %) and CO₂ (3 %), and CH₄ (77 %), N₂ (3 %) and CO₂ (20 %). Four different kinds of commercial devices were investigated: chilled mirror hygrometer, Fabry-Perot Interferometer, Tuneable-Diode Laser Absorption (TDLAS) and polymer sensor. The pressures of the carrier gas output from the flow mixing system were: 0.7 MPa, 3 MPa and 6 MPa. The temperature of the saturator was kept at 15 °C and the flows in the dry and wet lines were controlled in order to get a water dew-point temperature between -20 °C and +15 °C in the gas output from the flow mixing system. The measurements were performed in two runs.

Due to the complexity of the biogas system compared to the amount of measured data the definition of a suitable analytical function and model fitting is challenging. For these reasons a first approach with the well-known model of Greenspan [1] was used for each composition. The measurements intend to enlarge the limited amount of literature data on enhancement factors in biogas mixtures. With the developed experimental setups, further measurements can be carried out to support a better modelling of the enhancement factor.

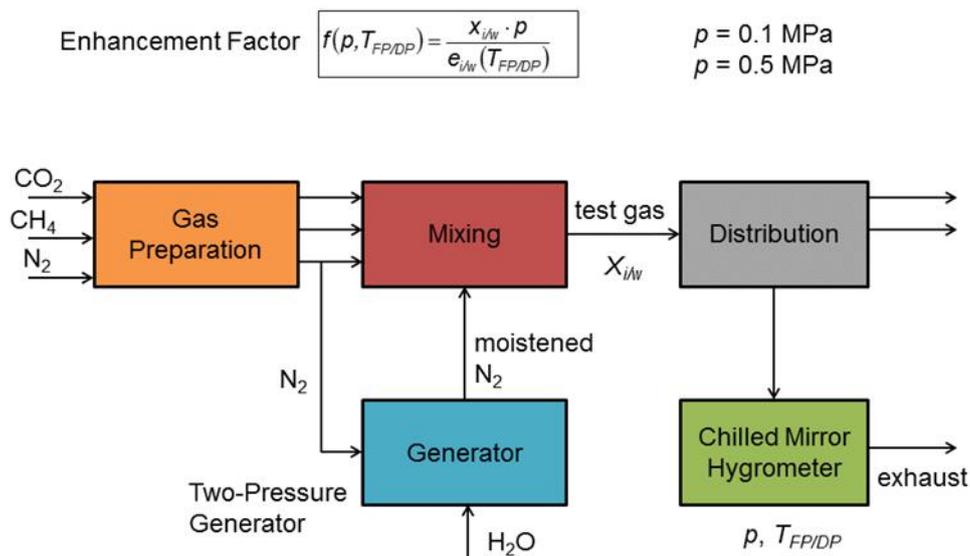


Figure 16 -- Scheme of PTB's experimental setup for the calculation of the enhancement factor

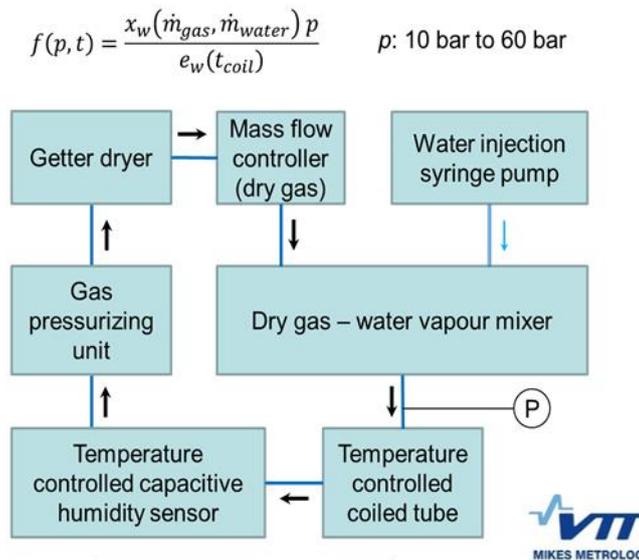


Figure 17 -- Principle of operation of the VTT MIKES system

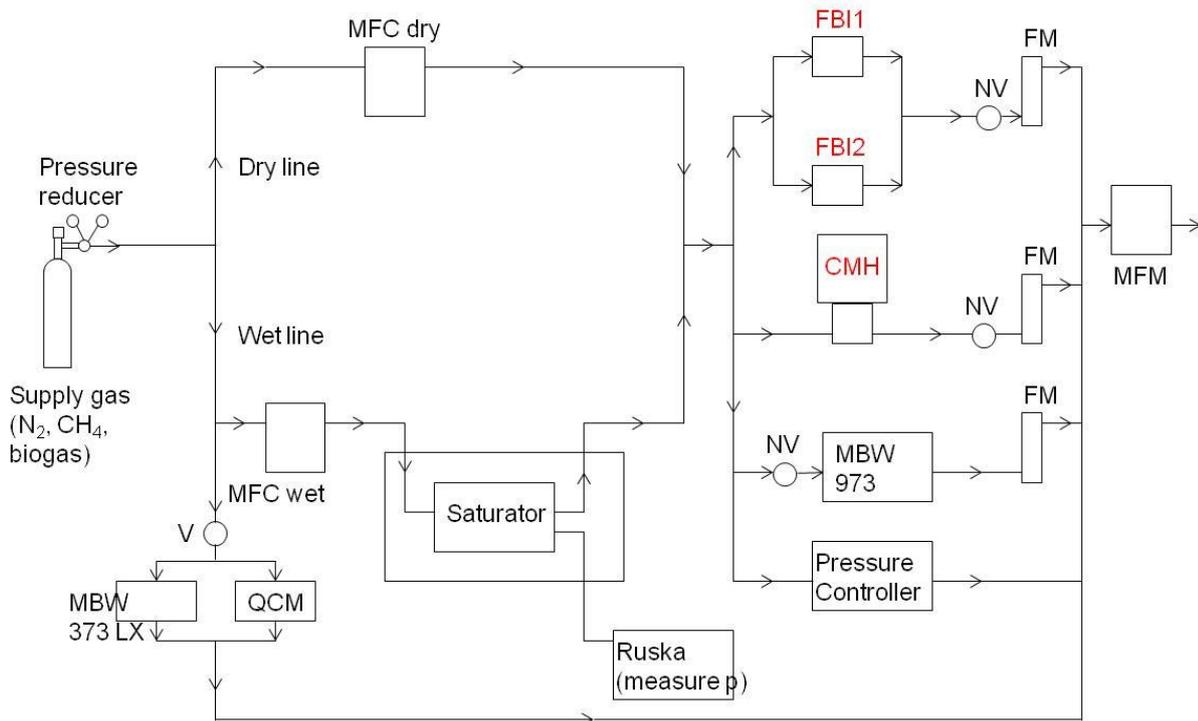


Figure 18 -- Outline of the experimental setup in Run 1 at VSL (FBI1 and FBI2 are the two Fabry-Perot Interferometer devices, CMH is the chilled mirror hygrometer)

For the low-pressure region and high methane content (i.e. low content of carbon dioxide) the behaviour of the biogas mixtures is similar to simple and well-known systems such as air/water or methane/water. The non-ideality increases with increasing content of carbon dioxide in the mixture. For binary systems, equations like Greenspan, VTT MIKES or the proposed approach by PTB seem to be sufficient.

