21NRM04 BiometCAP

Deliverable D1: Summary report on the development and validation of methods for the dynamic preparation of gas transfer standards, and multi-component static mixtures, for the EN 16723 impurities in biomethane with relative expanded uncertainties of 1 % - 10 %

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Deliverable Cover Sheet

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1 Summary

This report describes the results obtained within the first work package of the EURAMET European Partnership on Metrology project 21NRM04 “BiometCAP”. The work successfully achieved the development and validation of methods for the dynamic preparation of gas transfer standards, and multi-component static mixtures within the target relative expanded uncertainties of 1 % - 10 %.

2 Introduction

The aim of this work was to improve access to metrological traceability for the performance evaluation of the measurement systems used for biomethane conformity assessment. Although reference standards have been developed in previous projects (e.g. EMRP JRP ENG54 Biogas and EMPIR JRP 16ENG05 Biomethane), the high cost and non-portable nature of certain reference standards (specifically for nmol mol^{-1} amount fraction measurements of reactive gases) acts as a barrier to widespread implementation. Therefore, cost-effective and portable transfer standards were required in order to provide the required level of coverage for the industrial implementation of EN 16723-1 [1] and EN 16723-2 [2]. This work addressed this need by developing four novel standards (one static, three dynamic and one optical) containing multiple impurities which are typically found in biomethane (as defined in section 3), so that accessibility to traceable measurements against EN 16723 can be improved, particularly for locations in the field with logistical limitations.

3 Composition specifications

The specifications for the compositions used within the project were determined via a literature review led by NPL with support from VSL, followed by a stakeholder consultation survey to determine the applicability of the identified compositions. A total of 70 organisations were contacted as part of the stakeholder engagement, including the following 14 countries: Belgium, Denmark, Finland, France, Germany, Republic of Ireland, Italy, Japan, Netherlands, Spain, Switzerland, Taiwan, United Kingdom, and United States. 9 organisations responded to the survey. The organisations included varied representation from separate distinct fields including analytical laboratories, industry and standardisation associations, biogas producers, specialty gas producers, consultancies, gas infrastructure companies, instrument manufacturers, and universities.

Table 1: *Specifications considered for the composition of mixtures and the final vales selected for use in the project*

Component	Specifications from relevant standards				Stakeholder survey results						Unit (if not specified within row)	Relative Uncertainty target	Cylinder passivation example
					Lower Amount Fraction			Higher Amount Fraction					
	EN 16723-1:2016	EN 16723-2:2017	CEN/TR 17238:2018	EN 16726: 2015+A1:2018	Pre-survey	Post-survey	Final selected value	Pre-survey	Post-survey	Final selected value			
total silicon	0.3-1	0.3	-	-	0.3	0.01	**0.3**	1	1	**1**	mgSi m^{-3}	**6%**	BOC SPECTRA-SEAL
terpenes	-	-	-	-	0.01	0.01	**0.01**	10	50	**10**	µmol mol^{-1}	**5%**	Air products Experis
hydrogen chloride	-	-	-	-	1	1	**1**	n/a	n/a	**n/a**	µmol mol^{-1}	**10%**	BOC SPECTRA-SEAL
ammonia	10 (mg m^{-3})	-	-	-	10	0.1	**10**	20	20	**20**	µmol mol^{-1}	**5%**	BOC SPECTRA-SEAL
total sulphur	-	30	-	20*	5	1	**1**	20	50	**50**	mgS m^{-3}	**3%**	BOC SPECTRA-SEAL
Hydrogen sulphide + carbonyl sulphide (as sulphur)	-	As EN 16726	-	5**							mg m^{-3}		
halogenated VOCs	As CEN/TR 17238	-	1-63 (mg m^{-3})***	-	50	50	**50**	750	750	**750**	nmol mol^{-1}	**3 - 10%**	BOC SPECTRA-SEAL
hydrogen	-	2	-	-****	2	0.01	**0.01**	10	10	**10**	cmol mol^{-1}	**1%**	BOC SPECTRA-SEAL
nitrogen					2	0.01	**0.01**	10	10	**10**	cmol mol^{-1}	**1%**	BOC SPECTRA-SEAL
oxygen	-	1	-	0.001 or 1	0.001	0.001	**0.001**	1	1	**1**	cmol mol^{-1}	**1%**	BOC SPECTRA-SEAL
carbon monoxide	0.1	-	-	-	0.1	0.01	**0.1**	n/a	0.1	**0.1**	cmol mol^{-1}	**1%**	BOC SPECTRA-SEAL
Carbon Dioxide	-	-	-	2.5 or 4							cmol mol^{-1}		
Amines	10	10	-	-							mg m^{-3}		

* "For sulfur in high pressure networks and on interconnection points the maximum acceptable sulfur content for conveyance is 20 mg/m^3, where in high pressure networks non-odorized gas is current practice. However, for existing practices with respect to transmission of odorized gas between high pressure networks higher sulfur content value up to 30 mg/m^3 may be accepted."[8]

** "Hydrogen sulphide + Carbonyl sulphide (as sulfur)".[8] The limit for "Mercaptan sulfur without odorant (as sulfur)" is 6 mg m^{-3}.

***the examples given in CEN/TR 17238 are vinyl chloride, cis-1,2-dichloroethene, 1,1,1-trichloroethane (1,1,1-TCA), trichloroethylene (TCE), tetrachloroethylene (PCE), dichloromethane, trichloromethane (TCM), tetrachloromethane (TCC) and Tribromomethane

**** "At present it is not possible to specify a limiting hydrogen value which would generally be valid for all parts of the European gas infrastructure and, as a consequence, it is recommended a case by case analysis."[8]

4 Preparation and validation of static reference standards

4.1 Overview

Based on the results from the stakeholder survey, static gas mixtures were prepared for use during the project. Table 2 provides a summary of the mixtures prepared, the validation technique used, and the uncertainties achieved.

Table 2: *summary of static gas mixtures prepared during the project*

Component	Project partner(s)	Composition detail	Validation technique	Relative uncertainty target (k = 2)	Relative uncertainty achieved (k = 2)	Cylinder passivation
Total silicon	NPL	L2, L3, D3, D4, D5	GC-FID	6%	6%	Air Liquide MEGALONG
	VSL	L2, L3, D3, D4, D5	GC-FID		4 - 11%	Aculife IV
Halogenated VOCs	VSL	dichloropropane, 1,1,2-trichloroethane, dichloromethane, tetrachloroethylene trichloroethylene	GC-(TD)FID	3 - 10%	3 – 10 %	Aculife IV
terpenes	NPL	α-pinene, 3-carene, d-limonene	GC-MS/FID	5%	3%	Air Products Experis
ammonia	NPL	-	GC-NCD	5%	3.5%	BOC SPECTRA-SEAL
Total sulphur	CMI	H_2S, COS, CH_3SH, C_2H_5SH, $(C_2H_5)_2S$, $(C_2H_3)_3CSH$, C_4H_8S	GC-SCD/FID	3%		BOC SPECTRA-SEAL
	BFKH	H_2S, CH_3SH, $(CH_3)_2S$, C_2H_6S, C_3H_8S, $(CH3CH_2)_2S$	GC-SCD/FID		4.6%	BOC SPECTRA-SEAL
	NPL	H_2S, $CH_3SC_2H_5$, $(C_2H_5)_2S$, CH_3SH	GC-SCD/FID		2%	BOC SPECTRA-SEAL
	VSL	CH_3SH, C_2H_5SH, C_2H_6S, $C_4H_{10}S$ and C_4H_4S	GC-SCD		2 - 3%	Aculife IV
Bulk composition (CH_4, H_2, O_2, N_2, CO)	VSL	CH_4, H_2, CO_2, N_2	GC-TCD	1%	≤ 1%	Aculife IV
	NPL	CH_4, H_2, O_2, N_2, CO	GC-TCD	1%	≤ 1%	BOC SPECTRA-SEAL
	TUBITAK	CH_4, H_2, N_2, CO	GC-TCD	1%	≤ 1%	-
	CMI	CH_4, H_2, O_2, N_2, CO	GC-TCD	1%	≤ 1%	BOC SPECTRA-SEAL

4.2 Total silicon and siloxanes

NPL prepared four SI-traceable static primary reference materials containing between 0.3 and 1 mgSi m^{-3} total silicon (5503, 5516, 9299, and 9322), including L2, L3, D3, D4, and D5 siloxanes, in synthetic biomethane. The reference materials have expanded uncertainties of less than 6% for all components. The reference gas mixtures were prepared gravimetrically in 10 L Air Liquide “MEGALONG” passivated aluminium cylinders in three stages, designed to minimise the gravimetric uncertainty of the final mixtures. First, two high amount-fraction “grandparent” mixtures with approximately 100 mgSi m^{-3} total silicon were prepared directly from pure liquids, following ISO 6142-1. Solid D3 siloxane was added as a 5% D3 solution in *n*-hexane. These mixtures were then diluted with N6.0 grade methane to prepare two “parent” mixtures containing approximately 4.00 mgSi m^{-3} total silicon. Finally, these were diluted again with N6.0 grade methane to prepare four mixtures containing approximately 1 mgSi m^{-3} total silicon. The composition of each of the mixtures were validated via a direct comparison method using Gas Chromatography with Flame Ionisation Detection and Mass Spectrometry (GC-FID/MS) in accordance with ISO 6143.The purity of the source chemicals was analysed in accordance with ISO 19229.

VSL prepared reference gases containing L2, L3, D3, D4, D5 in methane in aculife IV passivated cylinders.

4.3 Halogenated VOCs

VSL prepared a reference material in methane containing 0.0526 µmol mol^{-1} of 1,2-dichloropropane, 0.0695 µmol mol^{-1} of 1,1,2-trichloroethane, 0.05 µmol mol^{-1} of dichloromethane, 0.0524 µmol mol^{-1} of tetrachloroethylene and 0.0528 µmol mol^{-1} of trichloroethylene.

4.4 Terpenes

NPL prepared two SI-traceable static primary reference materials containing between 0.01 – 10 µmol mol^{-1} of terpenes, comprising α-pinene, 3-carene, and d-limonene, in synthetic biomethane with less than 5% expanded uncertainty for all components. The reference gas mixtures were prepared gravimetrically in 10 L Air Products "Experis" passivated aluminium cylinders directly from the pure liquid components and N6.0 grade methane. The composition of the mixtures was validated via a direct comparison method using Gas Chromatography with Flame Ionisation Detection and Mass Spectrometry (GC-FID/MS).

4.5 Ammonia

NPL prepared two SI-traceable static primary reference materials containing between 10 – 20 µmol mol^{-1} ammonia in synthetic biomethane with less than 6% expanded uncertainty. The reference gas mixtures were prepared gravimetrically in 10 L BOC "SPECTRA-SEAL" passivated aluminium cylinders in two stages, designed to minimise the gravimetric uncertainty of the final mixtures. First, two high amount-fraction "parent" mixtures containing approximately 400 µmol mol^{-1} ammonia in synthetic biomethane were prepared directly from high purity (N5.0 grade) anhydrous ammonia gas using 100 mL stainless steel transfer vessels. These mixtures were diluted with N6.0 grade methane to prepare the two mixtures containing approximately 20 µmol mol^{-1} ammonia in synthetic biomethane. The composition of the mixtures was validated via a direct comparison method using Gas Chromatography with Sulphur Chemiluminescence Detection,

4.6 Total sulphur

NPL prepared two SI-traceable static primary reference materials containing between 1-50 $mgSm^{-3}$ total sulphur (D148923 and D148949), including hydrogen sulphide, methyl ethyl sulphide, diethyl sulphide, and methanethiol in synthetic biomethane. The reference gas mixtures were prepared gravimetrically in 10 L BOC "SPECTRA-SEAL" passivated aluminium cylinders directly from binary mixtures of individual sulphur compounds in synthetic biomethane, following ISO 6142-1. The two multi-component sulphur mixtures prepared contained approximately 20 $mgSm^{-3}$ total sulphur, with expanded uncertainties of less than 2% for all components. The composition of the two mixtures were validated via a direct comparison method using GC-SCD in accordance with ISO 6143.

