A2.1.2 – Review of the requirements for biomethane sample preparation and sampling including dynamic methods (flow through the analysers) and static methods

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Title		
Review of the requirements for biomethane sample preparation and sampling including dynamic methods (flow through the analysers) and static methods		

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Abstract

Standards EN16723 require analysis in a laboratory and therefore requires the collection and transport of a gas sample from the point of use. The sample taken must be representative of the gas supplied. Biomethane composition determination can to some extend also be done onsite. This report reviews the requirements for biomethane sampling including recommendations for maintaining the integrity of the biomethane sample, material compatibility and practical recommendations for dynamic and static gas sampling. A key aspect of the sampling of biomethane highlighted here is the risk of losing impurities through adsorption on the vessel´s wall. The selection of appropriate materials for the sampling vessel and sampling line is crucial. However, material compatibility tables tentatively proposed in this report are not yet extensively filled to help in this choice and more studies are needed to fill the gap in knowledge in this area.

Key words

Sample preparation, biomethane, dynamic methods, static methods, sampling

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Contents

1 - Introduction

Standards EN16723-1 [1] and EN16723-2 [2] require analysis in a laboratory and therefore requires the collection and transport of a gas sample from the point of use. Standard ISO 17025 [3] gives general requirements for the competence of testing and calibration laboratories.

The sample taken must be representative of the gas supplied; this assumes that no compounds are added to or removed from the gas during sampling and transport to the analysis laboratory. However, it is known that adsorption effects in the sampling vessel or sampling line can lead to a loss of the impurities to be analysed. Another risk is contamination of the sample by air or from carryover from a previous sampling. Some recommendations must be followed in order to guarantee the integrity of the sample. Recommendations are given in standard ISO 10715 [4] (originally intended for natural gas), which was revised 2022, and include a few considerations for biomethane. Issues have also been studied during previous metrology projects such as EMRP54 Metrology for Biogas [5] and 16ENG05 Metrology for Biomethane [6]. This report intends to review the requirements for biomethane sampling including recommendations for maintaining the integrity of the biomethane sample, material compatibility and practical recommendations for dynamic and static gas sampling.

Sampling can be divided in three primarily techniques: spot, continuous composite or continuous on-line sampling.

Spot sampling is essentially the simplest way to sample a gas: a sample vessel is connected to a pipe, opened until the pressure in the sample vessel reached that of the pipeline [7]. For natural gas, sampling is usually performed in cylinder. If the pressure is not too high, other types of vessels such as gas bags or sorbent tubes can be used for laboratory analysis of impurities.

Composite sampling is the middle ground between spot sampling and the continuous on-line analysis with use e.g. GC analyzers [8].

A composite gas sampler or gas sampling system consists of a probe, a sample collection pump, an instrumentation supply system, a timing system and a collection cylinder for sample transportation. Its sole objective is to collect and store over a period of time ("time proportional") or volume of flow ("flow proportional"), a representative composite sample at line conditions, allowing it to be transported to the laboratory for analysis, without changing the chemical composition, heating value, or physical characteristics of the products being sampled. This practice is also common in LNG sampling as described in ISO 8943:2007 [9].

A typical gas sampling system consist of tubing, valves, filters, heating elements, optional probes and sample cylinders.

2 – Sampling vessels

Different containers have been used for collecting biogas and biomethane samples. These include gas cylinders (of different materials, with or without treatment or passivation technologies), sampling bags (of different materials), canisters, adsorbent tubes and impingers [10]. Due to the variety of materials for bags, cylinders and sorbent tubes, the selection of appropriate vessels is a big challenge.

Several reviews [11] [10] have collected useful information on the different vessels that can be used to sample impurities. These studies are an important source of information to select vessels. For example, in [11], a table collects the physico-chemical features of common gas sampling bags according to the manufacturer's information (Tedlar, Altef, Kynar, Nalophan, Teflon). Another table collects the properties of common commercial adsorbents used in thermodesorption applications (including porous polymers, carbon molecular sieve and graphitized carbon black). For sorbent tubes, another useful source of information are the different tools developed for selecting a sorbent for thermal desorption applications [12] [13].

