21NRM04 BiometCAP

D6: Report on the effectiveness and reproducibility of the developed biomethane performance assessment protocol, across a wide variety of methods and compounds, based on application at a variety of laboratories and field sites

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Glossary

L2: Hexamethyldisiloxane
L3: Octamethyltrisiloxane
D3: Hexamethylcyclotrisiloxane
D4: Octamethylcyclotetrasiloxanne
D5: Decamethylcyclopentasiloxane
GC-IMS: Gas chromatography-based ion mobility spectrometry
GC-FID: Gas chromatography-based flame ionization detector
TD-GC: Thermally desorbed gas chromatography
OFCEAS: Optical feedback cavity enhanced absorption spectroscopy

FTIR: Fourier transform infrared spectroscopy
Far-UV: Far ultraviolet spectroscopy
LOD: Limit of detection
LOQ: Limit of quantification

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1 Summary

The report gives an overview of the effectiveness and reproducibility of the developed biomethane performance assessment protocol, across a variety of methods and compounds, based on the application at a variety of laboratories and field sites. Different measurement methods have been employed in several laboratories and biomethane production plants in different countries to measure impurities in biomethane. This report summarizes the results on impurity measurements within the 21NRM04 BiometCAP project.

2 Introduction

Biomethane, an upgrade of biogas or purified form of biogas, is a renewable source of energy produced from decomposition of organic waste, landfills, pulp sludge or manure [1]. Biomethane production plants and gas grid operators continuously monitor impurities (e.g. ammonia, siloxanes, terpens etc) for quality control of the produced biomethane before it is injected into the gas grid. The limit values of these impurities are documented in the EN16723 standard [2]. These limit values are set to prevent e.g. damage, caused by harmful impurities to the existing natural gas infrastructure and to end user appliances. To measure these impurities accurately, a biomethane assessment protocol [3] has been developed in 21NRM04 BiometCAP project, providing guidance on how to assess the performance, and on how to validate, the methods and analytical instruments used in the conformity assessment of biomethane. Therefore, this document reports on the effectiveness and reproducibility of the developed biomethane performance assessment protocol across in laboratories [4] and field sites [5].

3 Laboratory comparison on the performance assessment protocol

3.1 Laboratory based technique comparison (fixed analyte)

To assess the reproducibility of the protocol within laboratory settings, Table 1 shows results for L2 siloxane from different laboratories following the protocol, spanning three separate measurement techniques (GC-IMS, TD-GC-MS and GC-FID). Parameters such as the limit of detection (LOD), limit of quantification (LOQ) and expanded uncertainties were determined for the different measurement techniques.

Table 1: Results of the application of the performance evaluation protocol for L2 siloxane measurements employing three measurement techniques

Analyte	Technique	Laboratory and location	Parameter					
			Working range	Trueness	Precision (% relative)	LOD	LOQ	Expended measurement uncertainty (k = 2)
L2 siloxane	GC-IMS	NPL, UK	0.271 – 0.812 mg m^{-3}	0.36 %	Repeatability: 1.23 % Intermediate precision: 3.10 %	0.06 mg m^{-3}	-	6.7 %
	TC-GC-MS	RISE, Sweden	3 – 117 ng	4.56 %	Intermediate precision: 3.10 %	0.18 ng	0.61 ng	11 %
	GC-FID	VSL, Netherlands	0.30 – 4.00 µmol mol^{-1}	-0.39 – 0.34 %	Repeatability: 0.27 % Intermediate precision: 0.51 %	0.0016 µmol mol^{-1}	0.0052 µmol mol^{-1}	4 %

From the table 1, it is clear that the use of the protocol reproduces L2 siloxane measurement results with expected targeted uncertainties using three different measurement technique in three different laboratories. As these uncertainties have been obtained by following the protocol, the quality assurance of the data produced is ensured.

