21NRM04 BiometCAP

Deliverable D7: Good practice guide on ensuring the reproducible application of the developed biomethane performance assessment protocol

Organisation name of the lead participant for the deliverable: NPL

Due date of the deliverable: 30/09/2025

Actual submission date of the deliverable: 23/09/2025

Confidentiality Status: PU - Public, fully open (remember to deposit public deliverables in a trusted repository)

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or EURAMET. Neither the European Union nor the granting authority can be held responsible for them.

European Partnership Co-funded by the European Union

The project has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States.

TABLE OF CONTENTS

1 Summary 2
2 Choice of sampling materials 3
2.1 Sample Bags 3
2.2 Sorbent Tubes 3
2.3 Sample Tubing 3
2.4 Sample Cylinders 3
3 Ensuring representative sampling 4
3.1 Contamination Risks 4
3.2 Preventing analyte loss 4
3.3 Best practice from standardisation 4
3.4 Sampling media 5
3.5 Sampling and analysis methods 6

1 Summary

This good practice guide is a complimentary material intended to be applied alongside the instrument performance evaluation protocol developed during the EURAMET European Partnership on Metrology project 21NRM04 "BiometCAP". It covers key technical considerations to ensure the protocol is applied accurately and reproducibly. Best practice recommendations are provided for: material choice, sampling methods and biomethane analysis.

2 Choice of sampling materials

A summary of key points is provided below. Refer to the [BiometCAP A2.1.2 report][1] for comprehensive guidance on material compatibility for use with biomethane.

2.1 Sample Bags

- **Use only for short-term storage** and non-reactive compounds.
- **Avoid for high-boiling compounds** (>150 °C), which are prone to adsorption losses.
- **Minimize exposure time** and transfer gas to more stable media (e.g. sorbent tubes) promptly.
- **Material choice matters**: fluoropolymer bags (e.g. Tedlar) are better than polyethylene for reducing adsorption.
- **Humidity and temperature** influence adsorption—avoid sampling in high-moisture environments without proper conditioning.

2.2 Sorbent Tubes

- **Effective for many VOCs and semi-volatiles**, especially when used with Tenax TA or similar sorbents.
- **Not suitable for very volatile compounds** (boiling points <20–50 °C).
- **Good short-term stability** (up to one week) for many compounds.
- **Combine with bag sampling**: transfer gas from bag to sorbent tube immediately after filling to reduce losses.
- **Use high flow rates** during transfer, especially for moist biomethane, to avoid underestimation.

2.3 Sample Tubing

- **Use inert materials** such as PTFE, PEEK, or stainless steel with SilcoNert® coating.
- **Avoid materials prone to adsorption or reaction** (e.g. rubber, PVC).
- **Ensure leak-tight connections** and avoid dead volumes to prevent contamination and loss.
- **Purge thoroughly** before sampling to remove residual moisture and contaminants.

2.4 Sample Cylinders

- **Select based on impurity type and pressure conditions**:
    - High-pressure (>50–60 bar) cylinders reduce adsorption (e.g. for siloxanes).
    - Low-pressure (<10 bar) storage increases risk of adsorption (e.g. for toluene).
- **Use coated cylinders** (e.g. SilcoNert®, Spectraseal PT) for reactive species.
- **Validate cylinder performance** through stability studies:
    - Experis, PB, and Megalife cylinders showed good stability for siloxanes.
    - Performax and Spectraseal PT showed partial stability; some compounds degraded or increased.
- **Avoid uncoated stainless steel** for reactive or sticky compounds unless validated.





BiometCAP guide to biomethane sampling

3 Ensuring representative sampling

It is essential to ensure the sample reaching the analyser is representative of the gas to be measured. False positives may result from contamination; false negatives from loss of impurities.

3.1 Contamination Risks

- **Air ingress** (O_2, N_2, H_2O)
    - Occurs via dead volumes/dead ends in sampling lines and during transport if vessels are not properly sealed.
- **Minimise surface area** and **volume** for sampling connections.
- **Purging** is essential:
    - Removes O_2 and N_2 effectively.
    - Requires robust procedure for H_2O due to higher adsorption.
    - Take account of weather effects on humidity for outdoor work.
- **Perform check on the Leak-tightness of sampling lines** to esnure sample quality.
- **Carry-over contamination**:
    - From previous samples, especially if they contained “sticky” compounds.
    - Surface defects and materials like thread-seal tape increase adsorption risk.
    - Thorough purging is critical after sampling sticky compounds.