3.2.2 Particulate content

Among other parameters, the specification for biomethane and upgraded biogas requires that the gas should be particle free. At the moment, however, the particle concentration of biogas is not monitored. Three

National Metrology Institutes (NMIs) took part in this study, namely VTT Technical Research Centre of Finland Ltd Centre for Metrology MIKES (VTT MIKES) in Finland, Laboratoire National de Métrologie et d'Essais (LNE) in France and TÜBİTAK National Metrology Institute (TÜBİTAK UME) in Turkey. LNE determined the concentration and size distribution of particulates in one real gas sample using AFM, SEM and STEM and a gravimetric technique. TÜBİTAK characterised particles in one real gas sample for count and size distribution using SEM. Using AFM and a gravimetric technique VTT studied the efficiency of monitoring the pressure drop across a filter as a quality control method for particulates in a biogas line. LNE determined the most appropriate sampler design and sampling conditions (e.g. flow rate during sampling, size of the sample, adapted support) which can be used to produce a statically representative sample of the particle content.

Biogas was sampled at GASUM Kujala biogas production and refining plant in Lahti (Finland) where biogas is produced from bio-waste material. Both raw (unprocessed) and processed biogas was sampled into sample cylinders for further laboratory analysis using Scanning Electron Microscopy (SEM) and aerosol measurement instrumentation (Electrical Low Pressure Impactor, ELPI). In addition, the particle size distribution and concentration of raw biogas was measured on-site using ELPI and particles from raw biogas was sampled onto mica substrates for SEM analysis in the lab.

The ELPI laboratory measurements of bottled biogas indicate that the particle concentration of biogas is very low. The particle concentration of processed biogas cannot be distinguished from the concentration of laboratory air that has been sampled through a High Efficiency Particle Filter (HEPA) (Figure 19). In case of raw biogas, the particle concentration was an order of magnitude higher than for processed biogas, but still more than a magnitude lower than the particulate concentration of laboratory air. Due to the low particulate content, representative samples for SEM analysis could not be obtained.

On-site measurements with ELPI show that in reality the particle concentration of raw biogas is about 10 times higher than that measured in the laboratory (Figure 20), indicating that particulate losses caused by sampling biogas into cylinders are considerable. Despite this, the particle size distribution is well preserved and resembles the distribution found in the sample cylinder (results not shown here). Anyway, on-site measurements verified that the particulate content of raw biogas is very low, on average 2 000 particles per cubic centimetre, which was roughly one tenth of the ambient concentration during the measurements. ELPI and SEM measurements showed that most of the particles were below 100 nm in size.

This study showed that the particulate content of biogas produced at the Kujala plant is very low even before any processing (wet-scrubbing, filtering etc.). Based on these findings, measurement based quality control of particulate content might not be necessary in this case. However, the particulate content probably depends on the biogas production process and therefore, the particulate content should be assessed for every process separately. In any case, the particles are effectively removed by installing a HEPA filter in-line. Measurements of particle concentration should preferably be performed on-site, because sampling into gas cylinders results in significant particle losses. Moreover, on-site measurements using real-time aerosol measurement instrumentation, such as the ELPI, give an insight into the time dependent behaviour of the particle concentration in the process.

Particulate content of biogas (sample cylinder)

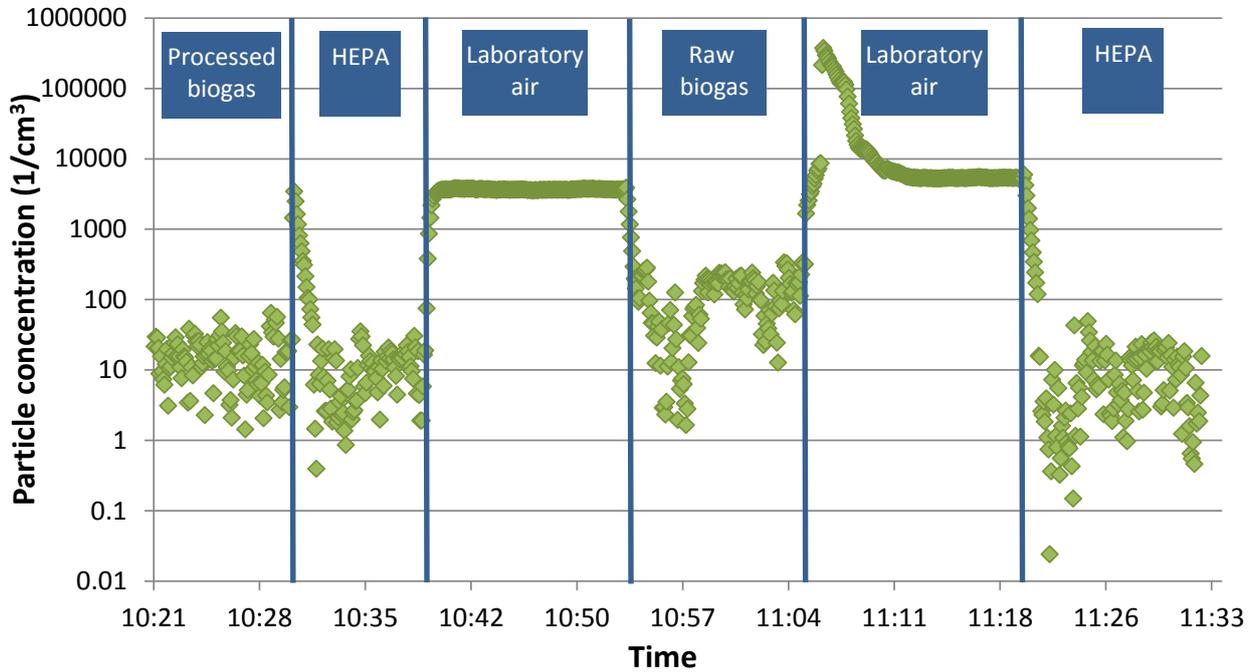


Figure 19 – ELPI results from laboratory measurements of particle number concentration of raw- and processed biogas samples. Particle concentration of laboratory air and HEPA filtered laboratory air is shown for comparison

Particulate content of raw biogas (on-site)

