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1 Overview

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

2 Need

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

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

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

3 Objectives

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

The specific objectives of the project were:

1. To improve the long-term stability (2-3 years for static standards) of the measurement standards and the performance of related calibration methods that are used in the measurement of the contents of VOC impurities in biomethane (*i.e.* the target relative expanded uncertainties are 3 % for total silicon and siloxanes, 3 % for halogenated VOCs, < 4 % for terpenes, and 5 % for amines).
2. To improve the long term stability (2-3 years for static standards) and the performance (*i.e.*, by eliminating biases in the instruments' readings caused by biomethane, for dynamic standards based on ISO 6145 methods) of the measurement standards and the related calibration methods that are used in the measurement of the contents of corrosive impurities and compressor oil in biomethane (*i.e.* the target relative expanded uncertainties are 3 % for ammonia, 3 % for HCl, 10 % for HF, 10 % for compressor oil).

3. To develop and validate novel test methods, based on existing calibration methods, for the regular conformity assessment of biomethane during which the content of total silicon and siloxanes, total fluorine and chlorine, ammonia, terpenes, compressor oil, amines, and biogenic methane (based on determining the $^{14}\text{CH}_4$ content in biomethane and blends of biogas and natural gas) are measured.
4. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (accredited laboratories, instrument manufacturers), standards developing organisations (CEN, ISO) and end users (energy sector, automotive industry).

4 Results

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

This project delivered novel measurement standards and related novel high accuracy reference methods for the content of amines and terpenes in biomethane (such standards did not exist). The lifetime of the measurement standards for measuring siloxanes and halogenated VOCs was also improved from 6 months to 1.5 – 2 years.

Improved stability of siloxane measurement standards

This goal has been achieved as follows. NPL prepared six siloxane reference standards in separate cylinder types and monitored stability over an 18-month period. The mixtures were prepared gravimetrically in a two-step process in accordance with ISO 6142-1. The preparation scheme was designed to minimise the gravimetric uncertainty in the final mixtures. This required conformity with pressure limitations caused by the dew points of the mixtures, so a calculation was performed at each stage to minimise uncertainty. Pure siloxanes L2 (hexamethyldisiloxane), L3 (octamethyltrisiloxane), D4 (octamethyltetra-cyclosiloxane) and D5 (decamethylpentacyclosiloxane) were purity analysed using Gas Chromatography with Flame Ionisation Detection and Mass spectrometry (GC-FID/MS) in accordance with ISO 19229.

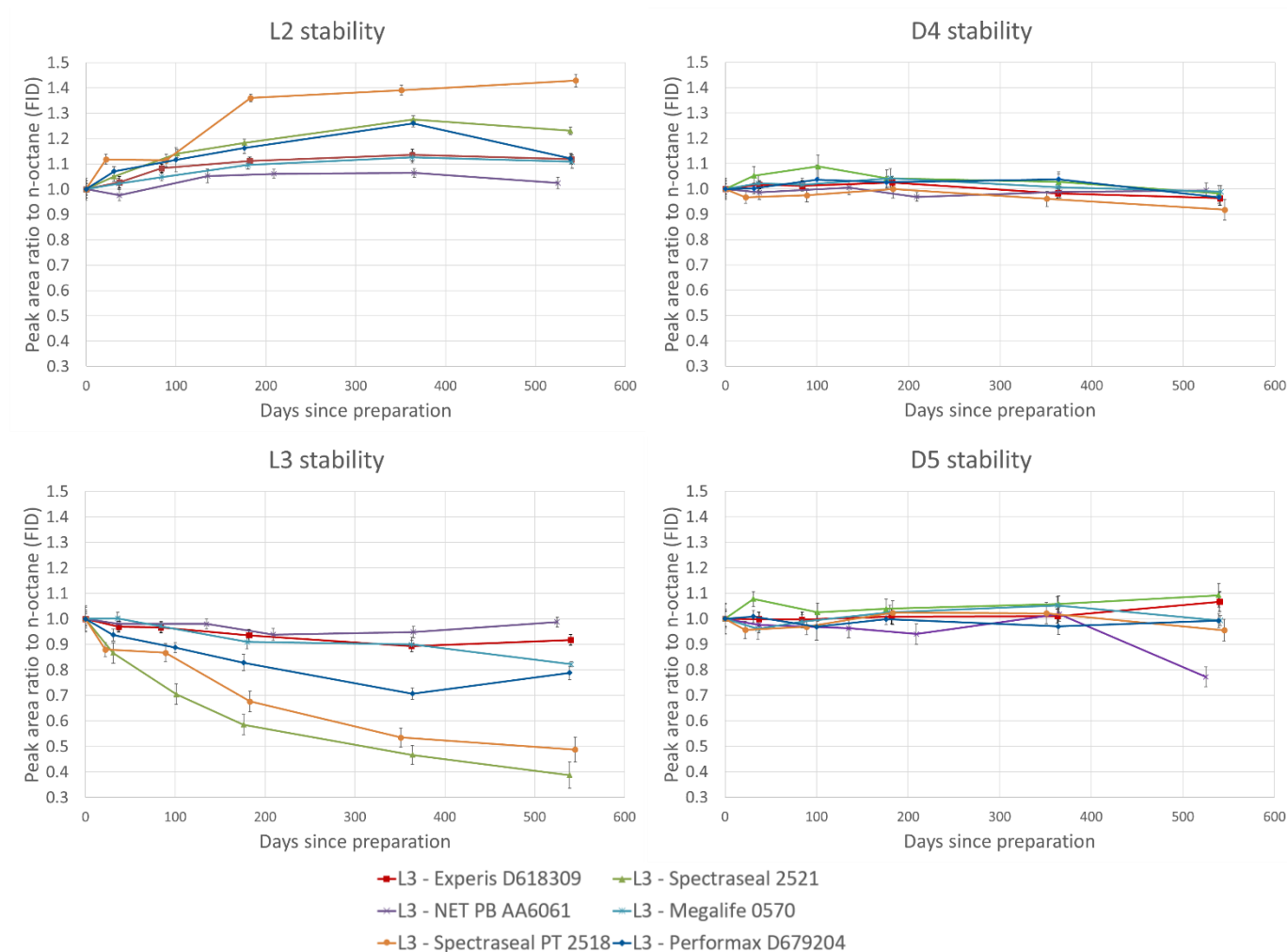


Figure 1: Siloxane stability over the 18-month period for the six cylinders studied

Stability was found to vary according to the cylinder passivation used, with notable variations observed between individual siloxanes. A clear relationship was established between L3 and L2 siloxane amount fractions in static standards, suggesting that decay of L3 and formation of L2 occurs within most cylinder types except for New Energy Technology (NET) PB. Due to this, dynamic standards were found to provide the best accuracy for L3 and L2 quantification when compared to static standards.

Stability study results have highlighted the instability of L3 siloxane in all cylinder types, with the exception of NET PB where L3 was stable within the 3 % target. Evidence for the conversion of L3 into L2 siloxane has been observed. Based on this, inclusion of L3 is not recommended in reference materials unless an appropriate uncertainty is applied to account for this for L3 and L2 (if L2 is also a specified mixture component). The most suitable cylinder type based on the 18-month stability considering all components was found to be Air Liquide Megalife (uncertainty < 18 % for L2 and L3; uncertainty < 3 % for D4 and D5) and the least suitable was found to be BOC Spectraseal PT (uncertainty < 52 % for L2 and L3; uncertainty < 9 % for D4 and D5). Overall the siloxane D4 was found to be the most stable across all cylinder types and is recommended for use in gas reference materials.

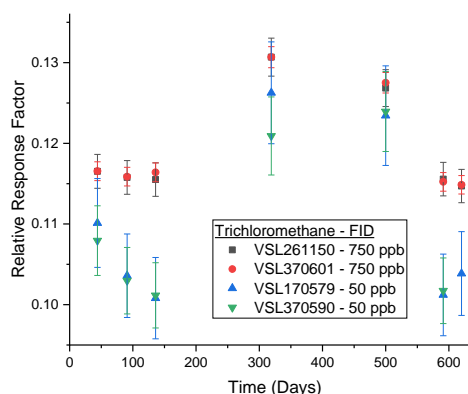
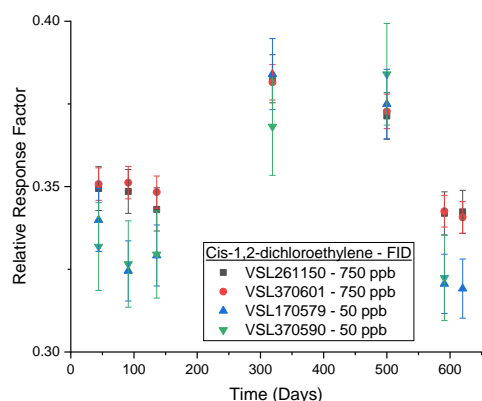
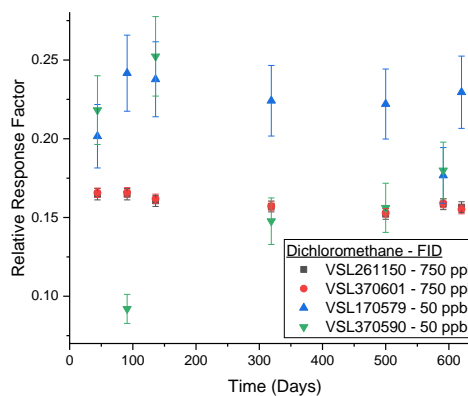
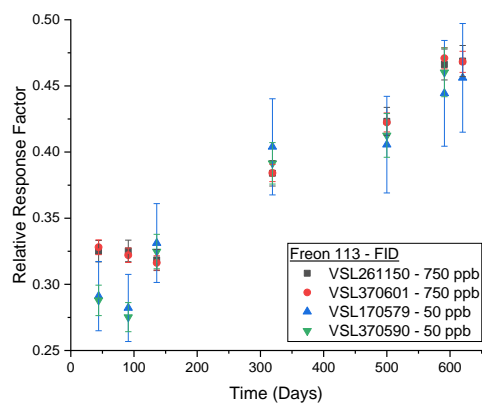
Two calibration methods were developed for the quantification of siloxanes in biomethane at the 0.5 mg m⁻³ concentration level. The expanded uncertainty of the methods was found to be between 2 % and 14 %, with higher uncertainties attributed to lower amount fractions in the nmol mol⁻¹ range.