3 - Sample collection and storage

The conditions at the facilities need to match the need for the diverse range of analytical instruments and sampling vessels used to assess the purity of biomethane [14]. Some parameters need to be known beforehand, for example, volume of gas required for each analysis, if pressurized gas is needed, what are the analytes or properties of interest to be measured (determines material compatibility or coating requirements); connections at the sampling point and on the sampling vessels. To achieve representative sampling, it is crucial to adhere to many of the sampling guidelines outlined in ISO 10715, including:

1. Choose an appropriate place to take the sample from. It should be in a flowing leg (receiving fresh biomethane), not on a dead leg
2. Use a sample probe if the line is not too small to allow good flow
3. Minimise the number of valves, regulators and other sampling equipment downstream of the sampler
4. Use valves with good flow paths (e.g. ball valves), similar/compatible materials and without deadlegs, exposed polymeric seals etc
5. Sample tubing should be defect free, coated for certain analytes and ideally be heated to reduce adsorption
6. A sampling protocol should be used, which involves appropriate heating, purging, filling of sampling equipment to get a representative sample and avoid unwanted adsorption prior top the sample container (bag, sorbent tubes, cylinder).

Note: 1-6 apply for all offline and online sampling methods. 7 applies only to spot sampling.

On Tables 1 and 2, some requirements are listed for each impurity and analytical method. Table 1 shows the requirements for the analysis instruments that will be used in BiometCAP, table 2 show general requirements for the different types of sampling vessels that can be used.

Table 1: list of requirements for analysis methods

Impurities	Partner	Analysis methods	Sampling vessel or Media	Connections between sampling media and instrument	Description of the transfer	Volume required (if pertinent)	Pressure required (if pertinent)	Comments
Siloxanes	RISE	TD-GC-MS(FID)	Sorbent tubes or bags/sorbent tubes	Not applicable	Thermal Desorption	Sorbent: 100 to 500 ml @ 50 to 500 ml/min onsite Bags: 2-3 liter	Low pressure onsite	The volume sampled is related to the detection limit therefore accurate measurement of flow, pressure, temperature of sample is crucial
	VSL	TD-GC-MS(FID)	High pressure gas cylinders/ sortbent tubes	Gas reducer, connector, sampling line	Volumetric sampling via GC system /Thermal Desorption	> 10 L	> 10 bar	
	NPL	GC-IMS	316 stainless steel cylinder with internal SilcoNert® 2000 passivation	1/16´´ diameter 316 stainless steel tubing with internal SilcoNert® 2000 passivation. Passivated pressure regulator and cylinder connections	Direct flow of gas into the GC sample loop volume via pressure gradient	> 5 L (to achieve flows of ~30 ml/min over a 2 hour period + stabilisation time)	> 10 bar	
	IMBIH	atomic/ionic emission spectrometry-based analyser	silicon inert (sampling) cylinder and mineral acids	direct analysis upon derivatistion in liquid media	Not applicable	2-20 litre at atmospheric pressure (Concentration dependable)	2-3 bar at least	Analytical form of silicon $[SiF6]^{2-}$
Ammonia	NPL	NDIR	316 stainless steel cylinder with internal SilcoNert® 2000 passivation	1/16´´ diameter 316 stainless steel tubing with internal SilcoNert®	Direct flow of gas into the cell volume via pressure gradient	>100 L (to achieve flows of ~400 ml/min over a 2 hour	> 10 bar	

				2000 passivation. Passivated pressure regulator and cylinder connections.		period + stabilisation time)		
		GC-NCD			Direct flow of gas into the GC sample loop volume via pressure gradient	> 10 L (to achieve flows of ~30 ml/min over a 2 hour period + stabilisation time)	> 10 bar	
	VSL	laser spectroscopy	High pressure gas cylinders and possibly polyester bags	Gas reducer, connector, sampling line	Sampling via coated mass flow controlller before the measurement cell and pressure controller and pump after the cell	~5 L	No requirement as measurement cell can operate at sub-atmospheric pressure.	Reasonable results have been obtained in literature for NH_3 using sampling in polyester bags [15].
HCl	VSL	laser spectroscopy	High pressure gas cylinders	Gas reducer, connector, sampling line	Sampling via coated mass flow controlller before the measurement cell and pressure controller and pump after the cell	~15-30 L	No requirement as measurement cell can operate at sub-atmospheric pressure.	
Halogenated VOC	RISE	TD-GC-MS(FID)	Sorbent tubes	Not applicable	Thermal Desorption	-	-	The volume sampled is related to the detection limit therefore accurate measurement of flow, pressure, temperature of sample is crucial
Sulphur compounds	BFKH	GC-FID-SCD GC-MSD	SilcoNert® 2000 - treated cylinder, aluminum (Luxfer, Aculife 4+3)	Special pressure reducing valve with SilcoNert® 2000 - treated tubing inside	Pressure regulator of GC	50 liters	>8 bar	Slightly above atmosphere pressure is enought for the GC, but proper flushing, due to adsorption and for the good reproducibility of area need higher pressure.
	CMI	GC-SCD	Aculife III/IV treated cylinder or sample bags	SilcoNert® 2000 - treated 1/8´´stainless steel tubing	Volumetric sampling via GC system	At least 1 liters for bags and 10 liters for cylinder	atmospheric for the bag and 10bars for cylinder	CMI
	NPL	GC-SCD-FID	316 stainless steel cylinder with internal SilcoNert® 2000 passivation	1/16´´ diameter 316 stainless steel tubing with internal SilcoNert® 2000 passivation		> 10 L (to achieve flows of ~30 ml/min over a 2 hour period + stabilisation time)		