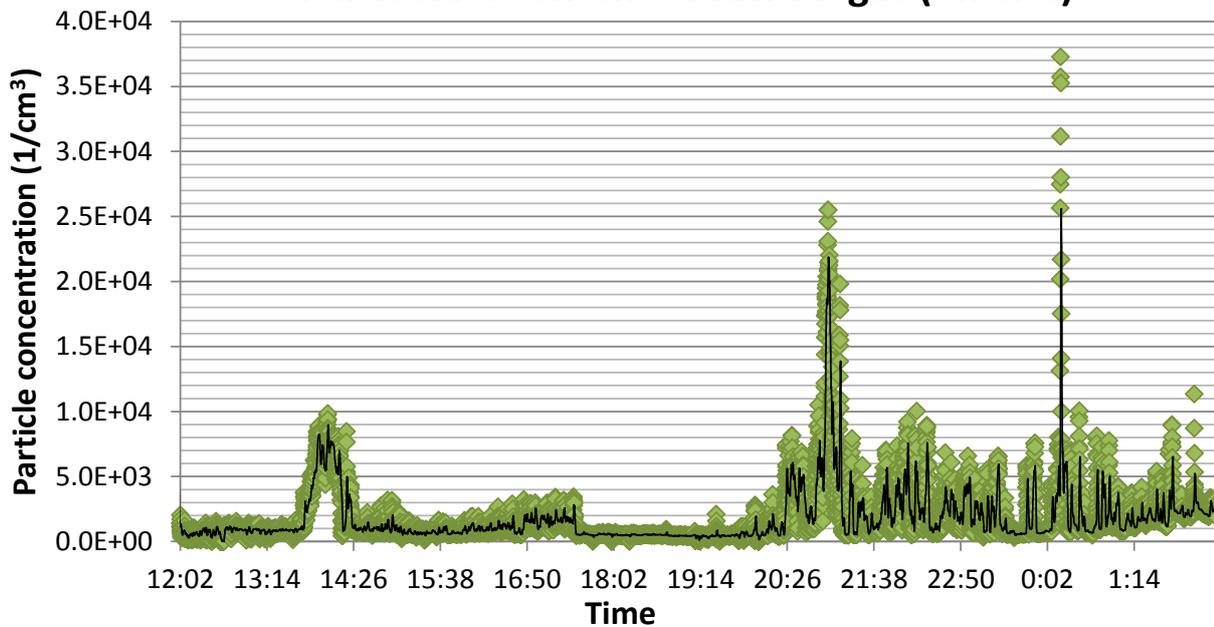


Figure 20 – Particle number concentration of raw biogas measured on-site. The solid line shows a 1 min moving average

3.3 Objective 3: To develop and validate methods for the measurement of calorific value, heat capacity, and density of biogas and biomethane.

3.3.1 Calorific value

The objective of this task was to provide the necessary gas mixtures for a successful execution of Task 4.2, i.e. calorimetric (direct) and analytic (indirect) determination of the calorific value (cf. Figure 3) of biogas and biomethane (upgraded biogas) using field and reference calorimetry and gas chromatography. The competence of NPL and VSL for the gas chromatographic analysis of biomethane alike mixtures has recently been proven by a key comparison. Reference calorimetry was performed at PTB and LNE, field calorimetry at PTB. The two field calorimeters employed, i) Cutler-Hammer calorimeter and ii) Union Instruments CWD 2005 calorimeter, require calibration by means of suitable calibration gas mixtures.

Seven ternary calibration gas mixtures were defined by PTB, RMG(Funge) and LNE with the aim to allow the separation of the influence of differing chemical and thermophysical properties on the measured values, in particular hydrogen content, calorific value, Wobbe number, density under standard conditions, and viscosity:

- Gases WP12-2, WP41-1, WP41-2 have the same calorific value, but different densities, Wobbe numbers and viscosities.
- Gases WP12-1, WP41-3, WP41-4 have the same density, but different calorific values, Wobbe numbers and viscosities.
- Gases WP31-1, WP41-3, WP41-4 have similar viscosities, but different calorific values, Wobbe numbers and densities.
- Gases WP12-2, WP41-3 have the same Wobbe number, but different calorific values, densities and viscosities.
- Gases WP41-1, WP41-3, WP41-4 have the same methane content, but different carbon dioxide contents, calorific values, Wobbe numbers, densities and viscosities.
- Gases WP12-2, WP41-3 have similar carbon dioxide contents, but different methane contents, calorific values, Wobbe numbers, densities and viscosities.

These gases were prepared gravimetrically by NPL and VSL at an uncertainty level of 0.1 %.

Table 1 – Selected biogas and biomethane sampling sites

Production site	Product	Raw Material	Sampling Pressure
Falköping (Sweden – 120 km NE from Gothenburg)	Biomethane	Household wastes, professional kitchen	100 bar
Vårgårda (Sweden – 80 km E from Gothenburg)	Biomethane	90% manure (cow, pig, fowl) and 10% slaughterhouse wastes, silage	100 bar
Lille (France – 230 km N from Paris)	Biomethane	Household wastes -food and wood wastes	50 bar
Kouvola (Finland – 140 km NE from Helsinki)	Biogas	Local wastewater sludge and separately collected biowaste, sludge and energy crops	5 bar

Seven potential biogas and biomethane sources were identified, of which four were finally selected, cf. Table 1. The sampling process must not alter the properties of the sampled gas, thus, the biogas was transferred to 50 l bottles at 4 bar by VTT MIKES, which rendered just enough gas for the field calorimeters, but it proved to be nearly too little for the LNE reference calorimeter. The biomethane from France could be filled into standard 5 l bottles, the biomethane from Sweden required a special sampling system developed at RISE for safe use at filling stations (Figure 21).

