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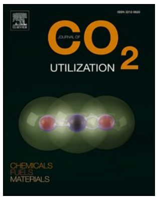

Quality of biogenic carbon dioxide stream from biogas plants including analytical method development

Karine Arrhenius [a,*], Sandra Hultmark [a], Iris de Krom [b], Luuk Meijer [b], Emma Henderson [b], Janneke van Wijk [b]

[a] *Research Institutes of Sweden AB (RISE), Frans Perssons väg, Göteborg 412 76, Sweden*
[b] *VSL, Thijsseweg 11, Delft 2629 JA, the Netherlands*

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ABSTRACT

The capture, use and storage of biogenic CO_2 from the biogas sector contributes to environmental benefits by reducing the overall greenhouse gas emissions. In several plants, CO_2 separated in the biogas upgrading process is captured and processed. Depending on the composition, some level of purification is needed before the biogenic CO_2 can be used, for example, in the food industry. In this article, we first present novel or adapted analytical methods which are both cost-effective and reliable to assess the purity of CO_2 streams. These methods concern not only species that are currently regulated in different standards but also allows for an extensive overview of the overall gas composition. The methods are then applied to samples of CO_2 stream collected from different biogas plants located in Sweden. Results from this campaign are presented together with some conclusions regarding the need to further purify the stream so the CO_2 even fulfill the most stringent requirements such as those set by the food industry. The need for purification concerns only a few species: water, methane, oxygen, nitrogen (for all samples), and hydrogen sulfide (in two cases). VOCs found specifically when the plants digest food wastes may also require a purification step, however, only some of these compounds are currently regulated.

1. Introduction

Carbon capture, utilization and storage (CCUS) are technologies that can play a role in achieving global energy and climate goals. Carbon capture with permanent storage (CCS) or utilization of the carbon dioxide (CCU) are effective tools to reduce carbon dioxide (CO_2) emissions [1] and contribute to reaching the climate goals set by the European Commission. New technologies for capturing CO_2 are being developed, some methods are already being applied to capture CO_2 from different sources. Many industries that contribute to CO_2 emissions can use these technologies, including cement plants, iron and steel plants, high-purity industrial sources such as natural gas processing, hydrogen production, biomethane production, coal/gas-to-liquids, ammonia production, pulp and paper industry, biofuel production etc.

Biogas produced from the anaerobic digestion of organic wastes is playing an increasingly significant role in the energy market [2]. Biogas is considered central to achieve carbon-neutrality by 2050 and help the EU become less dependent on external energy supplies [3]. To obtain biomethane, CO_2 and other unwanted impurities need to be removed in an upgrading process before it can be used as vehicle fuel. If the captured CO_2 is utilized or stored and originates from the digestion of biomass, it does not contribute to the increased emission of climate gases. Therefore, its capture and further utilization or storage could contribute to reducing the overall greenhouse gas emissions of the biomethane production process [4]. The capture and utilization of CO_2 from biogas production is not yet a common practice, but as studies are showing the potential benefits of its valorization, interest increases, and new projects are starting where the CO_2 from biomethane plants is valorized.

Depending on the source of CO_2 and the type of valorization chosen, a specific quality of CO_2 is often required to ensure process performance, components integrity, health and safety. Therefore, valorization options for CO_2 require composition analyses, possible treatment, and monitoring before implementation [4]. Additional CO_2 purification might be required, depending on the upgrading technology and the selected valorization option. In order to determine if the CO_2 quality meets the required specifications, reliable analytical methods are required. Novel

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* Corresponding author.
E-mail address: karine.arrhenius@ri.se (K. Arrhenius).

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or adapted analytical methods are necessary for CO_2 produced from these alternative energy sources such as biomass (biogas) to cover the large number of species to be analyzed. One of possible valorization method is using this CO_2 to produce beverages. A recent paper from the European Biogas Association (EBA) show the main utilization avenues and perspective markets opportunities for the biogenic CO_2 from the biogas industry [5]. The study underlines that policymakers should set drivers to facilitate the uptake of biogenic CO_2 and derived products. They also conclude that it already exists today purification and liquefaction processes capable of treating CO_2 from biogas sources and of generating a liquefied CO2 that is fully compliant even with the most stringent requirements.

Document 70–17 [6] from EIGA outlines specifications for the production and storage of liquid CO_2 in bulk production tanks and intermediate storage tanks at gas supplier depots. These specifications are designed for use in foods and beverages, specifically when CO_2 comes into direct contact with food or beverage as an ingredient or additive. The following compounds are required to be analyzed: acetaldehyde, benzene, carbon monoxide, carbonyl sulfide, hydrogen cyanide, methanol, nitric oxide, nitrogen dioxide, oxygen, phosphine, sulfur dioxide, hydrogen sulfide, total sulfur, total hydrocarbon content. In addition, any other impurities that can impact the quality of products should be quantified. Biogas is obtained by methanization of organic waste such as food wastes (from households or industry) or sludge from wastewater treatment plants, energy crops, plant or/and animal by-products and mostly mixtures of these. Biogas composition is therefore variable, complex and highly dependent on the feedstock used. Studies have shown that biogas can contain a large number of volatile organic compounds belonging to many different families such as terpenes, ketones, alcohols, siloxanes, hydrocarbons, esters, amines, sulfur compounds etc. Depending on the upgrading method, some of these compounds can follow into the CO_2 stream. To determine the composition, the choice of analytical instruments involves both technical factors (required limit of detection required, accuracy, possibility to analyze several impurities with one method, availability, etc.) and financial considerations. Methods developed for biogas and biomethane can be advantageously used for analyzing the CO_2 stream, but they need to be adapted to account for any possible matrix effect. Performing the whole set of analyses required in document 70–17 is time-consuming for any laboratory and will require a combination of several analytical techniques or instruments. Appendix D of the document enumerates general analytical techniques that can be used to demonstrate compliance with the specifications. The most common techniques mentioned in the document are based on gas chromatography, which is well suited for small organic species such as benzene, ethanol, acetaldehyde and amines. Infra-red spectroscopy is well suitable for compounds such as ammonia [7], hydrogen sulfide and carbon monoxide [8]. Additionally, mass spectrometry and colorimetric tubes are very simple to use but the presence of coexistent gases, which can interfere with the measurement, must be taken into account.

To this end, cost-effective (as the method allows the analysis of up to 10 compounds simultaneously within 10 min, this allows reduction of operational costs inclusive calibrants consumption and personal time) and reliable analytical methods are being developed as part of the projects 20IND10 Metrology for decarbonizing the gas grid (Decarb) [9] and 21GRD06 Metrology support for carbon capture utilization and Storage (MetCCUS) [10]. The method has been validated for the determination of carbon monoxide, hydrogen sulphide [11], and for methanol, ethanol, acetaldehyde, acetone and benzene [12]. For instance, an instrument composed of a gas chromatograph (GC) having three columns (two packed columns and a plot-column) and two detectors (FID and TCD) coupled in parallel to two Optical Feedback Enhanced Absorption Spectroscopy (OFCEAS) instruments has been developed and evaluated for the simultaneous determination of oxygen, carbon monoxide, carbon dioxide, water, hydrogen sulfide (all these species are analyzed with OFCEAS), nitrogen, methane, hydrogen and other hydrocarbons such as ethane, propane, butane, isobutane, methanol, ethanol and acetone, acetaldehyde, benzene (all these species are analyzed with gas chromatography). With this instrument, the sample can be introduced either from a cylinder or from a gas bag. Due to the low pressure of CO_2 streams produced in biomethane upgrading plants, bags can be a more suitable alternative as they can be filled directly using the slight over-pressure of the stream. However, the choice of the material for the bag is crucial and can only be made once the storage stability of the impurities has been established as satisfactory (for example, a criterion for satisfying stability can be “less than 10 % loss after 10 days of storage compared to the initial concentration”). Stability studies using four different bags were conducted as part of the MetCCUS project and some results are given in this article.

