



21GRD06 MetCCUS

Report A3.2.1: Literature survey on current state-of-the-art for the material compatibility of vessels for the sampling of CO₂ for CCUS

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Summary

This report was written as part of activity A3.2.1 from the Partnership on Metrology project Metrology for the support for Carbon Capture Utilisation and Storage (MetCCUS). The three-year European project started 1st October 2022.

In the report, we have reviewed the current state of the art for the material compatibility of the vessels (including cylinders, bags and sorbent tubes) that are used to sample CO₂. The choice of vessels depends on many parameters, including the pressure and temperature of the gas at the sampling point, safety aspects, requirements/ recommendations in standards, transport regulations and the suitability of the vessel. It is crucial to ensure that the sample provided to the laboratory is representative, which requires knowledge about the stability of the impurities in the carbon dioxide stored in sampling vessels. Risks of reaction inside the vessel or adsorption on the wall of the vessel must be avoided. Stability studies performed in adequate conditions (careful choice of the concentration, pressure for cylinders, possible interaction with other impurities) are often needed to ensure the suitability of any given vessel for a given impurity. The MetCCUS project will perform stability studies in bags in activity A3.2.3 and information on cylinder's suitability will be obtained from the activities performed in task 3.1.

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1 - Introduction

Carbon capture with permanent storage (CCS) or utilization of the carbon dioxide (CCU) are effective tools to reduce carbon dioxide (CO₂) emissions [1] and contribute to reach climate goals set by the European Commission. Many industries contribute to CO₂ emissions can use these technologies: cement plants, iron and steel plants, high-purity industrial sources such as natural gas processing, hydrogen production, coal/gas-to-liquids and ammonia production, pulp and paper industry, biofuels production etc. Depending on the source of CO₂ and the type of capture technology used, a certain quality of the CO₂ is generally required to guarantee process performance, components, health and safety. The document ISO/TR27291:2020 [2] describes the effects of the impurities present in the CO₂ stream on the storage (classified as physical, chemical, microbiological and toxicological). For example, impurities of the CO₂ stream can affect both the thermodynamic and transport properties (operating pressure, temperature, fluid density, safety considerations, fracture control and cloud dispersion). As for any application, allowable levels (maximal limits) of certain impurities are needed to guarantee process performance, components, health and safety.

Chemical analysis of CO₂ is critical to allow industry to accurately test the performance of new capture technologies to understand the degradation and purity of carbon dioxide and key impurities. In many cases, to assess the purity of CO₂ requires taking a sample onsite which is then sent to a laboratory for analysis. It is crucial to ensure that the sample provided to the laboratory is representative, which requires knowledge about the stability of the impurities in the carbon dioxide stored in sampling vessels.

The choice of vessels depends on many parameters, including the pressure and temperature of the gas at the sampling point, safety aspects, requirements/ recommendations in standards, transport regulations and the suitability of the vessel. One evident risk is the possible loss of impurities through adsorption on the wall of the vessels used to collect the gas.

A large effort has been done recently to assess sampling vessels suitability for other matrices than CO₂ in different metrology projects (ENG4 Metrology for biogas [3], 16ENG05 Metrology for biomethane [4], 16ENG01 Metrology for Hydrogen Vehicles [5], 19ENG04 Metrology for Hydrogen Vehicles 2 [6]) in particular for biomethane [7] and for hydrogen matrices [8].

The review uses input from A3.1.1 which dealt with gaps in Primary Reference Material (PRMs) and A3.1.2 (literature review on available cylinders for PRMs) and it includes material compatibility data in other matrices as mentioned above together with the possible effects of CO₂ on these results (matrix effects). This information is then used to identify the knowledge gaps in material compatibility and to specify some experiments needed to fill the gaps for the sampling of CO₂.

2 – Targeted impurities

As part of A3.1.1, a table of relevant impurities for CCUS was established (table 1 below)

Table 1 – Impurities and ranges relevant for CCUS (A3.1.1)

