21NRM04 BiometCAP

D2 - Report on the validation of the performance assessment protocol for EN 16723 impurities using existing reference methods with relative expanded uncertainties of 1 % - 10 %

RISE, NPL, VSL, CMI, BFKH, TUBITAK, IMBiH

Due date of the deliverable: 2024-05-31

Actual submission date of the deliverable: 2025-03-04

Glossary

AES : Atomic emision spectroscopy

TD-GC/MS/FID : Thermal Desorption Gas Chromatography/Mass Spectrometry/Flame Ionization Detection

GC-IMS : Gas Chromatography-Ion Mobility Spectrometry

TDLAS: Tunable diode laser absorption spectroscopy

GC-NCD : Gas Chromatography-Nitrogen Chemiluminescence Detection

GC-SCD-FID : Gas Chromatography-Sulfur Chemiluminescence Detection-Flame Ionization Detection

GC-TCD : Gas Chromatography-Thermal Conductivity Detection

VOC : Volatile organic compounds

L2 : hexamethyldisiloxane

L3 : octamethyltrisiloxane

D3 : hexamethylcyclotrisiloxane

D4 : octamethylcyclotetrasiloxane

D5 : decamethylcyclopentasiloxane

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1   Summary

The BiometCAP project has developed a comprehensive protocol for evaluating gas analyzers in biomethane conformity assessment applications. This protocol supports various measurement technologies, including laser-based, optical, and mass spectrometry systems, and ensures accurate results through best practices in sample preparation and sampling. The project partners have validated this protocol using methods like gas chromatography, spectroscopy, and spectrometry for impurities listed in EN 16723. The report highlights the validation process and the relative expanded uncertainties for each method, aiming for a goal of 1 % to 10 %, depending on the impurities targeted.

2   Introduction

Biomethane is widely used across Europe as a sustainable alternative to fossil fuels. Monitoring the quality of biomethane is crucial to prevent damage to the existing natural gas infrastructure and end-user appliances. Harmful impurities in biomethane must be kept below specified thresholds, as outlined in EN 16723 [1][2] for gas grids and vehicles.

Reliable and traceable purity measurements require equipment with known performance, validated through traceable evaluation parameters. Several analytical techniques are available to analyse specific impurities, and new techniques are being developed. Performance evaluation should be conducted after the initial installation of the analytical system to ensure that it meets its intended purpose. This evaluation can be challenging for parties lacking metrological training.

The list of method performance characteristics, their definitions, and how to assess those vary slightly depending on the source. Therefore, more specific guidelines together with practical applications of these guidelines can be very useful. While similar protocols exist for other green fuels like hydrogen, a specific biomethane evaluation protocol is still lacking.

The BiometCAP project is addressing the lack of validated protocol specifically designed for evaluating gas analysers in biomethane applications. The project has developed a comprehensive protocol to support both current and future measurement technologies. The protocol applies to various techniques used for biomethane conformity assessment, including techniques such as laser-based, optical techniques and mass spectrometry systems. It covers best practices in sample preparation and sampling to ensure accurate results, taking into account existing generic guidance on method validation. Partners of the BiometCAP project have demonstrated the fitness of purpose of this performance assessment protocol using a number of validated methods and technologies such as gas chromatography, spectroscopy and spectrometry for relevant impurities, which are already included in EN 16723, or which are under discussion to be included (e.g. total silicon, ammonia, amines, HCl/HF, halogenated VOCs, sulphur compounds, terpenes, siloxanes, carbon monoxide).

For this validation, only fit-for-purpose and laboratory-based methods developed during previous projects (EMRP JRP ENG54 Biogas [3] and EMPIR JRP 16ENG05 Biomethane [4]) and gas reference standards, produced in WP1 for different impurities, have been used. This report summarizes the validation of the performance assessment protocol for EN 16723 impurities and indicates the relative expanded uncertainties for each method (goal 1 % - 10 %).

3   Overview of the validation process

Table 1 shows the validation process for each partner together with the method used and the completion date.

Table 1 Overview of the validation process.

Activity	Partner	Targeted compounds	Analytical method	Standard	Completion date
A2.2.1	IMBiH	Total silicon	AES	ISO 2613-1:2023	July 24
	RISE	Siloxanes:L2, L3, D3, D4, D5	TD-GC/MS/FID	ISO 2620:2024	September 24
	VSL			ISO2620:2024	January 25
	NPL		GC-IMS	ISO 2613-2:2023	January 25
A2.2.2	VSL	Ammonia	TDLAS	ISO 2612 :2023	February 25
	NPL		GC-NCD	own method	February 25
A2.2.3	VSL	HCL	TDLAS	own method	Februari 25
A2.2.4	RISE	Halogenated VOC	TD-GC/MS/FID	ISO 2620:2024	September 24
A2.2.5	BFKH	Sulphur compounds	GC-SCD-FID	Modified ISO 19739	January 25
	CMI			Modified ISO 19739	
	NPL			Modified : ISO 19739	February 25
A2.2.6	NPL	Terpenes	GC/MS/FID	Modified ISO 2620:2024	December 24
	RISE		TD-GC/MS/FID	ISO 2620:2024	July 24
A2.2.7	NPL	H_2, CO, O_2, N_2	GC-TCD	ISO 6975:2002	January 25
	CMI			ISO 6974-6:2002	
	Tubitak			ISO 6974-1:2012	

AES : Atomic emision spectroscopy

TD-GC/MS/FID : Thermal Desorption Gas Chromatography/Mass Spectrometry/Flame Ionization Detection

GC-IMS : Gas Chromatography-Ion Mobility Spectrometry

TDLAS: Tunable diode laser absorption spectroscopy

GC-NCD : Gas Chromatography-Nitrogen Chemiluminescence Detection

GC-SCD-FID : Gas Chromatography-Sulfur Chemiluminescence Detection-Flame Ionization Detection

GC-TCD : Gas Chromatography-Thermal Conductivity Detection

VOC: Volatile organic compounds

L2 : hexamethyldisiloxane

L3 : octamethyltrisiloxane

D3 : hexamethylcyclotrisiloxane

D4 : octamethylcyclotetrasiloxane

D5 : decamethylcyclopentasiloxane

4 Results

Each partner produced a full report which can be found on the website of the project in their entirety. The reports are combined and summarized below.

4.1 Total silicon

The performance assessment protocol was applied and validated for the determination of total silicon.

4.1.1 AES (IMBiH)

The performance assessment protocol (A2.1.4) was applied and validated for the determination of total silicon using atomic emission spectroscopy (AES). AES is an analytical technique used to determine element concentrations by measuring light emitted from excited atoms or ions. Microwave Plasma Atomic Emission Spectrometry (MPAES) is a cost-effective and efficient form of AES that uses microwave energy to create a nitrogen plasma for sample excitation. This method is particularly useful for analyzing non-metals and metals, such as silicon, in complex matrices. Nitrogen is preferred for its inertness and cost benefits. Specific emission lines, like those at 251.6 nm and 288.1 nm for silicon, are selected for accurate measurement. Sampling from the gas phase was done using reference gas mixture NPL ID A623 containing silicon content of 0.500 mg/m^3 ± 0,08 mg/m^3.

- **Selectivity**: Stated elements are not present in the sample providing selectivity of the instrumental setting. Blank measurements - reagents and water - proved no contamination with silicon from outside sources.

- **LOD**: LOD was calculated to 0.0035 mg/kg.

- **Working Range and Linearity:** Figure 1 show linear equation and correlation coefficient related to each calibration curve. Correlation coefficient is close to 1, thus indicating a strong linear correlation between the measured response and analyte concentration. During method validation, the absence of a trend in the regression line confirms the method's ability to provide reliable and reproducible results.
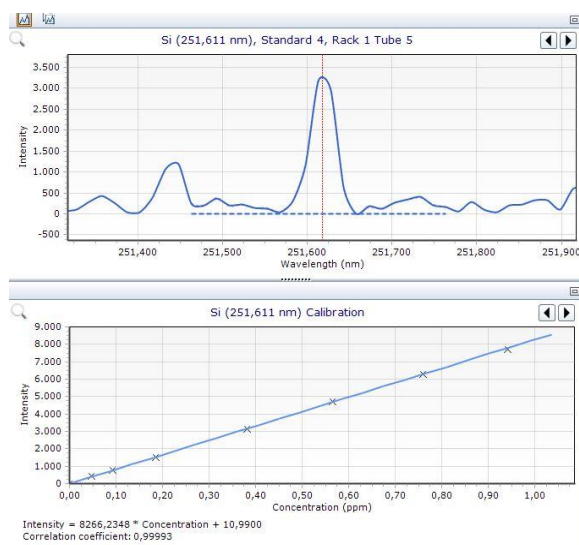
Figure 1 Examples of used calibration curves and emission peaks for silicon at selected analytical line.