As the determination of total species is also required (including total hydrocarbons, total sulfur) and many of these species included being organic, thermal desorption often coupled with gas chromatography is a good candidate for analyzing many compounds simultaneously. It is also a good complement to the OFCEAS/GC instrument. Total compounds family usually covers many species having different physical properties, making identification of all species almost impossible in routine analysis [13]. The analytical method has the advantage that it indirectly lowers the detection limits. Through pumped sampling, according to ISO 16017:2000 [14], organic impurities are trapped onto the sorbent whereas the CO_2 matrix passes through without being retained. The analyte’s boiling point is the key factor when deciding which sorbent type to use. The amount preconcentrated onto the sorbent can be calculated by measuring the gas flow rate and sampling time during sampling on the sorbent tube. To choose the most appropriate sorbent material, systematic recovery experiments and short-term stability tests at defined and relevant conditions (matrix and amount fraction) are necessary. To test the method for CO_2 matrix, a selection of compounds was made based on the specifications from the EIGA document 70–17 [6] and previous knowledge about biogas composition. Methanol and benzene were selected as they both have limits stated in the document (10 μmol mol^{-1} for methanol and 20 nmol mol^{-1} for benzene). Two sulfur compounds, 1-propanethiol and dimethylsulfide, were chosen as they have been commonly found in biogas samples. Two hydrocarbons, hexane and decane were added to cover a wider range of boiling points.

In this paper, the results from short-term stability studies on different sorbents are presented for these compounds. After discussion with sorbent providers and considering previous experiences, the following sorbents were chosen for the selected compounds: Chromosorb 106, Air Toxic, Tenax TA, Tenax TA/CarboGraph 5, Odour/Sulfur. Storage periods of two weeks were evaluated, as this is typically the time required to complete the collection, transport, and analysis of samples.

The methods described in this article were then applied to samples of CO_2 stream collected from different biogas plants located in Sweden. Results from this campaign are presented together with some conclusions regarding what a cleaning process of the stream should be able to handle in order to fulfill the requirements specified in EIGA document 70–17.

2. Methods and chemicals

The stability studies on sorbent tubes were carried out both at RISE and at VSL using thermal desorption gas chromatography coupled with mass spectrometry with or without flame ionization detection (TD-GC/MS-FID or TD-GC/MS). Different set-ups and instruments were used for the tests depending on the equipment at the test facilities).

The stability studies in bags were carried out at RISE using an OFCEAS-GC/FID-TCD.

2.1. TD-GC/MS-FID (RISE)

Sorbent tubes were desorbed using a Markes TD100 thermal desorber with a two stages desorption; a primary tube desorption

Table 1
Gas mixture used for the short-term stability tests on sorbents at RISE.

Components	Mole fraction (nmol/mol)	Expanded uncertainty (k = 2) (nmol/mol)
Methanol	1392	84
Benzene	571	34
1-propanethiol	585	35
Hexane	517	31
Decane	314	19
Dimethylsulfide	718	43

followed by a secondary trap desorption. Depending on the sorbents, different temperatures were used for the primary tube desorption (no inlet split): 275°C for 7 min for the Tenax tubes, 330°C for 7 min for the multi-sorbent tube (Air Toxic) and 220°C for 7 min for the Chromosorb 106 tubes. In the second stage, a cold trap (Air Toxics from Markes) (-10°C) was heated quickly (1.3 °C/s) to 300°C so the compounds were released and reached the gas chromatographic column where they were separated. The instrument used for the analyses was an Agilent technologies 6890 N coupled with a flame ionization detector and a 5975 C inert MSD mass spectrometer (electron impact, EI, mode). The GC column was a DB-MS5 non-polar capillary column (5 % phenyl polysilphenylene-siloxane, 60 m long, 0.32 mm internal diameter, 1 µm film thickness). The initial GC oven temperature was 35°C (hold 4 min). The oven temperature was then raised with three ramp rates: to 100°C at 3 °C/min, to 220°C at 8 °C/min and finally to 300°C at 15 °C/min. The temperature was then held at 300°C for 10 minutes. For detection, one part of the effluent was sent to a flame ionization detector and the other part to the mass spectrometer. Compounds can be quantified using both detectors; the FID or the MS. When quantifying with the MS, two modes can be used; the total ion chromatogram mode which represents the summed intensity across the entire range of masses being detected (*m/z* 29 to *m/z* 390) or an extracted-ion chromatogram mode where one *m/z* value characteristic for one compound are recovered from the entire data set. In this study, data were collected by extracting one ion per compound (*m/z* 78 for benzene, *m/z* 86 for hexane, *m/z* 142 for decane, *m/z* 76 for 1-propanethiol, *m/z* 62 for dimethylsulfide and *m/z* 31 for methanol).

The instrument was calibrated by spiking Tenax TA tubes using a solution containing all the compounds (2500 ng of each compound of the tubes).

2.2. TD-GC/MS (VSL)

Sorbent tubes were desorbed using a ATD 650, Perkin Elmer thermal desorber with a two stages desorption; a primary tube desorption followed by a secondary trap desorption. The temperature used for the primary tube desorption (no inlet split) was 250°C and the desorption time was 5 min. In the second stage, a cold trap (Air toxics, Perkin Elmer) (-30°C) was heated quickly (1.3 °C/s) to 275°C so the compounds were released and reached the gas chromatographic column where they were separated. The instrument used for the analyses was an Agilent technologies 7820 A coupled with a 5977E inert MSD. The GC column was a DB-1 capillary Agilent column, 60 m long, 0.32 mm internal diameter, 1 µm film thickness). The initial GC oven temperature was 30°C (hold 6 min). The oven temperature was then raised with one ramp rate to 225°C at 30 °C/min. The temperature was then held at 225°C for 12.5 minutes. The total ion chromatogram mode which represents the summed intensity across the entire range of masses being detected (*m/z* 40 to *m/z* 450) was used.

2.3. OFCEAS-GC/FID-TCD (RISE)

The setup for this instrument is similar to the setup described in [15]. The three instruments (two OFCEAS instruments and a GC system) were connected. The instrument combined a GC8860 Agilent 450-GC-TCD/FID (gas chromatograph/thermal conductivity detector/-flame ionisation detector) equipped with three columns with two OFCEAS instruments. The three columns in the GC are:

- A Hayesep Q, 80–100 Mesh, 1.8 m × 1/8 ″ × 2.0 mm connected to the TCD.
- A molecular Sieve 5 A, 60–80 Mesh, 1 m × 1/8 ″ × 2.0 mm connected to the TCD.
- A PoraBOND Q, 25 m × 0.53 mm × 10 µm connected to the FID.