VSL prepared standards containing CH_3SH, C_2H_5SH, C_2H_6S, $C_4H_{10}S$ and C_4H_4S in the range of 2 – 10 µmol/mol in a methane matrix.

BFKH prepared mixtures containing H_2S, CH_3SH, $(CH_3)_2S$, C_2H_6S, C_3H_8S, and $(CH3CH_2)_2S$ in the range of 20 – 106 µmol/mol in a methane matrix.

CMI prepared mixtures containing H_2S, COS, CH_3SH, C_2H_5SH, $(C_2H_5)_2S$,$(C_2H_3)_3CSH$, C_4H_8S in the range of 0.5 – 6 mg/m^3 in a methane matrix.

4.7 Bulk composition

NPL prepared four SI-traceable static primary reference materials containing the bulk components of biomethane, comprising CH_4, N_2, O_2, H_2, and CO with less than 1% expanded uncertainty for all components. The standards were prepared in two groups, the "high" group, containing approximately 10 cmol mol^{-1} H_2, 9.5 cmol mol^{-1} N_2, 0.2 cmol mol^{-1} O_2, and 0.2 µmol mol^{-1} CO in synthetic biomethane; and the "low" group, containing approximately 20 000 µmol mol^{-1} hydrogen, 20 000 µmol mol^{-1} nitrogen, 400 µmol mol^{-1} oxygen, and 1000 µmol mol^{-1} carbon monoxide in synthetic biomethane. The reference gas mixtures were prepared gravimetrically in 10 L BOC "SPECTRA-SEAL" passivated aluminium cylinders directly from pure gasses or

binary mixtures of pure gasses in methane. The composition of the mixtures was validated via a direct comparison using Gas Chromatography with Thermal Conductivity Detection

VSL prepared mixtures containing CH_4, H_2, CO_2 and N_2 at various amount fractions in order to optimize and validate their dynamic system.

TUBITAK prepared mixtures containing CH_4, H_2, CO and N_2 at various amount fractions for use throughout the project in comparison with NPLs dynamic system and for validation of the biomethane protocol developed within WP2 for the project. The O_2 was removed from the composition plan for the mixture for safety reasons.

CMI prepared mixtures containing CH_4, H_2, O_2, N_2, CO at various amount fractions for use throughout the project in comparison with NPLs dynamic system and for validation of the biomethane protocol developed within WP2 for the project.

4.8 Multi-component stability trial

NPL prepared a multi-component static gas standard consisting of L2, L3, D3, D4, D5 siloxanes, α-pinene, 3-carene, d-limonene, benzene and toluene in methane matrix. The standard was prepared gravimetrically according to ISO 6142-1 [3], in a 10L Air Liquide “MEGALONG” passivated aluminium cylinder. The gas standard was validated in accordance with ISO 6143 [4] using direct comparison method. The amount fractions of each component are listed in **Table 3**.

Table 3: *Amount fraction of multi-component static gas standard*

Component	Amount fraction (μmol mol^{-1})
L2 siloxane	0.085
L3 siloxane	0.056
D3 siloxane	0.056
D4 siloxane	0.043
D5 siloxane	0.033
Benzene	10
Toluene	10
α-pinene	3
3-carene	3
limonene	3
Methane	**Balance**

The mixture prepared and validated at day 0, D223088, and its stability monitored at 3 (M3), 6 (M6) and 9 (M9) months to evaluate long-term stability of the components in the static gas standard.

The technique used to assess the stability of D223088 after 3 months, is through direct validation where it is compared against a newly prepared and validated standard, D223089. The new standard was prepared following an identical method to D223088.

The results from the 3-month stability for the 10-components are shown in Figure 1 below.

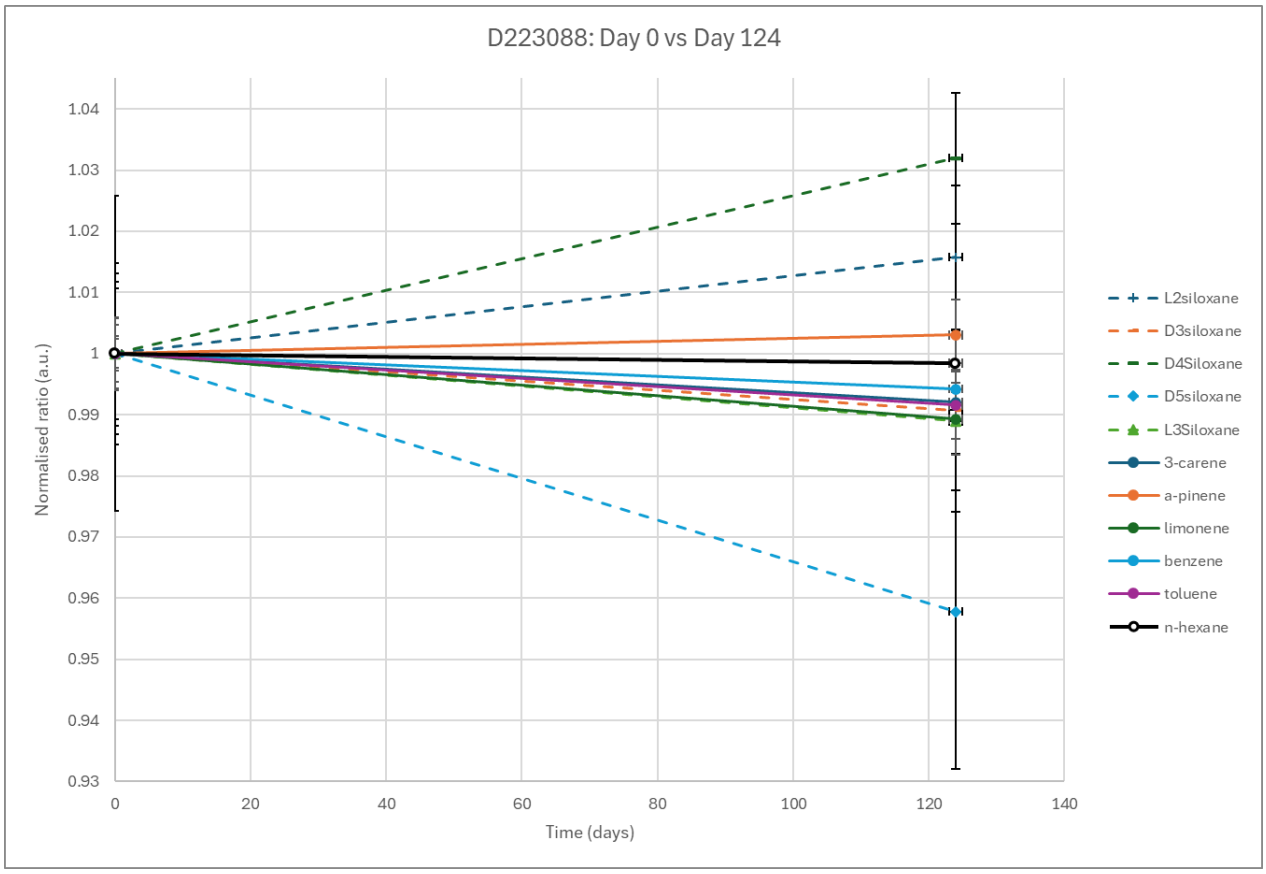

Figure 1: *Graph showing stability for all analytes in multi-component static reference standard D223088 over a 124-day period*

The study found that all components were stable to within 7% over a 124-day period. A further stability measurement is planned for reporting in paper format.

5 Development of lab-based and portable dynamic and optical reference standards

5.1 NPL

In activity A1.2.1, NPL developed a Dynamic dilution system, made using five thermal mass flow controllers (MFCs). A schematic of the system is shown in Figure 2.

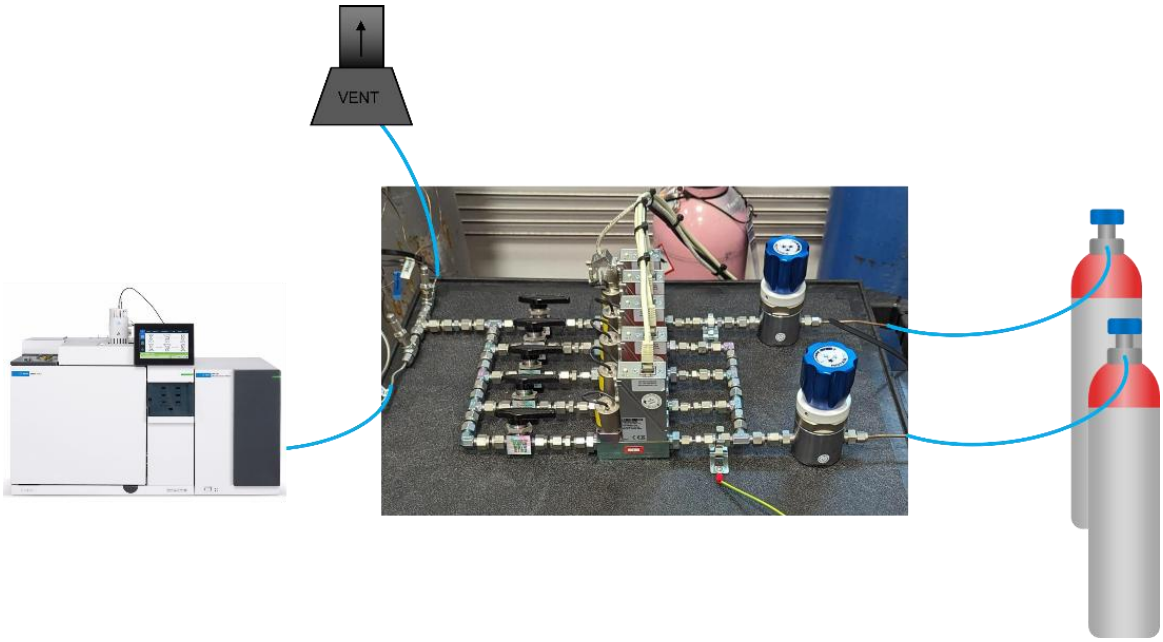

***Figure 2**: NPL dilution system schematic*

A reference material was connected to the 0-25 ml min^{-1} MFC input, and pure diluent gas was connected to the second input. One of four Bronkhorst MFCs (0-50 ml min-1, 0-125 ml min^{-1}, 0-625 ml min^{-1}, 0-3125 ml min-1) was selected, depending on the desired amount fraction of the blended gas. The MFC flow ratios were set according to the required amount fraction and minimised where possible to conserve gas. Flows below 20% of a controller's nominal flow rate were not used to minimise flow uncertainties.