Improved stability of halogenated VOC standards

Three calibration methods have been developed and validated by VSL, RISE and INERIS. The measurement uncertainties obtained for the methods developed are between 3 % and 10 %. The aim to set-up a high-accuracy analytical method with a < 3 % uncertainty has not been achieved entirely. The methods have been validated with the measurement standard developed by VSL containing 10 relevant halogenated VOCs in methane. The stability and uncertainty of the measurement standards is reported.

Based on stakeholder input, 10 halogenated volatile organic compounds were selected: chloromethane, dichloromethane, cis-1,2-dichloroethane, trichloromethane, trichloroethylene, 1,2-dichloropropane, 1,1,2-trichloroethane, tetrachloroethylene, trichloro trifluoroethane (freon 113) and vinyl chloride. n-hexane was added as an internal standard. Not all relevant halogenated VOCs could be used, as many (especially freons) have been banned.

The gas mixtures were prepared starting from a gravimetrically prepared liquid mixture. This mixture was prepared using a Liquid Mixture Robot (LMR) developed at VSL. The individual components, except for chloromethane and vinyl chloride, were added according to their boiling point in a decreasing order. The prepared liquid mixture contains specific amount-of-substance fractions of the different halogenated hydrocarbons calculated according to ISO 6142-1. All materials used underwent purity analysis as described in ISO 19229. The liquid mixture obtained is injected with a syringe into the cylinder then vaporised and diluted with methane, to obtain mother mixture 1. The mother mixture was diluted in two steps, first 2 gas mixtures with a nominal amount-of-substance fractions of 750 ppb nmol mol⁻¹ for all components were obtained. During this dilution step chloromethane and vinyl chloride which are gases at room temperature were added. Mother mixture 2 was further diluted to obtain 6 end gas mixtures containing amount-of-substance fractions of approximately 50 nmol mol⁻¹ for all components. For this purpose, all the gas mixtures were prepared in cylinders treated with an Experis VOC coating.



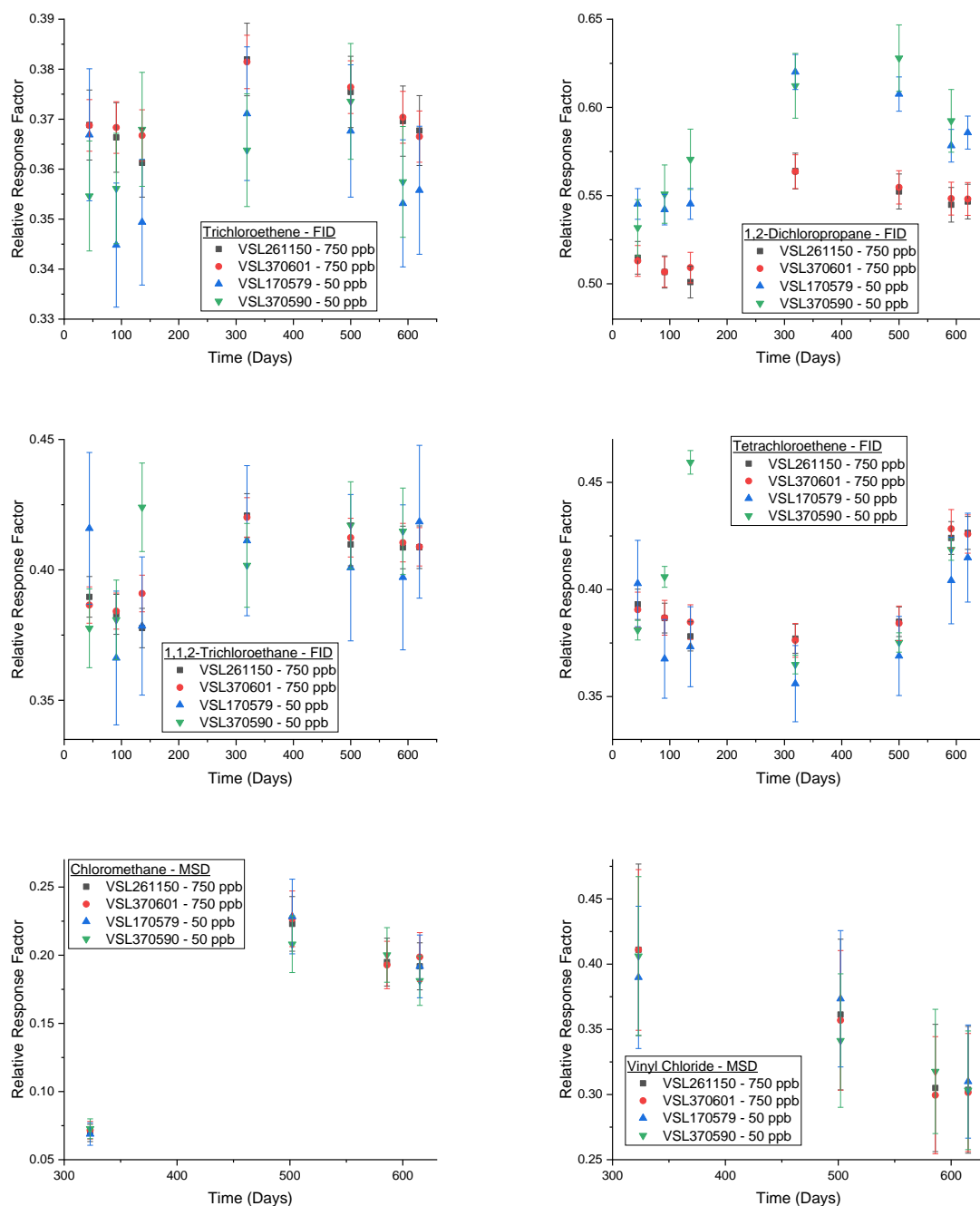


Figure 2: Results of stability measurements at VSL in the period from July 2018 until February 2020.

One of these measurement standards was analysed at RISE after sampling a known volume of the gas onto thermal desorption tubes. The samples were desorbed and subsequently analysed using TD-GC-FID/MS. At INERIS and VSL the measurement standards were connected directly to the TD-GC-FID/MS. After online sampling onto a cold trap the sample was analysed. Furthermore, at VSL a method has been developed using a GC-BID, which does not need preconcentration before analysis. The analysis of 50 ppb chloromethane and vinyl chloride was difficult or not possible using the validated calibration methods.

The measurement uncertainty for the halogenated VOCs using the TD-GC-FID/MS method at RISE was calculated to be around 10 %. At VSL the measurement uncertainty using the TD-GC-FID was determined to be between 3 % and 10 % using the 50 ppb measurement standards. On the other hand, when using the

GC-BID the measurement uncertainty could be decreased to ≤ 3.2 %. The aim to set-up a high-accuracy analytical method with a < 3 % uncertainty has not been achieved.

Both RISE and INERIS determined the stability of the halogenated VOCs in the measurement standard over a period of 1.5 years (RISE: except for chloromethane and vinyl chloride for which the sorbent used was found to be unsuitable due to large variations observed at the start of the test period). No losses could be detected during this period.

Based on the stability study performed at VSL, using the TD-GC-FID/MS, the relative expanded uncertainty of the developed measurement standards was determined. From the VSL measurements it appeared chloromethane, vinyl chloride, dichloromethane, cis-1,2-dichloroethylene, trichloromethane and trichloroethene showed losses. The other components appear to be stable, although, Freon 113 showed an increasing stability trend over the course of the stability study.

Overall, the relative expanded uncertainty of the developed measurement standards was determined from the analysis performed at VSL, using the TD-GC-FID/MS, it appeared to be between 6 % and 18 %, with dichloromethane (26 %), chloromethane (30 %) and vinyl chloride (50 %) as exceptions. These results do not render the measurement standards as unusable but underline the challenges for these parameters.

Measurement standards for terpenes

Terpenes, mainly *p*-cymene and limonene, are produced among other impurities during the digestion of food waste at biogas plants. Other substrates such as cow manure and deep litter are also known to lead to the formation of terpenes, in particular α -pinene, β -pinene and 3-carene. One of the main risks associated with the presence of terpenes in biomethane, is their ability to mask the already present odorants (e.g., tetrahydrothiophene) in the fuel. Moreover, at high concentrations, terpenes may also condensate in the natural gas pipelines and influence the integrity of the plastic pipelines.

Six Primary Reference Materials (PRMs) containing terpenes in biomethane (**Table 1**) were prepared by the Gas Metrology Group of the National Physical Laboratory (NPL). The selection of terpenes and amount fractions were based on those most commonly reported in the literature:

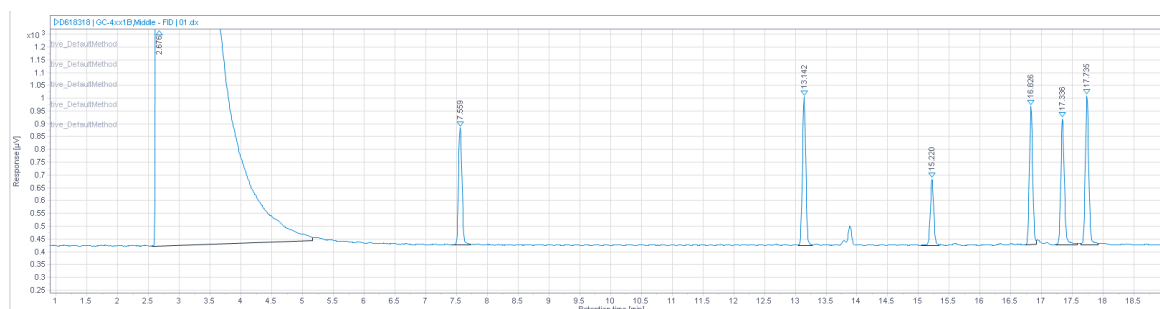
Table 1: Gravimetric amount fraction in $\mu\text{mol mol}^{-1}$ for each of the six PRM prepared at NPL.