	Porthos	TAQA (CO ₂ delivery specifications)	ZEP	Decarb WP 2,1,1	ENV23 NPL Report (Saline reservoir sequestration)	ISO 27913	CCUS Specifications Summary (NPL)	ECC (East Coast Cluster)	LBA (Liverpool Bay Area)	Amount fraction
component										
Carbon dioxide (CO ₂)	≥ 95 %	≥ 95 %	not defined	not defined		≥95%		≥96%	≥95%	≥96%
water (H ₂ O)	≤70	≤40	≤30	≤20	≤300	≤50 ppm	≤20-50 ppm	≤50 ppm	≤50 ppm	≤50 ppm
Sum [H ₂ +N ₂ +Ar+CH ₄ +CO+O ₂]	≤4%	≤4%								≤4%
H ₂	≤0.75%	≤0.75%	≤50	≤0.3%	≤4%	≤1%	≤0.005-2%	≤0.75%	≤0.75%	≤0.75%
N ₂	≤2.4%	≤2%				≤4%	≤1-4%	≤4%	≤4%	≤1-4%
Ar	≤0.4%	≤1%	not defined			≤4%	≤1-4%	≤4%	≤4%	≤1-4%
CH ₄	≤1%	≤1%	not defined			≤4%	≤1-4%			≤1-4%
CO	≤750 ppm	≤750 ppm	≤100 ppm			≤0.2%	≤0.01-0.2%	≤0.2%	≤0.2%	≤750 ppm
O ₂	≤40 ppm	≤40 ppm	≤10 ppm	≤100 ppm	≤4%	≤10 ppm	≤10-20 ppm	≤10 ppm	≤10 ppm	≤10 ppm
total sulfur-contained compounds (incl. mercaptan)	≤20 ppm					CS ₂ : ≤20 ppm				≤20 ppm
COS		≤0.1 ppm				≤100 ppm			COS and CS ₂ :≤5 ppm	≤5 ppm
DMS		≤1.1 ppm								≤1ppm
H ₂ S	≤5 ppm	≤5 ppm	≤9 ppm	≤20 ppm	≤5 ppm	≤5 ppm	≤5-20 ppm	≤5 ppm	≤5 ppm	≤10 ppm

SO _x		≤50 ppm	≤10 ppm	≤10 ppm	≤0.5 ppm	≤10 ppm	≤10-100 ppm	≤20 ppm	≤10 ppm	≤20 ppm
Total NO _x	≤5 ppm	NO ≤2,5 ppm, NO ₂ ≤2.5 ppm, NO _x ≤5 ppm	NO _x : ≤10 ppm	NO _x : ≤20 ppm	NO _x : 0.5 ppm	NO _x : ≤10 ppm	NO _x : ≤10-100 ppm	≤10 ppm	≤10 ppm	≤10 ppm (NO ₂ /NO)
Total aliphatic hydrocarbons (C2 to C10)	≤1200 ppm	≤1200 ppm				≤4.15%	≤1.15-6%		≤8.15%	≤1200 ppm
total aromatic hydrocarbons (C6 to C10, incl. BTEX)	≤0.1 ppm	≤0.1 ppm				BTEX: ≤15 ppm, Naphthalene: ≤100 ppb			BTEX: ≤15 ppm, Naphthalene: ≤100 ppb	≤0.1 ppm
Total volatile organic compounds (excl. methane, total aliphatic HC (C2 to C10), methanol, ethanol, and aldehydes)	≤10 ppm	≤350 ppm				≤48 mg/m ³	≤20-60 ppm		≤48 mg/m ³	≤10 ppm
total aldehyde compounds	≤10 ppm		acetaldehyde: ≤20 ppm formaldehyde: ≤20 ppm							≤10 ppm
										≤20 ppm
ethanol	≤20 ppm							≤500 ppm		≤20 ppm
methanol	≤620 ppm					≤350 ppm		≤500 ppm	≤350 ppm	≤350 ppm
hydrogen cyanide (HCN)	≤2 ppm	≤20 ppm		≤5 ppm	≤0.9 ppm					≤2 ppm
total amine compounds	≤1 ppm		≤10	not defined		≤100 ppb	≤0.08-10 ppm		≤100 ppb	≤1 ppm

total glycol compounds	follow dew point specification						≤0.025-0.05 ppm			≤0.025-0.05 ppm
ammonia (NH ₃)	≤3 ppm		≤10 ppm	≤50 ppm	≤25 ppm	≤10 ppm	≤10-1500 ppm	≤10 ppm	≤10 ppm	≤50 ppm
total carboxylic acid and amide compounds	≤1 ppm									≤1 ppm
total phosphorus-contained compounds	≤1 ppm									≤1 ppm
ethylene (etheen) (C ₂ H ₄)		≤1 ppm								
Cadmium (Cd)/Titanium (Ti)			≤0.03 (sum)							
Mercury (Hg)			≤0.03		≤0.002					
Solid particulates						≤1 mg/m ³	≤1 ppm	≤1 mg/m ³	≤1 mg/m ³	
Toxic metal						≤0.15 mg/m ³			≤0.15 mg/m ³	
Acid forming compounds						≤150 mg/m ³	≤10-70 ppm		≤150 mg/m ³	
Nitrosamines and nitramines						≤3 µg/m ³			≤3 µg/m ³	
Dioxins and furans						≤0.02 ng/m ³			≤0.02 g/m ³	
He										