Gas was allowed to flow for approximately 10 minutes to allow the system to passivate. The output flow was tuned to meet the specifications of the analyser connected to the system. For chromatographic data were acquired in this project, the output flow used was set to approximately 25 ml min^{-1}.

Static reference material(s), prepared in WP1, were used in the performance evaluation of the dilution system.

The uncertainty of the output flow was calculated according to Equation 1:

$$U(C_{total}) = C_{total}\sqrt{\left(\frac{U(C_{parent})}{C_{parent}}\right)^2 + \left(\frac{U(F_{diluent})}{F_{diluent}}\right)^2 + \left(\frac{U(F_{parent})}{F_{parent}}\right)^2} \qquad \textit{Equation 1}$$

Where C_{parent} and C_{total} are the gravimetric concentrations of the parent and combined output mixtures. $F_{diluent}$ and F_{parent} are flows of the diluent and parent mixtures respectively.

5.2 VSL

For activity A1.2.2, using the system developed in 16ENG05 Biomethane, VSL performed a multi-point calibration by dynamically preparing various H_2 in CH_4 standards, ranging from 100% CH_4 to 70% CH_4. During the initial tests it was observed that the dynamically prepared mixtures deviated -0.4% to -1.2% for H_2 and -0.4% to -0.5% for CH_4 compared to static mixtures, which was unsatisfactory.

A further look on the data is required, as not only the mixtures show a negative deviation, but also the pure CH_4 standard. During the experiment, the static mixtures were analyzed over the weekend on a GC-TCD, followed by two days of dynamic generation. The pure CH_4 standard was injected 30 times directly, and 7 times from the dynamic dilution system. The evolution of the GC response is shown in Figure 3 below.

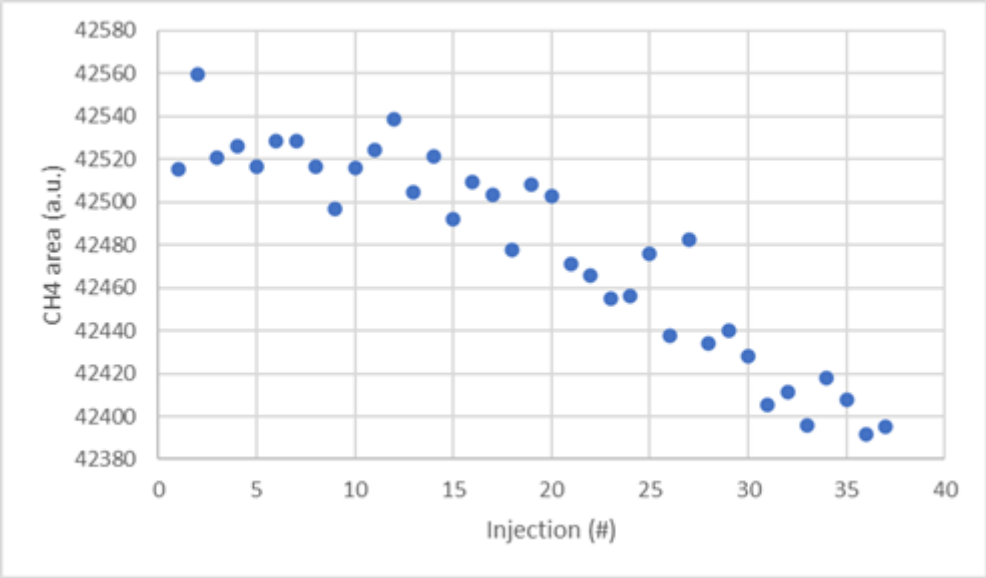

Figure 3: *Evolution of CH_4 response area as function of injection for the mixture consisting of 100% CH_4. Injection 1 – 30 is directly from a 100% CH_4 standard. Followed by injection 31 – 37 100% CH_4 using the dilution system.*

Interestingly, in the chromatogram of the dynamic 100% CH_4 mixture, no other components (H_2, CO_2, N_2) were observed. This indicates that the system did not leak, as N_2 and O_2 would be present in measurable amounts. After further investigation, it was observed that the ambient pressure increased from 101.25 kPa at injection 1, to 101.98 kPa at injection 30 (last of the static CH_4 standard) and up to 102.64 kPa at the injection 37 (last of the dynamic standards). Although a pressure correction was applied to correct the data it was found to be insufficient and future comparisons between the static and dynamic standards should thus be performed in a narrow time window, preferably measuring on a single day.

Next, a one-to-one comparison was performed using a 5% H_2 in CH_4 static standards and two dynamic standards at a total generation rate of 0.5 L/min and 1.0 L/min. To minimize the effect of ambient pressure, the measurement was performed on a single day. The analytical amount fraction H_2 of the dynamically generated mixture showed a deviation of -0.67% and -1.05%, respectively on the 1.0 L/min and 0.5 L/min generation rates. For CH_4, the deviation was 0.05-0.08%. The inconsistency in the deviation on the H_2 amount fraction depending on the flow rate requires some more attention.

To rule out effects of mixing and matrix gas, the one-to-one comparison was repeated using 30% H_2 in N_2. Resulting in a deviation of -0.5% for the H_2 amount fraction generated using both 0.5 L/min and 1.0 L/min flowrates compared to the static mixture.

As the largest deviation was observed repeatedly on the H2 amount fractions, it was decided to look into the flow calibration history of the H_2 MFC.

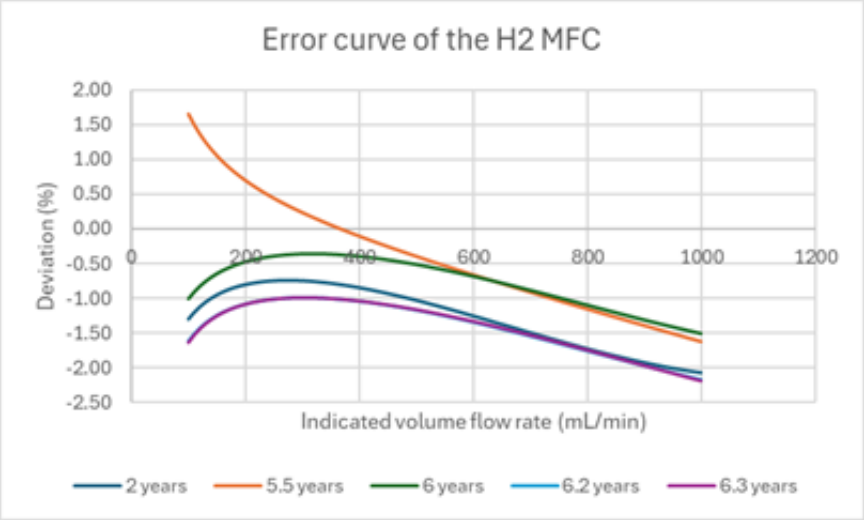

Figure 4: *Calibration curve (error curve) of the H2 MFC with a capacity of 1,000 mL/min. The various calibration fits of the error curve are shown upon their approximate age after receival at VSL.*

For the experiments described above, the calibration fit after 5.5 years (orange in Figure 4) was used. Just with the history of a single calibration fit a few years earlier, there was no comparison data available and the calibration of this MFC was followed in time. It was observed that after a few months, the calibration fit showed similar behavior and was negatively affected in comparison to the orange fit. On one hand, fitting of the original data with the newly obtained calibration fit did improve the results and lowered the deviation between static and dynamical gas standards. The deviation on the H_2 amount fraction was -0.46% to +0.10% and on the CH_4 amount fractions -0.38 to -0.61%. On the other hand, a last check was required and three mixtures were dynamically generated and compared to the static standards at amount fractions of 15 – 30% H_2 in CH_4. The resulting deviation between static standards and dynamic standards is -0.31% to -0.40% on the H_2 amount fraction and +0.17% to +0.21% on the CH_4 amount fraction.

In summary, after optimization of the system, these results show satisfactory equivalence between static biomethane standards and the dynamic dilution system of VSL, with an uncertainty below 1%.

5.3 PTB

PTB upgraded the optical feedback cavity enhance absorption spectroscopy (OF-CEAS) instrument to be operated as an optical gas standard for NH_3 in methane matrix targeting amount fractions in the range of 10-20 µmol mol^{-1}. The OF-CEAS analyser in Figure 5, comprised of a high finesse 'V'-shaped optical cavity with three high reflective mirrors (R>99.99%), allows the laser light to travel more than 10 kilometers of effective optical pathlength in the small volume of an optical cavity of geometrical length of ~40 cm. A distributed feedback diode laser operating at near ~1.5µm was used to probe the target ammonia absorption line. The light coming out from the cavity was measured by a photo detector placed behind the exit mirror along one arm of the 'V'-shaped cavity.

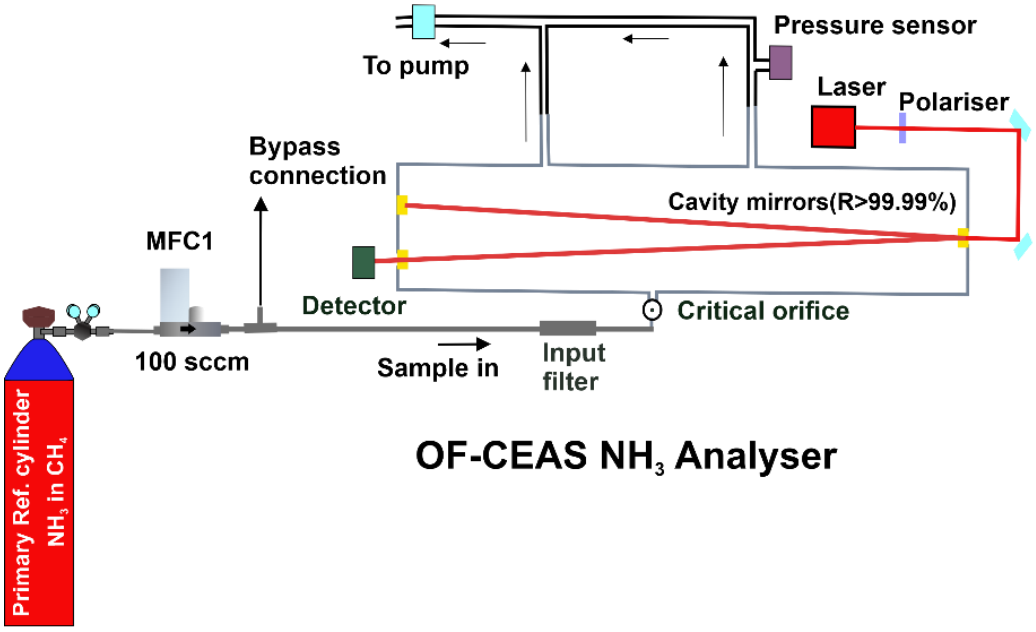

Figure 5: *schematic diagram of the PTB OF-CEAS experimental setup*

The schematic diagram of the OF-CEAS including the sample preparation system is shown in Figure 5. For spectroscopic measurements, a gas sample of about 19.7±1.1 µmol mol^{-1} NH_3 in CH4, provided by NPL, was used. A Silconert coated calibrated mass flow controller (MFC1, 100 sccm) was used control the NH_3 flow rate to the analyzer. During the measurement, the gas flow was maintained at a flow rate of 0.1 L/min and the gas pressure (*p*) as well as the gas temperature (*T*) were maintained at ~100hPa (*p*) and ~318.15K, respectively. The relative uncertainties of the measured gas temperature and the pressure are 0.3% and 0.31% respectively.