The instrument which has three 6-port valves includes a sampling loop of 100 µl is connected between the ports 2 and 3 of respective valves. The sampling loops are filled during 10 s after which the 6-port valves are switched. The content of the first loop is introduced into the first packed column (Hayesep), while the content of the second loop is introduced into the PLOT column. The third 6-port valve allows us to change the direction of the carrier gas in the second packed column to allow detection of methane, carbon dioxide, oxygen, nitrogen, carbon monoxide and hydrogen with the TCD.

Two custom-built optical feedback cavity enhanced absorption spectrometers (OFCEAS—ProCeas from AP2E) were developed for the measurement of oxygen (instrument 1) and methane, carbon monoxide, carbon dioxide, water, and hydrogen sulfide (instrument 2). Gas samples are introduced into the measurement cells at a flow rate of 100 ml min−1 through a sulfinert-treated stainless steel restrictor using an internal pump. These instruments were pre-calibrated, and the calibration has been verified by comparison with validated gas chromatographic methods [16].

3. Chemicals & materials

3.1. Stability studies of sorbent tubes RISE

1 µl of a reference mixture from Neochema GmbH, Bodenheim, Germany, containing the selected compounds each at 5000 µg/ml in n-octane was introduced in a 3L-gas bag (Altef, Restek, Centre County, PA, U.S) containing 2,7 liter of pure CO_2 to obtain a gas mixture containing all the targeted compounds at mole fractions between 300 and 1400 nmol/mol. The composition of the end gas mixture is given in Table 1.

A volume of 100 ml of this gas mixture was transferred onto 30 sorbent tubes (10 Chromosorb 106, 10 Air Toxic and 10 Tenax TA) on the starting day (D0). All the tubes were then stored in the freezer (-23°C) prior to analysis.

3.2. Stability study of sorbent tubes VSL

For the study a static gas mixture has been prepared in a high-pressure aluminum SPECTRA-SEAL® cylinder containing all the impurities in Table 1 in CO_2 as matrix gas (Fig. 1).

The final gas mixture was prepared in several steps according to ISO 6142–1:2015 [17] [17]. First, a liquid solution was prepared gravimetrically containing benzene, C6 and C10. The obtained liquid solution was injected with a syringe into an evacuated cylinder, then vaporized and diluted with CO_2 to obtain a gas mixture with a nominal fraction of 20 µmol mol^{-1} for the three impurities. An existing mixture of methanol in nitrogen (N_2) was diluted to 60 µmol mol^{-1} methanol in CO_2. Pure 1-propanethiol and dimethylsulfide were injected with a syringe into evacuated cylinders to obtain two binary mixtures with 20 µmol mol^{-1} of the impurities in CO_2. These four gas mixtures were combined to obtain one gas mixture with a nominal fraction of 1500 nmol mol^{-1} for methanol and 500 nmol mol^{-1} for the other impurities in CO_2. This mixture was further diluted with CO_2 to obtain the final mixtures with a nominal fraction of 60 nmol mol^{-1} for methanol and 20 nmol mol^{-1} for the other impurities. A higher fraction of methanol was prepared because methanol is known to adsorb to the cylinder walls. The composition of the final gas mixture used for sampling into sorbent tubes is given in Table 2.

For the preparation of a batch with homogeneously sampled sorbent

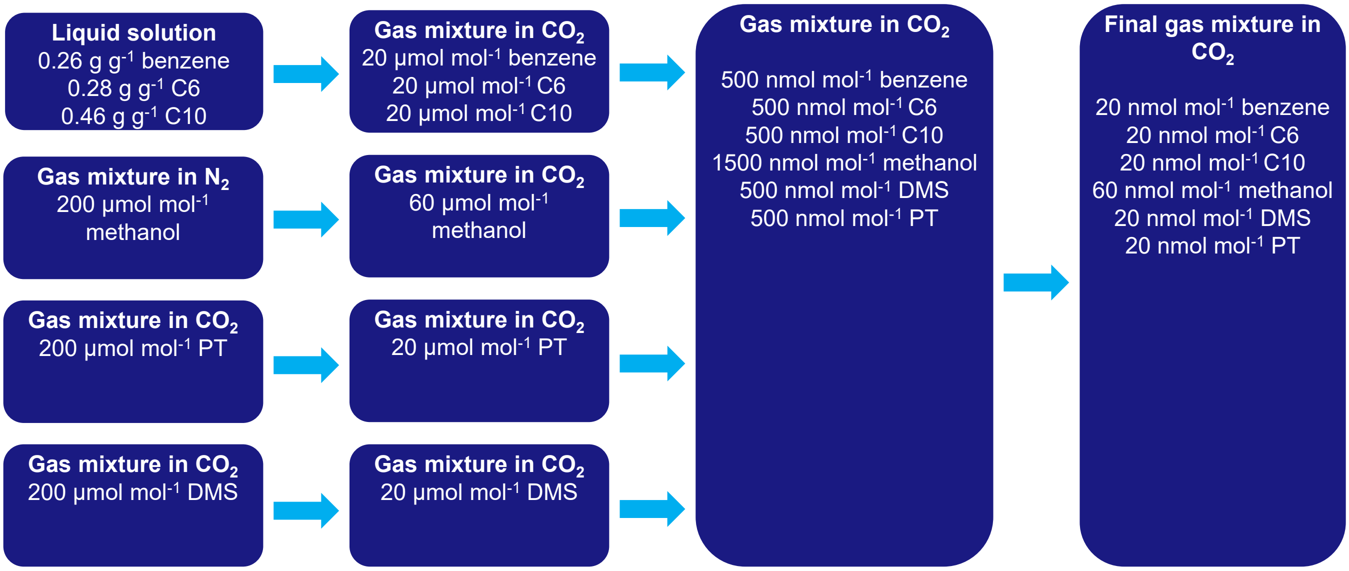

Fig. 1. Gas mixture preparation in high pressure cylinders with nominal amount fractions of the impurities in CO_2.

Table 2
Composition final gas mixture (VSL353926).

Impurity	Mole fraction (nmol mol^{-1})	Uncertainty (nmol mol^{-1}) ($k = 2$)
Hexane	18.159	0.014
Decane	18.002	0.012
Benzene	18.332	0.014
Methanol	62.409	0.016
Dimethylsulfide	20.028	0.006
1-Propanethiol	21.304	0.014

Table 3
Mass of each impurity per sorbent tube.

Impurity	Mass (ng)	Uncertainty (ng) ($k = 2$)
Hexane	65.3	0.7
Decane	106.8	1.2
Benzene	59.7	0.7
Methanol	83.4	1.0
Dimethylsulfide	51.9	0.6
1-Propanethiol	67.7	0.8

tubes, a specially designed sampling manifold was used. The manifold is equipped with mass-flow controllers (MFCs) and 2-way valves to allow for simultaneous sampling onto 12 sorbent tubes. For this study tubes were sampled with a volume flow rate of 50.16 ml min^{-1} for 20 minutes. The mass per impurity sampled into each sorbent tube is shown in Table 3.

Ten tubes with three different sorbent materials (in total 30 tubes) were sampled with the impurities in CO_2. After consultation with sorbent tubes providers and literature research, the following sorbents were selected for the feasibility study; 1) A double bed sorbent of Tenax TA/CarboGraph 5 (TTA/CG5), 2) Odour/Sulfur is a sorbent material developed to adsorb sulfur impurities and 3) TTA. All sorbent tubes used have been purchased at Markes International Ltd and have been treated with a SilcoNert® inert coating.