Terpenes	RISE	TD-GC/MS/FID	Sorbent tubes or bags/sorbent tubes	Not applicable	Thermal Desorption	Sorbent: 100 to 500 ml @ 50 to 500 ml/min onsite Bags: 2-3 liter	Low pressure onsite	The volume sampled is related to the detection limit therefore accurate measurement of flow, pressure, temperature of sample is crucial
	NPL	GC-MS/FID	316 stainless steel cylinder with internal SilcoNert® 2000 passivation	1/16´´ diameter 316 stainless steel tubing with internal SilcoNert® 2000 passivation	Direct flow of gas into the GC sample loop volume via pressure gradient	> 10 L (to achieve flows of ~30 ml/min over a 2 hour period + stabilisation time)	> 10 bar	316 stainless steel cylinder with internal SilcoNert® 2000 passivation
Main compounds (e.g. methane, nitrogen, carbon dioxide, oxygen, hydrogen, carbon monoxide)	Tubitak	GC-TCD GC-FID/methaniser	Al 5 L (Luxfer, Aculife III+IV) cylinders	DIN 477 No:1, 1/8" stainless steel tubing	Pressure regulator to GC autosampling system	5 L	>50 bar	
	CMI	GC-TCD/FID	Cylinder 5 – 40 liters	1/16´´stainless steel tubing	Volumetric sampling via GC system	At least 10 liters	> 10 bar	
	NPL	GC-TCD	316 stainless steel cylinder with internal SilcoNert® 2000 passivation Or Sample bags	1/16´´ diameter 316 stainless steel tubing with internal SilcoNert® 2000 passivation Or 1/8´´ diameter PTFE tubing	Direct flow of gas into the GC sample loop volume via pressure gradient	> 4 L (to achieve flows of ~30 ml/min over a 2 hour period)	> 10 bar	316 stainless steel cylinder with internal SilcoNert® 2000 passivation

Table 2 - List of requirements for the sampling vessels

Vessels	Volume required (l)	Flow (ml/min) to fill the vessel	Temperature (°C)	Connections	Pressure required	Problem med impurities or matrix	Comments
Bags	Different volumes exist, 1 to 20 L	Not exceeding 1-2 L/min	According to recommendation from provider	6 mm diameter, as short as possible, no silicon contained tubing	Slightly above atmosphere pressure. Over pressurization (>2 psi) can cause the bags to burst If too high, the pressure can be reduced using a valve	Check the oxygen, carbon dioxide and water vapor permeability Material depends on the compounds to be sampled	With fittings that 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
Sorbents	100 to 1000 ml	50 – 500 ml/min	Not exceeding 20°C for better trapping of lighter compounds	Stainless steel	Slightly above atmosphere pressure. Over pressurization can cause the sorbent to move inside the tube. If too high, the pressure can be reduced using a valve	Material depends on the impurities to be trapped	Requires using a calibrated flowmeter, and consequently stable flows
Cylinders	Different volumes exist, 0.1 to 50 L. Volume and pressure of gas are dependent on analytes.	N/A	Not to exceed 60°C. Depending on the dew points of the mixture, but usually the storage/use temperature should be ≥ 15°C	Gas reducer, connector, sampling lines 316 stainless steel tubing, All with appropriate internal passivation.	> 10 bar	Internal passivation choice depends on analytes.	Appropriate passivation is required for the cylinder. SilcoNert® 2000 is appropriate for a wide range.

4 - Integrity of the sample

In order to maintain the integrity of the sample from the moment the gas is sampled until it is analysed in the laboratory, contamination (leading to false-positive analysis results) and loss of impurities (leading to false-negative analysis results) must be avoided [16].

Contaminations occurs if the sampling procedure itself contaminated the sample, for example, an ingress of air (oxygen, nitrogen and water) into the biomethane sample. Air contamination entirely depends on the sampling line (presence of dead volumes or dead ends). Air contamination could also occur through ingress of air into the sampling vessel during transport (most probably before sampling). To minimize this risk, it is recommended to shorten the time between the preparation of the sampling vessel and the sampling. Oxygen and nitrogen are not as adsorptive to materials (stainless steel for example) compared to water, so an efficient purge should be enough to remove them while water it is more difficult to remove through purging. The water amount fraction in the vessel is highly dependent on the sampling system. Ensuring purging of the sampling system/line before taking the sample will avoid contamination from ambient humidity: sampling under the rain, or in dry summer. Ensuring that all parts of the sampling line is leak tight will reduce the number of purges required. Purging also ensures a fresh, representative sample is taken. To our knowledge, studies on the efficiency of purging methods for cylinders is not well-studied for biomethane and more effort should be put into performing purge testing in order to develop a protocol detailing the methods to apply.