Figure 2. shows example spectra for the 19.7 µmol/mol NH_3 in CH_4. The gas mixture used was provided by NPL. The data in Figure 2 was fitted with a Voigt profile to determine the integrated absorption coefficient for the targeted NH_3 line. To account for interference from neighboring absorption lines, 10 NH_3 and 22 methane absorption lines were fitted in the spectral window in Figure 6. The overlapping methane lines with NH_3 absorption lines made the overall spectra very complex. Thus, a careful fitting procedure is required to derive accurate and reliable amount fraction in methane matrix. Using the line area, the ammonia concentration was calculated according to Equation 2

$$x_{NH3} = \frac{k_B.\ T.\ \alpha_{int}}{S_T.\ p} \qquad \textit{Equation 2}$$

where the quantity k_B is the Boltzmann constant, α_{int} is the integrated absorption coefficient (area under the absorption coefficient curve= 'line area') and S_T is the line intensity of the probed molecular transition at gas temperature *T*. The amount fraction (concentration) results x_{NH3} is directly traceable to the international system of units (SI) if all the quantities in the right-hand side of equation (1) are traceable to the SI as well. As introduced, an instrument that can provide amount fraction results that are directly traceable to the SI can be referred to as an optical gas standard (OGS).

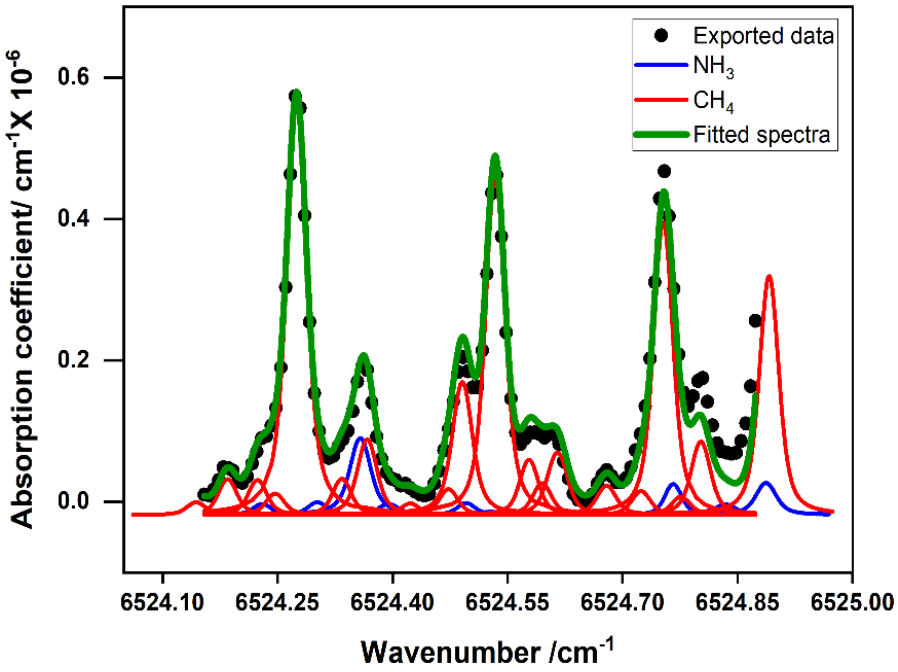

Figure 6: *(a) Measured spectra of 19.7 µmol/mol NH3 ammonia in methane matrix from the OFCEAS analyzer. The data is fitted with a Voigt profile.*

From the data in Figure 6, an amount fraction of 19.62 ± 0.98 µmol mol^{-1} ammonia in methane was derived. The relative uncertainty of the analyzers' results is 5 % (k = 1) as shown in the uncertainty budget in Table 4.

Table 4: *Uncertainty budget for OF-CEAS NH_3 amount fraction results*

Parameter	Relative uncertainty (k = 1), %	Index (% individual contribution)
Pressure	0.30	0.3
Temperature	0.31	0.4
Line strength	5.00	95.5
Line area	1.00	3.8
NH3 concentration (x_{NH3}) result	**5.0 (combined uncertainty)**	**-**

The spectroscopic NH3 amount fraction results, i.e. 19.62 ± 1.96 (k = 2) are in good agreement with the value (19.7 ± 1.1 µmol/ mol, k = 2) provided by NPL for the gas mixture. Direct traceability of the spectroscopic results is addressed via the traceability of the parameters in the right-hand side of Equation 2. The gas temperature (T) and pressure (p) have been measured with sensors traceable to respective PTB standards. The line intensity S_T was taken from the HITRAN 2024 and validated via separate FTIR measurements at PTB.

5.4 VTT

Operating principle

VTT's trace gas generator is based on liquid evaporation technique. It can be used for generating reference gases of water-soluble chemical compounds in a wide concentration range from µmol mol^{-1} (ppm) down to nmol mol^{-1} (ppb) levels. It is especially well suited for compounds which easily stick to surfaces and for which its challenging to produce traceable, long lived and stable static reference gas mixtures. It is also possible to make these systems portable, enabling their use both in laboratory and field conditions.

A schematic of the VTT trace gas generator is given in Figure 7. The operating principle is based on injecting a solution with known concentration into a carrier gas stream using an automatic syringe. Proper mixing and evaporation is ensured by applying a nozzle and evaporation heater. The carrier gas (methane in this study) was used as a carrier gas and the flow rate was controlled using a mass flow controller with a nominal flow range up of 10 L/min. Ammonium hydroxide (NH_4OH) was used as the solution for generating trace amounts of ammonia (NH_3) into the carrier gas. Distilled water is used to flush the system between measurement runs.

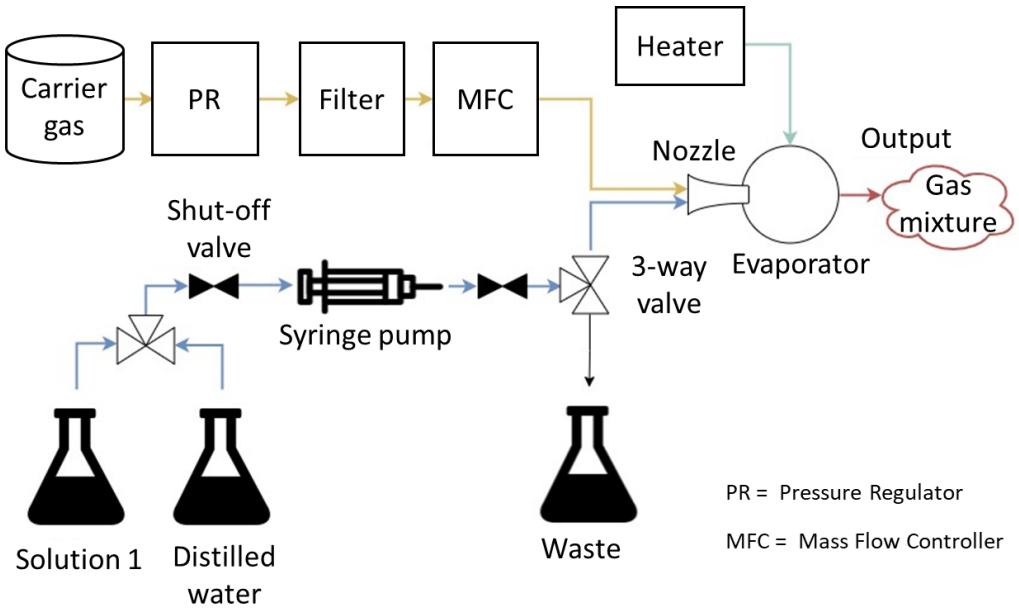

Figure 7. Schematic of operating principle of VTT trace gas generator.

Traceability

Traceability to the SI system of units is achieved by calibrating the mass flow controller and the syringe pump traceably to international standards and using certified solutions. To achieve the desired concentration, diluting the solution is in many cases necessary. This can be done using a calibrated weighing balance and a micropipette to dispense a known amount of the solution into water weighed by the balance.

Specifications

The VTT portable trace gas generator (Figure 8) can be applied for calibrating gas analyzers in the field. Any water-soluble chemical can be generated with the device, but it is especially well suited for generating ppm to ppb concentrations of reactive gases, e.g. NH_3, HCl, HF and Hg, which are difficult to realize as gas mixtures in cylinders due to their reactive nature and tendency to stick to surfaces. Moreover, any carrier gas can be used, as long as it is chemically compatible with the injected solution and the inner surfaces of the generator.

This makes the generator a versatile tool for flexible generation of a multitude of gas mixtures. In past and ongoing research projects the device has been successfully demonstrated for the following gas mixtures: Hg in air (16ENV01 MercOx [5]), HCL and NH_3 in hydrogen (21GRD05 Met4H2 [6]), NH_3 in carbon dioxide (21GRD06 MetCCUS [7]) and NH_3 in air (21GRD10 quantiAGREMI [8]). In the 16ENG05 Biomethane project [9] the generator was applied for generating trace amounts of HF and HCL in biomethane. In this project (21NRM04 BiometCAP [10]) the generator was further developed for generating µmol mol^{-1} levels of NH_3 in biomethane.

Figure 8: *VTT portable trace gas generator.*

More detailed specifications are given in Table 5.

Table 5*. Specification of VTT trace gas generator.*

Specification	Value
Generator output flow rate	up to 10 L/min
Generated gas concentration	ppm to ppb levels
Generated trace gases	Any water-soluble chemical (e.g. NH_3, HCL, HF, Hg)*
Carrier gas	Air, N_2, CH_4, H_2, CO_2*
Typical water concentration of generated gas	0.1 - 1.5 vol-%
Typical uncertainty of generated gas concentration	1.9 %

* As long as chemical compatibility with carrier and trace gas, and generator inner surfaces is ensured

6 Validation of dynamic reference standards

6.1 NPL validation of dynamic preparation facility

The static reference materials prepared in work package 1 were used to test NPLs dynamic dilution system. The PRMs were dynamically diluted to five amount fractions, linearly spaced over the ranges defined in A1.1.1. The gas chromatograph signal corresponding to each concentration was recorded, forming a calibration curve (Figure 9). NPL's XLGENLINE software was used to perform a weighted, linear least squares fit on the data and calculate gradient and y intercept uncertainties. R^2 was calculated to assess goodness of the linear fit for each data set, informing the viable working range for use in the future conformity assessment of biomethane.