Cylinder number	<i>n</i> -octane ($\mu\text{mol mol}^{-1}$)	α -pinene ($\mu\text{mol mol}^{-1}$)	β -pinene ($\mu\text{mol mol}^{-1}$)	3-carene ($\mu\text{mol mol}^{-1}$)	limonene ($\mu\text{mol mol}^{-1}$)	<i>p</i> -cymene ($\mu\text{mol mol}^{-1}$)
D618311	2.01	-	-	2.02	2.06	2.05
D618316	2.40	2.07	-	2.00	-	2.03
D618318	2.17	2.02	1.98	1.99	2.02	2.00
D618319	2.03	-	2.00	-	-	2.01
D618323	1.97	2.07	-	2.02	2.04	-
D723238	-	4.97	4.82	4.78	4.85	4.96

The mixtures were prepared in Air Products Experis passivated cylinders and pressurised at 7 MPa (70 bar), except D723238 which was pressurised at 4 MPa (40 bar). The mixtures were prepared following ISO 6142-1, by direct gas transfer from a higher amount fraction parent mixture prepared from a pure terpene and high purity methane. The purity of each terpene was assessed by quantitative nuclear magnetic resonance qNMR. The least pure terpene was 3-carene and its main impurity was identified as 1,4-cineole at approximately 7 cmol mol^{-1} ; also α -pinene was found as an impurity in limonene and β -pinene. The purity of the methane used for preparation (Methane N6.0, CK Gases) was assessed by performing an analysis by GC-FID; no detectable amount of terpenes were found at nmol mol^{-1} level. This purity data was taken into account to calculate the final composition of the five mixtures.

The first method developed by NPL used a gas chromatograph Varian 450 equipped with a flame ionisation detector (FID) and an Agilent capillary column DB-5 50 m long x 0.4 μm internal diameter. The oven was held at 60 °C for 3.5 min and ramped to 120 °C at 3 °C min^{-1} .

This method was used to assess the stability of the first five PRMs prepared in May 2018; the terpenes contained in each of the PRMs were compared against *n*-octane every two months until September 2018. The gas mixtures were connected to the GC using low volume connections. The flow rate was set to 25 mL min⁻¹ using an NPL custom-made flow restrictor. Mixtures were compared by running a sequence of a minimum of five consecutive injections. An example chromatogram is shown in **Figure 3**:



*Figure 3: Chromatogram showing the FID response for the PRM D618318, the order of elution is methane (RT=2.68), *n*-octane (RT=7.56), α -pinene (RT=13.14), β -pinene (RT=15.22), 3-carene (RT=16.83), *p*-cymene (RT=17.34) and limonene (RT=17.74). The small peak after α -pinene is an unidentified impurity.*

The expanded uncertainty for all the terpenes using the reproducibility as the uncertainty method is in the range 8 % – 12 %. β -pinene and *p*-cymene have the highest values with the β -pinene having a high contribution from stability and *p*-cymene from reproducibility.

The main contributor to the uncertainty is the reproducibility, however it is more accurate to use repeatability instead as the first is related with the robustness of the method and the latter is related with the uncertainty of the measurement. If *s* (*r*) for each component is used the uncertainty budget is the following: α -pinene = 1.96 %, β -pinene = 4.19 %, 3-carene = 2.13 %, limonene = 2.26 % and *p*-cymene = 3.12 %.

ENGIE developed and validated a fast and sensitive μ GC-TCD method for the analysis of the 5 terpenes selected in biomethane, in 6 minutes and over the range 1-10 ppm mol. The characteristics of this method are summarised in Table 2. This method demonstrates the use of a μ GC, which can also be used for onsite measurements.

Table 2: Characteristics of a rapid method for terpene analysis in biomethane.

Parameter	Outcome
Specificity	Excellent: No interference from the most likely trace constituents of biomethane (BTEX, hydrocarbons C ₂ - C ₁₁ , sulphur compounds)
Stabilisation	Signal stability reached after 13 injections (<1.5 hours)
Linearity	Excellent: one point forced through zero calibration can be performed
Repeatability	Satisfactory for trace compounds analysis α - et β -pinene: RSD % \leq 3% from 2 to 10 ppm Other terpenes: RSD % \leq 6% from 2 to 10 ppm (5ppm for 3-carene)
Accuracy	Excellent: error < 6 % from 2 ppm to 10 ppm (< 11 % for 3-carene)
LOQ	Excellent: ~ 1 ppm
Uncertainty (k=2)	Excellent: 5 % to 10 % from 3 ppm to 10 ppm 25 % at LOQ level (~ 1 ppm)

Measurement standards for amines

Due to the physical properties of amine components (high viscosity, high boiling point and low vapour pressure), instead of static preparation gas mixtures in high-pressure gas cylinders, the measurement standards were prepared on sorbent tubes (Tenax TA) by directly spiking liquid solution containing designed amounts of amines on the selected tubes. These measurement standards were developed for use as a transfer standard for the measurement of amine content in biomethane with metrological traceability. For the work, five light, commonly used amines were selected; Monoethanolamine (MEA), Piperazine (PZ, Diethylenediamine), Diglycolamine (DGA), Diethanolamine (DEA) and Methyldiethanolamine (MDEA). For all compounds save DEA, the stated purity was confirmed experimentally.

Different parameters were tested for the preparation of the spiked tubes, i.e., spiked mass (100 ng to 20 µg), flushing duration (10 min to 30 min), flushing media (air or nitrogen). The results demonstrated the feasibility of spiking 500 ng to 4000 ng of amine components on sorbent tubes to calibrate a gas chromatograph to address the threshold set by EN16723, i.e., 10 mg/m³. For the flushing duration and flushing media, the results did not show much dependence, so in the end 20 min flushing time with nitrogen was chosen.

Short-term (up to 8 days) and long-term stability (up to 7 months) tests were performed. The short-term stability test results did not show significant loss of amine components. The long-term stability results did not show a logical trend (e.g. the number of amines decreasing over time). This is probably due to the large reproducibility for preparing these measurement standards (such as the difficulty during preparation of the solution and to get the components out from the sorbent tubes due to their unfavourable physical properties).

ENGIE and GRTgaz developed, with the support of VSL, a measurement method using thermal desorption-gas chromatography with mass spectrometry (TD-GC-MS). Analyses were performed using an Agilent 7890B gas chromatograph (GC) coupled with an Agilent 5977B MSD Mass Spectrometer (MS) and an FID. The GC was equipped with a Thermal Desorption (TD) unit and a Cooled Injection System (CIS) packed with a Tenax TA sorbent. The initial temperature of desorption was 30 °C held for 2 min then raised to 290 °C at 60 °C/min and held for 10 min. Desorbed compounds were then cryofocussed on the CIS cooled at -30 °C with liquid nitrogen. At the end of desorption, CIS temperature was raised to 290 °C at 12 °C/s to inject the molecules in the column. Three columns were tested for their ability to properly separate the compounds: Rtx-Volatile Amine (30 m x 0.32 mm x 5 µm), HP-5MS Ultra Inert (30 m x 0.25 mm x 0.25 µm) and a DBWax (30m x 0.25 mm x 0.5 µm).

The Rtx-Volatile Amine column was the most suitable as it permitted a separation of the five amines in less than 25 minutes (Figure 4). For the separation, the GC oven was initially heated at 40 °C for 1.1 min then raised to 200 °C (with 10 °C/min) and maintained for 4.5 min, then raised to 270 °C (with 50 °C/min) and kept for 2 min.

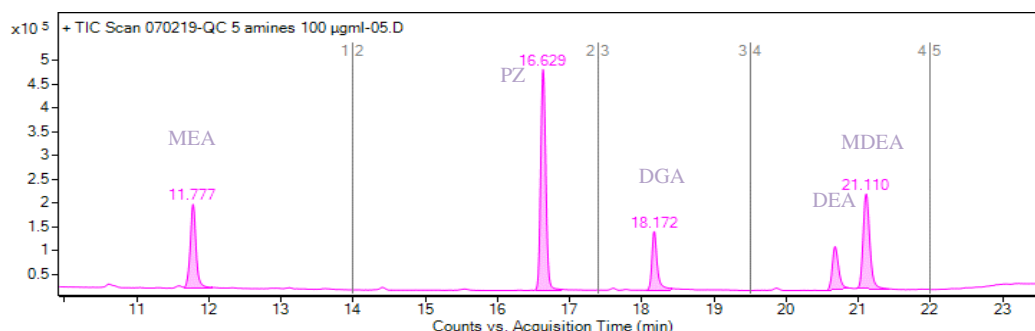


Figure 4. Separation of the five amines after liquid injection of a solution at 100 mg/L of each amine component in methanol with the column Rtx-Volatile Amine.

ENGIE and GRTgaz investigated biomethane coming from amine-based biogas purification, without success. Actually, no samples could be obtained with these impurities. A real biomethane sample was analysed, but it did not come from an amine purification process. Therefore, two chromatograms were overlaid: real biomethane and amines. The results obtained are presented in Figure 5. These results show that the method is not fully adapted for the analysis of amines in real biomethane. Indeed, the five amines show coelutions with other components present in biomethane. However, the use of mass spectrometry in SIM acquisition would

allow the specific detection of MEA, DGA, DEA and MDEA. Unfortunately, PZ is characterised by a m/z fragment also present in the biomethane interferent peak. Regarding FID, its use is not possible without any optimisation of the separation method.

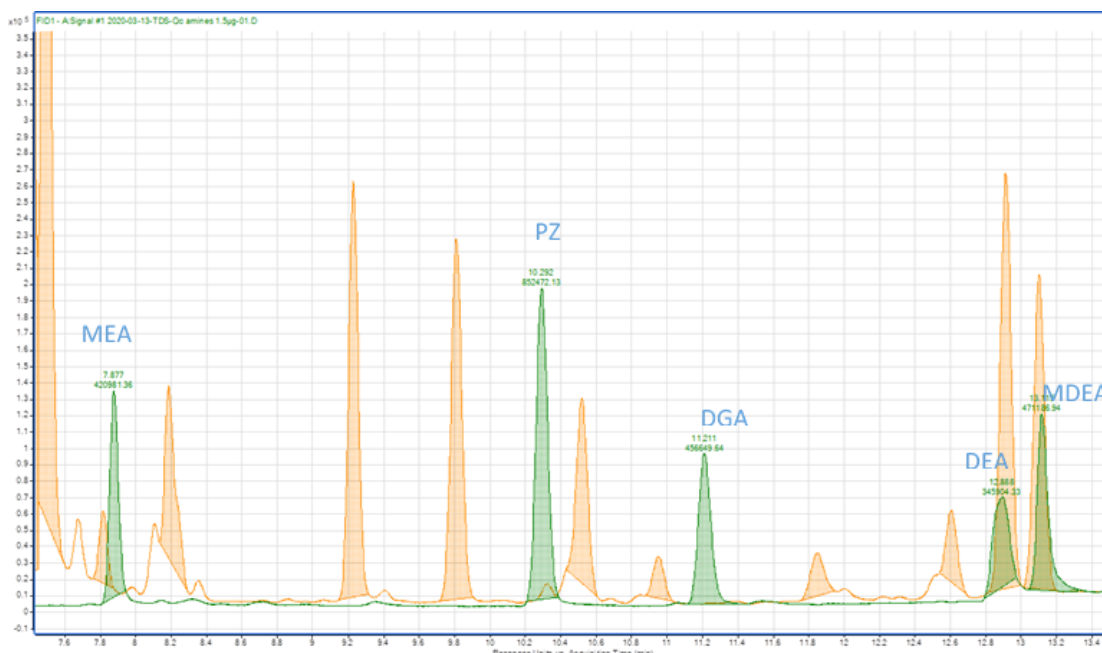


Figure 5. Overlay of biomethane (in orange) and amines (in green) chromatograms.