3.3. Stability studies in bags (RISE)

Gas mixtures in sampling bags were prepared by injecting a known amount of reference mixtures from Neochema GmbH, Bodenheim, Germany, containing the selected compounds, each at a concentration of 5000 µg/ml in n-octane, into 2–3 liter of pure CO_2. This was done to achieve the target concentrations of compounds (methanol, ethanol, acetone, acetaldehyde, benzene) ranging from 0.02 to 30 µmol mol^{-1}.

Four types of bags were tested: 3 L Altef gas bag (Restek, Centre County, PA, U.S), 3 L Multifoil gas bag (Restek, Centre County, PA, U.S), 3 L True Blue™ MLB gas bags (Airborne Labs International, New Jersey, USA), and 3 L Cali-5-Bond multi-layer foil gas bags (Calibrated Instruments, Illinois, USA). The bags were then stored at ambient temperature for the duration of the tests.

4. Results and discussion

4.1. Storage stability on sorbent RISE

Storage stability study on sorbent tube was performed by analysing the 30 tubes prepared as described in the section "Chemicals & materials - Stability studies of sorbent tubes RISE" on 5 different occasions, the day the tubes were prepared (D0), and then 1, 4, 8 and respectively 15 days after D0. Each time, duplicates were analysed.

The recovery yield (using the results at D0) was determined by

Table 4
Recovery yield obtained on Chromosorb 106, Air Toxic and Tenax TA (with MS).

	Chromosorb 106		Air Toxic		Tenax TA	
	Recovery (%)	Rel. standard deviation	Recovery (%)	Rel. standard deviation	Recovery (%)	Rel. standard deviation
Benzene	106.5	3.9	106.7	5.6	118.8	3.8
Hexane	109.8	3.6	112.9	4.1	113.8	6.3
Decane	103.2	5.0	100.4	7.4	100.0	5.2
1-Propanethiol	92.3	14.1	16.1	10.9	64.0	19.4
Dimethylsulfide	89.4	14.1	90.5	9.0	112.8	6.0
Methanol	87.5	23.8	49.3	73.1	34.6	48.0

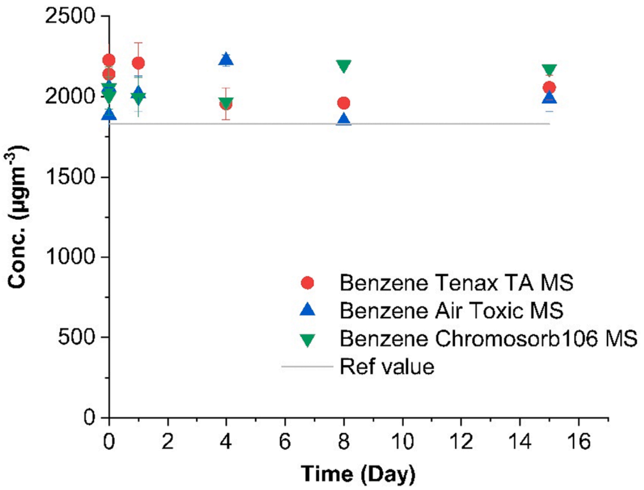

Fig. 2. Storage stability for benzene on the three sorbents.

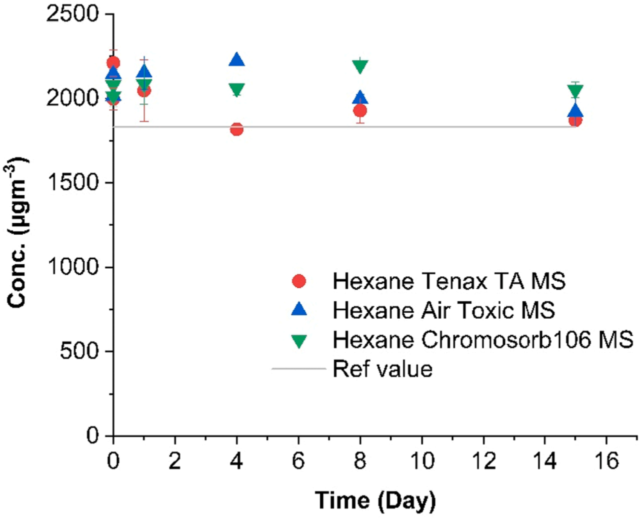

Fig. 3. Storage stability for hexane on the three sorbents.

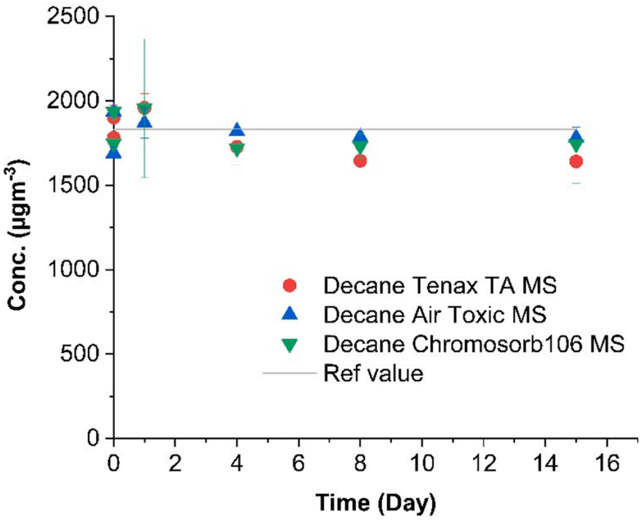

Fig. 4. Storage stability for decane on the three sorbents.

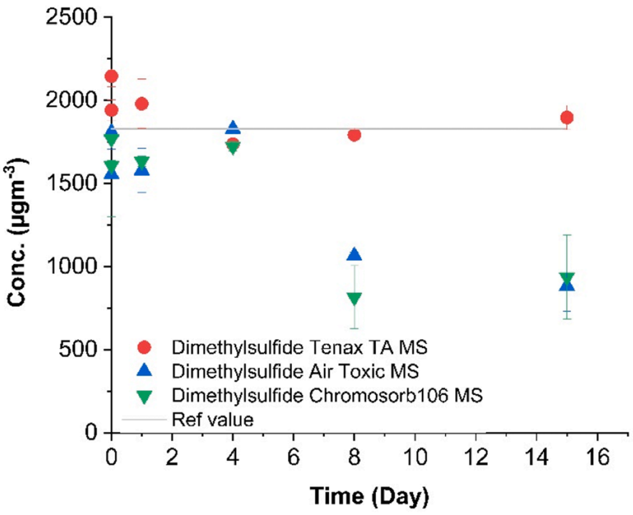

Fig. 5. Storage stability for dimethylsulfide on the three sorbents.

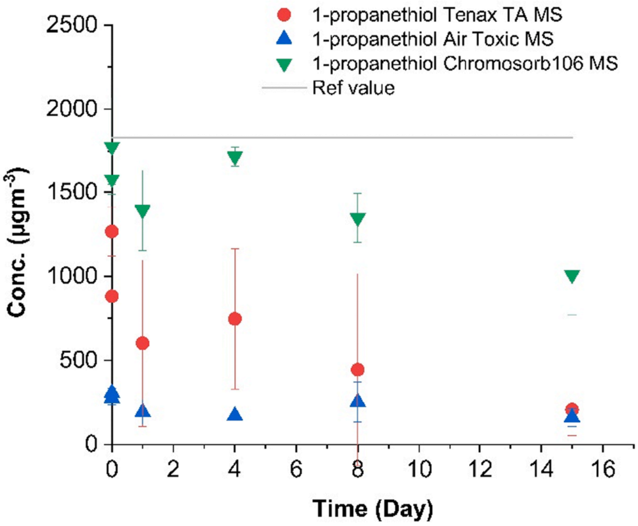

Fig. 6. Storage stability for 1-propanethiol on the three sorbents.

experimentally measuring and calculating the quantities of various substances using TD-GC/MS and dividing them by the known quantities of substances. Recovery yield was calculated for three different sorbents: Chromosorb 106, Air Toxic and Tenax TA. The results from the recovery yield studies using the MS are presented in Table 4.