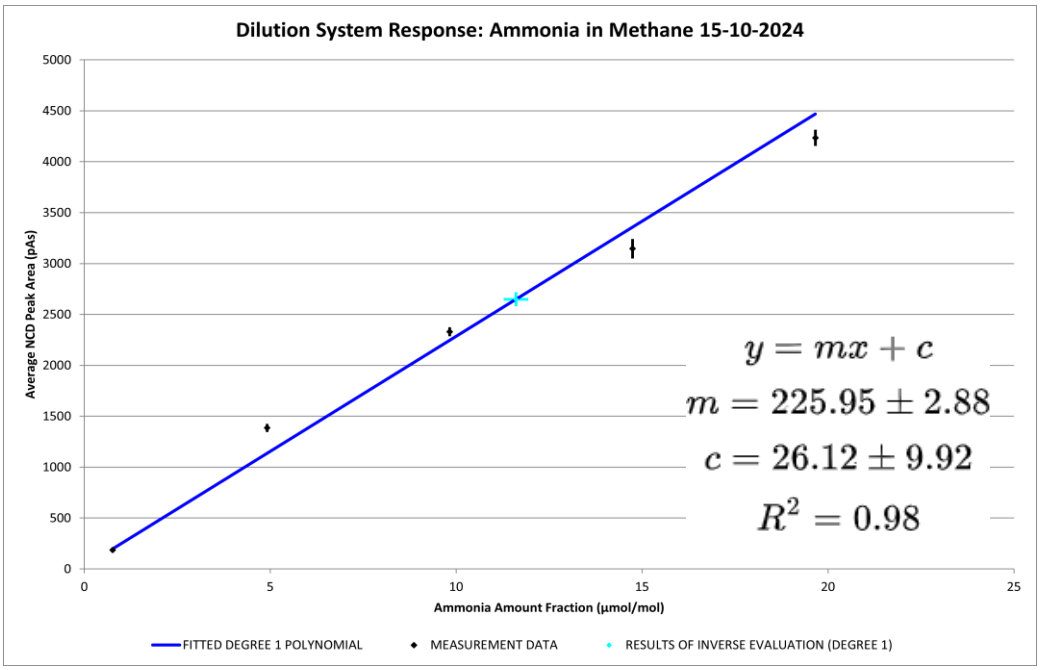

Figure 9: *Example data from the validation of NPL's dynamic dilution system. Performed using multiple dilutions of a 400 µmol mol^{-1} ammonia in methane PRM prepared by NPL. Measurement uncertainties do not account for deviation from fitted data in all cases, likely due to surface adsorption effects.*

There were cases, when working with sulphur and ammonia compounds, where the measurement uncertainty did not account for the deviation from the fitted data. This bias is believed to be due to sulphur and ammonia compounds' tendency to adsorb to metallic surfaces, combined with insufficient purging procedure for the dynamic system. If this method is to be used in the conformity assessment of biomethane, the system should be given sufficient time to appropriately passivate and stabilise to avoid introducing adsorption-related biases.

The dynamic standard was used to certify a sulphur reference standard provided by BFKH. The certified value was within 8% of the true value for total sulphur, with an uncertainty of 16%.

The sulphur mixtures from CMI were not provided within the required timeframe for comparison within WP1.

The dynamic standard was used to certify a reference standard containing CO (~0.1 cmol mol^{-1}), H_2 (~2 cmol mol^{-1}), and N_2 (~2 cmol mol^{-1}), provided by TUBITAK. The certified values was within 1% of the gravimetric value for CO, 4% for H_2 and 13% for N_2 with an uncertainty of 16%.

6.2 VSL validation of dynamic preparation facility

In order to validate their dynamic preparation facility, VSL compared nine dynamically generated reference gas mixtures containing the matrix gases CH_4, H_2, CO_2 and N_2 at varying compositions to relevant static-gravimetric synthetic biogas mixtures using GC-TCD + GC-FID on five consecutive days.

The results of this measurement are shown in Table 6. The indicated expected amount fraction in mol% (x) of the four matrix components H_2, N_2, CH_4 and CO_2 is given along with the relative standard uncertainty (u) of the dynamic dilution. The analytical determined amount fraction was calculated based on a quadratic fit using a set of static gas mixtures, which were measured on at least two different days, using a quadratic fit conform ISO 6143. Subsequently, the relative deviation (D) between the determined and expected amount fraction was calculated and is included in table 1.

For instance, BIO4J1501 is the dynamic gas mixture with a target composition of 15 mol% H_2, 20 mol% N_2 and 65 mol% CH_4. Based on the performance of the system, flow calibration of the individual MFCs and purity of the pure parent gases an amount fraction of 14.94 mol%, 19.92 mol% and 65.13 mol% was expected for, respectively, H_2, N_2 and CH_4. The uncertainty on the expected amount fraction ranges from 0.09% to 0.23%. After analysis, the amount fractions of the matrix gases in this gas mixture showed a relative deviation compared to the calibration fit between -0.11% for N_2 and +0.16% for H_2.

Typically, the deviation between analytically determined amount fraction and expected amount fraction was within 1% for all components: H_2 between 15 – 20 mol%, N_2 between 15 – 25 mol%, CH_4 between 25 – 85 mol% and CO_2 between 20 – 40 mol%. With the exception of the mixtures at lower amount fractions of H_2 as in the mixtures BIO4J1701 – BIO4J1703. In these mixtures the use of a replacement MFC with a smaller range to achieve lower amount fractions of H_2 in the range of 1.5 – 5.1 mol% resulted in larger deviations between expected and observed amount fractions of H_2 up to 2%. Replacement to the original MFC overcame these deviations, as observed for the H_2 deviation in BIO4J1801.

Table 6: *Comparison of the dynamically generated biomethane mixtures compared to static mixtures conform ISO 6143.*

Mixture	Hydrogen			Nitrogen			Methane			Carbon dioxide		
	x (mol%)	u (%)	D (%)	x (mol%)	u (%)	D (%)	x (mol%)	u (%)	D (%)	x (mol%)	u (%)	D (%)
BIO4J1501	14.94%	0.23%	0.16%	19.92%	0.22%	-0.11%	65.13%	0.09%	-0.07%	0.00%	51.37%	-
BIO4J1502	14.93%	0.26%	-0.01%	0.00%	58.97%	-	85.07%	0.05%	-0.41%	0.00%	55.32%	-
BIO4J1601*	19.99%	0.20%	-0.43%	14.95%	0.21%	-0.85%	45.10%	0.13%	-0.36%	19.95%	0.20%	0.47%
BIO4J1602	19.98%	0.20%	-0.52%	14.94%	0.21%	-0.88%	35.05%	0.16%	-1.54%	30.03%	0.17%	-0.63%
BIO4J1603	14.95%	0.21%	-0.4%	19.94%	0.20%	-0.74%	25.05%	0.19%	-0.16%	40.05%	0.15%	-0.89%
BIO4J1701	2.05%**	0.24%**	1.64%**	14.93%	0.22%	-0.44%	48.03%	0.14%	-0.16%	34.99%	0.17%	-0.66%
BIO4J1702	1.56%**	0.24%**	1.01%**	19.67%	0.21%	-0.45%	38.94%	0.16%	-0.33%	39.84%	0.16%	-0.75%
BIO4J1703	5.09%**	0.23%**	2.10%**	24.89%	0.19%	-0.41%	40.02%	0.15%	-0.65%	30.00%	0.18%	-0.74%
BIO4J1801*	19.98%	0.20%	-0.22%	14.94%	0.21%	-0.59%	45.07%	0.13%	0.26%	20.02%	0.20%	-0.18%

* Mixtures BIO4J1601& BIO4J1801 were replicates. ** A different MFC was used with a capacity of 100 mL/min instead of 1000 mL/min.

The included uncertainty budget for the dynamic mixtures consists of three main contributors (Equation 3). First a term related to the mass flow, including calibration uncertainty (0.205%), conversion from volume flow rate to mass flow rate (e.g. 0.033% for CO_2) and repeatability (0.200%). Secondly, the uncertainty associated to the molar weight of the pure components and thirdly, due to the purity of the parent mixtures.

$$u_{x,dynamic} = \sqrt{u^2_{mass\ flow} + u^2_{molar\ weight} + u^2_{purity}}$$ *Equation 3*

In general, the analytically assigned amount fractions for the four components H_2, N_2, CH_4 and CO_2 in the dynamic mixtures deviate up to 2 to 3 times the standard uncertainty dilution, but they are typically still within the desired 1% target uncertainty.

It was observed that duplicates of static mixtures showed to be reproducible within 0.5% for H_2 between 1.5 – 20 mol%, 0.4% for N_2 between 10 – 25 mol%, 0.4% for CH_4 between 38 – 75 mol% and 0.4% for CO_2 between 15 – 20 mol%. One dynamic mixture was repeated (BIO4J1601 and BIO4J1801) and showed a similar repeatability within 0.4% for all four matrix components. This reproducibility is mostly due to the length of the measurement (5 days) for which it is known that TCD detectors drift along the changing ambient pressure.

A one-to-one comparison was performed in order to neglect the influence of this changing ambient pressure and thus detector drift in time. Table 7 summarizes the results of this experiment. The response factors of CO_2, CH_4, N_2 and H_2 in the dynamically prepared gas mixture BIO4J0501 were compared to those of the gravimetrical gas mixture VSL144182.Subsequently, the relative deviations were calculated and were all well within the desired 1% regime. These results demonstrate again that the dynamic dilution facility operates in accordance with the target relative uncertainty of 1% as desired.

Table 7: *Results of a one-to-one comparison between a dynamically and gravimetrically prepared gas mixture representative of a synthetic biomethane matrix.*

Mixture	Component	Amount fraction (mol%)	GC area (au)	Response factor (area/mol/mol)	Deviation between dynamic and static (%)
VSL144182	CO_2	43.80%	29,844.92	68,136	-
BIO4J0501		43.82%	29,748.19	67,887	0.36%
VSL144182	CH_4	39.13%	18,666.26	47,701	-
BIO4J0501		39.23%	18,693.71	47,650	0.11%
VSL144182	N_2	14.99%	4,225.37	28,179	-
BIO4J0501		14.85%	4,191.44	28,209	-0.11%
VSL144182	H_2	2.00%	5,516.68	274,571	-
BIO4J0501		2.09%	5,786.97	276,823	-0.81%

Part 2 - Dynamic generation of HCl and NH_3 reference gas standards

The permeation technique relies on the continuous transfer of a substance from a device known as a permeator to the surrounding environment. This process leads to a steady loss of mass of the permeator, which is consistently monitored. Permeation devices are situated within a permeation chamber that ensures precise regulation of temperature and pressure, while being continuously purged with a stream of carrier gas. This method is primarily utilized for the dynamic production of highly accurate gas mixture standards, with substance concentrations varying from a few nanomoles per mole (nmol mol^{-1}) to 100 micromoles per mole (µmol mol^{-1}). It is especially effective for reactive analytes such as NO_2, SO_2, HCl, and NH_3 for which static reference gas standards often faces issues like limit stability, deviations from gravimetry, and long stabilization times (i.e., high gas use).

To assess the mass loss of the permeator, it is positioned within the magnetic suspension balance (MSB) (Rubotherm, TA instruments, The Netherlands), as illustrated in Figure 11.