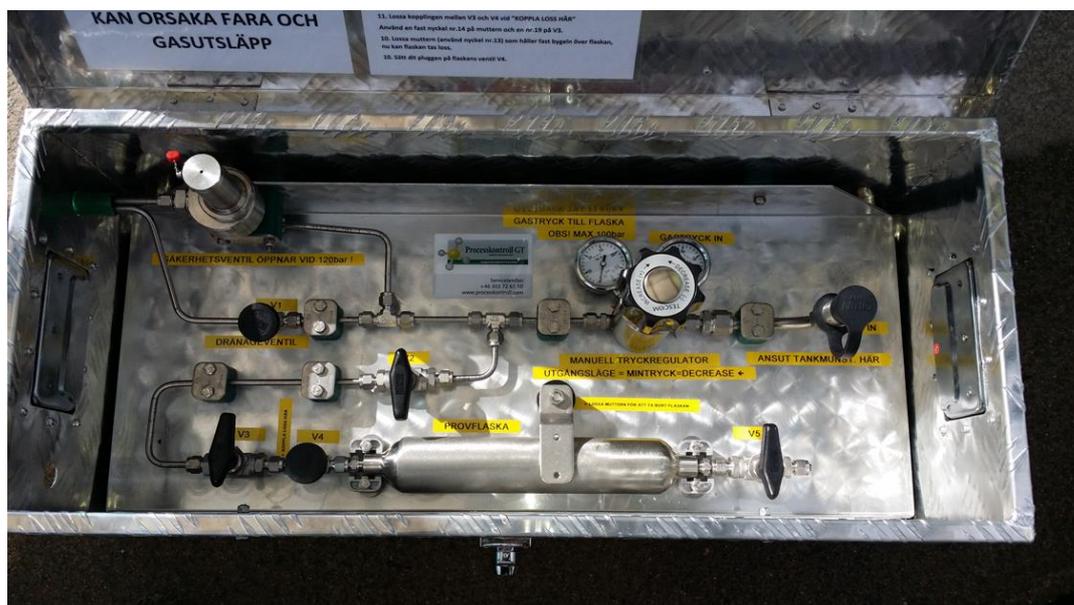


Figure 21 – The sampler developed at RISE for the safe sampling of biomethane at filling stations into 0.3 l stainless steel bottles

Three real biomethane samples and one real raw biogas sample have been tested by calorimetry and calorific values have been calculated from measurement series. Two of the biomethane samples have household wastes source (Falköping in Sweden and Lille in France), one biomethane has manure and slaughterhouse wastes and the raw biogas from Finland has local wastewater sludge and energy crops. Complete sampling systems have been developed at RISE and LNE for the project to sample the biomethane samples.

PTB with the help of RMG(Funge) calibrated the field calorimeters using seven reference mixtures prepared by NPL and VSL with different thermophysical properties (focusing on calorific value, density and viscosity). PTB and RMG(Funge) improved the calibration process with the aim of reducing the uncertainty of the instruments taking into account the calibration procedure, the calibration frequency, the number of calibration gases, the composition of the calibration gases and the evaluation algorithm. Two different calibration standards (DIN 51899 and ISO 6143) were applied to both calorimeters.

Calorific values of the real samples have been calculated and compared with all of the calorimeters used. For the biogas sample, the reference calorimeter at LNE has been adapted by modifying the experimental conditions by, among others, reducing the combustion period to 3 minutes. Unstable ignition and extinction conditions caused biased measurements and the calculations led to large standard deviations and a higher uncertainty on the calorific values. Nevertheless, the calculated calorific values agreed within their combined uncertainties for the biogas sample and a mean value of 20 057 kJ·g⁻¹ has been calculated. Uncertainties range from 0.2 to 2.6 ($k = 2$).

For the biomethane samples where only reference calorimeters have been tested, a conditioning problem on one sample has been observed at a level of tightness leading to a discrepancy in the calorific values. For the other Swedish biomethane sample, there is a very good agreement on the calorific values performed at PTB (9 experiments) and LNE (4 experiments) for one cylinder and the total combined uncertainties are in agreement with the objective initially claimed (between 0.1 % and 0.4 %, $k = 2$). After carrying out series of experiments on the different batches of biomethane samples, it turned out that sampling one unique bottle with enough pressure and volume ensures traceable and reliable comparison between laboratories through exchanging the sampling material or preparing smaller samples from the parent cylinder. That issue has been observed for the third biomethane sample.

The results obtained have been presented in different international conferences like the International Conference on Chemical Thermodynamics (2014), the Gas Analysis Symposium in 2015, EGATEC 2015 or the International Congress of Metrology in 2015. Results have also been presented at national events in Germany. One paper on the traceable measurement of the calorific value of real biogas is ongoing to be submitted for publication in the peer-reviewed journal *International Journal of Thermal Sciences*.

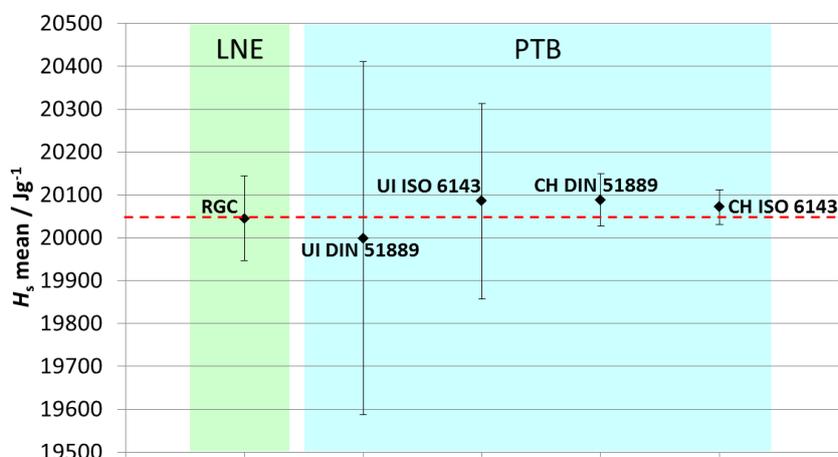


Figure 22 -- Superior calorific values and corresponding uncertainties in J g^{-1} for the biogas sample (CH for Cutler-Hammer, UI for Union Instruments calorimeter and RGC for Reference gas calorimeter)

3.3.2 Heat capacity and density

The objective of this task was to validate the current natural gas reference equations of state for their use with biogas and biomethane. To do that, the thermophysical behaviour of selected binary mixtures, as well as multicomponent biogas and biomethane synthetic mixtures have been experimentally studied in addition to real biogas samples.

The characterisations of all the mixtures prepared by the partners (CEM and SMU) have been concluded. The characterisations consisted of the determination of their density (REG(Funge) and SMU; Figures 21 and 22) and the isobaric heat capacity (REG(Funge)) allowing the complete knowledge of the thermodynamic behaviour and to accurately predict all the thermodynamic properties related with them.

Experimental densities of the synthetic biogas-like mixtures have been compared with the densities calculated from the GERG-2008 equation of state, which is the current reference equation of state for natural gas and related mixtures. Relative deviations between experimental data and estimates are within a $\pm 0.2\%$ band. However, data at $T = 275\text{ K}$ showed larger deviations up to 0.41% at pressures from (6 to 15) MPa. The results obtained are within the limits of uncertainty claimed by the GERG-2008 equation of state, which is up to 0.1% ; approximately 60 % of the measured data are below this limit. However, for mixtures with a high content of carbon dioxide, the deviations from the equation of state can be higher than 0.3% , but this fact has been registered only at the temperature of 275 K and pressures around 10 MPa.