Deviations with respect to the masses obtained from spiking were observed between 20 % and 40 % relative. The measurement uncertainty was estimated to be between 30 % and 60 % for higher spiked masses and the MS (SIM-mode).

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

This project delivered measurement standards and calibration methods for the content of HF and compressor oil in biomethane. Novel facilities for dynamic gas mixture preparation, for ammonia and HCl, were set up so that they provide SI-traceable gas compositions with a relative expanded uncertainty of 1 % - 3 %. The spectroscopic detection of HCl and long-term stability was also improved.

Improved stability of ammonia standards

A stability study of 10 $\mu\text{mol mol}^{-1}$ ammonia (NH_3) in biomethane mixtures in cylinders has been conducted at NPL. The gas mixtures were prepared in seven different kinds of cylinders to identify which one was most suitable for the stability of ammonia in biomethane at the above-mentioned concentration level. The following were used as storage passivation materials in cylinders: British Oxygen Company (BOC) Spectraseal that undergone an NPL proprietary in-house treatment with hydrogen sulphide (H_2S), Swagelok sulfinit, Experis (Quantum), Megalife, Effectech Performax, Air Products (TC1) and NET. For each stability measurement, two new mixtures of NH_3 in biomethane have been prepared at the same nominal ammonia concentration using new BOC Spectraseal cylinders (H_2S pre-treated). NPL's previous tests have confirmed that this kind of cylinder is suitable for the stability of NH_3 in nitrogen at this amount fraction. The nominal amount fraction of ammonia in biomethane in these gas mixtures was chosen to be 10 $\mu\text{mol mol}^{-1}$ to be aligned with the biomethane measurement requirements (1 mg m^{-3} - 20 mg m^{-3} i.e. 1.4 $\mu\text{mol mol}^{-1}$ - 28.7 $\mu\text{mol mol}^{-1}$).

The mixtures were analysed using a non-dispersive infra-red (NDIR) spectrometer (URAS 26, AO2000, ABB Instruments). At any given time during the measurement, two cylinders of the same nominal amount fraction were connected to a 3-way valve which led to the input of the analyser; the valve allowed rapid switching between either of the two cylinders connected to it. Cylinders were equipped with a Sulfinert®-treated minimal dead volume (MDV) connector, connected in turn to a Swagelok pressure regulator with a max inlet of 3000 PSI and an outlet of 1 L min⁻¹ to adjust the pressure of the gas to meet the requirements of the analyser. Most of the lines consisted of coated stainless-steel tubing (1/8" outside diameter) and the remaining was made of Perfluoroalkoxy alkane.

A permeation method following ISO-6145-10 was set up at VSL for the generation of ammonia in a variety of matrix gases such as (mixtures of) nitrogen, methane or CO₂. The mass of the permeation tube is continuously weighed using a highly accurate magnetic suspension balance (TA-instruments). A schematic overview of the employed flow system is shown in Figure 6. A small flow of nitrogen (50 ml/min) is led through a temperature-stabilised chamber containing the permeation tube. The pressure in the permeation chamber is kept at a constant value using a pressure controller. The outgoing gas mixture is mixed with either pure nitrogen (for experiments in nitrogen) or pure methane (flow rate up to about 5 L min⁻¹) to the required amount fraction. By changing the temperature of the permeation chamber, the NH₃ amount fraction can be varied (amount fraction increases as a function of temperature). The final relative expanded uncertainty of the dynamic standard was 1.6 % ($k=2$).

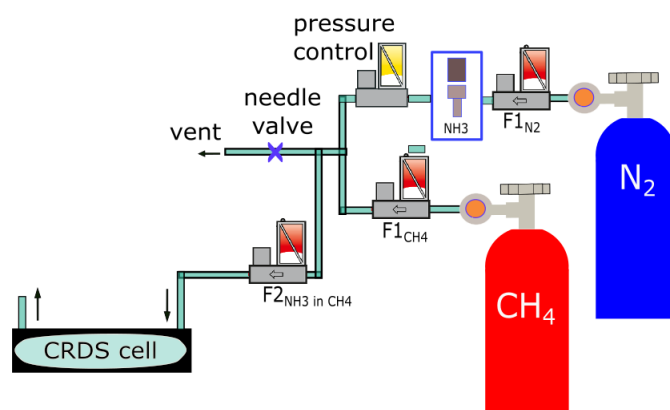


Figure 6 Schematic view of the dynamic generation system for ammonia in methane mixtures and the subsequent analysis by CRDS.

Further, the outlet of the permeation system can also be connected to the gas mixture preparation system (Figure 7) which has been developed at VSL within the framework of the biomethane project. This system is more flexible in terms of the number and type of components (suitable for reactive compounds due to the SilcoNert 2000 coating of the entire system) and provides a better mixing due to the presence of a mixing chamber.



Figure 7 Dynamic mixing facility based on mass flow controllers and a mixing chamber which can be used to generate various biogas compositions (a.o. CH_4 , CO_2 , N_2). This facility can be connected to the outlet of the permeation system.

The operation of the VTT setup has been optimised by testing and selecting different relevant physical and operational parameters, e.g. sample wetted parts materials (that come into contact with the sample gas) and their dimensions, gas and liquid flow rates, temperatures of heated system parts and output gas humidity as well as concentration ranges. This is made in such a way that they are optimal for the generation of ammonia, hydrogen chloride and hydrogen fluoride. The primary goal has been to minimise response time and memory effects for these acid and base compounds, in order to enable target uncertainties to be reached for all studied compounds. The design of this setup is such that it is applicable as a transportable reference gas generator for use both in laboratory and field conditions. The setup is portable and field deployable and furthermore its modular construction enables straightforward modification and tuning of critical system parts. A picture of the system is shown in Figure 8.



Figure 8 Dynamic generator calibration unit is portable and field deployable.

Liquid is injected using an automatic syringe pump and gas flow is controlled with a gas mass flow controller. Evaporation of the liquid solution takes place in a heated evaporation chamber, which has a selected coating. The whole system is built on a transportable container and it is operated with purpose-built control software running on an external laptop. The schematics of the system is shown in Figure 9.

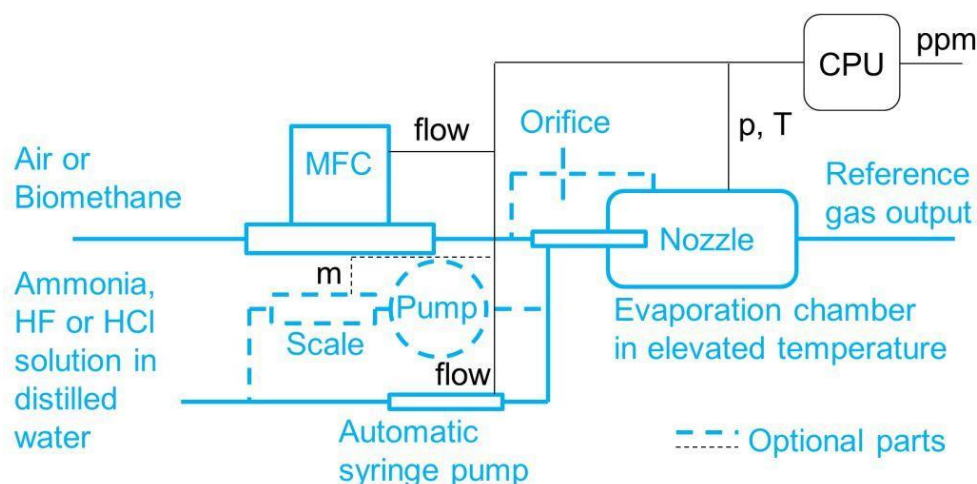


Figure 9 Schematics of the dynamic generator calibration unit based on the evaporation method.

The output concentration of the chemical is fixed by selecting the proper solution concentration, liquid flow and/or carrier gas flow. Typical water concentration of the generated gas is 0.1 % – 1 % (1 000 μmol – 10 000 $\mu\text{mol mol}^{-1}$). In general, humidity in calibration gas for reactive compounds decreases the response time and reduces memory effects. Elevated temperature is only used inside the evaporator (typically 120 °C) and after evaporation the gas may cool down to ambient temperature. High bypass gas flow (typically 7 L min⁻¹) is also used for better response time.

Concentration measurement of ammonia in methane using NPL's Tethys CEM500 Online Gas Analyser employing UV spectroscopy was made. Measurements included three separate reference gas cylinders for ammonia in methane prepared by NPL and calibration gas from the generator. Linearity and repeatability of the results for dynamically generated gas over the tested measurement range of 3 $\mu\text{mol mol}^{-1}$ - 22.5 $\mu\text{mol mol}^{-1}$ are good but due to problems in zeroing the analyser with dry (static standards) and humid (dynamic standard) gases, the absolute values show a negative offset of -1 $\mu\text{mol mol}^{-1}$ to -2 $\mu\text{mol mol}^{-1}$. The manufacturer of the analyser was not able to find a solution for this issue during the measurement period. The final relative expanded uncertainty of the dynamic standard was 2.37 % ($k=2$).

The results of the third stability measurement, performed 17 months after the first one, are presented in Table 3 where for each cylinder, the % change in amount fraction, the % relative expanded uncertainty and the % overall relative expanded uncertainty, are reported. This last uncertainty also takes into account the stability of the mixture that is the largest uncertainty contribution. A further stability measurement was planned for the 24 month point, but it was not possible to obtain this due to unanticipated delays.

Table 3 Results of the third stability measurement for the seven cylinders.

Cylinder type	Cylinder identifier	Change in amount fraction (% relative)	$U_{\text{rel}}(x)$, $k=2$ (% relative)	Overall $U_{\text{rel}}(x)$, $k=2$ (% relative)
Effectech	D679217	-2.5	1.1	5.2
Experis (Quantum)	D618312	7.7	1.9	15.5
NPL treated BOC Spectraseal	2426	-1.6	2.6	4.1
NET	L53103038	-12.8	1.6	25.6
Megalife	0606	-0.8	0.9	1.7
Air Products (TC1)	APEX1182786	2.8	1.6	5.9
Swagelok sulfinert	RK7065	-0.9	1.1	2.1

Reference standards containing ammonia in methane were produced via three methods; static standards in cylinders (expanded uncertainty of 5.18 %, $k=2$), dynamic standards via a permeation method (expanded uncertainty of 1.6 %, $k=2$) and dynamic standards via an evaporation method (expanded uncertainty of 2.37 %, $k=2$).