3.2 Laboratory based analyte comparison (fixed technique)

To further assess the reproducibility of the protocol within laboratory settings, the results of application of GC-FID technique were reviewed (see Table 2), spanning five separate analytes, these being: α-pinene, dichloromethane, dimethylsulphide, tetrahydrothiophene and L2 siloxane.

Table 2: Results of the application of the performance evaluation protocol employing GC-FID for five analytes at six laboratories.

Technique	Analyte	Laboratory and location	Parameter					
			Working range	Trueness (% relative)	Precision (% relative)	LOD	LOQ	Expended measurement uncertainty (k = 2)
GC-FID	**α-pinene**	Rise, Sweden	11 – 375 ng	1.8 %	Intermediate precision: 1.7 %	0.8 ng	2.7 ng	9 %
	α-pinene	NPL, UK	0.006 – 3.367 µmol mol^{-1}	2.8 %	Repeatability: 0.41 % Intermediate precision: 0.19 %	0.013 µmol mol^{-1}	0.042 µmol mol^{-1}	5.67 %
	dichloromethane	Rise, Sweden	12 – 61 ng	< 5%	Intermediate precision: 1.8 %	1.3 ng	4.3 ng	10 %
	dimethyl sulphide	BFKH, Hungary	0.105-0.732 µmol mol^{-1}	1.9 %	Intermediate precision: 1.62 %	0.306 µmol mol^{-1}	1.020 µmol mol^{-1}	5.62 %
	tetrahydrothiophene	CMI, Czechia	0.5 – 6.0 mg m	3.68 %	Intermediate precision: 0.986 %	0.031 mg m^{-3}	0.102 mg m^{-3}	5.58 %
	L2 siloxane	VSL, Netherlands	0.30 – 4.00 µmol mol^{-1}	-0.39 – 0.34 %	Repeatability: 0.27 % Intermediate precision: 0.51 %	0.0016 µmol mol^{-1}	0.0052 µmol mol^{-1}	4 %

The comparison shows that six different laboratories across Europe were able to successfully apply the protocol employing GC-FID for five different analytes, achieving relative expanded uncertainties for the results of ≤10 %. As these uncertainties have been obtained by following the protocol, the quality assurance of the data produced is ensured.

4 Field comparison on the performance assessment protocol

4.1 Field based technique comparison (fixed Analyte)

To assess the effectiveness of the protocol at a field site, the results for NH_3 measurement were reviewed, spanning three separate measurement techniques, these being: OF-CEAS, FTIR and Far UV spectroscopy, in a field setting as shown in Table 3.

Table 3: Results of the application of the performance evaluation protocol for NH_3 measurement using three measurement techniques at a filed site

Analyte	Technique	Field site	Working range	Result from field site	LOD
NH3	**OF-CEAS**	Denmark	0.05 – 100 µmol/mol	Process gas: 30-70 µmol/mol Product gas: <0.100 µmol/mol	0.01 µmol/mol
	FTIR	Denmark	0-3000 µmol/mol	Process gas: 45-75 µmol/mol Product gas: < 2 µmol/mol	0.1 µmol/mol
	Far-UV	Denmark	-	Raw Biogas: 20 µmol/mol Process gas: 55-105 µmol/mol	-

The measurement of NH_3 is very challenging at a biomethane production plant. The NH_3 amount fractions varies significantly at different stages of biogas upgrading processes. Before final filtration ("Process gas "), all three measurement techniques delivered NH_3 amount fraction ≤ 105 ppm as shown in Table 3. From Table 3, it is evident that the measured NH_3 amount fraction in the "Product gas" (= at final filtration, just before injection to the grid) employing the different measurement techniques is ≤ 2 µmol/mol/ (ppm), below the limit value as specified in the EN16723 standard.

Note: The Far-UV instruments could only measure the raw biogas (no filtration) and Process gas.

4.2 Field based analyte comparison (fixed technique)

To further assess the effectiveness and reproducibility of the protocol on field measurements, we compared the amount fraction of 12 analytes at two different field sites using the FTIR instrument.