- **Bias**: The total bias u_{bias} was calculated to 0.00404 mg/kg.

- **Precision**: For validation purposes, precision was quantified under intra-laboratory reproducibility conditions. Pooled standard deviation was used as a measure of precision of the method and it was calculated to 0.008 mg/kg.

- **Measurement Uncertainty**: The relative expanded measurement uncertainty was calculated to 1.9%.

Conclusions

The method is found to be fit-for-purpose, reliable and highly sensitive.

4.2   Siloxanes

The performance assessment protocol was applied and validated for the determination of siloxanes.

4.2.1   TD/GC-MS/FID (RISE)

The performance assessment protocol (A2.1.4) was tested and validated using the method ISO 2620:2024 for the determination of hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) in biogas/biomethane matrices using TD/GC-MS/FID.

Siloxanes in gas are enriched on adsorbent Tenax TA, thermally desorbed for gas chromatographic separation on a non-polar capillary column. The majority of the sample goes to a flame ionization detector (FID) and a smaller portion goes to a mass selective detector (MS) for identification of individual components and quantification.

A reference mixture produced by NPL in methane, as part of activity A1.1.2, containing (0.0874 ± 0.0044) µmol/mol of L2, (0.0557 ± 0.0034) µmol/mol of L3, (0.0542 ± 0.0038) µmol/mol of D3, (0.0429 ± 0.0026) µmol/mol of D4, and (0.0326 ± 0.0020) µmol/mol of D5 was used for validation.

Results

- **Selectivity**: D4 eluate close to a dimethyl-octene using FID but shows good separation when using MS.

- **LOD**: Varies between 0.18 and 0.9 ng, equivalent to 1.8 µg/m³ and 9 µg/m³, calculated with a volume of 100 ml.

- **Working Range and Linearity**: The correlation coefficient for all siloxanes measured with GC-MS/FID was close to 1, suggesting that the linear regression equation fits the data. This implies a linear working range within 3 to around 120 ng (0.03 to 1.2 mgm^{-3}, calculated with 100ml), see Figure 2. The distribution of residuals -calculated as the difference between the predicted and observed areas - is random, confirming the linearity and working range.
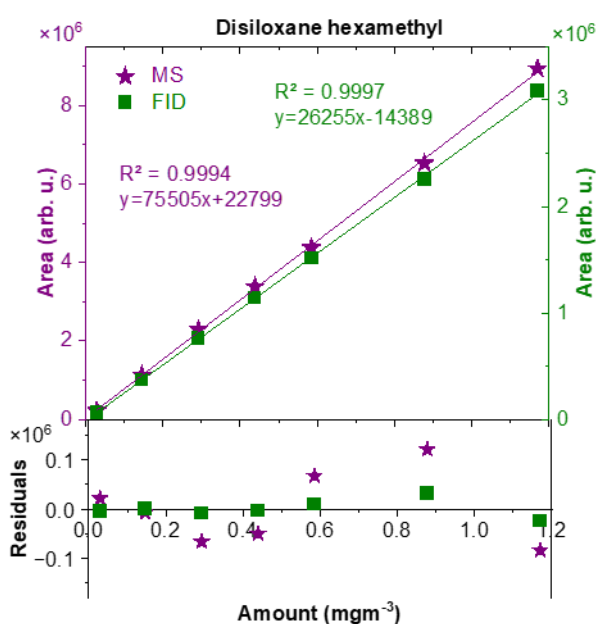

Figure 2 Results for disiloxane hexamethyl shows linear working range between 0.03 to 1.2 mgm-3, which was confirmed by the random distribution of residuals.

- **Bias**: The mean bias for L2 was calculated to be -21, and the relative bias to -3.6%. The standard deviation of the measured concentration, SRW, was 1.8%. Considering the uncertainty of the reference standard, the total bias, u(bias), was calculated to 4.56%, aligning well with the targeted value of 5%.

- **Precision**: Precision was assessed by measuring 10-12 duplicates of L2, L3, D3, D4, and D5 at varying quantities using TD-GC-MS/FID on several days. The standard deviation and relative standard deviation were determined, and the pooled standard deviation was calculated. The measured standard deviations varied between 0.8% to 3.9%. Considering the contribution of control samples (toluene), the within-laboratory reproducibility, u(Rw), was evaluated to be 3% for L2 using MS, slightly higher than the targeted value of 2.5%.

- **Measurement Uncertainty**: The expanded uncertainty (k=2) for L2 was calculated using the software MUKit, showing a measurement uncertainty of 11%.

Conclusions

ISO 2620:2024 is therefore found to be fit-for-purpose, reliable and highly sensitive. As the working range is at least 2 to 100 ng, it can be used to analyze samples with amount fractions of siloxanes from 2 nmol/mol to 1 µmol/mol (using volumes of 5 to 200 ml per tube).

4.2.2 TD/GC-MS/FID (VSL)

The performance assessment protocol was validated for L2, L3, D3, D4 and D5. The analysis was performed on a gas chromatograph with a flame ionization detector (GC-FID) with gas autosampler and a pressure controlling device. The GC column, the liners, tubing and reducers were all passivated. Seven Primary gas standards (PSMs) containing siloxanes in methane were prepared gravimetrically in high-pressure cylinders according to ISO 6142-1 (Table 2).

Table 2 Gravimetric composition including expanded uncertainty (k = 2) in µmol mol^{-1} of the seven PSMs.

	L2	U(L2)	L3	U(L3)	D3	U(D3)	D4	U(D4)	D5	U(D5)
VSL347730	0.299350	0.000043	0.201890	0.000034	0.207950	0.000396	0.063968	0.000095	0.043649	0.000078
PRM135744	0.900570	0.000213	0.795740	0.000178	0.597690	0.000151	0.575190	0.000126	0.400570	0.000100
VSL600656	3.001200	0.000415	1.995200	0.000200	1.990000	0.000205	0.596920	0.000150	0.420510	0.000217
VSL805228	3.002900	0.000610	2.014800	0.000409	1.998900	0.000429	0.594450	0.000114	0.435100	0.000076
VSL244858	3.003900	0.000456	2.006900	0.000305	1.993200	0.000335	0.803120	0.000307	0.394960	0.000246
VSL244251	3.977800	0.001249	2.501800	0.000807	1.601100	0.000576	0.575190	0.000126	0.400570	0.000100
VSL145000	4.000100	0.001279	2.515800	0.000826	1.610130	0.000587	0.807620	0.000313	0.397170	0.000248

Results

- **LOD:** Varies between 0.0012 and 0.0020 µmol mol^{-1}.

- **Working range and linearity:** The linearity of the GC-FID has been tested for each siloxane in different ranges. For a satisfactory fit of the data, it was required that the absolute value of the normalized residual was not exceeding 2. The normalized residual is the residual divided by the standard uncertainty. For the linearity test, the function used is a straight line ($y = ax + b$). All the normalized residuals were < 2, indicating this function is fit for purpose for all siloxanes under test.

- **Bias:** The bias for L2 ranges from -0.39% to 0.34%. The bias for L3 ranges from -1.55% to 1.77%. The bias for D3 ranges from -1.51% to 1.95%. The bias for D4 ranges from -0.93% to 1.32% and the bias for D5 ranges from -1.79% to 1.63%.

- **Precision:** Repeatability standard deviation (s(r), %) was calculated to between 0.3 and 1.6 % and reproducibility standard deviation (s(R), %) was calculated to 0.5-2.9% (The precision was below 2% save for siloxane D5 which had a reproducibility standard deviation of 2.9%).

- **Measurement uncertainty:** The measurement uncertainties were calculated to 4% for L2, 6% for L3, 8% for D3, 7% for D4 and 11% for D5 (k=2).