The speed of sound behaviour of the biogas-like mixtures is closer to that modelled by GERG-2008 at intermediate temperatures and pressures ($p \approx 6\text{ MPa}$ and $T = 300\text{ K}$), but smoothly tends to disagree at both low temperature and high pressure ($p \approx 12\text{ MPa}$ and $T = 273\text{ K}$). The same can be observed at the reverse state, high temperature and low pressure ($p \approx 1\text{ MPa}$ and $T = 325\text{ K}$), with deviations up to 1 part in 10^3 . Although, measurements are within the limits of uncertainty stated by the GERG-2008 in most cases, up to 0.1%

It is important to highlight that a comparison between the density measurements performed by REG(Funge) and SMU have also been carried out with perfectly compatible results and with no discrepancies with the results predicted by the GERG-2008 equation of state. The successful results of this comparison have ensured the reliability of this task outputs.

The results obtained have been presented in different international congresses like the 19th Symp. Thermophysical Properties (Boulder, CO, USA, June 2015) or the 11th Asian Thermophysical Properties Conference (Yokohama, Japan, October 2016). At the moment five papers have already been published in peer reviewed journals and one more is waiting for publication. A PhD thesis was also presented in February

2016. Other dissemination activities have been also carried out at a national level, like the publication of two articles in trade/professional press, in order to increase the impact of the findings among the non-metrological community.



Figure 23-- SMU primary standard densimeter



Figure 24 -- REG(Funge) Single sinker densimeter with a magnetic coupling



Figure 25 -- REG(Funge) Isothermal spherical resonator

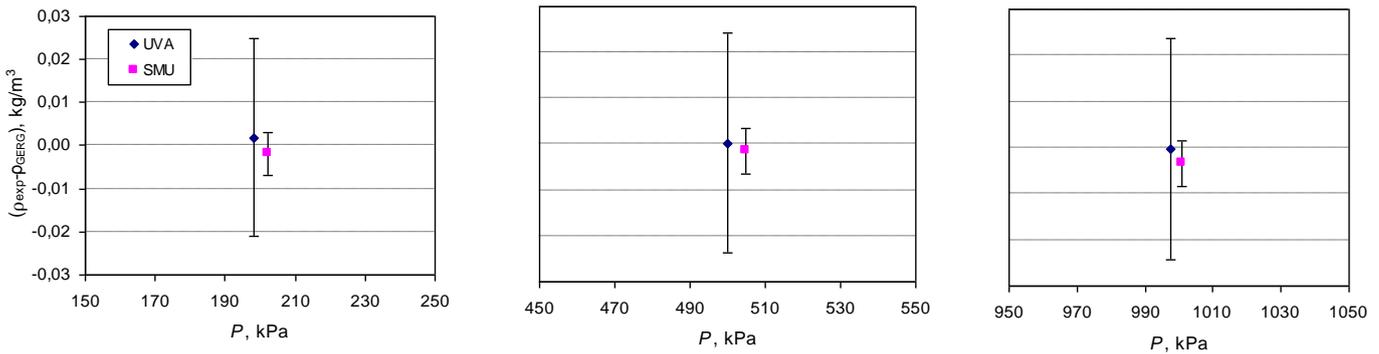
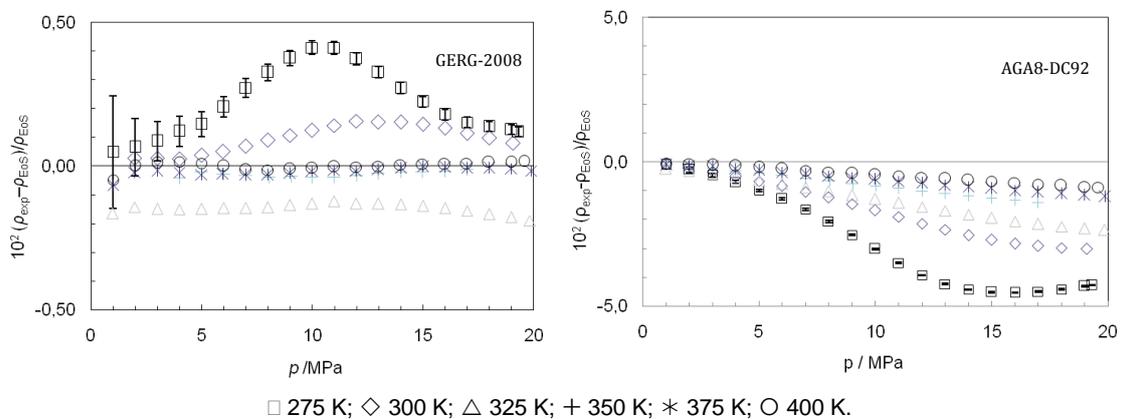
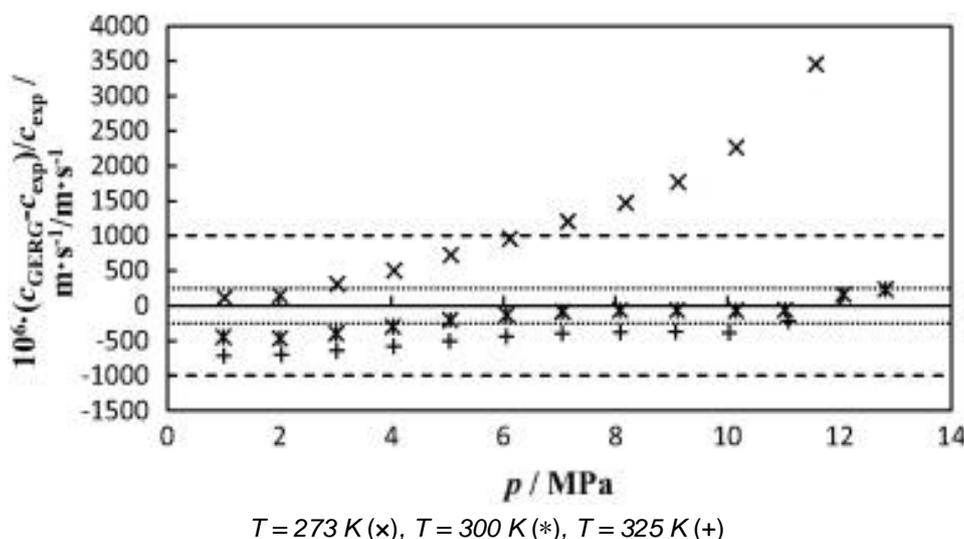


Figure 26 -- Result on the density comparison (measurements performed in a synthetic biogas mixture prepared by CEM)



R Hernández-Gómez, TE Fernández-Vicente, MC Martín González, ME Mondéjar, CR Chamorro
Integration of biogas in the natural gas grid: Thermodynamic characterization of a biogas-like mixture
 (2015) The Journal of Chemical Thermodynamics 84, 60-66.