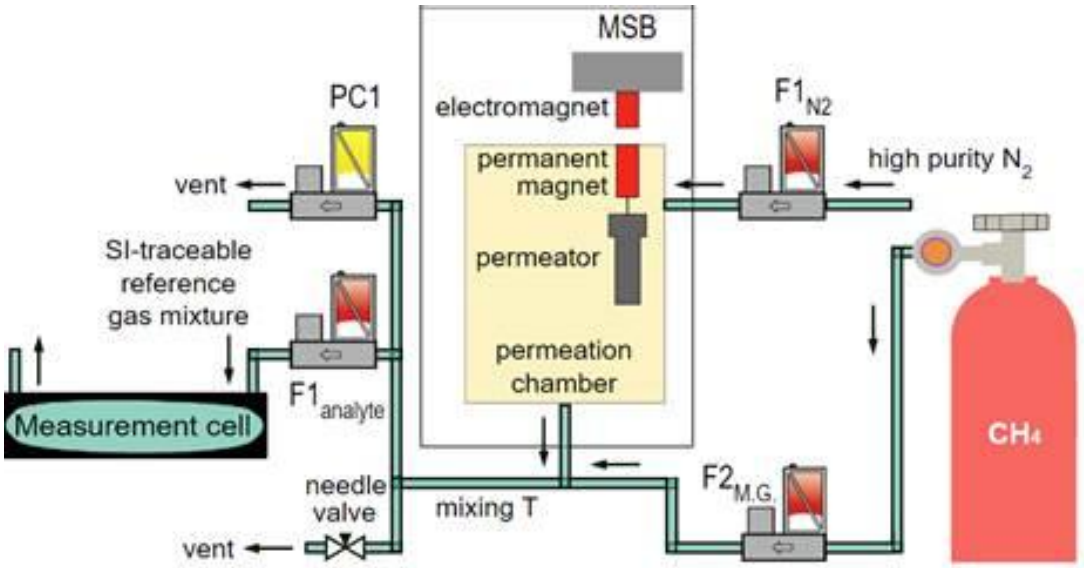

Figure 10: *Generation of HCl in CH_4 standards based on permeation following ISO 6145-10 (permeation) and ISO 6145-7 (thermal mass flow controllers).*

The permeators utilized in this study comprise a short polymer tube that is sealed at both ends with glass plugs and filled with the target analyte. The vapor of the analyte permeates into the polymer, diffuses through it, and is subsequently incorporated into the sample gas stream. The use of an MSB system facilitates continuous and uninterrupted mass measurements, as the temperature-controlled chamber, where the permeator is suspended, is physically separated from the balance itself. Within the context of the BiometCAP project, the MSB system is employed to produce trace amounts of HCl and NH_3.

Dynamic generation based on permeation following ISO 6145-10 [11] and using a magnetic suspension balance (MSB) as shown in Figure 2. Permeation tubes containing HCl or NH_3 were obtained from Fine Metrology and had a specified permeation rate for HCl of 600 ng/min at 50 °C and for NH_3 of 3500 ng/min at 30 °C. Part of the flow is directed to the vent while the flow directed to the analyzer is kept constant at 300 mL/min. Note that the permeation chamber itself is flushed with N_2 while the much larger dilution flow is CH_4, therefore there will always be some N_2 in the matrix gas.

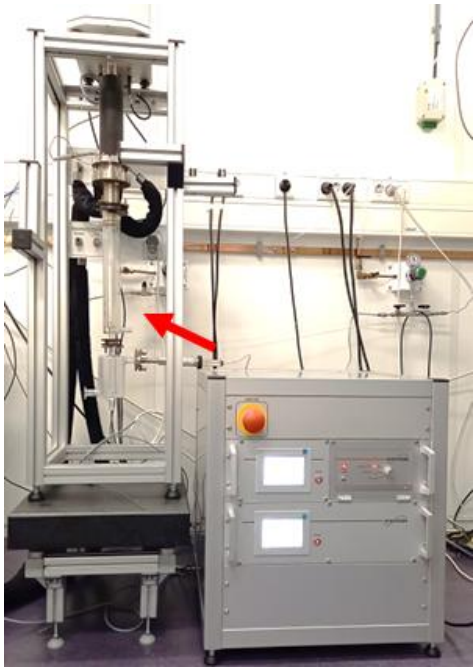

Figure 11: *Photo of permeation facility. The red arrow indicates the position of the permeation tube.*

Typical expanded uncertainty of the generated amount fractions of HCl and NH_3 is 3-4%. Major contributors include the temperature dependence of the permeation rate, the mass flow rate and the determination of the permeation rate from the mass loss date (in particular for some of the experiments done for BiometCAP, the suspension balance showed instabilities). A detailed description of the data analysis and the uncertainty calculations can be found in [12,13].

Part 3 – Calibration of sulphur analyser with the dynamic preparation facility

Five dynamically generated reference gas mixtures containing the at least CH_3SH, C_2H_5SH, C_2H_6S, $C_4H_{10}S$ and C_4H_4S in the range of 2 – 10 µmol/mol in a methane matrix were compared to static-gravimetric mixtures containing the sulfurs in the range of 1 – 10 µmol/mol in methane using GC-FID (and/or GC-SCD). A total of six dynamic gas mixtures were generated on two consecutive days, the nights and the day after gas generation were used to measure the gravimetric gas mixtures. The gravimetric mixtures were then used as calibration standards and an analytical amount fraction of the sulfurs was assigned to the dynamically generated mixtures conform ISO 6143 using a cubic fit. The relative deviation between the analytically determined amount fraction and expected amount fraction based on the dilutions is shown in table 3 below.

Table 8: *Composition and deviation between analytical and dynamical amount fractions of gas mixtures containing multiple sulfur compounds in methane.*

Mixture	CH_3SH		C_2H_5SH		DMS		DES		THT	
	x (µmol/mol)	D (%)	x (µmol/mol)	D (%)	x (µmol/mol)	D (%)	x (µmol/mol)	D (%)	x (µmol/mol)	D (%)
BIO4E1501	2.00	1.72%	1.99	2.06%	1.99	1.15%	2.02	1.02%	1.99	1.87%
BIO4E1502	2.50	1.52%	2.49	1.53%	2.49	1.14%	2.53	0.63%	2.49	1.56%
BIO4E1503	4.99	1.62%	4.98	1.62%	4.97	1.08%	5.06	0.82%	4.98	1.59%
VSL174288	0.99	2.19%	0.99	2.28%	0.99	1.15%	1.00	1.65%	0.99	1.43%
VSL184285	1.86	0.43%	1.84	0.84%	1.88	0.50%	1.85	0.71%	1.59	0.75%
BIO4E1601	7.40	1.72%	7.38	1.30%	7.37	1.14%	7.50	0.87%	7.38	1.24%
BIO4E1602	9.99	1.82%	9.96	1.91%	9.95	1.59%	10.12	1.59%	9.97	1.76%
BIO4E1603	2.00	1.20%	1.99	1.73%	1.99	1.35%	2.02	1.01%	1.99	1.73%

Two gravimetrically prepared gas mixtures (VSL174288 and VSL184285) were used as control mixtures and showed a deviation of 0.43% to 2.19% for the various components between analytical determined amount fraction and the amount fraction based on gravimetry. This deviation is indicative of the analytical precision of the measurement.

The dynamically prepared gas mixtures showed a deviation towards the calibration fit between 0.63% and 2.06% well within the analytical precision of the measurement. The repeatability of a dynamic dilution of multi sulfurs at the 2 µmol/mol level (BIO4E1501 and BIO4E1603) was within 0.5%. Thus, it was estimated that multi-sulfur gas mixtures can be generated within 2% uncertainty using the dynamic preparation facility. This uncertainty is within VSL's 2% - 3% CMC claim on the analysis of gravimetric gas mixtures for the various sulfur species at the investigated amount fractions.

Also, the performance of the dynamic generation system is in agreement with related normative requirements as specified for 5 - 6 mg m^{-3} for sulfurs in group H gases conform ISO 16726 and a 2 – 4 % relative repeatability and 25% relative proficiency agreement for sulfurs in a methane matrix conform ISO 19739. Thus demonstrating that performance of the dynamic preparation facility is satisfactory.

To summarize, VSL first performed a multi-point calibration for biomethane-related gas matrices by dynamically preparing gas mixtures of hydrogen, nitrogen, methane and carbon dioxide that were assessed against VSL's static synthetic biogas standards. The dynamic dilution facility performed within the target uncertainty of 1% for each of the four main components. Then five commonly encountered sulfur components were dynamically diluted in the range of 2 – 10 µmol/mol using a methane matrix and compared to static-gravimetric gas mixtures. The dynamically generated gas mixtures deviated up to 2% to the static-gravimetric gas mixtures, which is within VSL's CMC claim. Thus, the dynamical preparation facility operates satisfactorily, with <1% uncertainty on the matrix gas composition of biogas related mixtures and up to 2% uncertainty on various sulfur-containing components in a methane matrix.

6.3 PTB validation of the dynamic preparation facility

As mentioned in this report, PTB has used the static reference standard provided by NPL to validate the Optical gas standard for measurement of ammonia amount fraction in methane matrix. PTB has measured the sample with the upgraded OFCEAS analyser which will be used as an OGS for measurement of ammonia impurity in biomethane. The typical spectra of targeted ammonia line in methane matrix is shown previously in Figure 6. The spectra were post-processed with the fitting algorithm developed at PTB to evaluate the ammonia amount fraction in the gas mixture.

To evaluate the stability of the measurement provided by the instrument, we measured the NH_3 fraction of the same sample for a time duration of over 120 minutes. Figure 3 (a) inset shows a histogram depicting a normal distribution of the data results around the mean value.

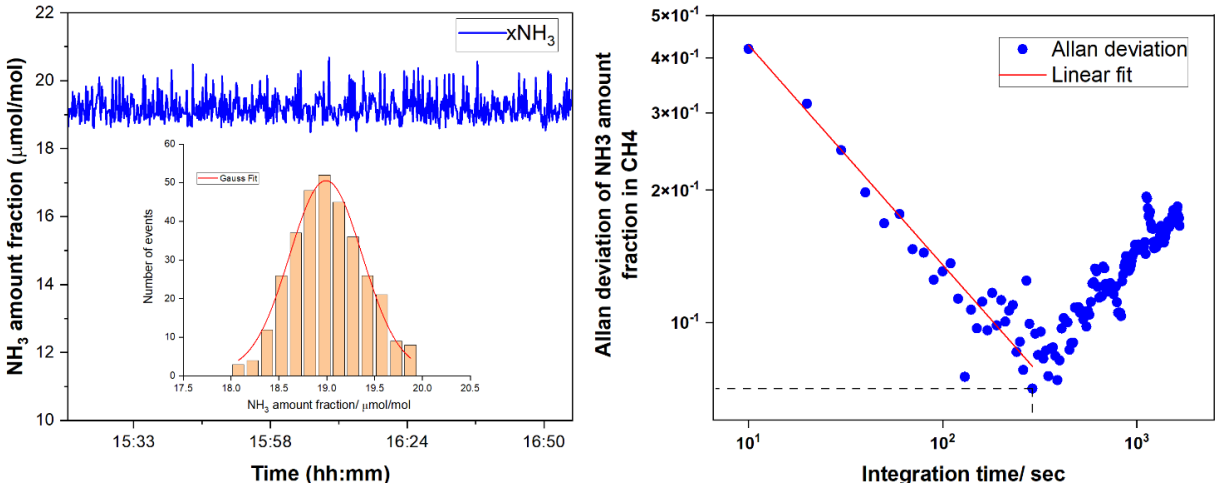

Figure 12: (a) Measured ammonia amount fraction in methane matrix. The inset in the figure shows a histogram of the results (b) Allan deviation of the results in Fig. 3a.

The optimal precision of the instrument is an important parameter to determine when targeting low (µmol/mol down to nmol/mol) NH3 amount fraction measurements. Figure 12b represents an Allan deviation of the data in Figure 12a. As shown in Figure 12b, an optimal precision of 70 nmol mol-^{1} (detection limit) has been achieved for the instrument at a time resolution of 290 second. This high precision of 70 nmol mol^{-1} demonstrates the capability of the instrument for precise NH_3 impurity measurements in methane and biomethane.