3.2 Preventing analyte loss

- Impurities may be lost during sampling or transport due to:
    - **Adsorption** onto vessel or line surfaces.
    - **Chemical reactivity** leading to degradation over time.
- **Sampling line material** must be compatible and appropriately passivated to prevent reactions.

3.3 Best practice from standardisation

The key messages to take from sampling standard **ISO 10715** [2] are as follows:

- When connecting an instrument to the process stream or to calibration gas, the point of sampling should be **within the gas flow path**, not on a dead-ended section of pipe without gas flow.
- **Minimise** the number of **valves, regulators, connections, and other sampling equipment** between the gas to be measured and the measurement equipment.
- Sample tubing should be **defect free, appropriately passivated for the analytes, and be heated where appropriate to reduce adsorption** from low vapour pressure and/or reactive components.
- A **validated sampling protocol** should be used, which involves appropriate **heating, purging, and filling** of sampling equipment to get a representative sample and avoid unwanted adsorption prior to the sample container (e.g., bag, sorbent tubes, cylinder).

The key messages from **ISO 17025** [3] are as follows:

- Laboratories must use a **validated sampling methodology** based on appropriate statistical methods.
- Records must include parameters such as:
    - Date and sample ID.
    - Personnel involved.
    - Equipment used.
    - Environmental conditions.
    - Sample transport conditions.

BiometCAP guide to biomethane sampling

3.4 Sampling media

Table *1* provides a summary of the best practice for selection of sampling media for biomethane analysis.

Table 1: Sampling media suitability for biomethane analysis

Method	Available sizes	Required flow rate	Sapling pressure required	Considerations
Sample bags 	1 – 20 L	Not exceeding 1-2 L / min	Slightly above atmosphere pressure. Over-pressurisation (>2 psi) can cause the bags to burst if too high. If required, the pressure can be reduced using a pressure regulating device of appropriate passivation.	• Check the oxygen, carbon dioxide and water vapor permeability. • Material depends on the compounds to be sampled. • Ensure fittings guarantee no loss of compounds by adsorption. • Bags may need to be warmed before analysis of some compounds. • Bags are often designed for single use.
Sorbent tubes 	100 – 1000 mL	50 – 500 mL / min	Slightly above atmosphere pressure. May require a vacuum pump. Over-pressurisation can cause the sorbent to move inside the tube. If required, the pressure can be reduced using a pressure regulating device of appropriate passivation.	• Material depends on the impurities to be trapped. • Requires a calibrated flowmeter and consequently stable flows. • Flow measurement for enriched gas blends (e.g., biomethane – natural gas - hydrogen) are challenging without prior composition knowledge.
Impingers 	Up to 20 mL of solvent typical	50 – 500 mL / min	Slightly above atmosphere pressure. May require a vacuum pump. Over-pressurisation can cause borosilicate glass to break. If required, the pressure can be reduced using a pressure regulating device of appropriate passivation.	• Impinger sampling is more complex compared to alternatives. • Acetone and methanol solvents are most suitable for siloxanes.
Cylinders 	1 – 20 L	N/A	> 10 bar Cylinders are available with maximum fill pressures up to 200 bar.	• Internal passivation choice depends on analytes.* • Appropriate passivation is required for the cylinder. E.g. SilcoNert® 2000 by SilcoTek is appropriate for a wide range of components.

* Examples of suitable passivation include SilcoNert® 2000 (SilcoTek), SPECTRA-SEAL (BOC), Aculife VII (Air Liquide), Performax (Effectech), Experis (Air products). A comprehensive material compatibility table is available from the BiometCAP project [1]

BiometCAP EURAMET

3.5 Summary of sampling and analysis methods

A list of methods for sampling and analysis of contaminants in biomethane are provided in Table 2.