Conclusion

The validation of the GC-FID method to analyse siloxanes L2, L3, D3, D4 and D5 was performed according to the performance assessment protocol. The GC-FID method was found to be fit-for-purpose, reliable and highly sensitive.

4.2.3 GC-IMS (NPL)

The performance assessment protocol developed in A2.1.4 was tested and validated using the method ISO 2613-2:2023 for the determination of L2, L3, D3, D4, and D5 siloxanes in samples of synthetic biomethane, using GC-IMS. The GC-IMS is a two-dimensional analytical technique, wherein the analytes are first separated using a GC capillary column using standard GC conditions. After eluting from the column, the components are transferred to a drift tube and ionised by a beta-radiation source. Inside the drift tube, the ionised analytes are subjected to an electrical field, causing the ions to move against the flow of carrier gas with a characteristic "drift time" based on their molecular weight and geometry. The ions are finally quantified by an electrometer at the end of the drift tube. Reference mixtures were used according to Table 3.

Table 3 Gravimetric composition of NPL PRMs used in this study.

Component	Amount fraction (mg m^{-3})			
	2952	**9300**	**D223101**	**9311-R1**
L2 siloxane	20.301	0.371	2.369	2.234
L3 siloxane	19.942	0.393	2.198	2.232
D3 siloxane	17.520	-	2.011	1.983
D4 siloxane	7.164	0.333	2.122	2.068
D5 siloxane	8.888	0.355	2.106	2.158
Hexane	135.399	-	15.480	15.262
Methane	Balance	Balance	Balance	Balance
Total silicon	26.840	0.468	3.936	3.919

Results

- **Selectivity:** Inspection of the chromatograms showed no regions of overlap between the interferent compounds and the siloxanes.

- **LOD:** The LOD analysis was carried out by diluting standard 2952 to a low amount fraction and comparing the peak heights to a blank run. The results are summarised in Table 4.

Table 4 Limit-of-detection analysis for siloxanes and total Si based on dilution of standard 2952.

Criterion	L2 Siloxane	L3 Siloxane	D4 Siloxane	D5 Siloxane	Total Si (based on D5)
Manufacturer's LOD	0.03	0.03	0.03	0.1	0.04
Calculated LOD	0.06	0.04	0.03	0.12	0.05

The value for total silicon meets the lower threshold requirements within both parts of EN 16723 (< 0.3 to 1 mgSi m^{-3}).

- **Working range and linearity:** Each of the five siloxanes were shown to exhibit a linear correlation with peak height and peak volume over the amount fraction ranges studied. The correlation coefficients were >0.9, indicating that the linear equations fitted the data well.

- **Bias:** The relative trueness was calculated to 3% for L2, 6% for L3, 3% for D3, 5% forD4, 11% for D5 and 4% for total silicon. The trueness uncertainty was noticeably large for the D5 siloxane component; this was due to the large standard deviation of the measured amount fraction for this component, which could be caused by sample absorption within the sampling lines.

- **Precision:** The repeatability of the measurement method was determined by seven repeat measurements of the check standard (9300) over three days. At least three measurements were performed on each day under repeatability conditions. The results were processed using Excel's one-way ANOVA function to determine the repeatability to between 0.4-1.6 % and intermediate precision to 1.4-3.1%.

- **Measurement uncertainty:** The expanded measurement uncertainty was calculated as 7% for L2, 8% for L3, 6% for D4, 6% for D5 and 3% for total silicon.

Conclusion

The validation of the method was performed according to the performance assessment protocol. ISO 2613-1:2023 was found to be fit-for-purpose, reliable and highly sensitive.

4.3 Ammonia

The performance assessment protocol was applied and validated for the determination of ammonia.

4.3.1 TDLAS (VSL)

The performance assessment protocol (A2.1.4) was tested and validated using a custom-built TDLS spectrometer utilizing a mid-infrared quantum-cascade laser (Alpes lasers, Switzerland) as light source. The laser operates in the 9537-9585 nm. To measure NH_3, an NH_3 absorption feature centered around 1046.4 cm^{-1} is used, consisting of various absorption lines with individual line strengths up to $S=3.648 \cdot 10^{-19}$ cm/molecule (HITRAN database). Since the threshold value for NH_3 in EN16723-1 is relatively relaxed (10 mg/m^3 or about 14 µmol/mol), a relatively short measurement cell with an optical path length of 3 m (cell volume is 100 ml) was used in this case The measurement cell was operated at a pressure of 100 mbar. Flow rate through the cell was typically 300 ml/min. Two different methods were used to prepare NH3 reference gas standards in methane at the required amount fractions:

a. Dynamic dilution of a static NH3 in biogas gas mixture (using a set-up similar as shown for HCl in Figure 1). For the static NH3 in biogas standard, two different biogas matrices were available.

b. Permeation based system identical to the system used for HCl. Also here, the permeation tube was obtained from Fine Metrology and had a quoted permeation rate of 600 ng/min at 50°C.

Results

- **Selectivity:** A low amount fraction of 1 µmol/mol NH3 was compared with the absorption of high amount fractions of CH4 (80 % mol/mol) and CO2 (20 % mol/mol). Interference due to absorption by these major components was relatively low for NH3 amount fractions even well below the EN threshold.

- **LOD and LOQ:** The LOD and LOQ for NH3 in CH4 were determined to be 10 nmol/mol and 34 nmol/mol, respectively.

- **Working range and linearity:** The linearity was assessed by dynamically dilution a NH3 in biomethane mixture with pure CH4 (see Figure 3 for a typical measurement). The goodness-of-fit value was 0.48 for a first-order linear regression fit. For a satisfactory fit of the data, it was required that the absolute value of the normalized residual was not exceeding 2, and therefore the analyzer can be considered linear over the tested range. The normalized residual is the residual divided by the standard uncertainty. All the normalized residuals were < 2, indicating this function is fit for purpose.
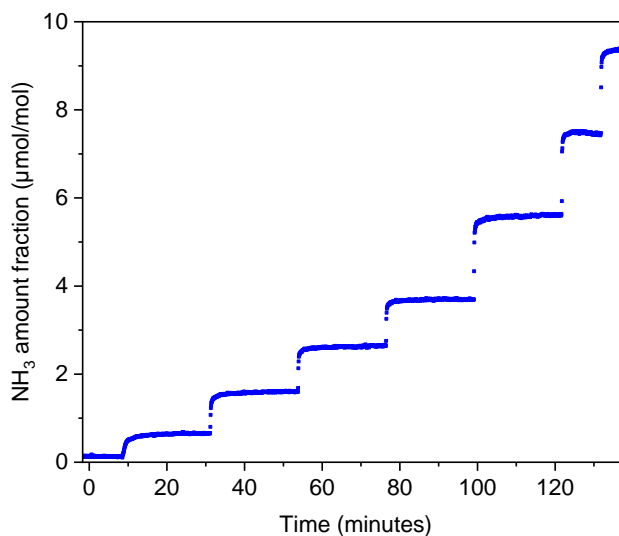
Figure 3 Example of measurement of NH3 using dynamic dilution with thermal mass flow controllers to assess the linearity of the analyzer.

- **Precision:** The precision was calculated using the pooled standard deviation as a measure of precision of the method. The resulting precision was 0.083 µmol/mol at 10 µmol/mol NH3 in CH4.
- **Measurement uncertainty:** Around the EN15723 threshold value for ammonia, the expanded measurement uncertainty (k=2) is 6% relative

Conclusions

The method is found to be fit-for-purpose, reliable and highly sensitive. Most parts of the protocol are fit for purpose, while some other parts should be more specific. As an example of the latter, the interference testing is not specified in detail. This leaves it more or less open to the user how many interferents and at which level the testing will be done, how it needs to be reported, and what are acceptable levels of interference.

4.3.2 GC-NCD (NPL)

The performance assessment protocol (A2.1.4) was validated using a method for quantification of ammonia in methane using a gas chromatograph with nitrogen chemiluminescence detector (GC-NCD). The dynamic amount fractions used in method validation were generated through dilution of a ~20 µmol mol-1 ammonia in methane static reference material (D148951) during two days (see Table 5 ,Table 6 and Table 7).

Table 5 Static reference material compositions.