Figure 27 -- Results of density measurements performed on CEM biogas-like mixtures



$T = 273 \text{ K} (\times), T = 300 \text{ K} (*), T = 325 \text{ K} (+)$

Lozano-Martín, D., Segovia, J.J., Martín, M.C., Fernández-Vicente, T., del Campo, D.
 Speeds of sound for a biogas mixture $\text{CH}_4 + \text{N}_2 + \text{CO}_2 + \text{CO}$ from $p = (1-12) \text{ MPa}$ at $T = (273, 300 \text{ and } 325) \text{ K}$ measured with a spherical resonator. (2016) *The Journal of Chemical Thermodynamics*. 102, pp. 348-356

Figure 28 -- Results of isobaric heat capacity measurement performed on CEM biogas-like mixtures

3.4 Objective 4: To develop a traceable method for determining the concentration of biomethane in samples of blended biomethane and natural gas.

The aim of this task was to develop and validate techniques for determining the biogenic methane concentration in a mixed gas sample. Isotopic composition carries information about the origin of methane. For example the radiocarbon ^{14}C isotope is depleted in natural gas due to radioactive decay, whereas biogenic methane contains close to ambient levels of newly produced ^{14}C . Radiocarbon analysis is a straightforward and accurate method for determining the age of the sample gas. The challenge arises from the low abundance of the radioactive isotopologue in the sample, thus requiring complex sample pre-treatment and detection routines.

VTT investigated the feasibility of using optical techniques for biogenic methane detection, by developing and validating an optical instrument for the detection of stable isotopologue ratios $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$ in methane. NPL prepared and validated traceable gas mixtures of ^{14}C -enriched methane in methane. These mixtures were used to validate a liquid scintillation counting analysis method, which was then used to perform the measurement of the ^{14}C content of samples of mixed biomethane and natural gas. TUBITAK used gas chromatography - isotope ratio mass spectrometry (GC-IRMS) to study the applicability of stable isotopologues of methane for the determination of the fraction of biomethane in mixed bio/fossil methane samples. HCP developed a tuneable mid-IR laser module, followed by the development of a sensing subsystem incorporating the developed laser module, an optical gas cell and an IR detector. These were used for measurements of the $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$ ratios of CH_4 .

The work on $^{14}\text{CH}_4$ confirmed that this method was ready for use and met elementary requirements of metrological traceability. This method has been in use for the determination of the biogenic methane content in blends of biomethane and natural gas. The prime focus was on developing an alternative route, based on the stable isotopologue ratios $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$ in methane. The principle was assessed based on spectroscopic measurements (Figure 14). The linearity of the method was also confirmed.

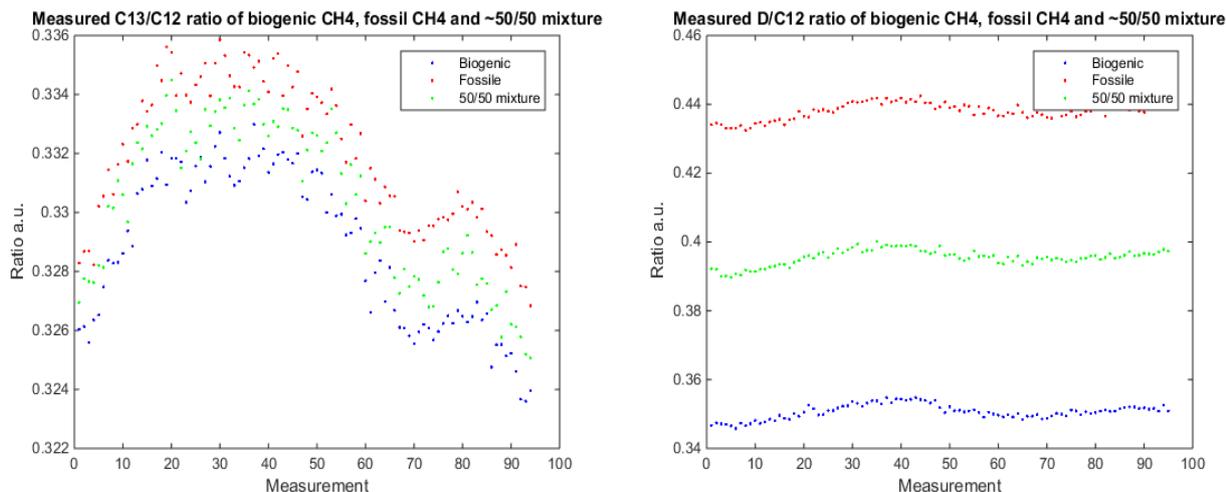


Figure 29 – Measured stable isotopologue ratios $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$ in natural gas, biomethane and a 50 %/50 % blend

An issue with both methods is the (assumed) background in natural gas and biomethane. This problem is larger for the method based on stable isotopologue ratios $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$, but not absent for the $^{14}\text{CH}_4$ method, for the contents of this isotopologue in biomethane and upgraded biogas which also varies from source to source.

3.5 Objective 5: To develop robust methods for sampling biogas and biomethane in the field, and to enable the biogas industry to perform robust and traceable quality assurance measurements.

The literature survey conducted by RISE, NPL and VSL on biogas and biomethane sampling pointed out that a combination of vessels is likely to be required to cover the wide range of impurities which have a wide range of boiling points, polarities, water solubilities, and reactivities (with the matrix and the impurities present in biogas). The choice of the sampling vessel to be used should be made only after fully assessing its short-term stability with respect to the component(s) of interest. The suitability of a vessel for a given compound or group of compounds is often assessed by measuring the recovery yield or the storage stability for a given compound. The recovery yield is defined as the ratio of the measured and the spiked content and it is expressed as a percentage. The storage stability is defined as the change in content for a given compound as determined at the end of the storage time compared to that determined at the start of the stability test.

After the literature survey, short-term stability studies for the storage of siloxanes, sulphur compounds, BTEX (Benzene, toluene, ethylbenzene and xylenes), halogenated hydrocarbons, ammonia and carbon monoxide were performed in cylinders (treated and untreated), sorbents and gas bags. The work was jointly undertaken by RISE, IMBiH, NPL, REG(INERIS) and VSL. The results of these short-term stability studies have been summarised. Several days storage of biogas or biomethane in gas cylinders appeared to be a reliable alternative if the gas is sampled at a relatively high pressure (> 50 bar) but may require several cylinders with different passivation treatments to store the different families of impurities to be analysed when assessing biomethane quality. At low pressure (less than 10^{-2} bar), adsorption effects on the inner surface of the cylinder were observed leading to an under-estimation of the concentration of targeted compounds.

Sorbents such as Tenax TA also appeared to be a reliable alternative for many compounds to be assessed in biogas/biomethane as they had good storage stability for a period of up to a week. However, these sorbents cannot be used for compounds with boiling points below 50 °C. Adsorption effects were observed for many components when using bags for the sampling of synthetic biogas. These effects are dependent upon the concentration of the compounds, and the more pronounced at lower concentrations. However, bags may also be a reliable alternative if analysis is performed shortly after the sampling (preferably in the next hours).