Another risk of contamination can arise from the sampling vessel itself if it is not sufficient clean (contamination from previous samples for example also called carry-over). The same risk exists for the sampling line. This is particularly important if the sample had previously contained "sticky" compounds that adsorb onto surfaces. The presence of surface defects and exposed surfaces such as thread-seal tape can also cause compounds to adsorb. Purging is even more important if the previous samples contained sticky compounds.

Loss of impurities occurs when impurities in the biomethane are lost either during the sampling or transport of the sampling vessel to the laboratory. Some of the impurities to be analysed have a propensity to adsorb on surfaces (adsorption in vessels and/or in sampling line (including regulators) while other impurities are reactive and may disappear from the sample over time.

Examples will be components such as sulphur containing compounds which may adsorb to sampling vessel [17] [18] or sampling line therefore would be lost or significantly reduced in the sample upon reaching the laboratory. It is important to perform the measurements as quickly as possible to avoid any under-estimation if reactive species are to be analysed (ex. ammonia). The use of an appropriate cylinder is a crucial contributory factor to the stability of some impurities. It is not only the cylinder that is important, but it is also essential that suitable sampling line materials and coating (where applicable) are selected.

The risk for reactions depends upon many factors including the vessels material and/or the concentration, the presence of other impurities etc... The use of appropriate coating or online analysis is important with reactive compounds.

To summarize, maintaining the integrity of the sample is crucial to deliver correct analysis results. False-positive and false-negatives must be avoided at all costs to guarantee that the sample that reaches the laboratory is representative of the gas onsite. Many parameters need to be thoroughly considered among them, the material for the sampling vessel and the sampling line (material compatibility), the preparation (conditioning) of the sampling

vessel beforehand, the thorough purge of the sampling line (and sampling vessel if necessary), the optimized time between the sampling vessel preparation and sampling and the time between the sampling and the analysis.

5 - Material compatibility

As discussed before, material compatibility is crucial to ensure that the sample will not change over time. Material compatibility is assessed by performing recovery studies and storage stability studies. The recovery yield [10] is defined as the measured concentration divided by the spiked concentration and expressed as a percentage. To assess the suitability of the sampling vessel after a period of storage, the storage stability, defined as the change in concentration for a given compound as determined at the end of the storage time compared to as determined on Day 0, is often measured. The conditions used for these tests are of high importance (concentration of the impurities, volume and pressure of the sampling vessel, matrix) and must be specified.

For the selection of materials for natural gas sampling, ISO10715 [4] refers to a table from another standard, ISO16664 [19], which provides material compatibility for a list of gases such as inert gases, oxygen, carbon dioxide, carbon monoxide, alkanes, alkenes, aromatics, nitrogen oxides, chlorine, hydrogen chloride, ammonia, hydrogen sulphide and sulfur dioxide and for a list of materials (stainless steel, copper/brass, Hastelloy/monel/nickel, aluminium, polytetrafluorethene, polyether-ketone silica-lined, glass/quartz, fluorinated ethene-propene and silica-lined stainless steel).

According to this table, stainless steel is suitable for most of the impurities mentioned, except for CO at a mole fraction above 1 % (of limited suitability) and for Cl_2 and HCl at all mole fractions (of limited suitability) and for H_2S at a mole fraction below 0.001 % (not suitable) unless SilcoNert® 2000 or other suitable coating is used [20]. Aluminium is also suitable for many of the impurities. However, there is no experience for NO_2 with a mole fraction below 1 % (aluminium is not suitable for NO_2 with a mole fraction above 1 %), for Cl_2 with a mole fraction between 0.001 and 1 % (aluminium is not suitable for Cl_2 with a mole fraction above 1 %) and for NH_3. Aluminium is not suitable for HCl at mole fractions above 0.001%. Hastelloy/monel/nickel, glass/quartz and silica-lined stainless steel are suitable for all impurities in the three ranges of mole fractions (<0.001%, >0.001 to 1%, >1%). The ISO10715 standard even recommends analysing reactive compounds on site using direct sampling methods when practical, as even coated cylinders cannot eliminate the risk of absorption of reactive species.