	Gravimetric Amount Fraction µmol mol^{-1}		
Component	**D148951**	**2426**	**1870**
NH3	19.66 ± 0.03	9.97 ± 0.01	10.00 ± 0.01
Methane	Balance	Balance	Balance

Table 6 Dynamic reference material summary 01-10-2024

Parent	Parent Flow (mL/min)	Diluent Flow (mL/min)	Generated Amount Fraction µmol mol^{-1}
D148951	6.5	1188	0.1
D148952	10	50	3.3
D148953	25	50	6.6
D148954	13	13	9.8
D148955	17	8	13.4
D148956	42	8	16.5
D148957	25	0	19.7
2426	25	0	10.0

Table 7 Dynamic reference material summary 15-10-2024.

Parent	Parent Flow (mL/min)	Diluent Flow (mL/min)	Generated Amount Fraction µmol mol^{-1}
D148951	13.5	336	0.8
D148951	6.5	19.5	4.9
D148951	12.5	12.5	9.8
D148951	19.5	6.5	14.7
D148951	25	0	19.7
1870	25	0	10.0

Results

- **Selectivity:** Amines were highlighted as a potential source of interference due to their occurrence in biomethane. While amines and ammonia are both detectable by GC-NCD, the difference in boiling points makes them easily separable for the column used with the method. As such, amines are expected to be fully resolved from the ammonia when using this method for biomethane conformity assessment.

- **LOD:** LOD was calculated to 0.03 µmol mol^{-1}.

- **Working range and linearity:** A minimum of 5 repeat runs were averaged for each of the dynamic amount fractions. NPL's XLGENLINE software was used to perform a weighted, linear least squares fit on the data and calculate gradient and y intercept uncertainties. Figure 4 show average NCD peak area for a range of evenly spaced dynamic amount fractions between 0 and 20 µmol mol^{-1}.

  The points where the linear fit does not pass through the measurement uncertainties were likely due to loss of ammonia through adsorption to the walls of tubing in the analyser and dilution system. Similarly, measurements of some low-amount-fraction dynamic standards may have been biased by residual ammonia from high-amount-fraction standards which were run shortly before. If this method is used for the conformity assessment of biomethane then dynamic amount fractions should be given adequate time to stabilise before measurements are made. The high number of repeat readings required in a single day to produce a calibration curve made it impractical to allow a long passivation time for each amount fraction. Further work is required to quantify the passivation time required for readings to stabilise.
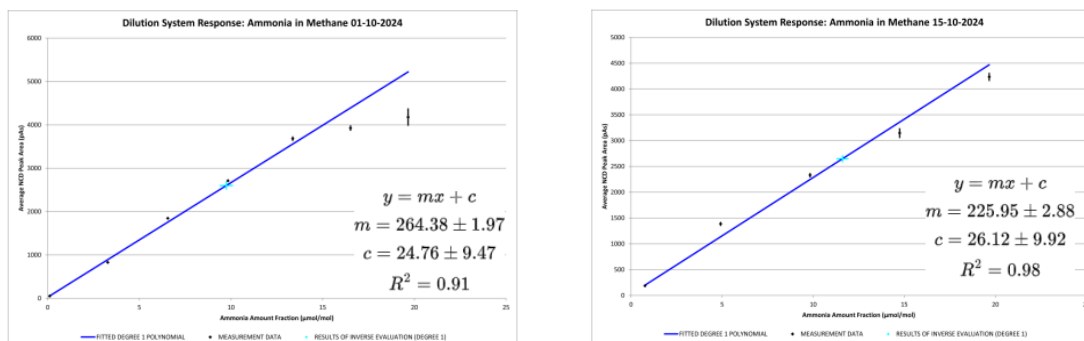
Figure 4 First figure is calibration curve from 01-10-2024 and second figure is calibration curve from 15-10-204, with cyan point showing static check standards.

Residuals are, for the most part, randomly distributed above and below the fit. The only exceptions being 16.5 and 19.7 µmol mol-1 on 01-10-2024 where a region of apparent non-linearity occurred.

- **Bias:** The bias was calculated to 0.22 µmol mol^{-1} for the static standard 2426 and to 1.61 µmol mol^{-1} for the static standard 1870. If the expanded uncertainty of the difference is smaller than the absolute difference between the mean measured value and the reference value, the difference is considered significant, which was the case for 1870.

- **Precision:** The repeatability was estimated as the relative standard deviation and calculated to 2.25%. A meaningful estimate of the intermediate precision could not be made.

- **Measurement uncertainty:** Since the intermediate precision could not be calculated therefore no expanded uncertainty was obtained for this method.

Conclusions

The intermediate precision could not be calculated and therefore no expanded uncertainty was obtained for this method. This is likely a result of purging and passivation effects associated with the sampling system causing bias in the calibration curves. Further work is needed to quantify the passivation time of the dilution system in the proposed working range before this method can be reliably used for the quantification of ammonia for the conformity assessment of biomethane.

4.4 HCl

The performance assessment protocol was applied and validated for the determination of hydrogen chloride.

4.4.1 TDLAS (VSL)

The performance assessment protocol (A2.1.4) was tested and validated using a custom-built TDLS spectrometer which employs an interband cascade laser (Nanoplus, Germany) with collimator. The laser is used to probe the P6 line of HCl centred at 3633.68 nm. The laser is tuned over the absorption line at a rate of 200 Hz. The laser beam is coupled into a multi-pass cell (Aerodyne, USA) with an effective path length of 76 m (cell volume is 0.5 l) via several silver-coated mirrors and the exiting light is focused using a parabolic

mirror on a 2-stage Peltier-cooled detector (PVI-4TE from VIGO, Poland). The pressure in the cell is maintained at 100 mbar using a combination of a pressure controller and a membrane pump. The flow rate through the cell was typically 300 ml/min. Two different methods were used to prepare HCl reference gas standards in methane at the required amount fractions:

1.   Dynamic dilution of a static HCl in CH4 gas mixture. For the static HCl in CH4 standard, a commercial mixture was used which had been certified shortly beforehand.

2.   Dynamic generation based on permeation following ISO 6145-10 and using a magnetic suspension balance (MSB).

Results

- **Selectivity:**

- **LOD and LOQ:** LOD and LOQ for HCl in CH4 were determined to be 10 nmol/mol and 33 nmol/mol, respectively.

- **Working range and linearity:** The linearity of the system has been tested over the range of 0.6 µmol/mol to 6 µmol/mol according to ISO 6143. The Goodness-of-fit value was 1.01 for a first order linear regression fit. For a satisfactory fit of the data, it was required that the absolute value of the normalized residual was not exceeding 2. The normalized residual is the residual divided by the standard uncertainty. All the normalized residuals were < 2, indicating this function is fit for purpose.

- **Precision:** The precision was calculated using the pooled standard deviation as a measure of precision of the method. The resulting precision is 0.05 µmol/mol at an HCl amount fraction of 12 µmol/mol.

- **Measurement uncertainty:** The expanded measurement uncertainty (k=2) is 7% relative for measurement of HCl in the lower µmol/mol range. This value increases with decreasing HCl amount fractions. The dominant sources are the uncertainty due to the reference standard and the bias.

Conclusions

The method is found to be fit-for-purpose, reliable and highly sensitive. Most parts of the protocol are fit for purpose, while some other parts should be more specific. As an example of the latter, the interference testing is not specified in detail. This leaves it more or less open to the user how many interferents and at which level the testing will be done, how it needs to be reported, and what are acceptable levels of interference.

4.5   Halogenated VOC

The performance assessment protocol was applied and validated for the determination of halogenated volatile organic compounds.

4.5.1   TD-GC/MS/FID (RISE)

The performance assessment protocol (A2.1.4) was tested and validated using the method ISO 2620:2024 for the determination of 1,2-dichloropropane, 1,1,2-trichloroethane, dichloromethane, tetrachloroethylene and trichloroethylene in biogas/biomethane matrices with TD-GC/MS/FID.

Halogenated VOCs in gas is enriched on adsorbent Tenax TA, thermally desorbed for gas chromatographic separation on a non-polar capillary column. The majority of the sample goes to a flame ionization detector (FID) and a smaller portion goes to a mass selective detector (MS) for identification of individual components and quantification. A reference mixture produced by VSL in methane containing 0.0526 µmol/mol of 1,2-dichloropropane, 0.0695 µmol/mol of 1,1,2-trichloroethane, 0.05 µmol/mol of dichloromethane, 0.0524 µmol/mol of tetrachloroethylene and 0.0528 µmol/mol of trichloroethylene was used for the validation.