$k=2$). An NDIR analytical method was developed, achieving a relative expanded uncertainty of 1.6 % ($k=2$). In all cases the developed standards and method improve upon the previous state of the art for biogas measurements (uncertainties of 5 % - 10 %). The dynamic measurement standards meet the target objective of having a relative expanded uncertainty smaller than 3 %.

Measurement standards for HF

The aim of having a measurement standard and analytical method for HF in biomethane has been met as follows. For the detection of hydrogen fluoride, VSL has developed an analytical method based on DAS with enhanced noise rejection of $2f$ -WMS. HF gas standards used in the calibration of the setup were realised using the permeation method as well as through the dynamic dilution of higher level static mixtures using thermal mass flow controllers (see Figure 6).

Figure 10 shows results of $2f$ -WMS measurements recorded using a static mixture of $10 \mu\text{mol mol}^{-1}$ hydrogen fluoride in nitrogen from a cylinder. The mass flow from this cylinder was mixed with the dilution flow of pure methane using thermal mass flow controllers. The obtained $2f$ -WMS signals of $1.88 \mu\text{mol mol}^{-1}$ hydrogen fluoride in methane and pure methane are plotted together with the background corrected $2f$ -WMS spectrum of HF and its simulated $2f$ -WMS lineshape based on HITRAN in Figure 10a. The observed interference of CH_4 is relatively small compared to that of the case of HCl at an amount fraction of $1 \mu\text{mol mol}^{-1}$. After subtraction of methane interference, the $2f$ -WMS spectrum of HF agrees well with the HITRAN-based $2f$ -spectrum. Background corrected WMS- $2f$ spectra of HF at different amount fractions are depicted in Figure 10b, demonstrating that HF in methane can be analysed in the nmol mol^{-1} and lower $\mu\text{mol mol}^{-1}$ range.

The total relative expanded uncertainty for the measurement of HF is 7 %. Given the relatively small background interference from methane, comparable measurement uncertainties can be achieved in a CH_4 matrix. The amount fraction of hydrogen fluoride in an unknown sample can be determined by comparing the absolute area of the experimentally obtained $2f$ -WMS spectrum against the absolute areas of the dynamic measurement standards. For the measurements in hydrogen, VSL found a limit of quantification of 9 nmol mol^{-1} . The sensitivity of the method can be improved by further optimisation of the optical alignment of the multi-pass measurement cell, allowing it to achieve longer effective path lengths and thereby enhanced sensitivity.

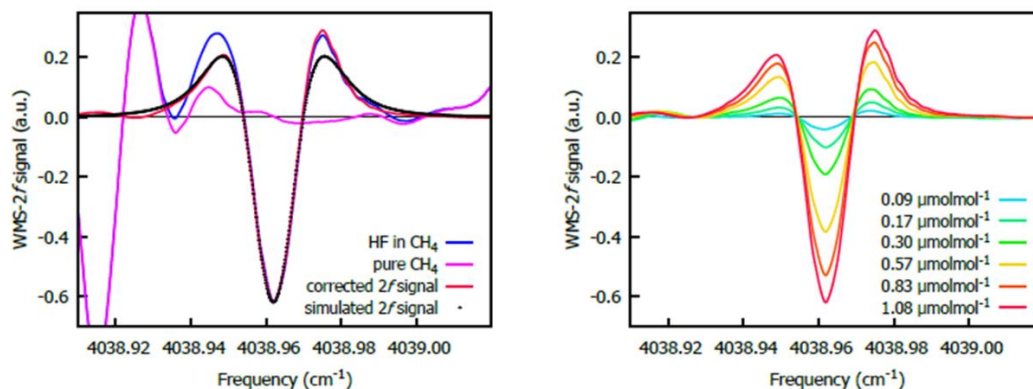


Figure 10 a) The WMS- $2f$ signal of $1.08 \mu\text{mol mol}^{-1}$ HF in methane (blue), pure methane (magenta), the background subtracted WMS- $2f$ signal of HF in methane (red) and HITRAN-based simulation of the $2f$ -lineshape of HF (black dots). b) Background subtracted WMS- $2f$ spectra of HF in methane collected at different amount fractions obtained by the dilution of a static mixture.

The portable generator of VTT (Figure 8) was also validated for HF. The uncertainty budget is given in Table 4, meeting the target of 10 %. The parameters are denoted as follows:

- c_{sol} concentration of the target chemical in solution [$\mu\text{g/l}$]
- $q_{v,g}$ flow rate of the carrier gas [l/min]
- $q_{v,w}$ flow rate of the evaporated water in the gas phase [l/min]
- $q_{v,\text{sol}}$ flow rate of the liquid solution [ml/min]
- δc_{eva} correction/effect of evaporator, due to adsorption losses [$\mu\text{g/m}^3$]
- δc_{rep} overall repeatability of the gas generator [$\mu\text{g/m}^3$]

Table 4: Overall uncertainty of the generated calibration gas for hydrogen fluoride in methane.

Term	Average value	Standard uncert.	Distribution	Sensitivity coeff.	Contribution	Relative contribution
c_{sol}	1012340 mg/m ³	0,89 %	norm.	0,00001	0,04 mg/m ³	0,45 %
$q_{v,g}$	7 L/min	0,07 L/min	norm.	-1,4	-0,05 mg/m ³	-0,49 %
$q_{v,w}$	0,087 L/min	0,001 L/min	rect.	-1,4	-0,0004 mg/m ³	-0,004 %
$q_{v,sol}$	0,07 g/min	0,42 µL/min	norm.	143	0,03 mg/m ³	0,30 %
δC_{eva}	0 mg/m ³	0,15 mg/m ³	rect.	1	0,09 mg/m ³	0,87 %
δC_{rep}	0 mg/m ³	0,4 mg/m ³	rect.	1	0,23 mg/m ³	2,31 %
c_{gen}	10 mg/m ³			$u(k=1):$	0,26 mg/m ³	2,57 %
				$U(k=2):$	0,51 mg/m ³	5,14 %

Measurement standards for HCl

A method for the CH₄ broadening coefficient for HCl was developed at PTB. Results of a new CH₄ collisional broadening coefficient for HCl measurements in CH₄/biomethane are presented. This collisional broadening coefficient (measured at PTB) is required to fit laser spectroscopic HCl in CH₄/biomethane spectra (e.g., measured at VSL) to improve the measurement speed, repeatability, and reproducibility of measurements. The broadening coefficient has also been tested and validated at PTB via spectroscopic (direct tuneable diode laser absorption spectroscopy) HCl amount of substance fraction measurements.

Figure 11a depicts example absorbance data measured (at different pressures) with the PTB dTDLAS instrument. Figure 11b shows a plot of the FWHM (full width at half maximum) as a function of the total gas pressure (dominated by the partial pressure of CH₄). A generalised linear regression was performed, taking into consideration the uncertainties of the Lorentzian full width and the total gas pressure. The slope (m) of the GLR applied to the data in Fig. 2b was $(1.0733 \pm 0.0016) \cdot 10^{-4} \text{ cm}^{-1}/\text{hPa}$ and the intercept (b) was $(-7.83 \pm 9.78) \cdot 10^{-5} \text{ cm}^{-1}$, $k = 2$. The intercept was insignificant, indicating that p_{CH_4} is equal to p_{total} within the uncertainty. Refitting the data using an equation without intercept ($y = m_1 x$) yielded a slope (m_1) of $(1.064 \pm 0.0144) \cdot 10^{-4} \text{ cm}^{-1}/\text{hPa}$, leading to a CH₄ broadening coefficient (γ_{CH_4}) of $(5.320 \pm 0.072) \cdot 10^{-5} \text{ cm}^{-1}/\text{hPa}$, $k = 2$, evaluated at the measured gas temperature of 294.8 K. The combined uncertainty of 0.072 cm⁻¹/hPa is 1.4 % of γ_{CH_4} ($5.320 \cdot 10^{-5} \text{ cm}^{-1}/\text{hPa}$).

A modified version of PTB's direct tuneable diode laser absorption spectroscopy (dTDLAS) instrument operating at 3.6 µm, which was developed in the course of the project, was set up and used. The instrument was used to calibrate three gas mixtures of hydrogen chloride in methane. The dTDLAS HCl amount of substance fraction of $(510.8 \pm 23.5) \mu\text{mol/mol}$ was in good agreement with values reported for a gravimetrically produced gas mixture of $(506.0 \pm 25.3) \mu\text{mol/mol}$.

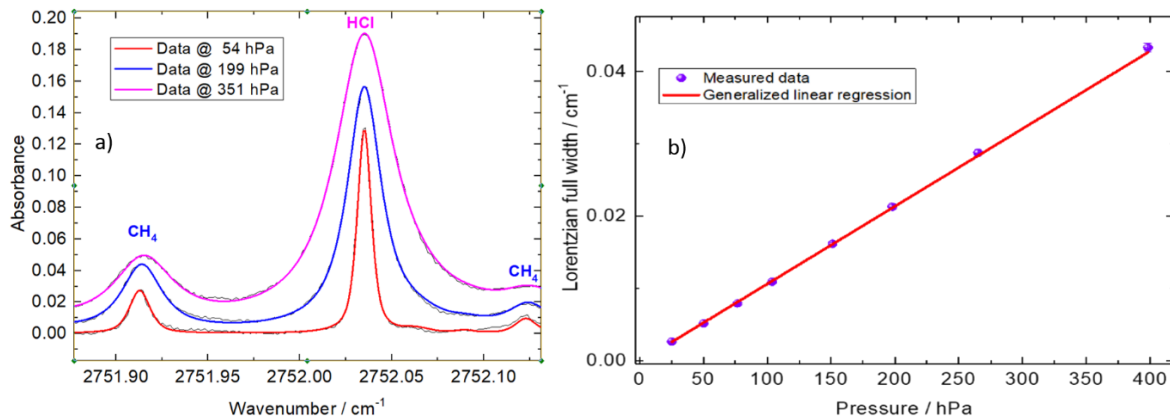


Figure 11: a) HCl absorbance spectra at different pressures. b) CH₄ line widths (FWHM) as a function of the total gas pressure. A generalised linear regression was applied to the data (red, slope m : $(1.0733 \pm 0.0016) \cdot 10^{-4} \text{ cm}^{-1}/\text{hPa}$, intercept $b = (-7.83 \pm 9.78) \cdot 10^{-5}$).