3 – Different vessels

Sampling can be done using two principles: with or without enrichment [7]. Sampling with enrichment implies that gas is collected onto a solid collection phase (using adsorbent tubes) or absorbed in a solution (using impingers) while the matrix passes without being retained. Sampling without enrichment consists in directly collecting a sample of gas in a vessel: bags, canisters, or cylinders of different materials, with or without treatment or passivation technologies. These vessels do not discriminate between compounds during collection; thus, all compounds are collected.

In this report, we focus on three sampling vessel types: sampling bags, cylinders and sorbent tubes.

4 – Material compatibility

4.1 – Sampling bags

Sampling bags are gas-tight bags made of different materials such as polyvinyl fluoride (tradename: Tedlar), polyethyleneterephthalate (tradename Nalophan), polytetrafluoroethylene (PTFE, tradename: Teflon), polyester aluminium, polyethyleneterephthalate-nylon-aluminium, polyvinylidene difluoride, and equipped with a valve (of different materials).

Sampling bags volumes vary typically from 0.5 liter to at least 250 liter, however the sizes 1-3 liter are the most common. The advantages of sample bags are; simple and quick sampling, sampling can be carried out by unskilled personnel, and little or no additional equipment, such as coolants and flowmeters is required. Moreover, multiple samples can be withdrawn from the bag for repetitive analyses. Bags can be filled using a little over pressure at the sampling point or by using a pump. Bags are also cheaper than other vessels but cannot be reused.

Disadvantages: Sampling bags can only be used in specific conditions. Most providers set limits for temperatures and pressures of the gas to be stored in the bag. Although careful selection of the bag material can minimize undesired effects, some limitations of sampling bags have been reported, such as permeation through the walls, leaks through the valves or physical leaks (holes), sorption losses and adsorption effects to the bag walls as well as chemical reactions [9]. Estimating the relative contributions from these factors is not an easy task, however, the loss of volatile species by adsorption between species and bag material is considered to be the dominant factor [9]. Moreover, the storability of species may be affected by such variables as initial concentration level, as demonstrated by Jo et al. [10]. Sampling bags may also require special storage conditions, such as low temperatures, to prevent degradation or contamination of the sample according to [11].

Most of the information available regarding the suitability of bags for different species are for air matrix. However, some information can also be found for biogas and biomethane. For CO₂, Airborne Labs International Inc (ALI) [12] has developed sampling equipment for beverage grade (according to ISBT) which include cylinders and gas sampling bags. In this case, the bags are called “True Blue MLB (multi-Layer Barrier) and True Blue Tedlar bags and are according to ALI, inert and rugged bag. The MBL is opaque for protection from light degradation and has very low gas permeability.

Multi-foil layers bags work well for gases such as CH₄, CO₂, CO and H₂S whereas Tedlar, or Teflon bags are mostly used for semi- and volatile organic compounds (SVOCs and VOCs). This is due to the gas permeability of the bag as shown in Table 2 for three different bags. Alternatives to Tedlar such as Altec [13] from Restek also exist. According to the manufacturer, these do not produce background levels of dimethylacetamide or phenol, have a very low VOC and sulfur background but are not recommended for ketones, acetates, hydrogen sulfide or permanent gases.

Table 2 – Gas permeability for Tedlar, Teflon and Multi foils Bags [14]

Permeability (g/m ² /day)	Tedlar	Teflon	Multi-layer foil
Oxygen	50	58	0.0078
Water vapor	9-57	12-15	0.0078
Carbon dioxide	172	172	0.0078

However, sampling bags are not always suitable for oxygen and nitrogen as it is very difficult to completely avoid introducing small amounts of air during the sampling.

Stability in bags have been tested by NMIs as part of project ENG01 Characterisation of energy gases [15] (H₂S in Flexfoil and Flexfoil in methane) (Figure below directly taken from the article) and ENG54 metrology for biogas [16] (for benzene, toluene, ethylbenzene, o-xylene, methylmercaptan, dimethylsulfide, dimethyldisulfide, tetrahydrothiophene, hydrogen sulfide and carbon sulfide in Flexfoil, or Altec in synthetic biogas).

