



**21GRD06 MetCCUS**

**Report A3.2.5: Good practice guide for the sampling of CO<sub>2</sub> for capture, transport storage, conversion, utilisation and recycling**

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## Summary

This report was written as part of activity A3.2.5 from the Partnership on Metrology project “Metrology for the support for Carbon Capture Utilisation and Storage” (MetCCUS). The three-year European project started 1<sup>st</sup> October 2022.

This report is a good practice guide for the sampling of CO<sub>2</sub> for capture, transport storage, conversion, utilization, and recycling to support the industry in specifying their operational conditions and in performing the required measurements. The guide also discusses material compatibility for sampling lines (relevant to both online and offline analytical methods) and sampling vessels (specifically relevant to offline methods) which is critical to keep the integrity of the sample.

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## 1 Introduction

Several standards contain requirements for CO<sub>2</sub> quality assessment for different applications. The quality of CO<sub>2</sub> can be assessed using offline methods (collection of a sample of CO<sub>2</sub>, transport, storage and analysis in a laboratory environment) or online methods (which would give directly information about the quality, but which is using limited to some impurities, not all of them and is mostly relevant to the CCS process monitoring).

Sampling is a prerequisite for offline analytical methods, the sample taken must be **representative** of the gas supplied (no removal or addition of compounds during the sampling, transport and storage). For online analytical methods, the same requirement applies to the sampling lines (or interface) and measurement systems (analyzers).

The main challenge is for species at trace levels for which the risk of loss of contaminants in the sampling systems, vessels and sampling lines must be taken into consideration:

- partial adsorption or irreversible adsorption
- reaction (chemical reaction between species or between species and the matrix)
- Diffusion through materials

For sampling, different types of vessels exist, e.g., gas cylinders, canisters, sampling bags, impingers or sorbent tubes. The material of the vessels needs to be carefully chosen; material compatibility is therefore critical to keep the integrity of the sample. For online methods, the influence of temperature, pressure, material, tubing length used for the sampling lines on the targeted impurities need to be known. Moreover, components of the online analyzer in direct contact with the gas should properly be assessed prior use. The good practice guide aims at supporting the industry in specifying their operational conditions and in performing the required measurements within CO<sub>2</sub> capture, transport and storage, conversion, utilization and recycling.

## 2 Expected specifications at industrial sites

The conditions at the facilities need to be carefully specified so the sampling campaign can be planned optimally. The conditions at the facilities must be adapted to the need for the diverse analysis instruments and sampling media used to assess the composition of carbon dioxide. It may require compressing or expanding the gas, reducing the flow etc. The examples below describe some conditions that can be expected to be actual at facilities.

### 2.1 CO<sub>2</sub> transportation

For CO<sub>2</sub> transportation in a pipeline as CO<sub>2</sub> should be compressed to ensure that a single phase is achieved, the most widely used operating pressure for the pipelines is between 7.4 and 21 MPa and temperature 5 -35°C [1]. For CO<sub>2</sub> transport in storage tanks, lower pressures and temperatures are typically used: e.g. 17 bar and -20 °C, respectively. Sampling will often require a pressure reduction. This step must be done with great care to minimize the risks to lose impurities. For more information, the MetCCUS report A3.2.2 [1] gives some guidelines and proposes two sampling approaches (direct pressure reduction from 60-200 bar to 1 bar) or two stages pressure reductions (from 100-200 bar to 40-70 bar to 1-2 bar). CO<sub>2</sub> sampling from high-pressure sources should be done using an adequately coated sampling line.

## 2.2 CCS process and major CCS projects

Carbon capture and storage (CCS) process is done at facilities where carbon dioxide (CO<sub>2</sub>) emissions are captured from industrial processes or power generation (heat and electricity). The captured CO<sub>2</sub> is then transported to, and then stored in sealed geological formations such as e.g. former gas or oil fields to prevent CO<sub>2</sub> leakage into the atmosphere. The CO<sub>2</sub> storage sites play a crucial role in mitigating climate change by reducing the amount of CO<sub>2</sub> released from industries such as cement, steel, and fossil fuel power plants.

CCS process typically involve three main steps:

- 1) Capture: CO<sub>2</sub> is separated from other gases produced by industrial processes.
- 2) Transport: The captured CO<sub>2</sub> is then compressed and transported via pipelines, tanks (ships, trucks) or other means to the storage site.
- 3) Storage: CO<sub>2</sub> is injected into deep underground rock formations, such as depleted oil and gas fields or saline aquifers, where it is securely stored long-term.