A rigorous validation using a traceable measurement standard was conducted by VSL using the permeation system (Figure 6). The composition of the calibration gas mixture is calculated from the permeation rate as well as the mass flow rates of the carrier N_2 and dilution gases CH_4 (in compliance with ISO 6145-10 and ISO 6145-7, respectively). At VSL a laser spectrometer combining direct absorption spectroscopy (DAS) and wavelength modulation spectroscopy (WMS) has been developed for the measurement of HF and HCl at trace levels in methane (CH_4). Both the HF and HCl spectrometer uses the same flow system, photodetector, measurement cell, and data acquisition system, but only the laser and laser drivers (i.e., current and temperature controllers) are different. For the detection of HF, a distributed feedback (DFB) laser operating at 2475.88 nm (4038.96 cm^{-1}) has been used. For the analysis of HCl, the spectrometer employs an interband cascade laser (ICL) with collimator (Nanoplus, Germany) to probe the absorption line of HCl centred at 3633.68 nm (2752.04 cm^{-1}). This line is not the strongest available HCl absorption line, yet it suffers less from methane interference than other strong HCl absorption lines. Wavelength modulation (WMS) has been applied to realise higher sensitivity and to reduce CH_4 interference compared to direct absorption spectroscopy, thereby allowing detection of low HF or HCl amount fractions in a methane matrix.

Enhanced sensitivity and lower detection limits were achieved by using $2f$ -WMS. Figure 10a shows the results of $2f$ -WMS measurements of pure methane, $0.99\text{ }\mu\text{mol mol}^{-1}$ HCl in CH_4 , the matrix-corrected $2f$ -signals of HCl and its simulated $2f$ -spectrum based on the HITRAN database. The methane matrix causes quite some spectral interference at these low HCl amount fractions, but as the CH_4 background signal is very stable this can be easily subtracted. The background-corrected signal shows good agreement with the simulated $2f$ -spectrum (see

Figure 12a).

Figure 12b depicts the matrix-corrected $2f$ -WMS spectra of the calibration gas mixtures with varying HCl amount fractions in CH_4 showing the high sensitivity and selectivity of the method, even for such a low HCl amount fraction in methane. Using the absolute area under the curves provides a robust measure of the HCl amount fraction and a good linearity (slope: $(6.77 \pm 0.19) \times 10^{-2}$) was observed (see

Figure 12c). The obtained straight line meets the requirements of ISO 6143 regarding the goodness-of-fit. A limit of quantification of 20 nmol mol^{-1} was found for the $2f$ -WMS measurement of HCl in CH_4 . The resulting expanded uncertainty for HCl analysis at $1.0\text{ }\mu\text{mol mol}^{-1}$ in CH_4 was 4 %.

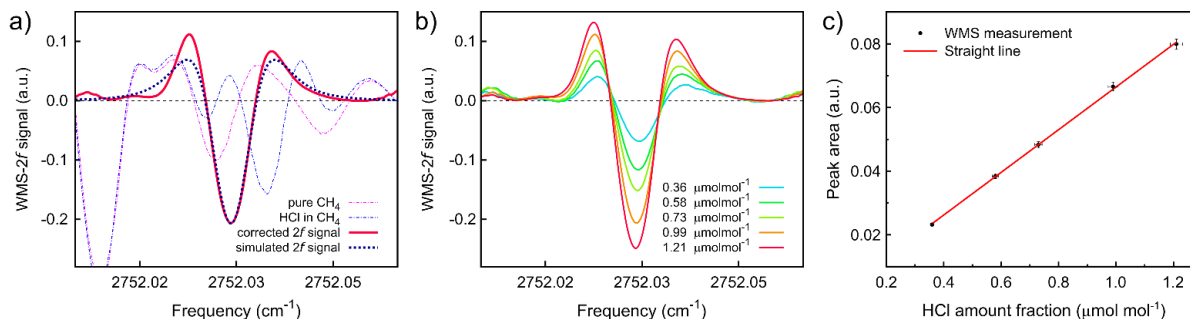


Figure 12 a) WMS-2f signal of pure CH₄ (magenta), 0.99 μmol mol⁻¹ HCl in CH₄ (blue), and the latter also corrected for the contribution from the CH₄ matrix (red). Further, a simulated spectrum based on HITRAN database (black) is shown. b) Background-subtracted WMS-2f spectra of HCl in CH₄ at different amount fractions. c) Dependence of the peak area on the HCl amount fraction. The slope of the straight line is $(6.77 \pm 0.19) \times 10^{-2}$ where the uncertainty is stated as standard uncertainty. The intercept is $(-1.09 \pm 1.15) \times 10^{-3}$ where the uncertainty is stated as standard uncertainty. The uncertainty bars plotted denote expanded uncertainties ($k=2$).

The dynamic standard developed by VTT (Figure 8) was validated for HCl as well. Its performance is summarised in Table 5. The measurement standard met the target uncertainty.

Table 5: Overall uncertainty of the generated calibration gas for hydrogen chloride in methane.

Term	Average value	Standard uncert.	Distribution	Sensitivity coeff.	Contribution	Relative contribution
c_{sol}	1012500 mg/m ³	0,74 %	norm.	0,00001	0,04 mg/m ³	0,37 %
$q_{v,g}$	7 L/min	0,07 L/min	norm.	-1,4	-0,05 mg/m ³	-0,49 %
$q_{v,w}$	0,087 L/min	0,001 L/min	rect.	-1,4	-0,0004 mg/m ³	-0,004 %
$q_{v,sol}$	0,07 g/min	0,42 µL/min	norm.	143	0,03 mg/m ³	0,30 %
δC_{eva}	0 mg/m ³	0,1 mg/m ³	rect.	1	0,06 mg/m ³	0,58 %
δC_{rep}	0 mg/m ³	0,2 mg/m ³	rect.	1	0,12 mg/m ³	1,15 %
c_{gen}	10 mg/m ³			u (k = 1):	0,15 mg/m ³	1,46 %
				U (k = 2):	0,29 mg/m ³	2,92 %

Methods for the measurement of compressor oil content

WAL, RISE and INERIS each developed an analytical method to measure oil carryover in compressed gas (Compressed Natural Gas (CNG), biomethane or a mixture of those) have been developed. The targeted measurement uncertainty for compressor oil content is 10 % relative. One of the evident challenges with oil is the complexity of the oil which usually consists of many compounds that cannot be fully separated from each other with gas chromatography. Each method was developed using the 3 selected oils corresponding chromatographically to 3 different types: oils being a complex mixture comprising many individual compounds often including hydrocarbons and additives that are unresolvable using gas chromatography, oils being a complex mixture mostly unresolvable using gas chromatography, but presenting some clearly dominant peaks (partially resolved) and oils with well separated peaks.

WAL developed an TI-FTIR analytical method for the analysis of compressor oil. Three target oils were analysed by direct injection into the gas cell of a Fourier Transform Infrared Spectrometer (FTIR) (MAX Analytical Technologies "crossmark" prototype). The FTIR gas cell was of a continuous flow "light pipe" type, with 10 cm pathlength and 1.6 ml internal volume. The gas cell was thermally insulated and maintained at a temperature of 300 °C. The spectrometer incorporated a Deuterated Triglycine Sulphate (DTGS) detector and spectra were obtained at 4 cm⁻¹ resolution and at a rate of 2.5 seconds per scan.

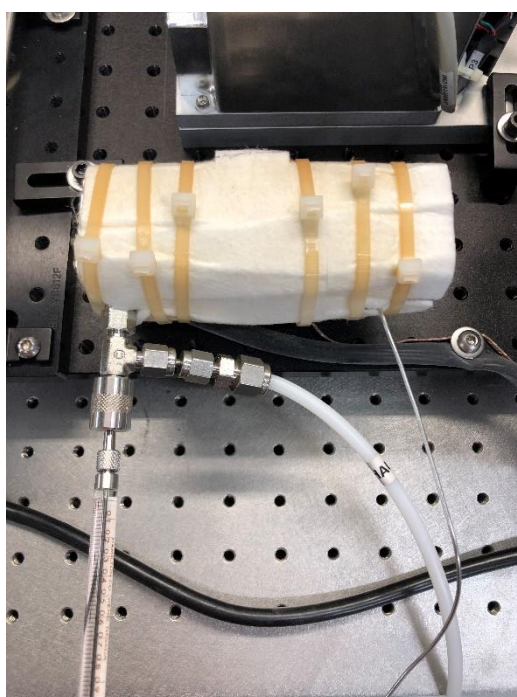


Figure 13: Sampling apparatus for compressor oil analysis.

Figure 13 shows the “light pipe” gas cell assembly which is heavily insulated and heated to 300 °C. A 1/8” Swagelok tee is connected to the inlet of the gas cell and is partially covered by the insulation of the oven. The other arms of the tee are connected to a Valco injection port with septum and a ¼-inch Teflon tube, which delivered nitrogen gas with a flow of 5 ml/min. On the exit port of the gas cell, a 1/16-inch stainless steel exhaust line was connected to vent the gas to a fume hood.

A second method was developed based on GC/FID. Oils are analysed by GC/FID after dilution in hexane. The analyses of these solutions are performed on a gas chromatograph coupled with a flame ionization detector. The gas chromatograph (Varian, CP3800) is equipped with a programmed temperature vaporiser (PTV) injector (Varian 1079) (injector temperature 50 °C for 0.1 min and programmed at 320 °C, the injections are performed in split-less mode) and a fused-silica capillary column (Rxi-5ms, 30 m, 0.25 mm i.d., 0.25 µm film, from Restek). The temperature program of the GC oven started at 40 °C for 5 min, then a ramp of 10 °C /min, until 300 °C for 20 min. The temperature of the detector is fixed at 300 °C. The injection volume was set at 1 µL. For the calibration, six standard solutions from 0.2 mg/ml to 6 mg/ml with different levels of concentration are prepared from liquid solutions of oils by successive dilutions in n-hexane. The standard solutions used for the calibration curve are a mixture of 3 selected oils (by volume) in order to cover the different types of chromatographic profiles:

- 1/3 of Mobil SHC 1025 oil
- 1/3 of Mobil Pegasus 1 oil
- 1/3 of UNIVIS TM N32 oil

The calibration is performed using these 6 standard solutions at various concentrations in n-hexane which are injected in gas chromatography.