However, due to the production methods, biomethane may contain species in traces that can have a negative impact on the equipment they come into contact with or on the pipelines when they are injected into the gas network which are not found in natural gas. Some of these impurities; siloxanes for instance, are regulated in the EN16723 standards. Other such as terpenes may be added in the future. Therefore, material compatibility for biomethane is specific and a similar table as the one in ISO16664 needs to be establish for this gas. However, due to the large number of vessels available (bags, sorbents, cylinders…), this task is a big challenge.

For this purpose, some recovery and stability studies for siloxanes, halogenated compounds and BTEX (benzene, toluene, ethylbenzene and xylenes) have been performed during the project Metrology for Biogas [21] in cylinders, bags and onto sorbent tubes. The studies showed that many factors, at least, concentration, pressure and the presence of water affect the suitability of a vessel. While storage in gas cylinders seemed to be a reliable alternative when the gas was taken at a relatively high pressure (> 50 bar to 60 bar as in the case of siloxanes D4 and D5), adsorption effects occurred directly on the inner surface of the cylinder at low pressure (less than 10 bar as in the case of toluene). The occurrence of adsorption on the walls of bags has been shown to be strongly related to the boiling point of the target species, which is consistent with information provided by bag manufacturers [22]. Compounds with a boiling point above about 150 °C tend to be more likely to be partially lost by adsorption in bags

than compounds with lower boiling points. The loss appears to be concentration dependent and to occur to a greater extent during the initial storage period when the internal surfaces become saturated [21]. Using sorbents as Tenax TA has also been found [23] to be a reliable alternative for many compounds to be assessed in biogas/biomethane as good storage stability for a period of up to a week has been obtained. However, these sorbents cannot be used for compounds with boiling points under 20-50°C (depending on the material). Combining sampling on tubes and sampling in bags by transferring a volume of gas from the bag into a sorbent tube immediately after filling the bag has been proposed as another sampling strategy, as it could provide a solution to overcome the disadvantages associated with both methods (adsorption effects in the bags and needs for rather complicated flow measurements for the sorbent tubes). However, this study [24] has shown that the transfer must be done at relatively high flow rates (Figure 3), especially if the gas contains a higher water content (as in biogas). If lower flow rates are used, the concentrations can be underestimated, which has a particular effect on compounds with higher boiling points (above 150 °C), probably due to adsorption on the walls of the bags.

Material compatibility was also investigated for different cylinders as part of the EMPIR project "Metrology for biomethane" [6], with tests to determine the long-term stability (1.5 years) of siloxane standards in six different types of cylinders: Spectraseal from BOC, Spectraseal with H_2S-treatment performed by NPL (called Spectraseal PT), Performax from Effectech, Megalife from Air Liquide, Experis from Air Liquide and PB passivation from New Energy Technology (deliverable D1). The targeted siloxanes were hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) in a methane matrix. These tests were carried out at a pressure of 100 bar and concentrations of 55 nmol/mol for L2, 35 nmol/mol for L3, 27 nmol/mol for D4 and 22 nmol/mol for D5. In these tests, measurements were performed on different cylinders 30 days after the preparation of the mixtures and the results were compared with measurements performed on the preparation day. With this time frame, these results can be used to assess material compatibility for sampling (mostly when found stable) even if it would also have been interesting to have results after a shorter period of storage (1 or 2 weeks) – for the cases where some compounds were found unstable. The results for the Experis, PB and Megalife cylinders showed that all siloxanes were stable (within 5% change) compared to day 0. The results for Performax and Spectraseal PT showed that only D5 and D4 were stable within the limit of 5 % change. L2 levels increased (+9% and +11% change compared to day 0 for Performax and Spectraseal PT, respectively) and L3 levels decreased (-8% and -12% change compared to day 0 for Performax and Spectraseal PT, respectively). The results for Spectraseal showed that only D4 was stable within a 5% change. The concentrations of L2 and D5 increased (+9 % change compared to day 0) and the concentration of L3 decreased (-12 % change compared to day 0).

Some stability studies have been done on sorbents for halogenated compounds and sulphur compounds in a hydrogen matrix [25]. The matrix doesn´t play an important role for sorbent as both methane and hydrogen passes through the sorbent without being retained but the thresholds required are much lower in hydrogen than in biomethane.

Based on these studies and standards, an attempt to summarize the results into a material compatibility table from the different stability studies is done. Another source of information is the experiences from the different NMIs involved in this activity. The time-period of testing is not standardized so some studies were performed over months while others were performed over weeks. The definition of the term "suitable" would need to be defined quantitatively which is not the case in these studies.