Results

- **Selectivity:** Dichloromethane eluates close to cyclopentyl acetylene using FID but shows good separation when using MS.

- **LOD:** The limit of detection and quantification was calculated with a Signal-to-Noise (S/N) approach. LOD varies between 0.5 and 2.6 ng which is equal to 5 µg/m3 and 26 µg/m3 calculated with a volume of 100ml.

- **Working range and linearity:** The correlation coefficient for all halogenated VOCs measured with GC-MS/FID were close to 1, suggesting that the equation for the linear regression fits the data. Figure 5 shows one example with results for dichloromethane. This observation implies that the method encompasses a linear working range within around 0.1 to around 1 mgm^{-3}. The distribution of residuals -calculated as the difference between the predicted and observed areas - was random, confirming the linearity and working range.
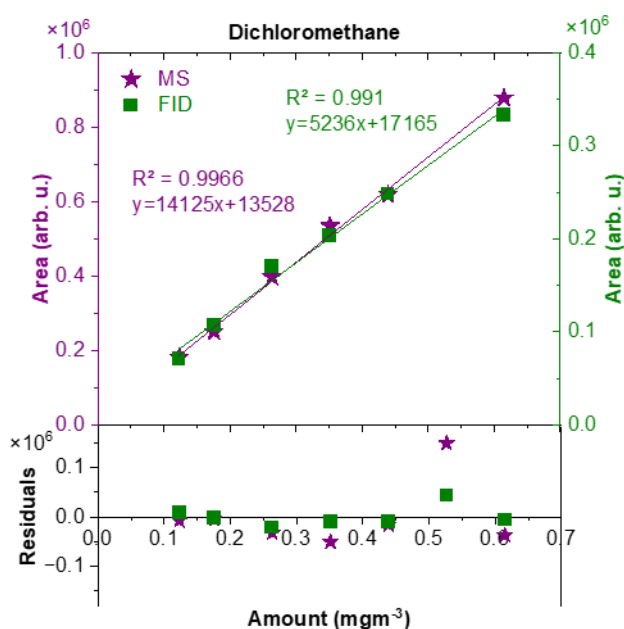

Figure 5 Results for dichloromethane shows linear working range between 0.1 to 0.6 mgm-3, which was confirmed by the random distribution of residuals.

- **Bias:** The mean relative bias was calculated to -3 % and the standard deviation to 1.8 % for dichloromethane. Taking into account the uncertainty of the reference standard, the total bias, u(bias), was calculated to be 4.11% which is in good agreement with the targeted value of 5%.

- **Precision:** Precision was assessed by measuring 10 duplicates at varying quantities using TD-GC-MS/FID on several days. Standard deviation, as well as relative standard deviation, were determined and the pooled standard deviation was calculated. The measured standard deviations, Sr, varies between 0.8 to 1.9 %. The measured pooled standard deviations vary between 0.8 to 1.9 %. Taking into account, the contribution of control samples (here toluene), the within-laboratory reproducibility, u(Rw), was evaluated to be 2.65% for Dichloromethane using MS, which is close to the targeted value of 2.5%.

- **Measurement uncertainty:** The expanded uncertainty (k=2) for dichloromethane was calculated using the software MUKit, showing a measurement uncertainty of 10%.

Conclusions

ISO 2620:2024 is therefore found to be fit-for-purpose, reliable and highly sensitive. As the working range is at least 10 to 100 ng, it can be used to analyze samples with amount fractions of halogenated volatile organic compounds from 10 nmol/mol to 1 µmol/mol (using volumes of 70 to 350 ml per tube).

4.6 Sulphur compounds

The performance assessment protocol was applied and validated for the determination of sulphur compounds.

4.6.1 GC-SCD-FID (BFKH)

The performance assessment protocol was validated for hydrogen sulphide, methyl mercaptan, dimethyl sulphide, ethyl mercaptan, ethyl methyl sulphide and diethyl sulphide with the method ISO 19739:2019 using capillary column with Sulfur Chemiluminescence Detector, SCD and Flame Ionisation Detector, FID. An 7890 Agilent GC FID detects most organic compounds, while combusts samples at a continuous flame as they exit the GC column. One of the combustion products under these flame conditions is a hydronium ion (CHO+), which is attracted to a polarized collector, creating an ion current that is measured by an electrometer.

The Agilent 8355 SCD, Sulfur Chemiluminescence detection is a dual-plasma burner that achieves high temperature combustion of sulfur-containing compounds to form sulfur monoxide (SO). A photomultiplier tube detects the light produced by the chemiluminescent reaction of SO with ozone.

Results

- **Selectivity:** The selectivity of the method was investigated by studying the analyte of interest in a sample which contained 6 closely similar compounds. All peaks were well separated with a good resolution.

- **LOD:** The limit of detection and quantification for the sulphur compounds was calculated with a Signal-to-Noise (S/N) approach. LOD was calculated to 0.001 – 0.025 ppm with SCD and 0.081- 0.306 ppm with FID. The results show that the method is sensitive and can be used to analyze samples with low amount fractions of sulphur compounds.

- **Working range and linearity:** For hydrogen sulphide between 2-3.7 ppm and methyl mercaptan between 0.308 to 0.718 ppm the linear line measured with GC-SCD was close to a value of 1.00, suggesting that the equation for the linear regression fits the data. The distribution of residuals was random, confirming the linearity and working range. For dimethyl sulphide between 0.105-0.732 ppm, ethyl mercaptan between 0.102 to 0.711 ppm, ethyl methyl sulphide between 0.105-0.735 ppm and diethyl sulphide between 0.108 to 0.753 ppm the linear line measured with GC-SCD and GC-FID was close to a value of 1.00, suggesting that the equation for the linear regression fits the data. The distribution of residuals was random, confirming the linearity and working range.

- **Bias:** The relative bias was calculated to between -0.022 and 0, thus biases were negligible.

- **Precision:** Precision was assessed by measuring 10 duplicates of sulphur compounds mixture at varying quantities using GC-FID/SCD on several days. Relative standard deviations were calculated to 0.9 to 2.1 %.

- **Measurement uncertainty:** The expanded uncertainties were calculated to between 3.3 to 8.1%.

Conclusions

The calculations show that measurement uncertainties were lower than 10 % and the method ISO 19739:2019 can therefore be considered fit-for-purpose, reliable and highly sensitive.

4.6.2 GC-SCD-FID (CMI)

The performance assessment protocol was tested and validated using the method based on ISO 19739 for the determination of hydrogen sulphide, carbonyl sulphide, methanethiol, ethanethiol, dimethyl sulphide, tert-butyl mercaptan and tetrahydrothiophene in biomethane matrices. The method is based on gas chromatography with a sulphur chemiluminescence detector.

Results

- **Selectivity:** A reference mixture containing the components of interest was used. The selectivity of the method was investigated by measuring the analyte of interest in the sample. Chromatograms showed that sulphur components eluate with a good separation.

- **LOD:** The limit of detection and quantification (LOD and LOQ) for sulphur components were calculated with a Signal-to-Noise (S/N) approach. LOD was calculated to between 0.014 and 0.031 mg/m^3. The results therefore show that the method is sensitive and can be used to analyse samples with low amount of components.

- **Working range and linearity:** The linearity was assessed by analysing different amounts of compounds (mg/m3). The results for sulphur components measured in the range 0.5 -6 mg/m3 are shown in Figure 6 and Figure 7.
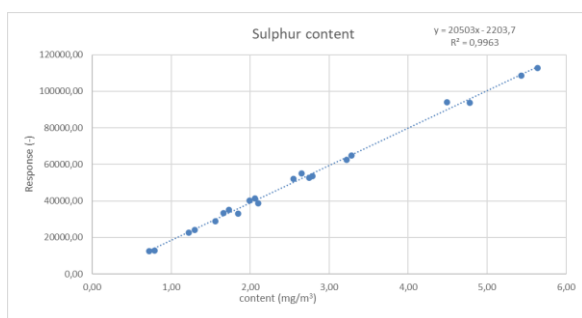

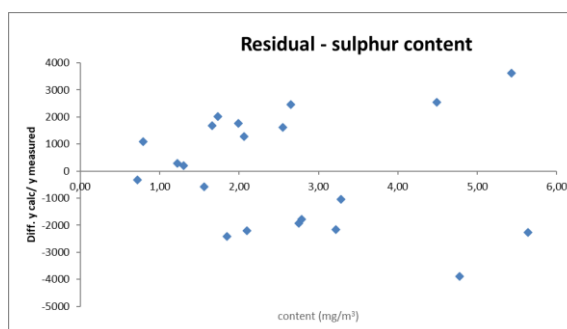*Figure 6 Correlation between the area measured with SCD detector and the known amount of sample in mg/m3.*

Figure 7 The residual of the difference between calculated area and measured area in GC-SCD plotted against known amount of sample in mg/m3.