The relative standard deviations obtained from five replicates were found to be lower than 7.5 % for the hydrocarbons on the three sorbents. High relative standard deviations (6–20 %) were obtained for the two sulfur compounds. As expected, even higher relative standard deviation (73 %) was obtained for methanol.

Recovery yields above 90 % were observed for the hydrocarbons and for dimethylsulfide on the three sorbents. Recovery yields above 115 % were observed in some cases, however that seemed to be due to calibration issues with the mass spectrometer as the same recovery yields were close to 100 % with the flame ionization detector.

Low recovery yields with high relative standard deviations were observed for methanol and 1-propanethiol except on Chromosorb 106. Dipropyl disulfide in significant amount was found on Air Toxic and on Tenax TA (only small amount of this compound was found on Chromosorb 106) showing a reaction of 1-propanethiol on these sorbents (dimerization).

Next, the stability of the substances on the different sorbents was

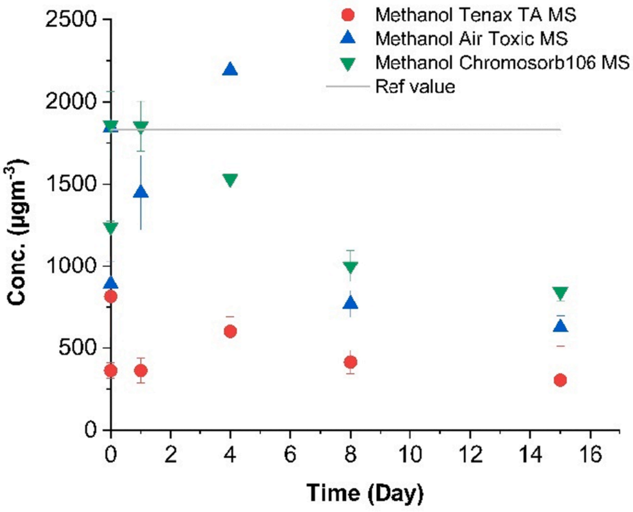

Fig. 7. Storage stability for methanol on the three sorbents.

Table 5
Results stability study: √ the impurity is stable and can be stored for a period of 14 days in the sorbent material within the relative expanded uncertainty of 5 % and 10 % for methanol and dimethylsulfide, x the impurity shows instability and can't be stored for a period of 14 days in the sorbent material.

Impurity	TTA/CG5	Odour/Sulfur	TTA
Hexane	√	x	√
Decane	√	√	√
Benzene	√	√	√
Methanol	√	x	√ (Breakthrough)
Dimethylsulfide	x	x	√ (Breakthrough)
dipropyl disulfide	√	√	√

Table 6
CO_2 streams sampled at biomethane plants.

Sample ID	Substrates	Upgrading techniques	Subsequent purification steps	Other comments
#1	Food wastes and Sludge from WWTP	Amine scrubber	no	
#2	Sludge from WWTP	Amine scrubber	no	Carbon filter before the upgrading
#3	Wastes from fish industry	Amine scrubber	no	
#4	Sludge from WWTP	Pressure swing adsorption	Catalytic oxidation	
#5	Sludge from WWTP	Water scrubber	Voxidiser	
#6	Sludge from WWTP	Water scrubber	no	Taken after a vacuum pump
#7	Food wastes + manure	Amine scrubber	no	

(WWTP: wastewater treatment plant)

investigated by measuring the concentration of the substance for 15 days. The results for the stability studies are presented in Figs. 2 to 7.

As it can be seen in Figs. 2 to 4, the hydrocarbons evaluated in this study were determined to be very stable (with D15 concentrations less than 10 % below the initial concentrations) on all three sorbents.

Decane results were very close to the expected value while benzene and hexane concentrations were overestimated by 10–20 %. The results using the FID detector were in much better agreement with the expected concentrations, showing that there may be some issues with the calibration of the instrument. Dimethylsulfide (Fig. 4) was found to be very stable (D15 concentrations less than 10 % below the initial concentrations) on Tenax TA but showed a decrease with time when stored on Chromosorb 106 and Air Toxic leading to a D15 concentration 50 % lower than the initial concentration. However, the decrease did not seem to occur during the first four days of storage.

As it can be seen in Figs. 6, 1-propanethiol showed a decrease with time when stored on Chromosorb 106 leading to a D15 concentration of 45 % lower than the initial concentration. However, the decrease did not seem to occur during the first four days of storage. Moreover, the results show relatively high deviations when analyzing three samples for each measurement. The same trend is observed on Tenax TA but with this sorbent, even recovery yield at D0 is relatively low (see Table 5, 64 %). This is due to a reaction of 1-propanethiol producing dipropyl disulfide on this sorbent as well as on Air Toxic. The sum of the concentration of 1-propanethiol and dipropyl disulfide on Tenax TA is close to the expected value. Dipropyl disulfide formation seems to be similar for each tube and at each measurement date on Chromosorb 106 and Air Toxic while it seems to vary from tube to tube on Tenax TA (as showed by the very large variations at each measurement date).

As already observed at D0 (recovery yields), methanol cannot be quantified on Tenax TA (loss of up to 85 % of the concentration is observed for example at D15). Methanol concentration showed a decrease with time when stored on Chromosorb 106 leading to a D15 concentration of 55 % lower than the initial concentration. However, the decrease is more pronounced at D8 and D15 than at D1 and D4. The same trend is observed on Air Toxic.

As expected, hydrocarbons (hexane and decane) could be quantitatively analyzed with all sorbents tested in this study and the analysis can be performed up to 14 days after the sampling without risk for losses. Even if the tests were performed at higher concentration, a detection limit of 20 nmol/mol for benzene (30 times lower than in this study) does not present a challenge.

Good results for dimethylsulfide were obtained when using Tenax TA. Chromosorb 106 and Air Toxic can also be used for this compound if the analysis is done within 4–5 days.

1-propanethiol dimerizes into dipropyl disulfide (mostly on Tenax TA and Air Toxic). The best option for this compound would be Chromosorb 106 if analysis is done in 4–5 days.

Methanol was the most challenging compound and none of the sorbents used in this study yielded quantitative results. However, using Chromosorb 106 and even Air Toxic when analysis is done in 4–5 days could give an indication of the presence of methanol. If so, another method needs to be used to quantify this compound.

Overall, the most versatile sorbent in this study was found to be Chromosorb 106 if the analysis is done within 5 days after sample collection and with storage in the freezer prior to analysis.

4.2. Storage stability for sorbent (VSL)

Storage stability study on sorbent tube was performed by analysing the 30 tubes prepared as described in the section "Chemicals & materials - Stability studies of sorbent tubes VSL" on 5 different occasions, the day the tubes were prepared (D0), and then 2, 6, 10 and respectively 14 days after D0. Each time, duplicates were analysed.