Major CCS projects around the World:

- Sleipner CO<sub>2</sub> Storage (Norway): One of the world's first large-scale CCS projects, storing CO<sub>2</sub> in a saline aquifer under the North Sea.
- Gorgon CO<sub>2</sub> Injection Project (Australia): Part of the larger Gorgon natural gas project, capturing and storing CO<sub>2</sub> from the natural gas processing facilities.
- Boundary Dam (Canada): A coal-fired power plant in Saskatchewan with integrated CCS technology.
- Petra Nova (USA): A coal-fired power plant in Texas that captures CO<sub>2</sub> and uses it for Enhanced Oil Recovery (EOR).
- Quest CCS (Canada): Captures CO<sub>2</sub> from Shell's Scotford Upgrader and stores it underground in a saline aquifer.
- Snøhvit CO<sub>2</sub> Storage (Norway): Similar to Sleipner, this project captures and stores CO<sub>2</sub> from natural gas processing.
- CarbonNet (Australia): An emerging project aimed at capturing and storing CO<sub>2</sub> from industrial sources in the Latrobe Valley.

CCS is considered a critical technology for achieving global climate goals, especially for sectors that are hard to decarbonize. Many countries are exploring new CO<sub>2</sub> storage sites and new technologies to improve the CCS process (more efficient and cost-effective). CCS activities are expected to have a significant boost in the coming next 10 years across the globe.

### 2.3 Other projects

Other processes are of interest for the carbon capture storage and utilization (CCUS) industry. For example, in biomethane plants, the stream of CO<sub>2</sub> produced during the upgrading process can be used in different ways; for CCS projects or utilized for the production of beverages [2]. Depending on the sampling point (directly after the upgrading process or after other purification stages), the conditions at the sampling point will differ, however the pressure is not expected to be more than 5 bar.

## 3 Consideration about sampling lines

Sampling lines refer to the systems and methods used to collect samples of gases, liquids, or solids at various stages of the carbon capture and storage process. These samples are typically analysed to monitor the efficiency, composition, and integrity of the system.

Here's how sampling lines might be used in each part of the CCUS process:

#### 1) Carbon Capture:

**Pre-combustion Capture:** Sampling lines could be used to monitor the composition of the gas mixture before CO<sub>2</sub> is separated. This could include samples of syngas or flue gases (from flue gas recycling), depending on the capture method.

**Post-combustion Capture:** In post-combustion systems, sampling lines collect gas samples from the exhaust stream before and after CO<sub>2</sub> separation. These samples help monitor the efficiency of capture systems (e.g., amine scrubbing) by assessing the amount of CO<sub>2</sub> captured.

**Oxy-fuel Combustion:** Samples from the flue gas can verify the purity of CO<sub>2</sub> and the presence of other gases like nitrogen, which are minimized in this process.

#### 2) Carbon Utilization:

When captured CO<sub>2</sub> is used in industrial processes, such as in enhanced oil recovery (EOR) or chemical production, sampling lines may monitor the composition and quality of the CO<sub>2</sub> before it is injected into the process. They can also help detect impurities that may affect downstream processes.

#### 3) Carbon Storage:

During the transport phase, sampling lines monitor the purity and composition of CO<sub>2</sub> being transported via pipelines or in tanks to ensure safe and efficient transport.

In geological storage, sampling systems are essential for the monitoring of the injected CO<sub>2</sub> to ensure its proper containment within a storage reservoir. Samples may also be collected from monitoring wells to detect any potential leaks or chemical reactions that could compromise storage integrity.

In CCUS projects, sampling lines are vital for compliance with regulations, safety assessments, and operational optimization. Their design varies depending on the physical state of CO<sub>2</sub> (gas or liquid), the environmental conditions, and the specific monitoring requirements.

## 4 Selection of sampling vessels

Before choosing a vessel (gas cylinders, canisters, sampling bags, impingers or sorbent tubes and the materials for the vessels), some considerations must be taken into account:

- 1) The conditions at the sampling point must fit the requirement for the vessels (enough pressure or a pump would be needed), maximal operating temperature
- 2) The requirement for the vessels must fit the conditions of the analytical instruments. Enough volume sampled to perform all analyses (all replicates) and all instruments, enough pressure if needed by the instruments which implies that pressure from the vessels may need to be reduced.
- 3) Materials in contact with gases that may contain reactive impurities should be impermeable to all species and should have a minimum of sorption and chemical inertness to the constituents being sampled [3]

In this good practice guide, we focus on gas cylinders, sampling bags and sorbent tubes for which information regarding the suitability has been obtained in different activities of the MetCCUS and Decarb projects.

## 5 Requirements for different vessels

### 5.1 Sorbent tubes

Sorbent tubes have been showed to be a good alternative to determine the content of organic impurities in CO<sub>2</sub> (for example, hydrocarbons, alcohols or organic sulphur compounds).