6.4 VTT validation of the dynamic preparation facility

To validate the performance of the VTT trace gas generator, a comparison against a static gas reference produced by NPL was performed using DTU far-UV analyser as a comparator. The NPL static gas reference was connected through a (uncoated) pressure regulator and Ø3 mm SilcoNert2000 coated SS tubing to the far-UV analyzer. The NPL reference gas was prepared gravimetrically to realize an ammonia concentration of (19.6 ± 1.1) ppm in methane. The concentration was verified by means of gas chromatography.

Measurements with the DTU far-UV analyser from the output of the NPL reference gas cylinder show a concentration around 20 µmol mol-1, which corresponds well to the certified concentration of NPL reference gas (Figure 13). Vertical error bars show uncertainty of the NPL reference gas. A possible NH3 desorption from the cylinder walls (vertical arrow) has been observed.

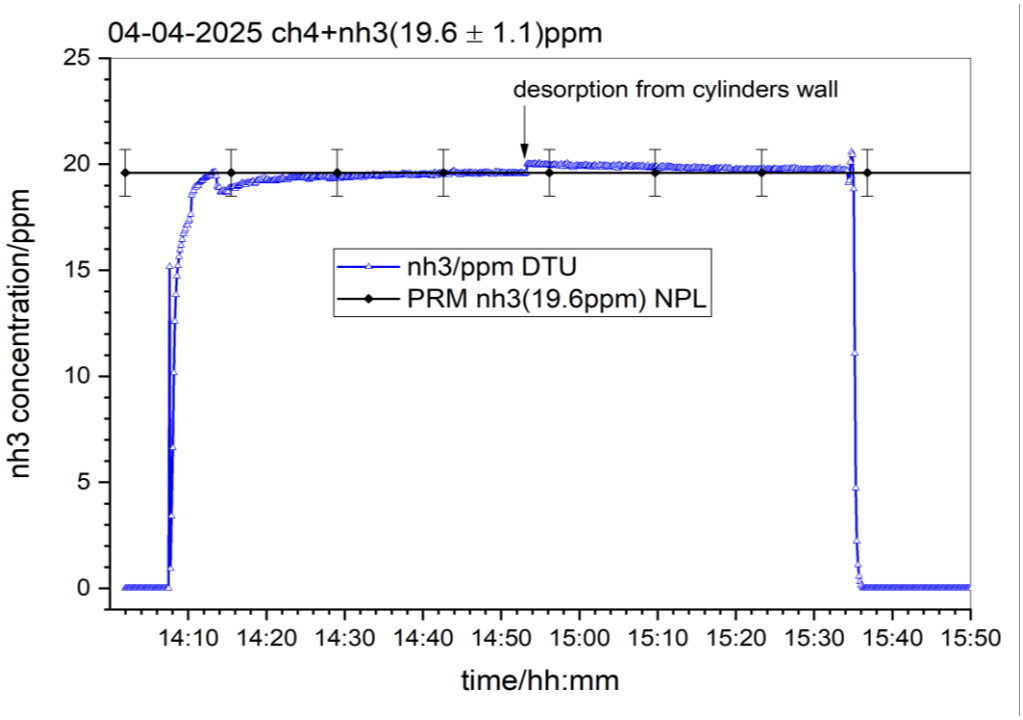

***Figure 13**: Ammonia concentrations measured with DTU far-UV analyser from NPL reference gas containing 19.6 µmol mol^{-1} (ppm) of ammonia in methane at about 1 bar pressure and 24ºC in the analyser.*

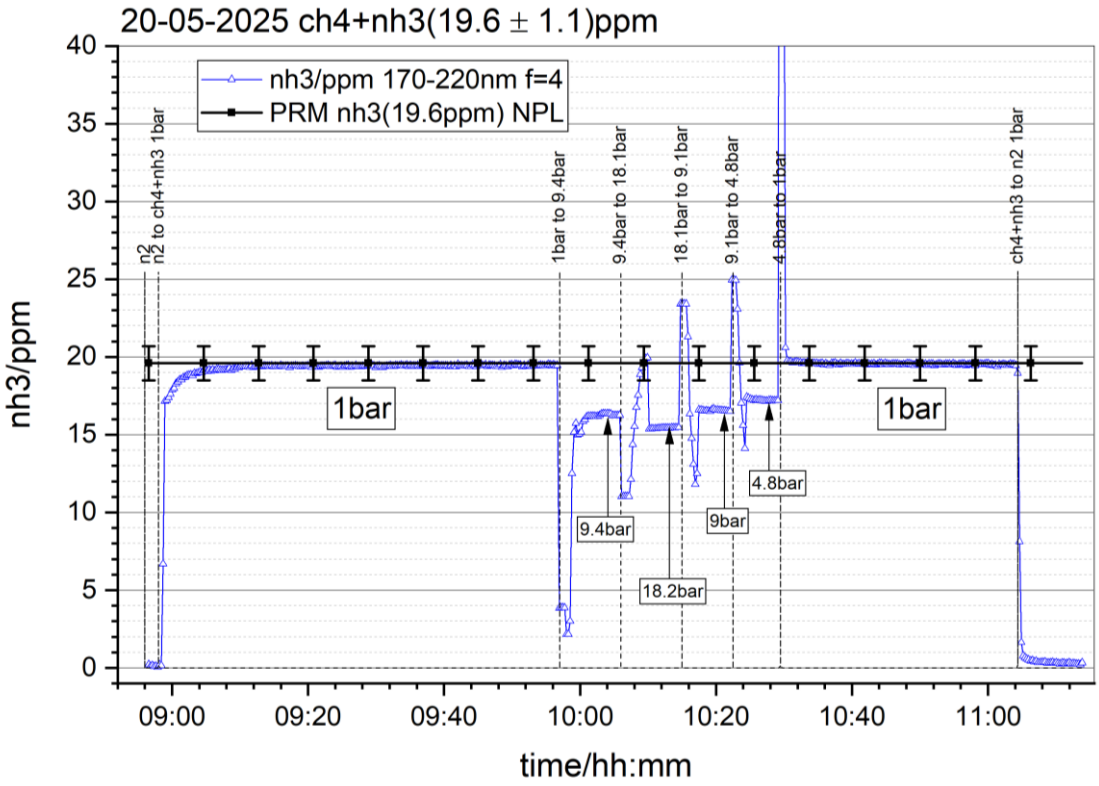

***Figure 14:** Ammonia concentrations measured with DTU far-UV analyser from NPL reference gas containing 19.6 µmol mol^{-1} (ppm) of ammonia in methane. The measurements were done around 1½ months after the measurements in Figure 13. Some measurements (marked by vertical solid lines with arrows) were made from about 5 bar to about 18 bar pressure in the analyser and temperature of about 24ºC.*

Figure 14 shows repeated after around 1½ months measurements from around 1 bar to around 18 bar pressure in the analyzer. The measurements followed the protocol developed in the WP2 of the BiometCAP project: the measurements started and ended with N_2 reference gas in the analyser. No NH_3 losses in the NPL reference gas at 1 bar have been observed over a given time span. The NH_3 amount fraction in the gas phase, however, decreases by a few µmol mol^{-1} at pressures above 1 bar. This is caused by a forced surface NH_3 adsorption on the inner walls at elevated pressures.

Measurements were repeated using the VTT trace gas generator as a source of ammonia to realize an output NH_3 concentration of 19.6 µmol mol^{-1}. The generator produces an H_2O+NH_3 gaseous mixture through a H_2O+NH_4OH solution evaporation. The generator has a modified atomiser section which mimicked an original hand-made glass one. That section consists of a set of needle-size stainless tubes used to generate a solution mist in the carry gas, prior to gas injection into the evaporator. The original atomiser was accidentally damaged during a startup operation in one of the measurements.

A commercial 5.0 M NH_4OH solution from Honeywell, traceable to NIST SRM was used. In house available milli-Q water was used to prepare a final H_2O+NH_4OH solution. The generator was connected through an unheated Ø6 mm PTFE tubing to the far-UV analyser. The results of the NH_3 measurements are shown in Figure 15. The "noisiness" in the NH_3 and H_2O concentrations is attributed to a non-homogeneous injection of the solution into the atomiser. This non-homogeneity, however, should not affect the steady-state NH_3/H_2O concentrations. The measured NH_3 (26.8 µmol mol^{-1}) and H_2O (1.37%) concentrations are much higher than the expected values of 19.6 µmol mol^{-1} and 1.07 %, respectively. The reason for this discrepancy is not fully understood. Further investigations are ongoing to verify the MFC and syringe pump performances and to ensure that the device has not undergone chemical or physical degradation because of extensive travels among project partners.

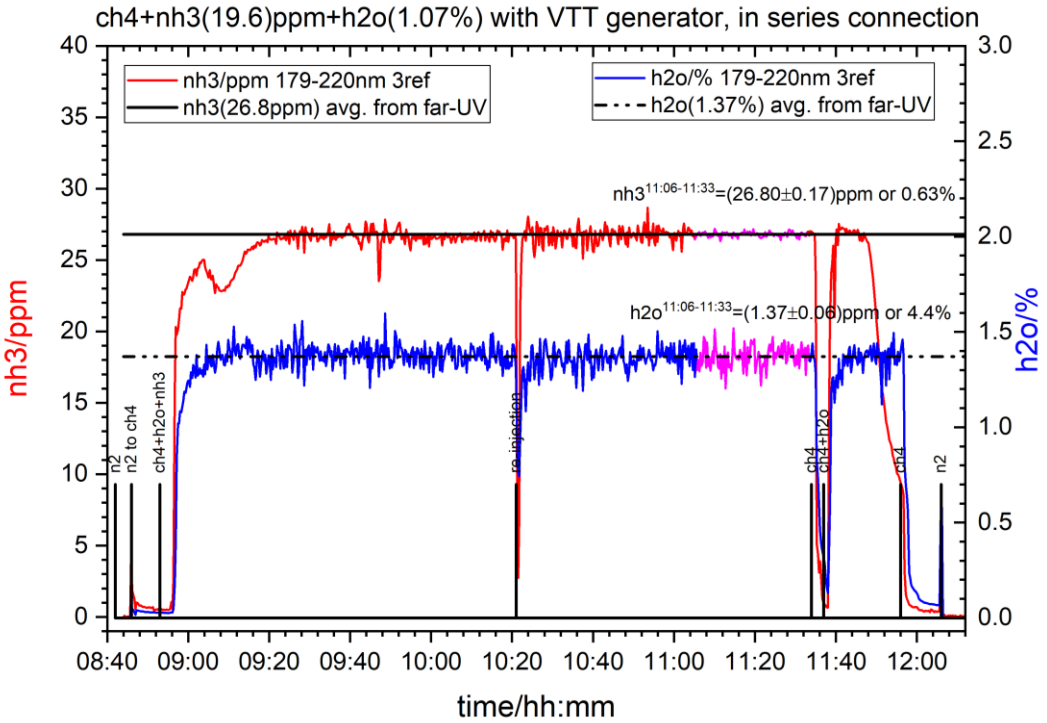

Figure 15: *Ammonia (left) and water (right) concentrations measured with DTU far-UV analyser from the VTT trace gas generator output with a nominal concentration of 19.6 ppm ammonia in methane-water-ammonia mixture at about 1 bar pressure and temperature of about 25°C.*

In the meantime, additional measurements were made with use a reserve VTT generator, so-called generator Nr,2. This generator has a different atomiser design than the one with the modified atomiser. The generator was connected to the far-UV analyser via a similar Ø6 mm PTFE tubing as in above-described measurements. The results are shown in Fig. 16,