Table 2: List of experimentally validated biomethane analysis and sampling methods by component

Component	Analysis method	ISO standard	Sampling method	Gas volume required
Siloxanes	TD-GC-MS/FID	ISO 2620	Sorbent tubes / sample bags then sorbent tubes	Sorbent: 100 to 500 ml @ 50 to 500 mL/min Bags: 2-3 litre
	GC-MS	ISO 2620	316 stainless steel cylinder with internal passivation* / sample bags with polypropylene valves and PTFE tubing / direct analysis with PTFE or passivated stainless steel tubing	> 1 L (bags) > 5 L (cylinders)
	GC-FID	ISO 2620	316 stainless steel cylinder with internal passivation* / sample bags with polypropylene valves and PTFE tubing / direct analysis with PTFE or passivated stainless steel tubing	> 1 L (bags) > 5 L (cylinders)
	GC-IMS	ISO 2613-2	316 stainless steel cylinder with internal passivation* / sample bags with polypropylene valves and PTFE tubing / direct analysis with PTFE or passivated stainless steel tubing	> 1 L (bags) > 5 L (cylinders)
	GC-AES	ISO 2613-1	direct analysis upon derivatisation in liquid media	> 2 L
Ammonia	GC-NCD	-	316 stainless steel cylinder with internal passivation* / sample bags / direct analysis	> 1 L (bags) > 5 L (cylinders)
	Laser spectroscopy	ISO 2612	316 stainless steel cylinder with internal passivation* / sample bags / direct analysis	> 1 L (bags) > 5 L (cylinders)
Amines	TD-GC-MS/FID	ISO/TS 2610	316 stainless steel cylinder with internal passivation* / sample bags / direct analysis	> 1 L (bags) > 5 L (cylinders)
Hydrogen chloride **Hydrogen fluoride**	Laser spectroscopy	ISO 2611-1	316 stainless steel cylinder with internal passivation / direct analysis	15 – 30 L
Halogenated VOCs	TD-GC-MS/FID	ISO 2620	Sorbent tubes	> 100 mL
Sulphur compounds	GC-SCD	ISO 6326	316 stainless steel cylinder with internal passivation* / sample bags / direct analysis	> 1 L (bags) > 5 L (cylinders)
Terpenes	TC-GC-MS/FID GC-MS/FID	ISO 2620	Sorbent tubes / sample bags then sorbent tubes 316 stainless steel cylinder with internal passivation* / sample bags / direct analysis	> 1 L (bags) > 5 L (cylinders)
Methane	GC-TCD	ISO 6974	316 stainless steel cylinder with internal passivation* / sample bags / direct analysis	> 1 L (bags) > 5 L (cylinders)
Nitrogen	GC-TCD	ISO 6974	316 stainless steel cylinder with internal passivation* / sample bags / direct analysis	> 1 L (bags) > 5 L (cylinders)
Carbon dioxide	GC-TCD	ISO 6974	316 stainless steel cylinder with internal passivation* / sample bags / direct analysis	> 1 L (bags) > 5 L (cylinders)
Oxygen	GC-TCD	ISO 6974	316 stainless steel cylinder with internal passivation* / sample bags / direct analysis	> 1 L (bags) > 5 L (cylinders)
Hydrogen	GC-TCD	ISO 6974	316 stainless steel cylinder with internal passivation* / sample bags / direct analysis	> 1 L (bags) > 5 L (cylinders)
Carbon monoxide	GC-TCD	ISO 6974	316 stainless steel cylinder with internal passivation* / sample bags / direct analysis	> 1 L (bags) > 5 L (cylinders)

* Examples of suitable passivation include SilcoNert® 2000 (SilcoTek), SPECTRA-SEAL (BOC), Aculife VII (Air Liquide), Performax (Effectech), Experis (Air products). A full compatibility table is available from the BiometCAP project (Arrhenius, Fateev, Culleton, & Li, 2023).

References

[1] Arrhenius K, Fateev A, Culleton L, Li J. Review of the requirements for biomethane sample preparation and sampling including dynamic methods (flow through the analysers) and static methods. 2023.
[2] ISO 10715:2022, Natural gas — Gas sampling 2022.
[3] ISO 6141:2015/Amd 1:2020 - Gas analysis — Contents of certificates for calibration gas mixtures — Amendment 1: Cross reference list to ISO Guide 31:2015 and ISO/IEC 17025:2017 2015.