Table 3 – Material compatibility for gas cylinders

| | Stainless steel | | | | Aluminium | | | | | | | | | | | | | | | | | | | |
| | Untreated | | Sulfinert® | | Untreated | | Aculife VII | | Performax | | SPECTRA-SEAL | | SPECTRA-SEAL PT | | Experis | | Megalife | | PB | |
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
Inert compounds (N2 for ex.)	S [19]	S [19]	X	X	S [19]	S [19]	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Methane	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Carbon dioxide	S [19]	S [19]	X	X	S [19]	S [19]	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Oxygen	S [19]	S [19]	X	X	S [19]	S [19]	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Carbon monoxide	S [19]	S* [19]	X	X	S [19]	S [19]	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Siloxanes	i.d.	i.d.	S† [21]	S† [21]	i.d.	i.d.	i.d.	i.d.	S† [6]	S† [6]	S† [6]	S† [6]	S† [6]	S† [6]	S [6]	S [6]	S [6]	S [6]	S† [6]	S† [6]
Ammonia	S [19]	S [19]	S [6]	S [6]	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	S [26]	S [26]	S [26]	S [26]	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.
Hydrogen sulphide	NS [19]	S [19]	S [26]	S [26]	NS [26]	S [19]	S [26]	S [26]	X	X	S [26]	S [26]			i.d.	i.d.	i.d.	i.d.	i.d.	i.d.
Sulphur compounds	NS [26]	i.d.	S	S	N [26]	i.d.	i.d.	i.d.	i.d.	i.d.	S [26]	S [26]	S	S	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.
Halogenated compounds																				
Hydrocarbons	S [19]	S [19]	X	X	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	X	X	X	X	X	X	i.d.	i.d.		
Terpenes	i.d.	i.d.	S [27]	S [27]	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	NS [27]	i.d.	NS [27]	NS [27]	S [27]	S [27]	i.d.	i.d.	i.d.	i.d.

*According to ISO16664, stainless steel cylinders have a limited suitability for CO for mole fractions above 1 vol-%

† Suitability demonstrated for siloxanes L2, D3, D4, D5. Instability observed when L3 siloxane present.

a: at EN16723 threshold: Siloxanes: 0.3 mg Si/m^3, H$_2$: 2 %, O$_2$: 1%, CO 1000 ppm, NH$_3$ 10 mg/m^3 – 14 ppm, H$_2$S+COS, 5 mg/m^3 1 -3 ppm, S total 30 mg S/m^3, Amine 10 mg/m^3

b: at Higher concentrations (i.e. 50 times EN16723)
X: should be suitable
S: suitability demonstrated (* more than 80% stability over at least a month)
I: Issues were found (ex. of issues: need careful selection of the cylinder, initial loss, not all compounds from one family are stable…)
i.d.: Insufficient data
NS: not suitable

Table 4 – Material compatibility for sampling bags

Commercial bag name	Film composition	Pressure (P) and temperature (T) working range	Measured permeability to permanent gases at 1 bar filling	Experiences with biomethane/biogas matrix including stability studies	Experiences with other matrices than air or biomethane including stability studies
Tedlar	Polyvinyl fluoride [11]	Max operating T: PP valve 82 ∘ C; SS valve 202 ∘ C Max filling P relative to atmospheric P: ~0.14 bar or	O$_2$: 50 cc/m^2/ day H$_2$O vapor: 9–57 g/ m^2/day CO$_2$: 172 cc/ m^2/day [11]	Siloxanes [21] (short storage stability for compounds with high boiling points but high recovery yield)	

		≤80% filled [11]			
Altef	Polyvinylidene Difluoride [11]	Max operating T: 82 ◦ C Max filling P relative to atmospheric P: ~0.14 bar or ≤80% Filled [11]	O_2: 58 cc/m^2/day H_2O vapor: 12–15 g/m^2/day CO_2: 172 cc/m^2/day [11]	Siloxanes, sulfur compounds, hydrocarbons [21] (short storage stability for compounds with high boiling points but high recovery yield)	
Kynar	Polyvinylidene Difluoride [11]	Max operating T: PP valve 93.3 ◦ C; SS and PTFE valves 107.2 ◦C [11]			
Nalophan	Polyethylene-terephthalate [11]				-
Teflon	Fluorinated ethylene propylene	PTFE valve working T range: -60 to 150°C Max filling P relative to atmospheric P: 0.06 bar or ≤90% filled	O_2: 2400 cc/ m^2/day H_2O vapor: 1.3 g/m^2/day [11]		
Multi-foil	Several layers for example: Nylon, metalized aluminum foil, polyethylene [28]	Max. Operating Temp.: 87 °C [28]	O_2: 0.0006 cc/m^2/day H_2O vapor: 0.0006 g/100 square inches/day CO_2: 0.0005 cc/100 square inches/day [28]	Permanent gases, H_2S [26], O_2 due to low permeability (as long as contamination with air can be avoid during filling), CO_2 due to low permeability	