- **Bias:** The relative bias was calculated to -1.5 % for hydrogen sulphide, -3.6% for COS, -2.7% for methanethiol, 3.4% for ethanethiol and 3.7% for tetrahydrothiophene.

- **Precision:** Precision was assessed by measuring 10 duplicates on several days. Relative standard deviations were calculated to between 1-3 %.

- **Measurement uncertainty:** The expanded measurement uncertainty was calculated to 6% for DMS, TBM and THT respectively.

Conclusions

The validation of the method ISO 19739 was performed according to the performance assessment protocol. The measurement method is reliable, sensitive and found to be fit-for-purpose.

4.6.3   GC-SCD/FID (NPL)

The performance assessment protocol was tested and validated with GC-SCD using a method based on ISO 19739 for the determination of total sulphur.

Results

- **Selectivity:** A sulphur chemiluminescence detector was used which is designed to respond only to sulphur-containing compounds. The separability of different sulphur species using this method was not considered since measurements were of total sulphur.

- **LOD and LOQ:** Limit of detection (LOD) and limit of quantification (LOQ) were evaluated using the signal-to-noise approach, assuming a signal-to-noise ratio (SNR) of 3 for LOD and SNR of 10 for LOQ. LOD was calculated to 0.1 µmol mol^{-1} and LOQ to 0.33 µmol mol^{-1}.

- **Working range and linearity:** The linearity was measured three times. For the first measurement, the R² value was 0.88, for the second measurement it was calculated to 0.98, and the final measurement was 0.91. Residuals show random distribution around zero.

- **Bias:** The bias was calculated to be 0.18% for the first measurement, 6.52-7.2% for the second measurement, and 7.73% for the third measurement.

- **Precision:** The repeatability of the measurement method was determined using six consecutive measurements of the static check standard D521792. Repeatability was estimated as the relative standard deviation of the GC-NCD peak area to 0.87% for the first measurement, 0.6-1.73 % for the second measurement and 2.29% for the third measurement. For intermediate precision, measurements of a static standard were made on 3 separate days. Relative standard deviation of the measured values was used to evaluate the intermediate precision. Intermediate precision was calculated to 10.43 µmol mol^{-1} for the first measurement, 11.17 µmol mol^{-1} for the second measurement (average of two measurements) and 9.64 µmol mol^{-1} for the third measurement. The total RSD was then 7.33%.

- **Measurement uncertainty:** The expanded uncertainty (k=2) was calculated to 15%.

4.7 Terpenes

The performance assessment protocol was applied and validated for the determination of terpenes.

4.7.1 GC/MS/FID (NPL)

The performance assessment protocol was validated against d-limonene, α-pinene and 3-carene using a GC-MS/FID. The GC uses helium carrier gas, and separation is achieved through a 75m length 0.53 mm inner diameter DB-624 fused silicon column. Components are identified and quantified by the FID or the quadrupole mass spectrometer (MS) detector. A gas mixture containing 3.28 µmol/mol d-limonene, 3.367 µmol/mol alpha-pinene and 3.123 µmol/mol 3-carene was diluted according to Table 8, and used for validation.

Table 8 Calculated amount fractions generated by dilution with N 6.0 purity grade methane.

Dilution factor	d-limonene (µmol mol^{-1})	α-pinene (µmol mol^{-1})	3-carene (µmol mol^{-1})	Total terpenes (µmol mol^{-1})
1.0	3.280	3.367	3.123	9.769
1.6	2.050	2.104	1.952	6.106
5	0.656	0.673	0.625	1.954
50	0.066	0.067	0.063	0.195
600	0.005	0.006	0.005	0.016

Results

- **Selectivity:** To evaluated selectivity, a mixture of five siloxanes, three terpenes, and two BTEX was measured to cover the common impurities found in biomethane. The chromatograms show good separation of the three terpenes and the interferent compounds for both FID and MS.

- **LOD:** LOD was calculated using FID to 12 nmol/mol for d-limonene, 13 nmol/mol for alpha-pinene and 12 for 3-carene. When using MS the LOD was calculated to 7 nmol/mol for d-limonene, 8 for alpha-pinene and 7 nmol/mol for 3-carene.

- **Working range and linearity:** For the FID detector, calibration curves were calculated for four amount fractions between 0.066 to 3.280 µmol/mol d-limonene, 0.067-3.367 µmol/mol alpha-pinene and 0.063 to 3.123 µmol/mol 3-carene. For the MS detector, calibration curves were calculated for five amount fractions between 0.003.28 µmol/mol for d-limonene, 0.006-3.367 alpha-pinene and 0.005-3.123 µmol/mol 3-carene. Visual inspection of the calibration curves indicated that the responses for both detectors were linear over the amount fraction ranges studied. The calculated correlation coefficients suggest that the linear regression fit the data well. A random distribution of residuals with no clear trend indicated that the regression model is valid over the working range.

- **Bias:** The relative bias using FID was calculated to 0.94% for d-limonene, 2.8% for alpha-pinene and 0.12% for 3-carene. The relative bias using MS was calculated to 4.9% for d-limonene, 5.8% for alpha-pinene and -3.5% for 3-carene.

- **Precision:** Repeatability was estimated as the maximum standard deviation from the measurement. For FID the repeatability was calculated to 0.85% for d-limonene, 0.41% for alpha-pinene and 1.1 % for 3-carene. For MS the repeatability was calculated to 0.44 % for d-limonene, 0.66% for alpha-pinene and 0.7% for 3-carene.

- **Measurement uncertainty:** The expanded uncertainty (k=2) using FID was calculated to 11% for d-limonene, 5.7% for alpha-pinene, 2.3% for 3-carene. When using MS, the expanded uncertainty was calculated to 14% for d-limonene, 10.5% for alpha-pinene and 9.2% for 3-carene.

Conclusions

The expanded uncertainty for d-limonene can be improved by excluding outlying data from the reproducibility analysis.

4.7.2   TD-GC/MS/FID (RISE)

The performance assessment protocol (A2.1.4) was tested and validated using the method ISO 2620:2024 for the determination of alpha pinene, 3-carene and R-limonene using TD-GC/MS/FID.

Terpenes in gas are enriched on the adsorbent Tenax TA, thermally desorbed for gas chromatographic separation on a non-polar capillary column. The majority of the sample goes to a flame ionization detector (FID) and a smaller portion goes to a mass selective detector (MS) for identification of individual components and quantification. A reference mixture produced by NPL in methane as part of activity A1.1.2 containing 3.32 ± 0.1 µmol/mol of alpha-pinene, 3.00 ± 0.1 µmol/mol of 3-carene and 3.18 ± 0.1 µmol/mol of R-limonene was used for the validation.

Results

- **Selectivity:** Dimethyl-octadiene eluate close to alpha-pinene and 1-Methyl-2-piperidinone eluate close to 3-carene using FID but shows good separation when using MS.

- **LOD:** Varies between 0.11 and 0.81 ng which is equal to 1.1 µg/m^3 and 9.1 µg/m^3 calculated with a volume of 100ml.