The presence of water when storing biogas will most certainly impact the storage stability of compounds in most vessels as compounds may to some extent dissolve in condensed water resulting in lower storage

stability than under dry conditions or alternatively water could compete with targeted compounds for adsorption on active sites of the vessel inner surfaces, which would result in higher storage stability than under dry conditions.

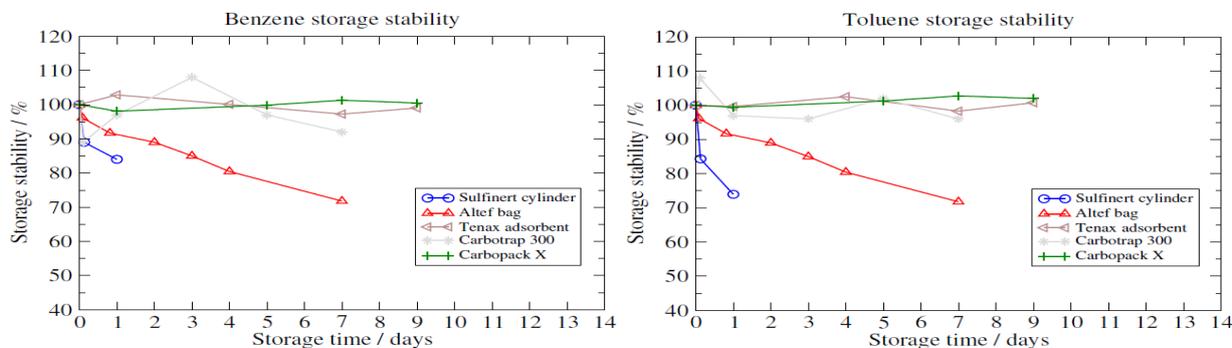


Figure 30 -- Short-term stability study results for benzene and toluene

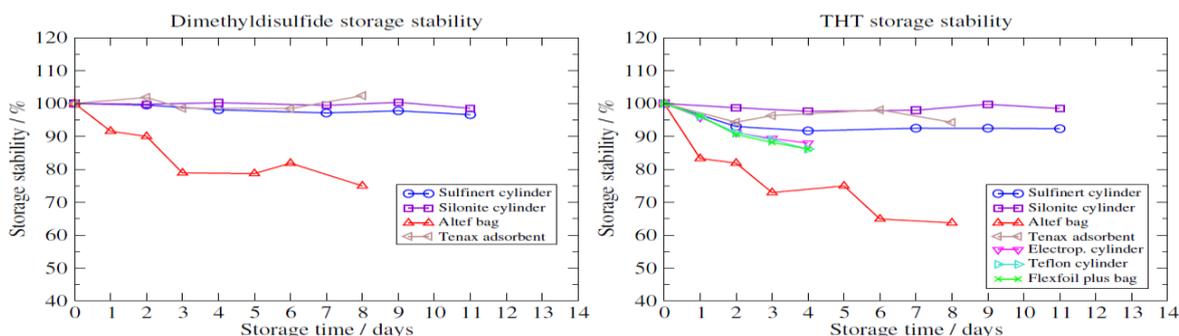


Figure 31 – Short-term stability results for dimethyl sulphide and tetrahydrothiophene

One of the greatest challenges with sampling is to collect biogas and biomethane samples so that the composition of the samples does not change between the time of sampling and the analysis. Biogas as well as air is a relative complex matrix due to the fact that all kinds of chemical compounds are present therein (organic and inorganic): dust, particulate matter, water vapour, aerosols etc. Biogas is, generally, very humid and this point should be addressed. The current standard for sampling natural gas (ISO 10715) provides very little guidance with respect to sampling natural gas, biogas and biomethane for impurities.

For sampling to be performed without altering the composition of the biogas, it is necessary to control the conditions at the facilities so that they comply with the requirements of the sampling techniques. Relevant parameters to be checked are, for example pressure, volume, flow and temperature.

In many production sites, taking samples may be challenging because of the lack of adequate sampling points or the relative low pressure at which these facilities operate. During this project, five facilities located in the south of Sweden were visited in order to identify the existing sampling points and the conditions (working pressure, temperature, flow, existing connections) which prevail at these sampling points.

The results of this study, conducted by RISE, LNE and INERIS, showed that facilities already had a number of sampling points at different stages of the process but their location did not always allow us to work in convenient conditions because of the height, the lack of space and the configuration. Most of the sampling points were located outside which implies that the person performing the sampling must evaluate the weather so it does not affect the sampling (e.g. high humidity).

For biogas and biomethane before compression, the pressure prevailing at sampling points has been identified as the critical parameter. Some analysers in the lab required the gas to be sampled at several bar while facilities often operate at low pressure (mostly for biogas). However, local consumption of biomethane in the vicinity of the plant is common and a pipe is laid from the production plant directly to one or more users. In that case, the biomethane is compressed up to a pressure of 200 bar.

For biogas, the flow (often more the 100 m³/h, 6 L/min) and the temperature (often from 10 °C to ambient temperature) prevailing at sampling points are not likely to be an issue for many analytical techniques.

The requirements for all of the analysis methods used in this project to assess the chemical or physical properties of biogas have been listed with regard to the sample media used, the connection between the sampling media and the instrument, the transfer to the instrument and the volume and pressure required.

In order to sample biomethane at 200 bar, RISE has developed a sampler that allows biomethane or CNG/biomethane to be sampled directly from a dispenser. This sampler can be used to take the biomethane samples for the analysis of both impurities and physical properties. The sampler is equipped with a 300 ml-cylinder having a maximum working pressure of 100 bar. The cylinder has two ball valves, one at each end as well as a needle valve. The cylinder and the three valves are mounted and certified according to the TPED (Transportable Pressure Equipment Directive 2010/35/EU). This part can easily be removed after sampling and sent to laboratories.

A good practice guide describing how to handle vessels commonly used to sample impurities in biogas has been produced. Vessels covered in this report are sorbent tubes, bags and cylinders. Aspects such as vessel conditioning or cleaning prior to sampling, labelling, transport and how to perform the sampling were thoroughly described in the report.

Finally, a report describing protocols for sampling at biogas facilities with a focus on spot sampling (indirect sampling onsite before transport to the lab) was written. Direct sampling and incremental sampling were not considered in the report. As part of this report, the applicability of ISO 10715 for biogas/biomethane was discussed. The feed stocks used for producing biogas differ substantially, as do the processes for producing the biogas and upgrading it to biomethane which means that a larger number of parameters than for natural gas need to be specified, in particular with respect to critical impurities. In addition, aspects specific to biogas sampling; such as the sampling of impurities; that are therefore not included in ISO 10715, were then discussed.