The breakthrough of the impurities during sampling was determined. During the sampling two tubes were placed in series. The first tube containing all impurities and the second tube left empty. All three sorbent materials were checked for breakthrough. The TTA/CG5 and Odour/Sulfur tubes showed no breakthrough for any of the impurities. However, when using the TTA sorbent tubes breakthrough was observed for methanol and DMS at 10 % and 30 % respectively. Shorter sampling times could help reduce breakthrough.

The desorption efficiency of the impurities from the sorbent tubes during analysis with TD-GC-MS was determined. After the initial

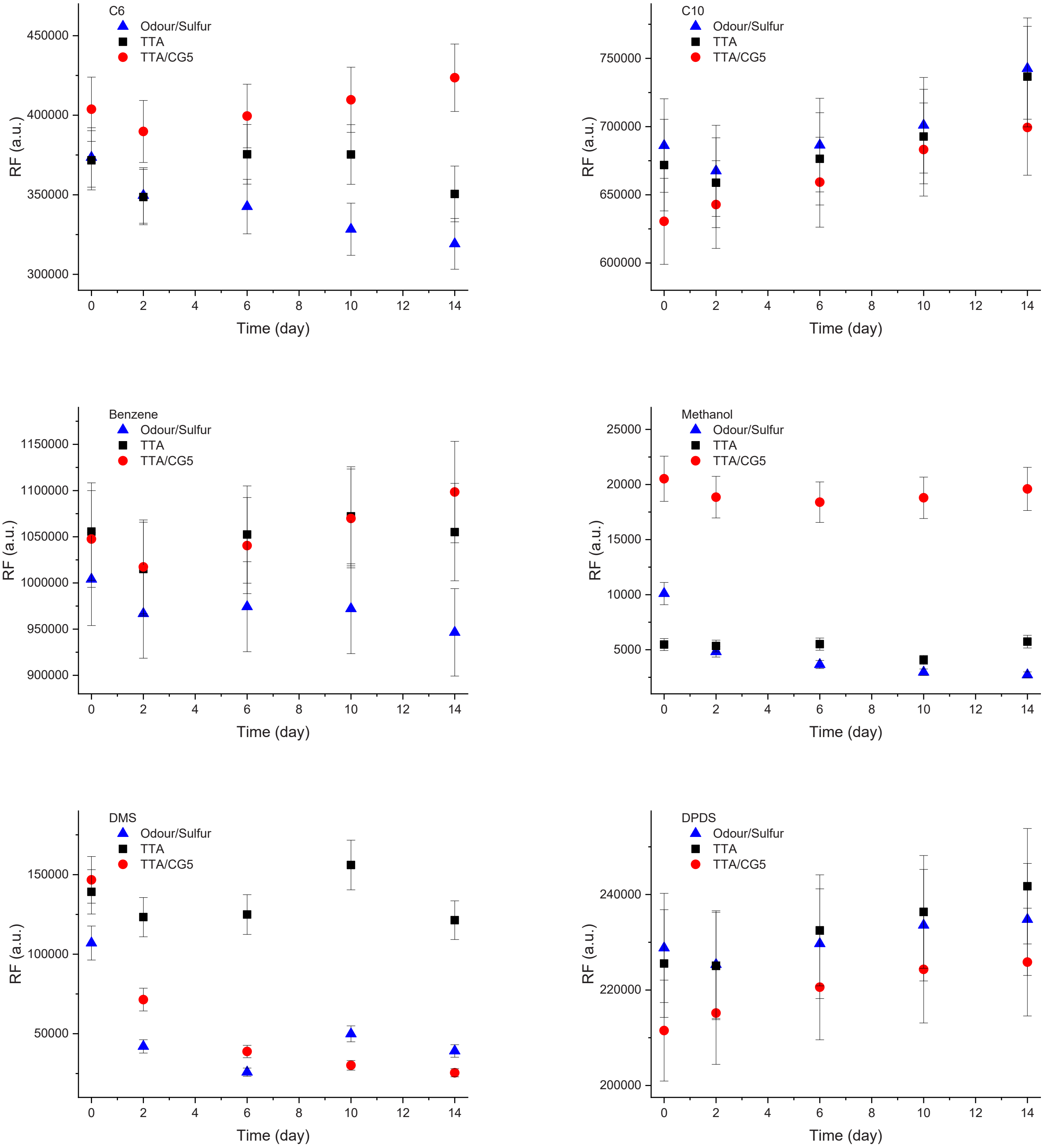

Fig. 8. Results stability study, C6 = hexane, C10 = decane, DMS = dimethylsulfide and DPDS = dipropyl disulfide.

analysis of the sorbent tubes, they were analyzed a second time with the tubes left empty. All three sorbent materials were checked for desorption efficiency and the results showed 100 % desorption efficiency of all the impurities during the first analysis.

After sampling of the sorbent tubes, 2 tubes of each sorbent material, and 1 or 2 blanks, were analyzed on five different days during a period of 14 days to determine the stability. During these 14 days the sorbent tubes were stored in the laboratory at 20 °C. The peak area of the 2 tubes was averaged and response factor (RF) was determined. Based on the RF the stability of the impurities was determined. The RFs per measurement day for each impurity per sorbent material are plotted against the measurement day (Figure B). Like RISE, VSL observed the dimer dipropyl disulfide instead of 1-propanethiol after analysis of the sorbents. Analysis of the gas mixtures from the cylinder using TD-GC-MS also showed dipropyl disulfide instead of 1-propanethiol. Also, during analysis of the gas mixture without preconcentration, using GC with a sulfur chemiluminescence detector (SCD), no 1-propanethiol could be detected, both dimethylsulfide and dipropyl disulfide were detected. SCD is known for its equimolar response for a sulfur atom, the peak area of dipropyl disulfide (577 µV s-1) compared to dimethylsulfide (1578 µV

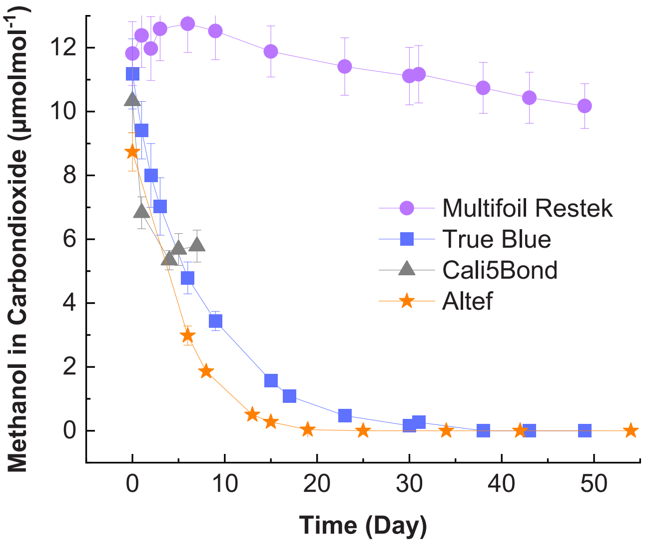

Fig. 9. Storage stability of methanol in CO_2 (amount fractions: 9 µmol mol^{-1}) in different bags.

s-1) indicate that not all 1-propanethiol was converted to dipropyl disulfide. This could indicate that part of the 1-propanethiol decomposed or reacted with the cylinder wall during or after preparation of the gas mixture.