- **Working range and linearity:** The correlation coefficient for all terpenes measured with GC-MS/FID were close to 1, suggesting that the equation for the linear regression fits the data. This observation implies that the method encompasses a linear working range within 0.05 to 44 mgm^{-3} (as an example for 3-carene, see Figure 8). The distribution of residuals - calculated as the difference between the predicted and observed areas- is random, confirming the linearity and working range.
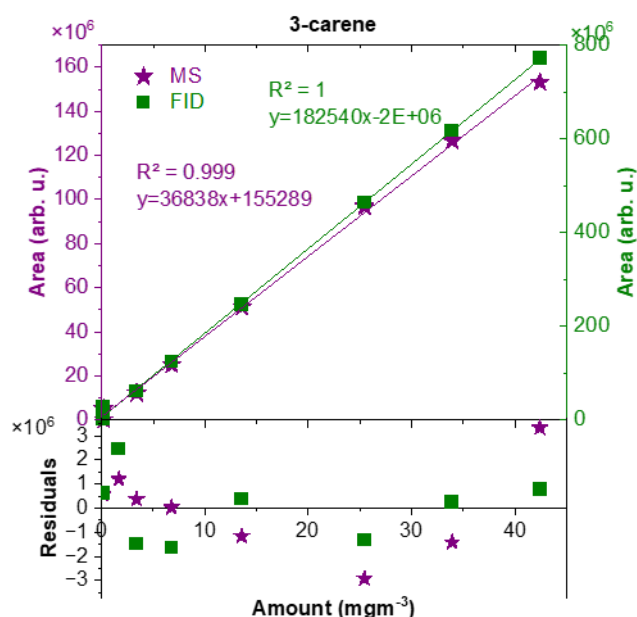
Figure 8 Results for 3-carene shows linear working range between 0.05 to 44 mgm-3, which was confirmed by the random distribution of residuals.

- **Bias:** The relative bias was calculated to 1.8 % for Alpha-pinene, 0% for 3-carene and -0.2% for R-limonene. Taking into account the standard deviation of the measured concentrations and uncertainty of the reference standard, the total bias, u(bias), was calculated to be 3.41 for Alpha-pinene, 3.31 for 3-carene and 3.12 % for R-limonene which is in good agreement with the targeted value of 5%.

- **Precision:** Precision was assessed by measuring 13 duplicates at varying quantities using TD-GC-MS/FID on several days. Standard deviation, as well as relative standard deviation, were determined and the pooled standard deviation was calculated. The measured standard deviations, Sr, varies between 1.7 to 2.4 %. Taking into account, the contribution of control samples (here toluene), the within-laboratory reproducibility, u(Rw), was evaluated to be 2.49% for Alpha-pinene, 2.62% for 3-carene and 2.76% for R-limonene, which is close to the targeted value of 2.5%

- **Measurement uncertainty:** The expanded uncertainty (*k*=2) for L2 was calculated using the software MUKit. The calculations show that the measurement uncertainty is 9% for Alpha-pinene, 3-carene and R-limonene.

Conclusions

ISO 2620:2024 is therefore found to be fit-for-purpose, reliable and highly sensitive. As the working range is at least 10 to 400 ng, it can be used to analyze samples with amount fractions of terpenes from 10 nmol/mol to 5 µmol/mol (using volumes of 25 to 200 ml per tube).

4.8   H2, CO, O2, N2

The performance assessment protocol was applied and validated for the determination of hydrogen, carbon monoxide, oxygen and nitrogen.

4.8.1   GC-TCD (NPL)

The analytical methods used to determine the concentrations of hydrogen (H_2), carbon monoxide (CO), oxygen (O_2) and nitrogen (N_2) in methane matrix using gas chromatography thermal conductivity detector (GC-TCD) were validated in accordance with the performance assessment protocol developed in A2.1.4. The TCD operates by measuring the thermal conductivity of the gases flowing through it. It contains a heated filament in a flow cell, where the carrier gas establishes a baseline. When the static standard flows through it, the gases that have different thermal conductivity to the carrier gas changes the heat dissipation from the filament, causing a shift in temperature and electrical resistance. The resistance change alters the voltage, which generates a signal proportional to the concentration of the gases in the static standard. The concentrations of the reference standards are reported in Figure 11.

Table 9 Gravimetric compositions of PRMs used in the validation.

Component	Amount fraction ($\mu mol\ mol^{-1}$)	
	D133074	D133080
Hydrogen	104060.886	20160.221
Carbon monoxide	962.805	1009.282
Oxygen	1922.799	406.6774
Nitrogen	94213.246	19973.566
Methane	Balance	Balance

Results

- **LOD:** LOD were calculated to 1.7 $\mu mol\ mol^{-1}$ for hydrogen, 39.7 $\mu mol\ mol^{-1}$ for carbon monoxide, 19.2 $\mu mol\ mol^{-1}$ for oxygen and 24.7 $\mu mol\ mol^{-1}$ for nitrogen.

- **Working range and linearity:** Visual inspection of the linear curves indicates that the TCD response for hydrogen (Figure 9), carbon monoxide, oxygen and nitrogen are linear for the tested amount fractions. The calculated correlation coefficients (R2) were above 0.995 suggesting that the linear regressions fit the data well. The distribution of residuals is random, confirming the linearity and working range.
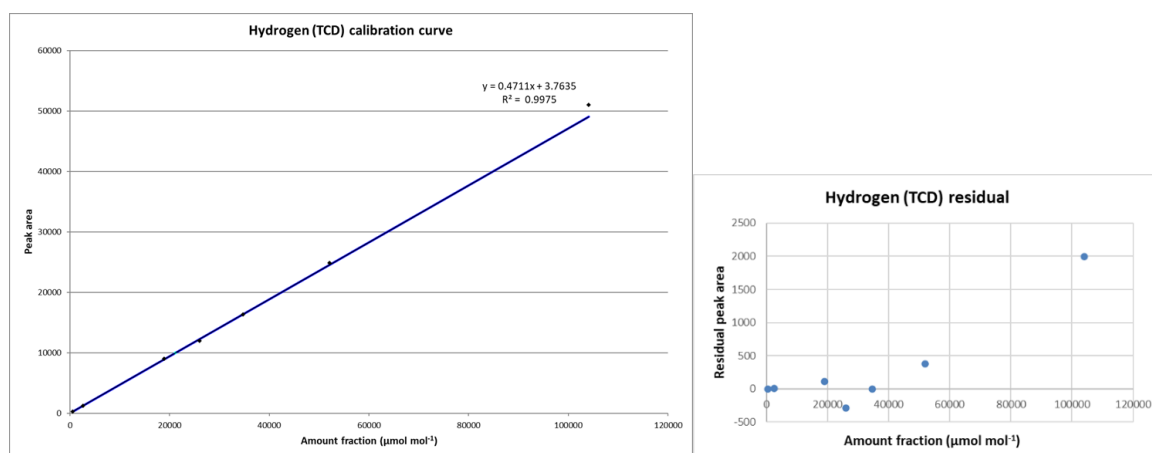

Figure 9 Calibration curve and plot of residual peak area against amount fraction for hydrogen.

- **Bias:** The relative bias was calculated to 5% for hydrogen, 0.2% for carbon monoxide, 6% for oxygen and 2% for nitrogen.

- **Precision:** The repeatability of the measurement method was determined by 3 repeat measurements. The repeatability RSD was calculated to 0.04 – 0.58 %. Intermediate precision was calculated through at least 3 repeats on each day. The relative standard deviations were calculated to 0.15 to 2.04 %.

The reproducibility for the four components of interest is below 5%, which indicate that the method is suitable for the measurement of these analytes.

- **Measurement uncertainty:** The expanded uncertainty was calculated to 10.5 % for hydrogen, 0.5 % for carbon monoxide, 13.5% for oxygen and 6% for nitrogen.

Conclusions

The method for the analysis of hydrogen, carbon monoxide, oxygen, and nitrogen in biomethane using the TCD detector is valid except for oxygen. The expanded uncertainties for hydrogen, oxygen and nitrogen can be drastically improved by sufficient purging of the MFC dynamic dilution system for 5-10 minutes to remove remaining gas from the previous standard as well as ambient air.

4.8.2 GC-TCD (CMI)

The performance assessment protocol was tested and validated using the method based on ISO 6974-6 for the determination of H2, N2, CO, O2, methane in biomethane matrices. The method is based on gas chromatography with a thermal conductivity (GC-TCD).

Results

- **LOD:** LOD was calculated to 0.006 10^{-2} mol/mol for hydrogen, 0.012 10^{-2} mol/mol for oxygen, 0.012 10^{-2} mol/mol for nitrogen and 0.01 10^{-2} mol/mol for carbon monoxide. The results show that the method is sensitive and can be used to analyse samples with low amount with components of interest.