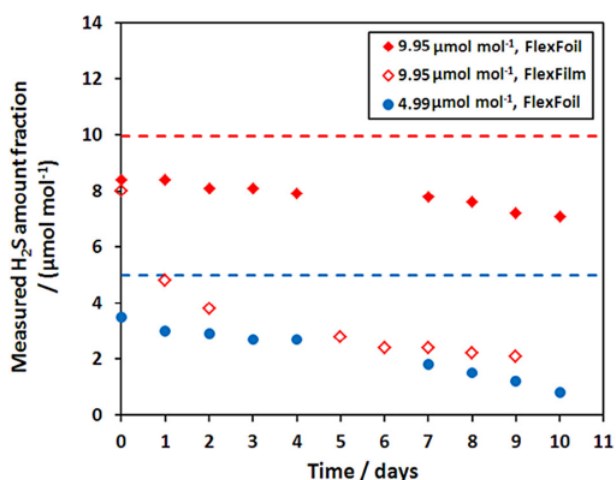
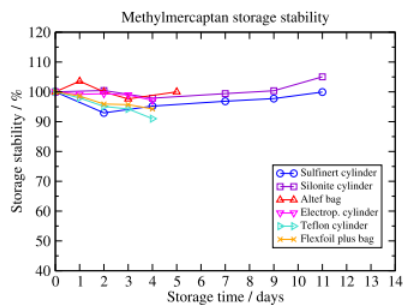
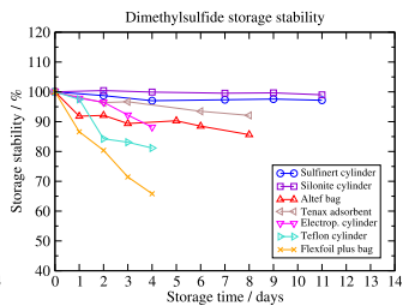


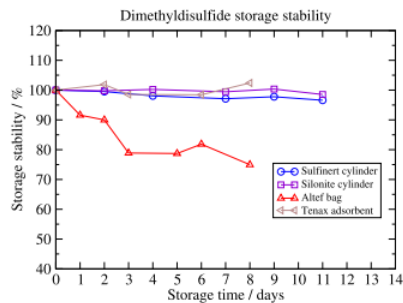
Fig. 4. Measured amount fractions of a 9.95 μmol mol⁻¹ hydrogen sulfide in methane gas standard after storage in sampling bags of FlexFoil (filled red diamonds) and FlexFilm (open red diamonds), and the measured amount fractions of a 4.99 μmol mol⁻¹ hydrogen sulfide in methane gas standard after storage in a FlexFoil sampling bag (filled blue circles). The dashed lines represent the amount fraction of the mixtures in cylinders (before sampling into the sample bags). The relative expanded uncertainty of each measurement is ~5%.