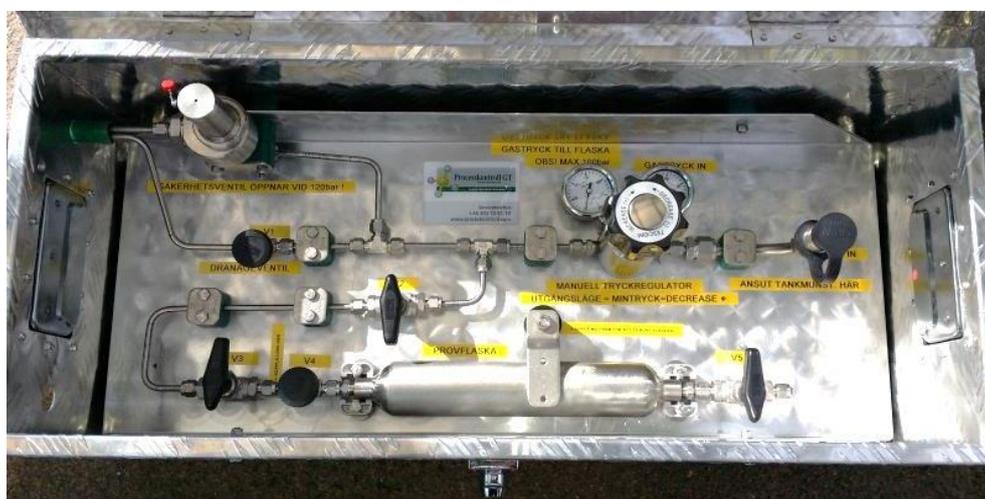


Figure 32 -- Sampling being performed at a refuelling station



Figure 33 -- removable part of the sampler

4 Actual and potential impact

Dissemination

32 presentations on calorimetry, calorific value, density and heat capacity were given at conferences such as the International Congress of Metrology, Conference of the European Biogas Association and Biogas Science. Fifteen articles were published in peer-reviewed journals such as The Journal of Chemical Thermodynamics and Analytica Chimica Acta.

An e-learning course entitled 'Metrology for Biogas' was developed, and this aims to make the work of the project more accessible to industry and end users such as biogas producers and transmission companies, helping them to comply with regulations. The course is available on the NPL website.

Four training courses on various aspects of biogas analysis were run for external delegates from industry, higher education and public research organisations.

Early impact

This project created an infrastructure for delivering calibration services and certified reference materials (CRMs) for the contents of key impurities (siloxanes, sulphur-containing components, aromatic hydrocarbons, halogenated VOCs, ammonia, hydrogen cyanide, carbon monoxide and hydrogen chloride) in biomethane and upgraded biogas at relevant content levels with established metrological traceability and known uncertainty. Laboratories will be able to use these services and CRMs provided by the partners for developing and delivering measurement services to the industry for the conformity assessment of biomethane and upgraded biogas in accordance with EN16723-1 and prEN16723-2. The methods for particulate matter and water content will enable laboratories to deliver corresponding services to the biogas producers and upgraders.

Companies and other organisations will be able to use the new measurement capabilities at NMIs to test and validate instruments, processes and methods. This will mean that calibration work based on the new measurement capabilities will be available at NMIs/DIs as a result of the project.

The work on field calorimetry will enable biogas producers and grid owners to use field calorimeters with known performance as an alternative to gas chromatography. This provides benefit, especially to small biogas producers, as the costs of ownership of gas chromatographs is high.

The dedicated models and methods for water dew point will enable the industry to rely on measurement results with similar accuracy to those in conventional natural gas. The water content will be measured more reliably and accurately than is currently possible. This in turn will enable the gas treatment to be optimised so that the water dew point specification can be reliably met, without drying the raw biogas any more than is needed.

Contribution to standards

The work of the project provided input to the following draft documentary standards:

- ISO/C 158 Analysis of gases
- NEN 310 408 Biomethane (Netherlands Standards Institute)

A new working group WG25 Biomethane was formed by the consortium, CEN/PC 408 and ISO/TC193/SC1, to work on the standardisation of test methods for the conformity assessment of biomethane and upgraded biogas. It will use the work on impurities (siloxanes, sulphur-containing components, aromatic hydrocarbons, halogenated VOCs, ammonia, hydrogen cyanide, carbon monoxide and hydrogen chloride) to develop ISO-methods, supporting the European specification EN 16723.

A best practice guide (available from the project website) about sampling and sample collection was written. ISO/TC193/WG20 is interested in using these results to feed into the revision of ISO 10715 (Natural gas -- Sampling guidelines). This written standard is being updated and extended to cover, among others, the sampling of biogas, biomethane and upgraded biogas for, e.g. impurities.

The experience on working with dynamic methods for calibration gas mixture preparation is being shared with ISO/TC158/WG5 in preparation for the further development of the ISO 6145-series of standards.

Future potential impact

The standardisation committees, will benefit through project reports, method descriptions and other building blocks that foster standardisation of measurement methods to support the specification for biomethane.

Equipment manufacturers will benefit from the project's results in that the novel measurement methods will direct their research and development activities towards new or improved technological solutions for measuring biomethane quality.

The Member States of the EU will benefit from this project in particular through the improved access of green gas to the national natural gas grids. This access is a prerequisite for the expansion of the biogas-producing community in order to meet the targets of the Renewable Energy Directive. The increased use of biogas adds to the diversification of sources of natural gas from non-conventional sources, which has a stabilising effect on both the supply and the natural gas price, because of a reduced dependence on imported gas.

The increased use of biogas and biomethane will help to reduce the emission of greenhouse gases, as biogas is produced from renewable sources, such as organic waste, landfills, or manure. Biogas does not compete with food and feed production with regard to its feed stocks. It can be transported in an environmentally friendly way through existing natural gas grids.

This project output will allow producers to reduce biogas upgrading costs by optimising these processes so that they are adjusted to what is actually needed to meet the specifications, thereby optimising revenues. A reduction in the production and upgrading costs of between 10 % - 30 % is possible. These developments will foster growth in the production of non-conventional energy gases from renewable sources by 50 % over the next 5 years. This growth in turn will reduce the dependency of the EU on imported natural gas and it will have a stabilising effect on energy prices for industry and consumers.

5 Website address and contact details

A public website has been open, where the main public deliverables have been made available for the end-users: to keep them informed about project meetings and events: <http://projects.npl.co.uk/metrology-for-biogas/>

The contact person for general questions about the project is Dr. A.M.H. van der Veen, VSL (avdveen@vsl.nl).

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<http://dx.doi.org/10.1016/j.jct.2016.01.020>

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