- **Working range and linearity:** The correlation coefficient for hydrogen measured with GC-TCD/TCD is close to a value of 1.00, suggesting that the equation for the linear regression fits the data (Figure 10). This observation implies that the method encompasses a linear working range within 0.99 to 8 10^{-2} mol/mol. The distribution of residuals is random, confirming the linearity and working range (Figure 11).
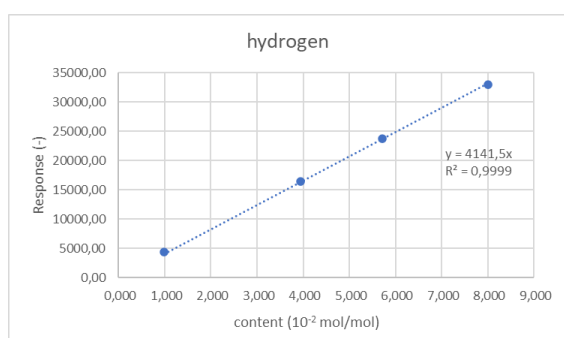

Figure 10 Correlation between the area measured with TCD detector and the known amount of sample in 10^{-2} mol/mol
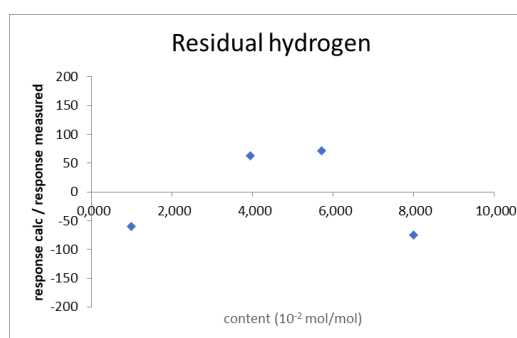

Figure 11 The residual of the difference between calculated area and measured area in GC-TCD/TCD plotted against known amount of sample in 10^{-2} mol/mol

- **Bias:** The mean relative bias was calculated to 0.3% for hydrogen, -1% for oxygen, 1% for carbon monoxide and 0.2% for nitrogen.

- **Precision:** Precision was assessed by measuring 10 duplicates of hydrogen, oxygen, carbon monoxide, nitrogen and methane on several days. The mean relative standard deviation was calculated to 0.1 % for hydrogen, 0.7% for oxygen, 1,1% for carbon monoxide and 0.6% for nitrogen.

- **Measurement uncertainty:** Measurement uncertainties were calculated to 1.6% for hydrogen 0.8% for carbon monoxide 1.6% for oxygen and 0.4% for nitrogen.

Conclusions

The method for the analysis of hydrogen, carbon monoxide, oxygen, and nitrogen in biomethane according to ISO 6974-6 and using the TCD detector is valid and fit for purpose.

4.8.3 GC-TCD (TUBITAK)

The performance assessment protocol was tested and validated for the determination of H2, N2, CO in biomethane matrices using GC-TCD. Reference mixtures were used according to Table 10.

Table 10 Concentrations of the gas mixtures prepared for method validation study (k=1).

Component	Unit	Composition (Mixture 1) (Cylinder: PSM206700)	Composition (Mixture 2) (Cylinder: PSM206696)
Hydrogen	cmol/mol	1.954 ± 0.001	9.974 ± 0.003
Nitrogen	cmol/mol	2.044 ± 0.001	10.051 ± 0.001
Carbon monoxide	µmol/mol	979.3 ± 0.6	997.9 ± 0.6
Methane	-	Balance	Balance

Calibration of the instrument was carried out using TUBITAK UME's reference gas mixtures. The gas mixtures with the compositions given in Table 11 are used as reference gas mixtures during method validation study for N_2 and H_2 components.

Table 11 Amount of fractions of the reference gas mixtures of N2 and H2

Cylinder No	Amount of Fraction (cmol/mol)	
	N_2	H_2
UME499821	0.122	-
UME499775	0.649	0.973
UME298291	14.917	0.502
UME499803	17.918	4.054
UME499802	20.421	7.444
UME499796	24.962	9.985

A binary mixture (CO in methane) is used for method validation study of CO. It was diluted to 3 different concentrations according to ISO 6145-7. The amount fraction of CO in the reference gas mixture and the target CO calibration points are given in Table 12.

Table 12 Amount of fractions of the gas mixtures obtained for method validation study of CO

Cylinder No	Amount of Fraction (cmol/mol)	Diluted to (µmol/mol)
PSM206723	2.997 ± 0.001	500
		1000

		2000

Results

- **Selectivity:** GC method provides successful separation of the components without any interference.

- **LOD:** LOD was calculated to 4.8 µmol/mol for CO, 4.6 µmol/mol for N2 and 8.7 µmol/mol for H2.

- **Working range and linearity:** The analyses of diluted mixtures and two sample mixtures were carried out in three different days. The correlation coefficient was close to 1 (R2 > 0.999) and there was a linear relationship between the response for each gas mixtures measured with GC-TCD.

- **Bias:** The relative bias was calculated to 2.5% for CO in cylinder PSM206696 and 2% in cylinder PSM206700. The relative bias was calculated to 0.4% for N2 in cylinder PSM206696 and to -0.3% in cylinder PSM206700. For H2 the relative bias was calculated to -0.1% in cylinder PSM206696 and to -0.4% in cylinder PSM206700. Uncertainty from bias, Ubias, was calculated to 0.5 % for CO, 0.06 % for N2 and 0.08 % for H2.

- **Precision:** Precision was evaluated using ANOVA (one way), taking into consideration replicates within days (10 injections) as well as replicates between days (3 sets). The precision was calculated to 0.36% within days and 0.1% between days for CO in PSM206696 and to 0.35% within days and 0.1% between days in PSM206700. Precision was calculated to 0.37% within day and 0.1 % between days for N2 in PSM206696 and to 1.7% within days and 0.5% between days for N2 in PSM206700. Finally, the precision was calculated to 0.17% within days and 0.05% between days for H2 in PSM206696 and to 0.28% within days and 0.08% between days in PSM206700.

- **Measurement uncertainty:** The relative expanded measurement uncertainty was calculated to 0.63% for CO, 1.1% for N2 and 0.35% for H2 in PSM206700 and to 0.63% for CO, 0.35 for N2 and 0.33% for H2 in PSM206696.

Conclusions

The method for the analysis of hydrogen, carbon monoxide, and nitrogen in biomethane is fit for purpose reliable and highly sensitive.

5   Measurement uncertainty

The project's partners have validated the protocol using multiple validated methods and technologies, addressing relevant impurities as per EN 16723 standards. The Table 13 summarizes the measurement uncertainty obtained for each method.

Table 13 Targeted compound, analytical methods and measurement uncertainties for the different methods used for validation of the protocol.

Partner	Targeted compounds	Analytical method	Measurement uncertainties
IMBiH	Total silicon	AES	2%
RISE		TD-GC/MS/FID	11%
VSL			4-11%

NPL	Siloxanes (L2, L3, D3, D4, D5)	GC-IMS	3-8%
VSL	Ammonia	Laser spectroscopy	6%
NPL		GC-NCD	-
VSL	Hydrogen chloride	Laser spectroscopy	7%
RISE	Halogenated VOC	TD-GC/MS/FID	10%
BFKH			3-8%
CMI	Sulphur compounds	GC-SCD-FID	6%
NPL			15%
NPL		GC/MS/FID	2-14%
RISE	Terpenes	TD-GC/MS/FID	9%
NPL	Hydrogen, carbon monoxide, oxygen, nitrogen	GC-TCD	Hydrogen 10% Carbon monoxide 0.5% Oxygen 13% Nitrogen 6%
CMI			Hydrogen 1.6% Carbon monoxide 0.8% Oxygen 1.6% Nitrogen 0.4%
Tubitak			Hydrogen 0.4% Carbon monoxide 0.6% Nitrogen 0.4%

6   Conclusions

The BiometCAP project has successfully developed and validated a comprehensive protocol for evaluating gas analyzers in biomethane applications. This protocol supports various measurement technologies and ensures accurate results through best practices in sample preparation and sampling. The project's partners have demonstrated the protocol's effectiveness using existing reference methods/ validated methods and technologies, addressing relevant impurities as per EN 16723 standards. Targeted relative expanded uncertainties as recommended in the protocol (1 to 10 % relative) are met for most of the methods used here.

7 References

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