Table 4: Results of the application of the performance evaluation protocol for 12 analytes measurements using FTIR at two biomethane production field sites in Denmark.

Technique	Analyte	Working Range	LOD (µmol/ mol)	Results from field site measurement	
				Field Site 1 (Denmark)	Field Site 2 (Denmark)
FTIR	CO2	0-1000µmol/mol	0.1	Process gas: 0.6 - 1.2% Product gas: 0.4 - 1.8%	Product gas: 1.2%
	H2O	0-20%	1	Product gas: <5 µmol/mol	-
	Ethylene	0-100 µmol/mol	0.2	Product gas: 2 - 2.5 µmol/mol	Product gas: 0.4 µmol/mol
	Propylene	0-10 µmol/mol	0.3	Product gas: 3 - 4 µmol/mol	Product gas: 4.8 - 6.4 µmol/mol
	NH3	0-3000 µmol/mol	0.1	Process gas: 45 - 75 µmol/mol	-

				Product gas: < 2 µmol/mol	
	Limonene	0-1000 µmol/mol	0.3	Product gas: <4 µmol/mol	Product gas: 3 µmol/mol
	CO	0-4000 µmol/mol	0.1	Product gas: 0-0.4 µmol/mol	-
	D3	0-30 µmol/mol	0.1	Product gas: 12-56 nmol/mol	Product gas: 45 nmol/mol
	D4	0-50 µmol/mol	0.1	-	Product gas: 200-250 nmol/mol
	D5	0-50 µmol/mol	0.1	-	Product gas: 30 nmol/mol
	L3			-	Product gas: 20-70 nmol/mol
	Methane	Methane:0-98%	Matrix gas	Product gas: 98-99%	Product gas: 99%

Table 4 shows that the amount fractions of the impurities at different field sites could be accurately determined using online techniques and were found to be well below the limit values specified in the EN16723 standard. Site 1 shows presence of higher level of ethylene in the product gas compared to site 2.

5 Conclusions

From the above-mentioned comparisons (Tables 1-4), it is clear that the reproducibility and effectiveness of the protocol have been successfully assessed via different laboratories and field-based measurements for several impurities in biomethane. Employing the performance assessment protocol, Table 1 shows the comparison of siloxane measurement results obtained from three different techniques in three different laboratories and Table 2 indicates the GC-FID measurement results of six analytes in six different laboratories which demonstrate the applicability of the protocol to reproduce the measurement results in laboratories within the respective target uncertainties. Table 3 shows a comparison of NH_3 measurements in “Process” and “Product” gas using three different analysers at a field site. Similarly, Table 4 shows the comparison of 11 different impurities measure in biomethane at two different field sites using FTIR spectroscopy which demonstrates similarities in the amount fraction levels of identified impurities in biomethane (except ethylene) at two field sites. The presence of impurities with their respective amount fraction in the biomethane depends on the origin of raw materials, the process parameters and the upgrading technique. However, at both sites the “Product gas” was free from siloxane, and the CO_2 level was well below the limit value set in EN16723.

6 References

[1] Arrhenius, K., Culleton, L., Nwaboh, J. *et al.* Need for a protocol for performance evaluation of the gas analyzers used in biomethane conformity assessment. *Accred Qual Assur* **29**, 69–76 (2024). https://doi.org/10.1007/s00769-023-01562-x

[2] EN16723-1:2016 Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network, part 1: Specifications for biomethane for injection in the natural gas network, Bruxelles, Belgium: European Committe on Standardisation, 2016

[3] BiometCAP A2.1.4: Protocol for the performance evaluation of gas analysers used for biomethane conformity assessment

[4] *BiometCAP D2*: Report on the validation of the performance assessment protocol for EN16723 impurities using existing reference methods with relative expanded uncertainties of 1 % - 10 %

[5] *BiometCAP D4*: Report on the field-based performance evaluation, of selected industrial gas analyzers and reference instrumentation, using the developed biomethane performance assessment protocol

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