In order to verify that the analytical system has correctly performed the injection, a known amount of n-decane was spiked in each standard solution. These standard solutions are used for the characterisation of the calibration curve and the validation of the limit of quantification.

Oil	Type	
Mobil Rarus SHC 1015	Type 1: GC characteristic: well separated peaks	
Mobil Pegasus 1	Type 2: Globally unresolved peaks with some dominant peaks	
Mobil Univis TM N32	Type 3: Unresolved mixture	

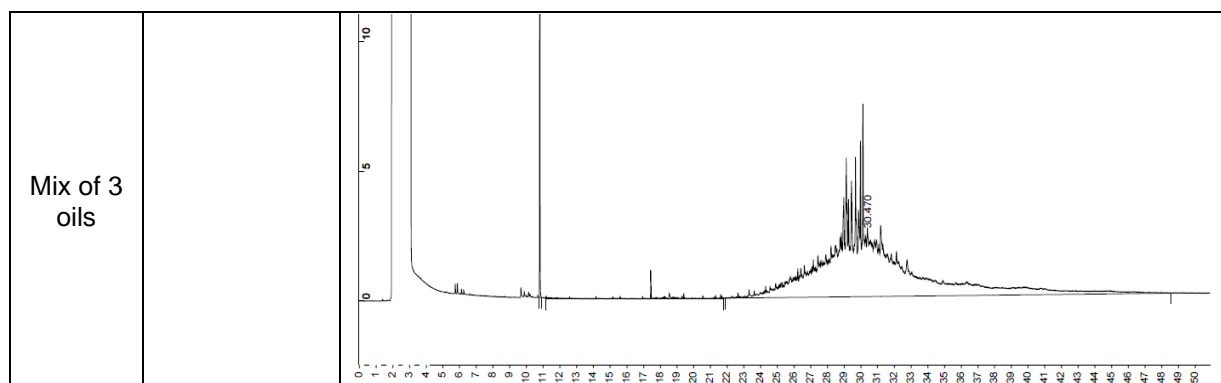


Figure 14: Three target oils and their GC/FID chromatograms.

A third method is based on GC/MS. Oils are analysed by GC/MS after dilution in dichloromethane. The analyses of the oil solutions were performed on a gas chromatograph coupled with a mass spectrometer. The gas chromatograph (Agilent, 6890N) was equipped with a split/splitless injector (injector temperature 325 °C, split ratio 4:1) and one fused-silica capillary column (HP-5MS Phenyl Methyl Siloxane, 30 m, 0.25 mm i.d., 0.25 µm film, Agilent Technologies). The temperature program was initial temperature 80 °C (hold 2 min). The temperature was then raised with a ramp rate of 12 °C /min up to 325 °C (15 min); for the mass selective detector (Agilent, 5975) the ion source temperature was set to 230 °C. The MS was operated in the electron impact (EI) ionization mode at 70 eV. When quantifying with the MS, two modes were used; the total ion chromatogram mode which represents the summed intensity across the entire range of masses being detected (m/z 29 to m/z 430) or an extracted-ion chromatogram mode where one m/z value characteristic for one compound are recovered from the entire data set.

For each method, the following performance parameters were estimated: selectivity, limit of detection and of quantification, working range, precision, trueness, ruggedness. Finally, the measurement uncertainties were calculated. The FTIR method and the GC/MS method both resulted in measurement uncertainties close to 20 % rel. while the GC/FID method resulted in a higher measurement uncertainty (around 30 % rel. at concentrations above LOD). However, for this method, the contribution due to the sample preparation was also included. The mass spectrometer has the advantage of a better selectivity as it allows the selection of specific ions from the total ion chromatogram mode. The selectivity of the FTIR method is improved by using some of the smaller characteristic peaks in the fingerprint region for quantification.

4.3 To develop and validate novel test methods, based on existing calibration methods, for the regular conformity assessment of biomethane during which the content of total silicon and siloxanes, total fluorine and chlorine, ammonia, terpenes, compressor oil, amines, and biogenic methane (based on determining the $^{14}\text{CH}_4$ content in biomethane and blends of biogas and natural gas) are measured.

This objective has been met by proposing the following nine methods. Some methods have variants, to further smoothen the take-up by laboratories. Apart from these nine methods, VSL and PTB developed methods based on their spectroscopic systems (see section 4.2), but these require own-built instruments and are currently deemed to be unfit for standardisation.

Test method for total silicon concentration

The method has been developed by IMBIH with the help of NPL and VSL to directly determine the concentration of silicon in biomethane and biogas. The silicon species are trapped using a liquid impinger and converted into hexafluorosilicate. The solution containing the silicon can then subsequently be analysed using an instrumental method. In the project, Microwave Plasma Atomic Emission Spectrometry (MWP-AES) has been used for this purpose.

For the gas sampling, a gas flow meter is needed which is calibrated for methane (biomethane, or biogas). Nitric acid is used as a liquid adsorbent, in two or three serially connected bubblers. After adsorption, the silicon

species are derivatised using sodium hydroxide and hydrogen fluoride. Sodium hydroxide is added until a slight basic pH is reached. Then, hydrogen fluoride is added and the pH is adjusted to 3.5 to optimise the stability of the derivatised sample. The sample obtained can be further concentrated or diluted to ensure that the concentration is within the working range of the analytical instrument.

The instrument calibration is performed using a stock solution of a soluble silicon salt, such as $(\text{NH}_4)_2\text{SiF}_6$. The method can also be applied with other mechanisms for generating a plasma, such as ICP (Inductively Coupled Plasma). The AES can be operated at different wavelengths, which have different sensitivities for silicon. The preparation of the solutions necessary for the calibration of the instrument involves regular gravimetry and volumetry to prepare the stock solution and calibration solutions.

Three different blanks are used: calibration blanks (nitric acid), a reagent blank, and a rinse blank. The latter is used to flush and check the instrument's uptake and a nebuliser system is used to reduce memory effects. The instrument performance is checked with a calibration control sample (elemental solution with a known concentration of silicon), a derivatisation control sample to assess the completeness of the derivatisation, and a calibration gas mixture containing low levels of siloxanes and other silicon-containing volatile organic compounds is used to assess the performance of the entire method.

Test method for siloxanes concentration

This activity aimed at developing and validating a method for the determination of the siloxanes content by means of gas chromatography with ion mobility spectrometry (GC-IMS). The work was carried out by NPL. The method can be employed both in the laboratory and for onsite analysis. Another method, based on a thermal desorption gas chromatography Fourier Transform infrared (TD-GC-FTIR) spectrometer prototype, was tested by WAL. However, from the results, it was determined that the sampling technique requires further development to improve siloxane recovery. This equipment is not yet commercially available and remains in a prototype form. The linearity, trueness, repeatability, within-laboratory reproducibility, limit of detection, and the selectivity have been assessed.

The sampling of biomethane should be performed with great care. Passivation of surfaces in contact with the sampled gas is required. Also the temperature of gas lines, vessels etc. is important to mitigate effects from adsorption and to prevent condensation. Pressure regulators should also be compatible with the calibration gas mixtures used. The injection pressure of the calibration gas mixtures and the sample(s) should be the same.

The instrument calibration is performed with calibration gas mixtures containing relevant siloxanes in methane. The stability of the amount fraction of the siloxanes in these calibration gas mixtures is generally limited. Especially the contents of L2 and L3 are prone to instability. Alternatively, dynamically prepared or diluted static gas standards can be used for instrument calibration to mitigate effects from the limited stability of the calibration gas mixtures. In the validation, a system comprising passivated mass flow controllers has been used to record the calibration curves.

The results for L2, L3, and D4 agreed within 14 % of the gravimetric values of the calibration gas mixtures, which is consistent with the uncertainty of the instrumental analysis. D5 was slightly overreported due to adsorption effects. The repeatability of the method was 3 % or better; the reproducibility was 7 %. The limit of detection of the instrument used was equivalent to 0.28 mg/m^3 total silicon.

Limited interference testing was performed. Interferences with hydrocarbons (C6-C10) were absent. There is some interference with sulphur-containing species with L2 with the instrument used for the method development.

Test method for hydrogen fluoride and hydrogen chloride

An analysis method was developed for HCl and HF using ion chromatography by INERIS and ISSI. The work aims at replacing the methods currently described in EN 16723. The proposed method provides traceable measurement results and is dedicated to biomethane and biogas. The method has been evaluated using a dynamic system for calibration gas mixture preparation based on the quantitative evaporation of an aqueous solution of HCl or HF. The system provides a humid calibration gas mixture of known composition.

The use of glass impingers works well for HCl but poorly for HF. Better performance for HF is obtained using PTFE impingers. An 0.01 mol L^{-1} solution of NaOH is used to trap the HCl and HF. Method 1 uses a quartz

fibre filter impregnated with 500 μL of an aqueous Na_2CO_3 solution. The trapped compound is extracted from the filter. Alternatively, cartridges can be used.

The analysis method is based on ion-exchange chromatography. The instrument is calibrated using a multipoint calibration.

Test method for halogenated VOCs

A method has been developed for the halogenated volatile organic compounds. There was a problem with obtaining pure freons, which were high on the priority list, but these substances have been banned and hence could not be obtained. One freon (113) was still available and has been added to the suite of ten compounds. Calibration gas mixtures have been prepared gravimetrically at the 50 nmol mol^{-1} level. The analytical methods developed used thermo desorption or preconcentration of the sample. Also a method without preconcentration was developed.

A method based on gas chromatography with a barrier ionisation detector (GC/BID) has been developed by VSL. This detector uses a helium plasma and is very sensitive. For most components, a detection limit of 50 nmol mol^{-1} or lower can be achieved.

Methods involving thermal desorption (TD) have been developed using different sorption tubes by RISE and INERIS. The TD was coupled with GC/MS (mass spectrometry). The detection limit obtained was 10 ng, which corresponds to 10 nmol mol^{-1} . The bias is better than 4 %; the precision is also better than 4 %. There is a substantial influence of the choice of sorbent. A Tenax TA/Carboxen 1003/Carbograph 1 combination yielded a relative expanded uncertainty between 8 % and 13 %.

The method based on a thermal desorption gas chromatography Fourier Transform infrared (TD-GC-FTIR) spectrometer prototype used by WAL for siloxanes was also tested with a halogenated VOC standard. Recovery rates were poor, particularly for the lighter components and it was concluded that the method and sampling technique requires further development for these compounds.

Direct analysis methods have been developed using GC/BID and ATD-GC-FID/MS. Generally, repeatability of 2 % or better is obtained using the BID and MS, both at 750 nmol mol^{-1} and 50 nmol mol^{-1} . The FID gives for some components a higher repeatability standard deviation. The best uncertainties are obtained using GC/BID (2 % -- 6.4 %). Higher uncertainties are obtained for ATD-GC-FID (3.2 % – 20 %) and ATD-GC-MS (12 % -- 32 %).