**Table 5 – Material compatibility for sorbent tubes**

		Volatility Range (Carbon & boiling point) [13]	Suitable Analytes [13]	Weakness/Caution [13]	Experiences with biomethane/biogas matrix including stability studies	Experiences with other matrices than air including stability studies
Graphitized carbon black	Carbopack X (Carbotrap X	C3 - C5 80 - 45°C	Light hydrocarbons: 1,3-Butadiene, benzene, toluene, and xylene	Some activity with labile compounds. Friable	Hydrocarbons [21]	
	Carbopack B (Carbotrap B) [Anasorb GCB1] {Carbograph 1}	C5 ~ C12 >75°C (C5 ~ C12) [C5 ~ C12]	A wide range from medium to high volatility: ketones, alcohols, and aldehydes (not formaldehyde). Nonpolars within volatility range. Perfluorocarbon trace gases. Aliphatic and aromatic hydrocarbons	Lower desorption efficiency than Tenax for higher molecular weight compounds when used in saturated atmosphere. Some activity with labile compounds. Friable	Siloxanes [21]	

	Carbopack C (Carbotrap C) [Anasorb GCB2] {Carbograph 2}	C8 ~ C20	Extends the capability of Carbopack B to higher molecular weight analytes. Alkyl benzenes and large aliphatics (C8-C20). As multi-sorbent with PCB, PAH	Some activity with labile compounds. Very low surface area. Friable	As multi-sorbent with Carbotrap B and Carbosieve SIII (Carbotrap 300), sulfur compounds, hydrocarbons [21]	
Carbon molecular sieves	Carbosieve SIII	C2 - C4 60 80°C	Permanent gases (H2, O2, Ar, CO and CO2) and C2-C4 hydrocarbons, chloromethane	Low desorption efficiency for polar compounds. Less retentive capability than charcoal. Easily and irreversibly contaminated by high boilers.	Tenax TA: hydrocarbons, sulfur compounds, halogenated compounds, ketones, alcohols, esters, terpenes, siloxanes [11]	-
	Unicarb (Spherocarb)	C3 - C8 -30 -150°C	Both nonpolar and polar compounds especially very volatile, but spatially large molecules	Easily contaminated by high boilers. Expensive		As a multisorbent with Tenax TA for Sulfur compounds in hydrogen [25]
Porous polymer	Tenax TA	C6-C26 100 - 400°C	Aromatics (except benzene), nonpolars (BP>150°C), semi-volatile polars (BP>150°C).	Low breakthrough volume. May form some artifacts when heated, reported sources are: CO2, benzene, toluene, benzaldehyde, acetophenone	Hydrocarbons, terpenes, chlorinated and fluorinated hydrocarbon; esters; ketones, furans, sulfur compounds, siloxanes [29], [11], [21]	Sulphur compounds, Halogenated compounds, Hydrocarbons in hydrogen [25]
	Chromosorb 106	C5 - C12 50 - 200°C	Low-boiling hydrocarbons, benzene, labile compounds, volatile oxygenated compounds	Low temperature limit. High artifacts (10ng), batch-to-batch variations		Halogenated compounds, hydrocarbons in hydrogen [25]

6 – Dynamical (flow through) gas sampling

Dynamical (or on-line) gas sampling is a part if on-line gas quality control. The gas can continuously flow through an analyzer at pipelines temperature and pressure, or a (very) small gas flow can be taken for an analysis. The gas is typically vented out after the analyzer.