Storage of the impurities in the sorbent materials is stable if the RFs do not deviate more than the relative expanded uncertainty of 5 %, and 10 % for methanol and dimethylsulfide over the measurement period of 14 days (Table 6). On the TTA/CG5 sorbent material as it can be seen on Fig. 8, all impurities are stable over a period of 14 days. The RF of dimethylsulfide decreased gradually with 80 %. For the Odour/Sulfur sorbent material methanol and dimethylsulfide show instability with respectively 70 % and 60 %. The other impurities are stable on this sorbent material over a period of 14 days. All the impurities are stable on the TTA sorbent material over a period of 14 days. However, breakthrough of methanol and dimethylsulfide was observed when using this sorbent material.

The results from the stability study summarized in Table 5, show that reactive impurities such as 1-propanethiol cannot be stored in a high-pressure cylinder as part of the 1-propanethiol dimerized to dipropyl disulfide the rest decomposed or reacted with the cylinder wall during or after preparation of the gas mixtures. For very volatile impurities such as methanol and dimethylsulfide stronger sorbents are needed to prevent breakthrough of the impurities during sampling. The different sorbent materials show different behavior for the different impurities. TTA/CG5 is suitable for all impurities save from dimethylsulfide, the Odour/Sulfur sorbent material is not suitable for hexane, methanol and dimethylsulfide. The impurities are all stable on the TTA sorbent material over a period of 14 days nevertheless, breakthrough of methanol and dimethylsulfide was observed during sampling.

4.3. Stability studies for bags (RISE)

Storage stability study in bags was performed by analysing the gas prepared in four different bags (Altef, Cali5Bond, True Blue and Restek Multifoil bags) as described in the section "Chemicals & materials - Stability studies in bags RISE" in four on 10–15 different occasions, the day the tubes were prepared (D0), and then regularly (every working day) during a period of 50 days. Each time, duplicates were analysed. The effect of the change of volume in the bag is considered to be negligible as only 60 ml of gas is needed for each analysis (2 % of the volume of the bag).

Among the species studied, alcohols were the most challenging compounds. Amount fractions of acetone ranging from 3 to 25 µmol mol^{-1} were found to be stable in Cali5Bond bags, Multifoil bags and True Blue bags even if the concentrations slightly decreased during the test period (the decrease was less than 10–15 % of the initial concentration after 50 days of storage). Amount fractions of acetaldehyde from 0.5 to 5 µmol mol^{-1} were found to be stable in Multifoil and True Blue bags even if the concentrations slightly decreased during the test period (the decrease was less than 10 % of the initial concentration after 10 days of storage).

The stability of methanol amount fractions in CO_2 was tested in all four types of bags. Several different amount fractions were produced, ranging from 3 to 25 µmol mol^{-1}. The results of the stability studies are presented in Fig. 9 for Altef bags, Cali5Bond bags, True Blue bags and Restek Multifoil bags.

Low amount fractions of methanol (here around 9 µmol mol^{-1}) in CO_2 were not stable in either Altef or True-Blue bags. Methanol showed a decrease of response with time when stored inCali5Bond bags, with a pronounced drop during the first days of storage and a more stable trend during the rest of the test duration. The best results were obtained when low amount fraction of methanol in CO_2 were stored in Restek Multifoil bags even if a slight decrease of concentration was observed with time. However, the decrease is not dependent on the initial concentration and is less than 20 % after almost 50 days storage at all amount fractions tested.

5. Analysis of CO_2 streams collected in biogas upgrading plants

The methods described in the section above were then applied to the analysis of real samples of CO_2 stream collected from different plants digested diverse substrates and using different upgrading techniques. Samples of CO_2 from seven different biogas plants in Sweden were collected to investigate the gas quality in comparison with CCUS documents or standards.

Table 6 gathers the information regarding the collected samples.

Sampling was done on sorbents and bags that were found to be the best alternative from the results obtained during the stability studies (see results and discussion). All samples were taken right after the upgrading stage except for two samples (#2 and #4), which were taken after a subsequent purification step (catalytic oxidation or voxidiser, se Table 6). Due to the conditions at the sampling point (low pressure; no more than 1 bar over atmospheric pressure and temperature not exceeding 40°C), the sampling line (max 20 cm of silicon tubing) didn't contain any sample conditioning equipment (for temperature or pressure). When needed, flow rate was restricted using the ball valve at the sampling points. All analyses were performed at RISE. For each sampling point, two different 3-liter sampling bags (Restek Multfoil and Restek Altef, Centre County, PA, U.S.A.) were first filled according to the manufacturer's instructions. Then within 15 minutes, gas from the Altef bag was transferred to four Tenax TA packed sorbent tubes (two with 50 ml gas and two with 100 ml gas) using a 100 ml gas-tight syringe (order of connection: bag – tube – syringe) for the analysis of the VOCs according to the method described in the section "TD-GC/MS-FID (RISE)". The Multifoil bag was used to perform all analyses on the OFCEAS-GC/FID-TCD instrument (carbon dioxide, water, hydrogen sulfide, ammonia, acetaldehyde, carbon monoxide, hydrogen, methane, nitrogen, methanol, ethanol, hydrocarbons (C2-C5)) according to the method described in the section "OFCEAS-GC/FID-TCD (RISE). Analyses of sulfur dioxide, nitric oxide, nitrogen oxide, carbonyl sulfide and carbon disulphide were done from the Restek Multifoil gas bags using colorimetric tubes (Dräger, Lübeck, Germany or Gastec Corporation, San Diego, CA, U.S.A.). To minimize the risk of loss of impurities in the sampling vessels, analyses were performed within 48 hours of the sampling.

The results of the gas analysis of the seven CO_2 streams are presented in Table 7.

The results showed that some kind of purification is needed for all

Table 7
CO_2 streams gas composition.