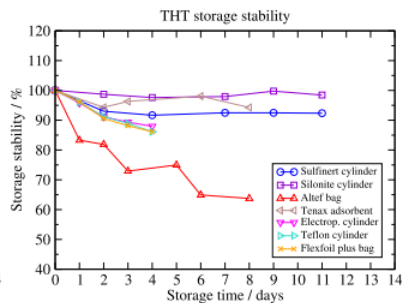
(a) Methylmercaptan storage stability



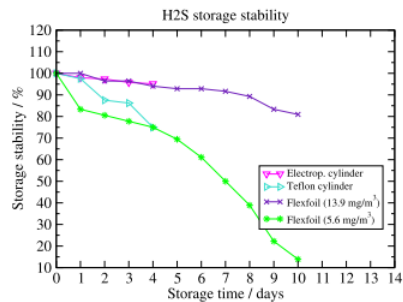
(b) Dimethylsulfide storage stability



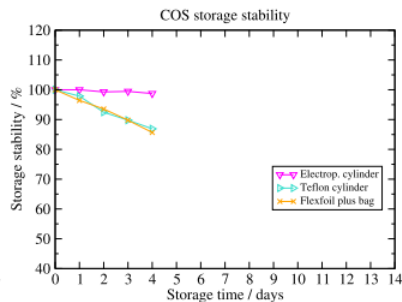
(c) Dimethyldisulfide storage stability



(d) Tetrahydrothiophene storage stability



(e) Hydrogen sulfide storage stability



(f) Carbon sulfide storage stability

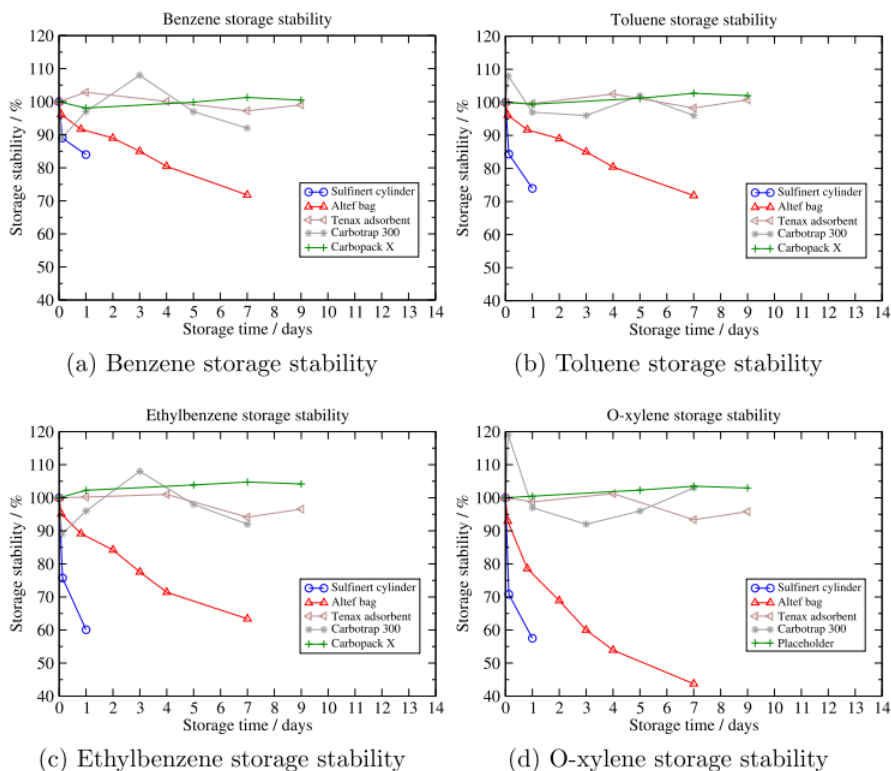


Fig. 2. Short-term storage stability in cylinders, bags and on adsorbent for BTEX.

Both studies showed that it is recommended to analyze the sample as soon as possible after the sampling to avoid losses due most probably to adsorption. The study on H₂S also showed that limited adsorption can also occur directly. However, there are bags for which given impurity is stable for a relative long time (> 10 days), for example methylmercaptan in Altef bags.

4.2 – Cylinders

Cylinders are made of different materials. The most common materials used today are aluminium, steel, alloys and composite materials. However, these materials are prone to absorbing certain species (for example sulfur compounds) onto the surface. One possible way to avoid absorption is passivation which consists of occupying active areas onto the vessel's surfaces.

There are a multitude of different methods used to passivate the internal surface of cylinders. The treatments are often to make the surface inert to targeted compounds. Passivation is a technique used to occupy the active areas on the surface of a vessel. For instance, Sulfinert[®] passivation technique bonds an inert silica layer onto the surface of stainless steel, preventing reactive compounds from reacting with or adsorbing to the steel.

However, as most of these technologies remain proprietary information, not a great deal of detail is known about these technologies [17]. Three categories of treatment can be distinguished:

- 1) Cleaning, polishing of the internal surface (electro) chemically or mechanically
- 2) Chemical treatment without targeting structural change of the surface

3) Multi-molecular layer coverage of the initial surface

Cylinders can be single-ended cylinders or double-ended cylinders. The use of double-ended cylinders allows more flexibility as for example for purging the cylinder before sampling. Some manufacturers also developed cylinders with a dip tube fitted internally to a dual port valve which allows a purge of the cylinder.

Information regarding the suitability of cylinders for different species relevant to CCUS can be found for air matrix, hydrogen matrix and methane matrix. However, some information can also be found for carbon dioxide.

4.2.1 – Cylinder suitability in other matrices than CO₂

Material compatibility for sampling vessels has been discussed for other matrices and some material compatibility tables are available. Information on these tables have often been obtained by experimental testing. However, it is also important to notice that the time-period of testing is not standardized so some studies are performed over months while others may be performed over weeks. Other parameters have also not well been defined in these studies, for example, the pressure in the cylinders is not always indicated. Possible cross-interferences have not been studied enough. The definition of the term “suitable” would need to be defined quantitatively and the conditions used during the tests need to be specified (among others, pressure, concentration, matrix...).