The gravimetric calibration gas mixtures are stable for a period of 18 months, save for vinyl chloride and chloromethane. For the others, the stability is confirmed within the experimental uncertainty.

Test method for ammonia

The specification for the ammonia concentration in biomethane is 10 mg m^{-3} (EN 16723). Several techniques have been probed, including various forms of laser spectroscopy, ion chromatography and gas chromatography. Two spectroscopic techniques have been chosen for developing a standardised test method: OFCEAS (Optical Feedback Cavity-Enhanced Absorption Spectroscopy) and UV/vis spectroscopy. The methods have been developed by NPL and GRTgaz. The proposed method is similar to methods known from air quality, i.e., the measurement of the concentration ammonia in air. In the sampling, specific attention is paid to material compatibility, the absorptiveness of ammonia, taking up experience from previous research into the improvement of the analysis of ammonia in air.

Multipoint calibration is required if the analyser is installed, underwent maintenance and drift in excess of the performance specifications. The use of multiple static reference standards should be in accordance with ISO 10723. Alternatively, dynamic methods as described in ISO 6145 can be used. High-purity methane is in the latter case required. High-purity nitrogen is needed as the purge-gas.

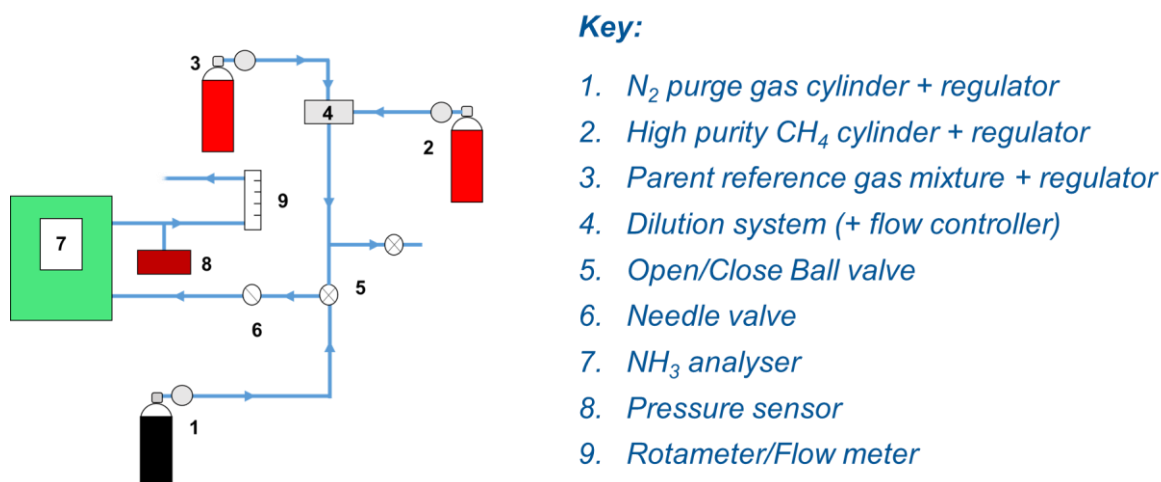


Figure 15 -- Schematic layout of the instrumentation needed for the analysis of ammonia in biomethane.

Test method for terpenes

Terpenes are odorous compounds which can be present in biomethane, depending on the feedstock. Their presence interferes with natural gas odourisation and they may accumulate in gas grids and in refuelling stations. Finally, they also affect the integrity of polymer pipelines. There was a need for a method for monitoring terpenes concentration and thus also for measurement standards of relevant terpenes in methane.

Measurement standards have been developed for selected terpenes in high-purity methane with amount fractions between $2 \mu\text{mol mol}^{-1}$ and $6 \mu\text{mol mol}^{-1}$. A method using micro-gas chromatography ($\mu\text{GC/TCD}$) was developed as a test method for monitoring terpene levels in biomethane. The method is suited for onsite and offsite analysis. It has a low gas consumption. The analysis time is less than 6 min.

The method can be used with a straight line through the origin. This has been confirmed by a multipoint calibration over the range from $1 \mu\text{mol mol}^{-1}$ to $10 \mu\text{mol mol}^{-1}$. The repeatability was 3 % for α - and β -pinene, and better than 6 % for the others. The limit of detection is about $1 \mu\text{mol mol}^{-1}$. The overall measurement uncertainty was between 5 and 10 % ($k = 2$).

Test method for the determination of compressor oil carryover

Compressor oil can be entrained in gas streams during refuelling and form deposits in gas vehicle tanks. EN 16723 does not specify a fixed limit but requires that the level should not have an impact on the application. Oil is carried over in two forms: aerosol and vapour. ISO 8573-2 describes methods for oil aerosol in compressed air. Because of varying flows and the presence of security systems that prevent sampling from an open end, the sampling method had to be redesigned. A novel sampler was developed by RISE using coalescing filters. By this process, small droplets are accumulated in larger droplets and eventually the oil is accumulated until purged.

Methods were developed by RISE and INERIS to recover oil from the buffer tank of the sampler. Also a method for the extraction of the oil from the filter was developed. For calibrating the equipment, it is optimal to use compressor oil of the same make that is present in the biomethane. Otherwise, an alternative oil should be used. Calibration standards are obtained by diluting the oil in a solvent. A backup filter is used so that malfunctioning of the sampling filter can be detected and the oil can still be collected.

Two extraction procedures have been developed, one using an ultrasonic bath, and a second using a pressurised fluid extraction apparatus. Also two recovery methods for oil from the buffer tank have been developed. The relative measurement uncertainty varies between 11 % and 17 %, depending on the type of compressor oil. It is recommended to use the same oil for calibration to be at the lower end of the observed measurement uncertainty. The profiles should ideally match as closely as possible. RISE and INERIS tend to see very similar profiles.

Test method for amines

Alkanolamines are used in the cleaning of biogas to remove hydrogen sulphide and carbon dioxide. No agreed method is available, neither are measurement standards. Hence, alkanolamines cannot be monitored. A method was developed for five amine compounds: methyldiethanolamine, diethanolamine, monoethanolamine, piperazine and diglycolamine. The vapour pressure of these compounds is too low to prepare gas standards. Instead standards on sorbent tubes have been developed. As the compounds are potentially sensitive to oxidation, it is important to use nitrogen when preparing the measurement standards on adsorption tubes.

An analytical method was developed using gas chromatography with mass spectrometry (TD-GC-MS). The Rtx-Volatile Amine columns provide a proper separation of the components. Linearity was confirmed between 0.4 µg – 10 µg. The LoQ ranged from 0.03 µg to 0.1 µg. The repeatability at higher levels ranged from 7 % to 19 %, going up to 75 % at 0.4 µg. The relative deviation from values from preparation was between 11 % and 42 %. The measurement uncertainty was estimated to be between 29 % and 90 %. The use of MS is necessary to avoid interferences, save for PZ for which further measures are taken.

The method can potentially be further optimised to improve the performance characteristics. This process is laborious, as the alkanolamines are viscous liquids and not too easy to handle. A further observation that should be made is that these amines are not encountered in practice, neither in biomethane and upgraded biogas, nor in natural gas. The question arises whether it is necessary to have this parameter in the specification for biomethane (EN 16723).

Test method for biogenic methane content (¹⁴C method)

A method was needed to distinguish fossil gas from renewable gas. The ¹⁴CH₄-method is still preferred, because the use of stable C-isotopes is limited in use, selectivity and quantification ability. The quantification ability is within ± 3 % of the biogenic methane fraction. It is potentially suitable as a standardised method. The measuring range was between 1.5 % and 100 % biogenic methane.

Existing standards include ASTM D6866 and EN/TS 16640 for bio-based products. Also standards exist for waste, flue gas CO₂, plastics, and rubber. Five laboratories using AMS (Accelerated Mass Spectrometry) participated in an interlaboratory comparison. Three blends and two biogases have been distributed. The methods described in these standards can largely be adopted. The work of RUG demonstrates that only the sample preparation needs to be adapted to be suited for biomethane conformity assessment.

Labs can use their own sample preparation and use their own equipment. Labs should use reference gases to check their sample preparation. The measurement uncertainty that is attainable is in the order of 3 % relative.

For the purpose of verifying whether biogas is produced from 100 % biogenic origin or mixed with natural gas, uncertainties in the ¹⁴C-based method results are for fractions above 90 % dominated by the uncertainty in the used ¹⁴C reference value for 100 % biogenic carbon. ¹⁴C measurement variability (as measured in this inter-comparison for AMS-based single ¹⁴C measurements) is in general much smaller and offsets due to isotope fractionation correction including the fossil carbon contribution are negligible. As long as the methane fraction of the sample is included in the ¹⁴C measurement, carbon fractionation does not significantly change the ¹⁴C-based bioC results.

For measuring the biogenic carbon fraction in gases with unknown mixtures of biogas and natural gas, carbon fractionation can significantly affect the final results, if not prevented from occurring between gas sampling and ¹⁴C measurement. For blends, the ¹⁴C composition of the entire gas should be measured. For gases with 25 % - 75 % bioC, offsets of a maximal ±2.5 % can be expected in the calculated bioC value due to isotope fractionation including the fossil carbon contribution. Unless the δ¹³C value of the biogas in the blend is known, a correction for this anomaly is usually not possible.

To verify the applied ¹⁴C lab-method on unknown gas samples, a reference gas standard with a known ¹⁴C amount is necessary. For the verification of biogases this requires a reference standard with 100 % biogas and a known ¹⁴C amount and for the quantification of the biogenic carbon fraction in blends a reference standard with 50 % - 80 % biogenic carbon and a known ¹⁴C amount would be required.

5 Impact

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

Impact on industrial and other user communities

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

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

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

Impact on the metrology and scientific communities

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

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

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

Impact on relevant standards

The project delivered nine NWIPs which are necessary for extending the portfolio of international standards supporting natural gas, biogas and biomethane characterisation and quality assessment. The nine NWIPs extend the current methods for natural gas properties by providing methods for assessing supplementary

parameters relevant for biomethane. These NWIPs have been submitted to the ISO/TC193/SC1/WG25 Biomethane Working Group. WG25 discussed the proposals in October 2020 in preparation for creating projects within ISO. Once these are completed, it will lead to new international standards.

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

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

Longer-term economic, social and environmental impacts

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

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

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

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

6 List of publications

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