Sample ID		1	2	3	4	5	6	7
Compounds	unit							
Carbon dioxide	mol mol^{-1}	97.8 ± 0.5	8.1 ± 0.1	97,2 ± 0.5	10.4 ± 0.1	99.1 ± 0.5	92.7 ± 0.5	97.9 ± 0.5
Water	μmol mol^{-1}	15600 ± 2000	11000 ± 2000	13000 ± 2000	11100 ± 2000	5000 ± 1000	9900 ± 2000	11100 ± 2000
Oxygen	μmol mol^{-1}	ca 400	18.7 ± 0.2	1000 ± 500	18.3 ± 0.2	< 0.1	0.2 ± 0.1	0.15 ± 0.05
Sulfur dioxide	μmol mol^{-1}	< 10	< 10	< 1	< 10	n.a.	< 10	n.a.
Nitric oxide	μmol mol^{-1}	< 2.5	< 2.5	< 0.2	< 2.5	n.a.	< 2.5	n.a.
Nitrogen dioxide	μmol mol^{-1}	< 2.5	< 2.5	< 0.2	< 2.5	n.a.	< 2.5	n.a.
Hydrogen sulfide	μmol mol^{-1}	50 ± 6	< 1	< 1	< 1	260 ± 30	< 1	< 1
Amine	μmol mol^{-1}	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Ammonia	μmol mol^{-1}	< 2	< 2	< 2	< 2	< 2	< 2	< 5
Acetaldehyde	μmol mol^{-1}	< 2	< 2	2.5 ± 0.5	< 2	1.8 ± 0.5	< 2	2 ± 0.5
Carbonyl sulfide	μmol mol^{-1}	< 1	< 1	< 1	< 1	< 1	< 1	n.a.
Carbon disulfide	μmol mol^{-1}	n.a.	n.a.	4 ± 1	n.a.	n.a.	n.a.	n.a.
Carbon monoxide	μmol mol^{-1}	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Hydrogen	μmol mol^{-1}	< 500	< 500	n.a.	< 500	< 500	< 500	< 500
Methane	μmol mol^{-1}	1200 ± 100	3200 ± 200	750 ± 60	< 2	920 ± 75	47000 ± 1000	840 ± 65
Nitrogen	mol mol^{-1}	0.55 ± 0.05	71.8 ± 0.7	1.3 ± 0.1	70.2 ± 0.7	0.25 ± 0.1	1.3 ± 0.1	0.7 ± 0.1
Methanol	μmol mol^{-1}	< 2	< 2	< 3	< 2	< 2	< 2	< 2
Ethanol	μmol mol^{-1}	< 2	< 2	< 3	< 2	1.1 ± 0.5	< 2	< 2
Hydrocarbon (C2 +)	μmol mol^{-1}	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Total VOC excl. Methanol and ethanol	μmol mol^{-1}	< 5 *	< 5	ca 60	< 5	ca 8	< 5	ca 350
p-cymene	nmol mol^{-1}	< 20	< 20	13000	< 20	55	< 20	260000
2-butanone	nmol mol^{-1}	< 30	< 30	3000	< 30	2700	< 30 (in the blank)	95000
Monoethylene glycol (MEG)	μmol mol–1	< 0.2	< 0.2	n.a.	< 0.2	n.a.	< 0.2	n.a.
Tri-ethylene glycol (TEG)	μmol mol–1	< 0.2	< 0.2	n.a.	< 0.2	n.a.	< 0.2	n.a.
Benzene	nmol mol^{-1}	< 20	< 20	< 20	< 20	350	< 20	45
VOC distribution		Only some toluene found at 900 nmol mol^{-1}	All VOC < 20–30 nmol mol^{-1}	p-cymen, D-limonen, eukalyptol, 1-propanethiol, 2-butanol, 2-butanone, pentanones, Dietoxyetan, isopropanol, ethoxy-ethene, methylbutanol,	All VOC < 20–30 nmol mol^{-1}	dimethylsulfide, 2-butanone and other ketones, methylfuran, benzene, toluene, p-cymene	Only some toluene found at 1300 nmol mol^{-1}	p-cymene, D-limonene, alpha-pinene, beta-pinene, other terpenes, 2-butanone, other ketones, 2-butanol

CO_2 streams taken directly after the upgrading step. The need for purification concerns only a few species which need to be removed in order for the CO_2 to be compliant with the specifications given in CCUS documents or standards in particular document 70–17. This is the case for water (all samples, from 0.5 to 2 mol mol^{-1}), methane (all samples), hydrogen sulfide (in some cases, sample ID 1 and 5), oxygen (all samples), nitrogen (all samples), and VOCs specifically if the plants digest food wastes (samples ID 3 and 7) including benzene (samples ID 5 and 7). The gases before cleaning steps are already compliant with specifications given in CCUS documents or standards with regards to methanol (limit in 70–17: 10 μmol mol^{-1}), carbon monoxide (limit in 70–17: 10 μmol mol^{-1}), ammonia (limit in 70–17: 2.5 μmol mol^{-1}), sulfur dioxide ((limit in 70–17: 1 μmol mol^{-1}), NOx (limit in 70–17: 2.5 μmol mol^{-1}). The VOCs found in the CO_2 are coming from the biogas. It would be interesting to study the proportion of VOCs in the biogas that will follow with the CO_2 stream. In this study, the biogas and the CO_2 stream were sampled on the same day for sample ID 3 (upgrading technique, amine scrubber) and it was found that around 8 % of the p-cymene and 3 % of D-limonene follows with the CO_2 stream. The concentration of ketones such as 2-butanone was found to be higher in the CO_2 stream than in the biogas. A study [18] comparing the VOC in biogas and biomethane found that the adsorption tower in the amine scrubber removed ketones and esters effectively from the biogas without significantly affecting the composition of other contaminants. This is because ketones and esters contain a carbon-oxygen group with a double bond (C═O) (in other words, they share a structural element with carbon dioxide, O═C═O) which reacts with amines in the same way as carbon dioxide, so they will undergo the same fate.

The gas samples taken after treatment with a voxidizer or catalytic oxidation (sample ID 2 and 4) are very clean but have a low amount fraction of CO_2 (8.1 respective 10.4 mol mol^{-1}).

The high concentration of water found is all samples may impact the results reported in Table 7, mostly for VOCs. Two different phenomena resulting in opposite effects have been reported when storing wet gases [19]:

1) Dissolution of compounds in condensed water under the humid conditions
2) Competitive adsorption of water vapour on actives sites of the vessel, water occupies active sites on vessel walls, thereby increasing the inertness of the vessel.

These effects can be opposite, or have a synergistic effecte leading to e.g. an aerosol formation in a gas phase followed by its surface adsorption.

6. Conclusion

This study presents analytical methods to determine the purity of CO_2 streams and applies these methods to sample CO_2 collected at different biomethane plants in Sweden. The fit-for-purpose of the methods regarding stability of relevant species in different sampling vessels, sorbent tubes or gas bags is shown as stability studies conducted using reference gaseous mixtures. The study demonstrates that sampling of CO_2 will imply collecting the gas in several vessels, which could be a combination of cylinders, gas bags and sorbent tubes. The study also showed some examples of possible reaction such as the one observed for 1-propanethiol which dimerizes to dipropyl disulfide on different sorbents and in high-pressure cylinders (SPECTRA-SEAL®). The study also shows that among the small organic compounds to be analyzed, alcohols are the most challenging species to sample in gas bags. Moreover, due to their low boiling point, none of the sorbents used in this study leads to quantitative results for methanol.

However, these stability studies have not fully taken into account the possible interactions between species present potentially simultaneously in the CO_2. Suitability of the sampling vessels to avoid interactions between compounds should also be studied: the presence of some compounds may stabilize other compounds; the presence of some compounds may lead to cross-interactions. However, these effects are not always related to the vessel itself, but sometimes only to the compounds.

Another study to be undertaken is the comparison of the gas composition of CO_2 streams from upgrading plants with the biogas to understand which proportion of VOCs will follow with the CO_2 stream depending on the substrates and on the upgrading technique. A test performed in this study showed that with an amine scrubber, 8 % of the main VOC; p-cymene was found in the CO_2 stream but that ketones were found in higher concentrations in the CO_2 stream than in the biogas. The proposed study will give valuable information on further purifications needed but also may highlight the need to optimize the process so the streams coming from the upgrading plant are already as clean as possible which will in turn require less effort to remove the impurities to the levels required in the different specifications.

CRediT authorship contribution statement

Luuk Meijer: Writing – review & editing, Methodology. **Iris de Krom:** Writing – review & editing, Methodology, Investigation. **Janneke van Wijk:** Writing – review & editing, Methodology, Investigation. **Emma Henderson:** Writing – review & editing, Methodology. **karine arrhenius:** Writing – original draft, Methodology, Investigation. **Sandra Hultmark:** Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: All authors reports financial support was provided by EURAMET European Metrology Programme for Innovation and Research. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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