For sampling of natural gas, the standard ISO 10715:2022 [18] refers to the material compatibility is given ISO 16664 [19] for components such as O₂, CO₂, CO, alkanes, Cl₂, HCl, NH₃, H₂S. Most of these impurities are also relevant for CO₂ except HCl and Cl₂. It is important to notice that this table is intended for PRMs.

According to this table, stainless steel is suitable for most of the impurities mentioned with the exception of CO at mole fraction above 1% (of limited suitability), for Cl₂ and HCl at all concentrations (of limited suitability) and for H₂S at mole fraction below 0.001% (not suitable). Aluminium is also suitable for many of the impurities. However, there is no experience available for Cl₂ at mole fraction between 0.001 to 1% (aluminium is not suitable for Cl₂ at mole fraction above 1%) and for NH₃. The MetNO₂ project provides relevant information regarding NO₂ [20]. In the project deliverable, a stability study was performed using reference standards consisting of 10 µmol/mol of NO₂/N₂ and NO₂/air. The study revealed a decline in the concentration of NO₂ over time across all tested cylinder types. The outcomes demonstrated that the AlphaTech cylinders produced by Air Liquide exhibited good performance, exhibiting minimal NO₂ drift and consistently reliable results.

Aluminium is not suitable for HCl at mole fraction 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%).

In the standard ISO10715, it is even recommended to analyse reactive compounds on site with direct sampling methods when practical since even coated cylinders may not eliminate the risk for absorption of reactive species.

For the sampling of hydrogen used as vehicle fuel some of the species are also the ones targeted in CO₂ matrices when used in CCUS applications, but the thresholds in CO₂ are less stringent than the ones required for hydrogen.

The results from the available stability studies together with experience from industry were gathered in a table in a recent article [8], the table is reproduced here (Table 3):

Table 3 – Cylinder suitability for a time period of 4 months (table from [8])

	Stainless steel				aluminium										
	Untreated		Sulfinert®		Untreated		Aculife VII		Performax		SPECTRA-SEAL		Untreated SGS		
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	
C ₂ H ₆	X	X	X	X	X	X	X	X	X	X	X	S	S	S	S
He	X	X	X	X	X	X	X	X	X	X	X	S	S	S	S
N ₂	X	X	X	X	X	X	X	X	X	X	X	S	S	S	S
Ar	X	X	X	X	X	X	X	X	X	X	X	S	S	S	S
CO ₂	X	X	X	X	X	X	X	X	X	X	X	S	S	S	S
CO	i.d.	S	i.d.	S	S	S	i.d.	i.d.	i.d.	i.d.	S	S	S	S	
H ₂ S	i.d.	I/S	X.	S	i.d.	I	i.d.	I	i.d.	i.d.	I	I	S	i.d.	
HCl	i.d.	i.d.	i.d.	I	i.d.	i.d.	i.d.	I	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	
CH ₂ O	i.d.	i.d.	i.d.	S*	i.d.	i.d.	i.d.	i.d.	i.d.	S*	I	I	I	i.d.	
CH ₂ OH	i.d.	i.d.	i.d.	i.d.	i.d.	X.	i.d.	i.d.	i.d.	i.d.	S	S	I	i.d.	
NH ₃	i.d.	i.d.	i.d.	X	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	I	X	I	i.d.	
O ₂	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	S ¹	S ¹	S ¹	S ¹	
H ₂ O	i.d.	i.d.	X ²	X ²	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	S ²	S ²	S ²	S ²	

a: at ISO14687:2019 threshold

b: at higher concentrations (i.e. 50 times ISO14687)

X: should be suitable

S: suitability demonstrated (* more than 80% stability)

I: Issues were found (ex. of issues: need careful selection of the cylinder, initial loss...)

i.d.: Insufficient data

¹ oxygen stability seems to vary between cylinders of same internal treatment

² oxygen reactivity may affect the amount fraction of water through the reaction in hydrogen matrix

4.2.2 - Cylinder suitability in CO₂

For CO₂, Airborne Labs International Inc (ALI) [12] has developed sampling equipment for beverage grade (according to ISBT) which include cylinders and gas sampling bags. In this case, the cylinders to sample liquid CO₂ to perform an extensive set of key ISBT impurities (not precise which ones) are passivated single-ended 5.9 L aluminium cylinders (passivation type not precised but the PTFE washer assembly is Silcotek passivated). ALI [12] has also dedicated equipment to flash vaporized liquid CO₂ for easier shipment. In that case, several vessels are used including a 150 ml double-ended passivated cylinder (passivation type not given) with 1.7 bar check valve and 11 bar burst disk.