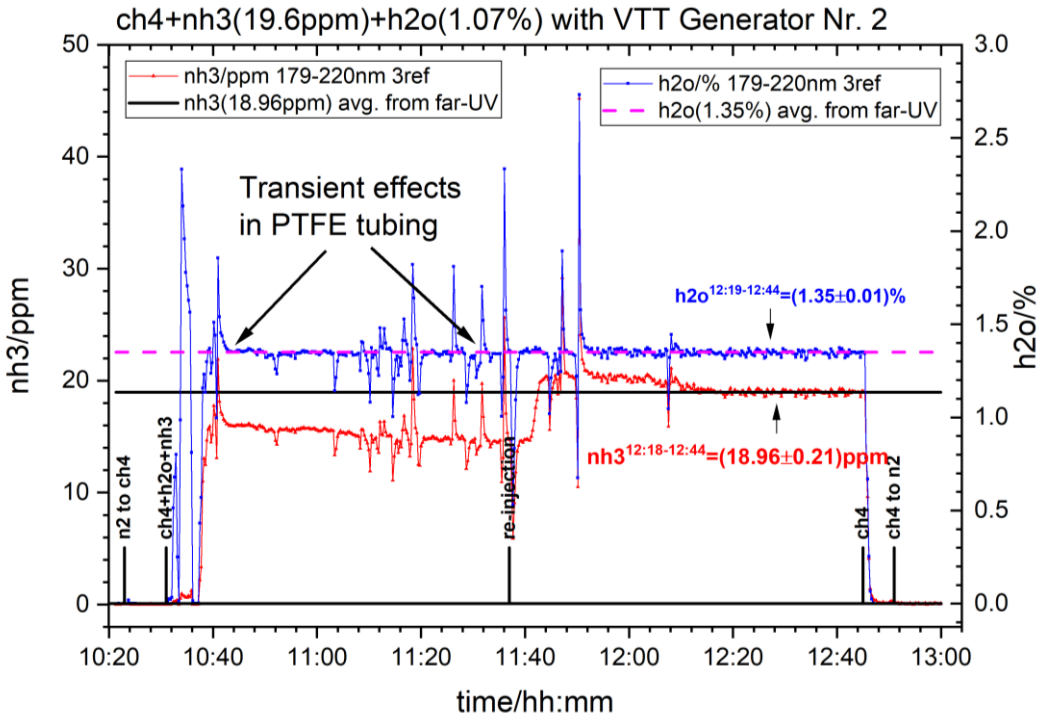

Figure 16: *Ammonia (left) and water (right) concentrations measured with DTU far-UV analyser from the VTT trace gas generator Nr. 2 output with a nominal concentration of 19.6 ppm ammonia in methane-water-ammonia mixture at about 1 bar pressure and temperature of about 24°C.*

As one can see from the Fig. 16, NH_3/H_2O time-dependent concentration profiles are less noisy (compared to ones in the Fig. 15) and stable NH_3 and H_2O concentrations are achieved after the second H_2O+NH_4OH solution injection in the syringe pump at about 11:38. The NH_3 steady-state concentration achieved was about 19 µmol mol^{-1} which is a bit lower than the nominal set point: 19.6 µmol mol^{-1}. This agreement (within 3%) between NH_3 measured and NH_3 set point can be considered as a very good one, taking into account the complexity of the measurements at the low NH_3 concentrations.

The H_2O concentration is somehow higher: 1.35%, than the nominal one (1,07%) but close to the H_2O concentration in the Fig. 15.

Other observation from the Fig. 16 is that it takes around 1 hr and an additional solution injection to get a steady-state NH_3 concentration time-profile. This is because of transient effects in Ø6 mm PTEF tubing. Measurements under MetCCUS project when the original generator was connected via various stainless-steel coated and PTFE tubing to other DTU's UV-analyser have shown that the noisiness in NH_3/H_2O time-concentration profiles is mainly caused by tubing diameter and not the tubing material.

The spikes in NH_3/H_2O concentrations in the Fig. 16 between 10:40 and 12:10 correspond to sudden NH_3/H_2O concentration variations in the gas phase and are not related either to an analyser noise or any other analyser operation artefacts. The (time-correlated) H_2O/NH_3 spikes reflect a non-homogeneous mist/aerosol generation in the generator from the operation start up at low solution dosing flow rate (0.04 ml min^{-1}) and seems to be smoothed out with time. This is in an agreement with the previous results shown in the Fig. 15, when e.g. a steady-state NH_3 concentration was achieved at the late time of the measurements.

6.5 Uncertainty estimations

The uncertainty of generated ammonia (NH_3) concentrations was determined based on the measurement model (Equation 4) and the operation parameters (Table 9).

$$x_{NH_3}[mol/mol] = \frac{n_{NH_3}[mol/min]}{n_{gas}[mol/min] + n_{H_2O}[mol/min]} = \frac{c_{NH_3}[mol/l] \cdot \frac{q_{m,H2O}[g/min]}{\rho_{H2O}[g/l]}}{\frac{q_{v,gas}[l/min]}{V_m[l/mol]} + \frac{q_{m,H2O}[g/min]}{M_{H2O}[g/mol]}} + \delta_{ev} + \delta_{rep}$$

Equation 4

The uncertainty of molar concentration of generated ammonia (NH_3) is given in Table 9 for the nominal concentration of 10 µmol mol^{-1}. From the table it can be seen that the largest source of uncertainty is the concentration of the solution, which is mainly caused by the uncertainty of the micropipette used for preparing the solution. The uncertainty of pipetting is estimated as the maximum permissible error (mpe) as stated in the ISO 8655 standard [14]. Combining all the uncertainty components results in an expanded uncertainty (k = 2) of 1.9 %. In the typical operational range of the generator, the relative values of the uncertainty components are considered constant, therefore the expanded uncertainty of 1.9 % can be applied in the whole operational concentration range.

***Table 9**: Uncertainty budget for generated trace concentration of ammonia (NH_3).*

symbol	quantity	unit	value	uncertainty	sensitivity coefficient	uncertainty / mol · mol^{-1}	type	probability distribution	divisor	contribution to standard uncertainty	
c_{NH3}	Concentration of NH_3 solution	mol · l^{-1}	3.48E-02	2.31E-04	2.87E-04	6.64E-08	B	normal	1	6.64E-08	
$q_{m,H2O}$	Liquid mass flow of syringe	g · min^{-1}	8.41E-02	5.05E-04	4.05E-07	2.04E-10	B	normal	2	1.02E-10	
$q_{v,gas}$	Volume flow at standard temperature (23 °C)	l · min^{-1}	7.01E+00	7.01E-02	-1.40E-06	-9.85E-08	B	normal	2	-4.92E-08	
δn_{ev}	Evaporation losses	mol · mol^{-1}	0	6.00E-08	1	6.00E-08	B	rectangular	1.73	3.47E-08	
δn_{rep}	Repeatability	mol · mol^{-1}	0	6.00E-08	1	6.00E-08	B	rectangular	1.73	3.47E-08	
	Molar fraction of NH_3 (x_{mol_NH3})		1.00E-05	mol · mol^{-1}				combined standard uncertainty		9.61E-08	
			10.0	**ppm**				**expanded uncertainty (k=2)**		1.92E-07	
										0.2	**µmol/mol**
										1.9	**%**

The complete evaporation of the gas-liquid mixture is critical to ensure reliable performance of the trace gas generator. The evaporation has to be complete and adsorption of the mixture to the generator surfaces needs to be minimized. Evaporative losses were thoroughly investigated in previous research by Sari S. et al. [15] for oxidized mercury. This value can be used as a worst-case estimate of generation losses for ammonia (NH_3), because the relative influence of evaporative losses is minimal.

7 Summary and Conclusion

Static gas reference standards were developed by NPL, CMI, BFKH and TUBITAK for use in the development and validation of novel dynamic and optical gas standards for use with biomethane conformity assessment. The vast majority of the static gas standards were produced within their target uncertainties (6% for siloxanes, 5% for terpenes, 5% for ammonia, 3% for total sulphur, 1% for bulk composition gases, H_2, N_2, O_2, CO).

A novel static reference standard was developed by NPL, containing siloxanes L2, L3, D3, D4, D5 (35 - 60 nmol mol^{-1}), terpenes α-pinene, 3-carene, d-limonene (~3 µmol mol^{-1}), benzene (~10 µmol mol^{-1}) and toluene (~10 µmol mol^{-1}). The amount fractions of the components were all found to be stable to within 7% within a 124 day period, with work ongoing to quantify stability up to a 9 month period. D5 siloxane exhibited the largest change, which is expected to be due to its high boiling point and tendency to adsorb to surfaces, highlighting

the importance of suitable passivation and sampling of biomethane and the advantages of use of dynamic generation of gas standards.

Dynamic gas standards were successfully developed by VSL, VTT and NPL and an optical gas standard was developed by PTB. The NPL dynamic system was validated with uncertainties ranging from 1-16%. The reason for the higher 16% uncertainty was attributed to bias in trueness value caused by the purging procedure used for flushing the system prior to analysis. This was particularly evidence when analysing trace analytes (µmol mol^{-1} and below) that are vulnerable to sorption effects, such as ammonia and sulphur. Results for 1000 µmol mol^{-1} carbon monoxide were within 1% uncertainty, demonstrating the potential of the system should sorption effects be mitigated through an improved purging procedure.

VSLs dynamic standard was optimised using blends of H_2, N_2, CH_4, CO_2. It was found that pressure correction is important to apply for GC techniques if using the calibration over time periods > 1 day, and it was recommended to perform measurements within a short timeframe (1 day) to ensure accuracy. The calibration of MFCs was also highlighted as an important factor to consider within the uncertainty budget when using dynamic MFC-based systems for performance evaluation. Following optimisation five commonly encountered sulfur components were dynamically diluted in the range of 2 – 10 µmol/mol using a methane matrix and compared to static-gravimetric gas mixtures. The VSL dynamic preparation facility was found to operates with <1% uncertainty on the matrix gas composition (H_2, N_2, CH_4, CO_2) and up to 2% uncertainty on various sulfur-containing components in a methane matrix.

PTB developed and validated an optical gas standard and tested this using a traceable static reference standards containing ammonia in methane. The results demonstrated the optical standard is capable of measuring ammonia in biomethane to within 5% uncertainty. The limit of detection of the standard was calculated as 70 nmol mol^{-1}.

VTT developed and validated a liquid evaporative generator using a traceable static reference standard containing ammonia in methane with a far-UV analyser produced by DTU used as a comparator. An expanded uncertainty of 1.9% was achieved for the initial test, however when the test was repeated a large bias was observed, requiring further investigation. Measurements with a reserve generator have shown much better agreement (within 3%) between NH_3 measured and NH_3 set point which is considered as a very good one, taking into account the complexity of the measurements at low NH_3 concentrations.

In conclusion, the BiometCAP project has successfully developed static, dynamic and optical gas standards for use with biomethane conformity assessment for use in laboratory and field settings. These standards support the traceable and accurate monitoring of impurities and main constituent components of biomethane according to the requirements of stakeholders. The target relative uncertainties for the gas standards (1 – 10 % relative) were achieved for the large majority of cases, and useful scientific data obtained for cases where uncertainties were not achieved, allowing for future improvement of capability beyond the BiometCAP project.

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