An example of a commercial GC analyzer installation used for natural gas measurements is shown in Fig. below [Elster EnCal 3000 BTU analyzer]:
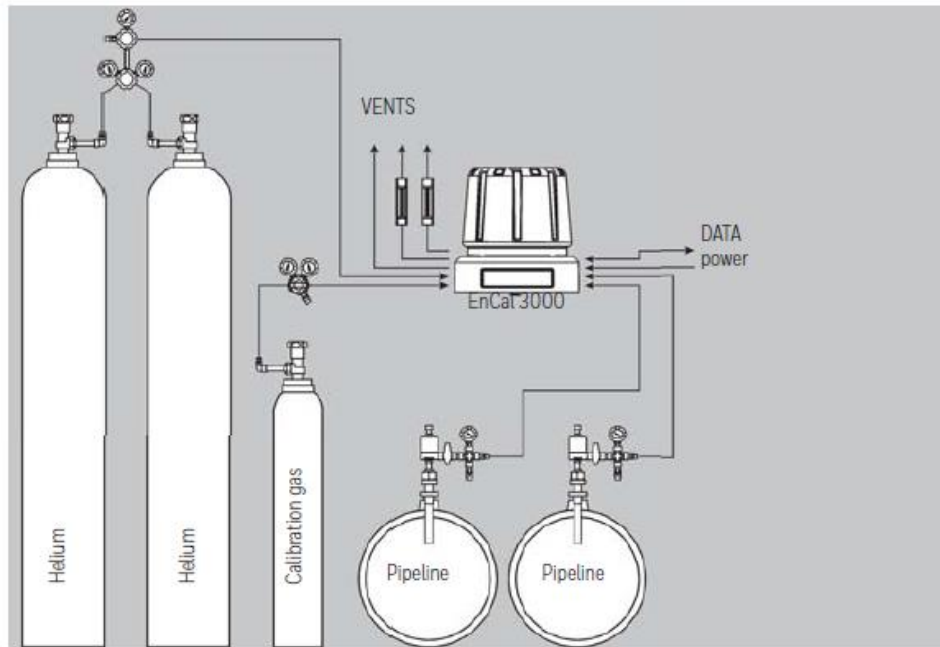
Most of analyzers require a reference and/or calibration gas. These gases have to be O2 -free and the calibration gas has to comply to gas mixture over-time stability requirements. This is highly related to materials compatibility discussed in the previous section.

The analyzer itself has to be at least ATEX approved (for permanent installations). The sampling line between the gas intake point and the analyzer should be leak free for given pressures and temperatures,

Major components of an on-line gas sampling line are essentially the same as for the composite gas sampling [30].

The main components of a gas sampling line are:

Regulators
On-line analysis normally use regulators to reduce the pressure to the analyzer. They will reduce the gas volume to the sampler, thus minimizing the time delay between the sample point, via the regulator, to the analyzer.

Valves
If shut-off/isolation valves present a restriction that causes a pressure drop, it is possible that condensation could occur. When used with a gas collection cylinder it is important that there are no leaks from the gland.

Filters
For on-line analyzers, it is sensible to install a filter, unless the gas is very clean. Proper selection of the filter flow capacity and the particle size capacity should be encouraged.

Relief valves
Regulators should have a relief valve installed down-stream, if the equipment downstream is not able to withstand full upstream pressure.

Pipework

Should be as short and as small a diameter as possible. This will assist in minimizing the time delay from sample point to the analyzer or cylinder. It will also help maintain the sample integrity. For on-line analyzers, sample delivery lines should slope upward from the probe to the analyzer to prevent condensation and impurities entering the analyzer. Lead lines to continuous samplers should slope back towards the pipeline. Inner coatings can be beneficial.

Heating Elements
There is sufficient evidence to show that heating all components of a sampling system is a prudent step in having a reliable and accurate sampling system. The hydrocarbon dew point of a natural gas stream is a critical issue in obtaining a representative gas sample.

Probes
The correct placement is at the top of the pipe, into the center one third or at least 200 mm for larger diameter pipes; in an area of minimum turbulence, that is, away from headers, bends, valves, etc. Turbulence will stir up the contaminates that usually reside at the bottom of the pipeline and are therefore not normally part of the gas stream. By having the probe at a point of turbulence these contaminates will be taken into the analyzer, giving a sample that is not representative. The key is to have the probe in the center of the line in the correct spot (positive velocity/no turbulence) with a proper valve on the outlet. Field applications have shown that mounting the probe on the top of the pipeline is the preferred location. Side or horizontal mounts can easily encourage free liquids (if present) to migrate into the sample system.

Sample Pump
A pump is needed to extract the gas from the line and to transfer that to the analyzer (if there is not enough pressure there (or there is a high flow resistivity) to draw the gas through the analyzer).

Conclusion

This report discusses requirements for sample preparation and sampling for both static and dynamic methods. The report includes a discussion on how to maintain the integrity of the sample from the moment the sampling is performed until the sample is analysing. The conditions at the facilities need to match the need for the diverse range of analytical instruments and sampling vessels used to assess the purity of biomethane. The report underlines the need to define some parameters beforehand, for example, volume of gas required for each analysis, if pressurized gas is needed; connections at the sampling point and on the sampling vessels and gives examples for a series of analytical methods.

Another key aspect of the sampling of biomethane is the risk of losing impurities through adsorption on the vessel´s wall. The risk for reactions depends upon many factors including the vessels material and/or the concentration, the presence of other impurities etc... Therefore, the selection of appropriate materials for the sampling vessel and sampling line is crucial. However, due to the lack of knowledge gathered while performing so called storage stability studies, material compatibility tables tentatively proposed in this report are not yet extensively filled to help in this choice. Moreover, studies available have concentrated on one family of compounds in one vessel. It currently lacks studies for several families present at the same time in the biomethane.

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