Vessel suitability assessments data can also be found in the calibration gases industry, but the timeline differs; for sampling, stability shall be assessed over some weeks up to a month whereas for gas calibrants, stability often needs to be demonstrated for over a year.

The available information on cylinders and surface passivation treatments for impurities in CO₂ is limited. Most of the data is obtained from literature and contact with cylinder providers. There is also some information available from experience gained through participation in National Metrology Institutes and other metrology projects, but this information is typically for other matrices such as hydrogen, air, and methane. Nonetheless, it has been found that aluminum cylinders treated with Spectraseal or Experis are suitable for storing volatile organic compounds like aliphatic and aromatic hydrocarbons, formaldehyde, and sulfur-containing compounds such as H₂S, SO_x, and total sulfur-containing compounds. The stability of DMS in aluminum cylinders with special surface treatments was found to be 9-12 years, whereas stability without these treatments varied from 1.5 to 3.5 years. On the other hand, the stability of NO₂ was limited to about one year in Spectraseal coated cylinders. Moreover, aluminum cylinders were observed to be more resistant to adsorption/desorption processes for CO₂, CO, CH₄, and H₂O than steel cylinders. These findings provide valuable insights into the selection of appropriate cylinder materials and surface treatments for gas storage and transportation.

4.3 – Sorbent tubes

Sorbent tubes are typically made of glass or stainless steel (with or without treatment) and contain various types of solid adsorbent material. Commonly used sorbents include activated charcoal, silica gel, and organic porous polymers such as Tenax and XAD resins. Solid sorbents are selected for sampling specific compounds in air because they trap and retain the compound(s) of interest but not the matrix. This leads to an enrichment of the targeted compounds, which can be desorbed by heating, or extracted with solvents, for analysis. The advantage of using sorbent tubes is that they are relatively simple to use, store and transport to the laboratory.

The factors to consider when selecting suitable sorbents include the strength of the sorbent-sorbate interaction, the temperature, the artefacts, the hydrophobicity, the inertness (some sorbents contain chemically active materials and are generally unsuitable for reactive species – sulphur compounds, amines etc.) and the mechanical strength (friability) [21]. Sorbent strength is usually measured in terms of retention or breakthrough volumes which is defined as the volume of carrier gas per gram of adsorbent that causes the analyte molecules to migrate from the front to the back of the adsorbent bed at a specific temperature. The highest breakthrough volumes would therefore correspond to the most suitable adsorbent materials.

Some of the impurities to assess in CO₂ used in CCUS processes are organic (see Table 1, example: sulfur compounds aliphatic hydrocarbons, aromatic hydrocarbons, methanol, ethanol and glycol). Thermal desorption often coupled with gas chromatography is a common speciation method used to determine the content of organic impurities. The analytical method has the advantage that it indirectly lowers the detection limits by a considerable factor. By means of pumped sampling, according to ISO 16017:2000 [22], organic impurities are trapped onto the sorbent whereas the carbon dioxide matrix passes through without being retained. However, no existing sorbent tubes are sufficiently universal as to trap all possible impurities, and therefore a selection process is required.

The suitability of sorbents for three hydrocarbons (Benzene, hexane and decane), two sulfur compounds (1-propanethiol and dimethylsulfide -DMS) and for methanol was assessed as part of activity A2.5.2 of the EMPIR project Metrology for decarbonizing the gas grid (Decarb) [23]. Different sorbents were tested at RISE (Chromosorb 106, Air Toxic and Tenax TA) and at VSL (Tenax TA, Odour/Sulfur and Tenax TA/Carbograph 5).

The results showed that Chromosorb 106, Air Toxic and Tenax TA were suitable for the three hydrocarbons on all sorbents. Good results were obtained for DMS on Tenax TA. The results showed that it is possible to use Chromosorb 106 and Air Toxic if analysis done within 4-5 days of the sampling. However, some issues were identified for 1-propanethiol as the formation of dipropyldisulphide from 1-propanethiol were observed mostly on Tenax TA and Air Toxic. It was shown that only Chromosorb 106 was suitable for this compound and under the condition that the analysis done within 4-5 days of the sampling. None of the sorbents were found suitable for methanol due to instability in the results. However, sorbents can be used to give an indication of presence of methanol using Chromosorb 106 and even Air Toxic when analysis within 4-5 days of the sampling.

The results obtained at VSL showed that for very volatile impurities such as methanol and dimethylsulphide stronger sorbents are needed to prevent breakthrough of the impurities during sampling. Tenax TA/Carbograph 5 is suitable for all impurities except for dimethylsulphide, the Odour/Sulfur sorbent material is not suitable for the volatile impurities hexane, methanol and dimethylsulphide. The impurities are all stable on the Tenax TA sorbent material over a period of 14 days nevertheless, breakthrough of methanol and DMS was observed during sampling.

For efficient sampling of all the impurities at CCUS sites it is preferred to select a sorbent material for all impurities, unfortunately, there is not a single sorbent material that seems to work for all these impurities. Overall, best results were obtained with Chromosorb 106 and Tenax TA/CarboGraph 5. Using these two sorbents could enable the quantitative analysis of all the selected compounds.

5 – Matrix effects

Even if it is a good source of information, the material compatibility obtained for a given specie in a matrix cannot be used directly to assess the compatibility in another matrix; the matrix effects need to be studied first. The matrix effect is the effect on a given specie by main component of the sample (here CO₂). Matrix effects are observed either as a loss in response, resulting in an underestimation of the amount of analyte (mainly due to a reaction between the species and CO₂), or as an increase in response, producing an overestimated result.

6 – Knowledge gaps in material compatibility

For cylinders, new information will be obtained as the results of the activities performed in task 3.1 where primary reference material standards that are required by industry in order to specify operational conditions and to perform the measurements required within CO₂ capture, transport and storage will be developed. Two-year stability study will be performed on the mixtures and the first results (at month 6) could be a good indication of the suitability of cylinders (in the case the mixture is found to be stable).

For sorbents, the tests performed in activity A2.5.2 during the Decarb project already give a good overview about the suitability of these vessels for organic impurities to be analysed in CO₂ streams.

Finally, for sampling bags, only few information is available and new tests are needed in order to assess the suitability of different sampling bags for different impurities relevant for CO₂.

7 – Plan for experiments needed to fill the gaps

To fill the gaps in knowledge of material compatibility, RISE plans to perform different stability studies in sampling bags. The choice of bags is also motivated by discussion with Swedish stakeholders who indicated that the pressure is very low at the required sampling points making bags an obvious alternative. Relevant impurities will be for example CO, O₂, NO₂, H₂S, SO₂, methanol, ethanol, acetaldehyde and benzene. Different bags can be selected; classical bags such as multifoil bags or Altef, but also bags specially designed for CO₂ such as True Blue from Airborne labs International Inc. The mixtures for these tests will be obtained from IPQ and/or CMI. For some impurities which are not included in the mixtures prepared by the NMIs will be directly prepared at RISE using pure substances.

8 – Conclusions

Chemical analysis of CO₂ is critical to allow industry to accurately test the performance of new capture technologies to understand the degradation and purity of carbon dioxide and key impurities. In many cases, to assess the purity of CO₂ requires taking a sample onsite which is then sent to a laboratory for analysis. The choice of vessels depends on many parameters, including the pressure and temperature of the gas at the sampling point, safety aspects, requirements/ recommendations in standards, transport regulations and the suitability of the vessel. It is crucial to ensure that the sample provided to the laboratory is representative, which requires knowledge about the stability of the impurities in the carbon dioxide that is stored in sampling vessels. Sampling can be done with (by collecting the gas onto a solid collection phase) or without enrichment (by directly collecting a sample of gas in a vessel: bags, canisters, or cylinders).

One evident risk is the possible loss of impurities through adsorption on the wall of the vessels used to collect the gas or reaction of impurities in the vessels. The available information on cylinders and surface passivation treatments for impurities in CO₂ is limited. Most of the data is obtained from literature and contact with cylinder providers but mostly for other matrices. Even if it is a good source of information, the material compatibility obtained for a given species in a matrix cannot be used directly to assess the compatibility in another matrix; the matrix effects need to be studied first. New information will be obtained as the results of the activities performed in task 3.1 where primary reference material standards will be prepared.

Decarb project provided some information about the suitability of sorbent tubes for impurities such as benzene, hexane, decane, dimethylsulphide, 1-propanethiol and methanol. Using Chromosorb 106 and Tenax TA/CarboGraph 5 could enable the quantitative analysis of all the selected compounds. However, sorbents are not an option for many other impurities (among others for CO, O₂, NO₂, H₂S, SO₂).

In activity 3.2.3 of MetCCUS, stability studies for a number of impurities will be performed at RISE in order to fill gaps in knowledge of bag's material compatibility.

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