To avoid contamination from previous sampling or occurring during storage periods in between sampling and to minimize interferences due to artefacts, sorbent tubes should be conditioned using an appropriate tube conditioning system.

It is very important to respect the flow direction along the tube, mostly in case of multi-sorbent tubes. Usually, the printed arrow on the sorbent tube shows the direction of gas flow.



The sampling line should be as short and simple as possible. The effect of all components used must be assessed in order to choose the proper material.

The pressure should be limited on the sorbent to just above atmospheric pressure and the temperature during the sampling should be as low as possible and no more than the ambient temperature.

Performing active sorbent sampling requires knowledge about the volume sampled. There are several ways to proceed (for example, using a flowmeter and recording time, or using a syringe of known volume).

Tests performed as part of the Decarb project [4] have demonstrated the suitability (and limitations) for different sorbent tubes for benzene, hexane, decane, dimethylsulphide, 1-propanethiol, and methanol (see section 5, material compatibility).

## **5.2 Gas cylinders**

In this report, we only discuss two-ended valves cylinders. The cylinder must be cleaned before utilization using an appropriate cleaning procedure. Relevant information about the sampling shall be communicated to the laboratory as for example, the filling pressure, information about the sampling point, the gas, sampling datum, etc.

As for any vessel, the choice of the cylinder (size, material, working pressure and temperature) should be properly addressed (see section 5). Sample cylinders containing gas under pressure shall be transported in accordance with relevant regulations. Cylinders shall be protected against damage during transportation and storage. During transportation, the cylinders shall also be protected against conditions of temperature which could create overpressure or condensation of sample.

## **5.3 Sampling bags**

Gas bags have often a valve (sometimes two) enabling collecting of the gas sampled inside the bag and a label so information about the sample and the sampling can be written directly on the bag. Some of the advantages of using bags are that their operation does not require skilled personnel and that it is not necessary to use additional step for sample preparation. Drawbacks are the risks for adsorption to the wall of the bags or diffusion through the walls (see section 5, material compatibility). One of the disadvantages of sampling bags is that the pressure and flow rate must be controlled and reduced which may require specific equipment (pressure reducer for example) on the sampling line. Impurities present in the gas may adsorb inside these devices leading to underestimating their concentration. This phenomenon needs to be taken into account while choosing sampling bags.

It is very important not to exceed the volume defined by the manufacturer. Exceeding this volume can cause irreversible unsealing of the bag. Avoid filling any bag with more than 80% of its maximum volume. But bags should be filled so as there is enough gas for the analysis. Depending on the material of the bag, the proper preparation/cleaning of the bag prior to sampling is an important step. This step is often done by repeated washing of the container inside with a high purity gas. The bags shall be flushed three times with an inert gas.

For the sampling, the pressure in the tubing should not be more than a little bit higher than the atmospheric pressure and the temperature should not exceed the temperature recommended by the manufacturer. Carefully flush the tubing with the gas to be sampled before connecting it to the bag to avoid contamination of the sample by air. Only once the conditions (flow, temperature, pressure) at the sampling point are known, can the sampling line be designed. If necessary, the sampling line shall be equipped with pressure reduction valves and sample conditioning equipment to control the temperature.

## 6 Material compatibility

### 6.1 Sorbent tubes

Totally, five different sorbents were tested based on previous experiences or discussion with sorbents providers:

- Chromosorb 106
- Air Toxic
- Tenax TA
- Tenax TA/CarboGraph 5
- Odour/Sulfur

The results of the studies conducted as part of A2.5.3 of the Decarb project [5] show that sorbents can be used for the organic impurities to be analysed in CO<sub>2</sub> streams but will probably require using at least two different sorts as none of the sorbents selected were found suitable for all the selected impurities. Hydrocarbons didn't present any challenges, they can be sampled on all the sorbents chosen in these studies with the exception of hexane on Odour/sulfur where this impurity showed some instability. 1-propanethiol dimerizes to dipropylsulfide both in cylinders at high pressure and on most of the sorbents, however to a lesser extent on Chromosorb 106. The best sorbent for methanol was found to be Tenax TA/CarboGraph 5 (which was the only sorbent that could be used to quantitatively analysed methanol). The studies were somewhat inconclusive for dimethylsulphide on Tenax TA; some results tend to show that it is stable, while in another case, some instability was observed. This could be due to differences in the analytical instruments for example, the material used in the cold trap or other settings.

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.

### 6.2 Gas cylinders

Cylinders and available surface passivation treatments have been reviewed as part of A3.1.2 and the summary of this information is presented in the table below. Note that this review is not intended for sampling but for the preparation of gas mixtures. The timeline is very different (stability needed for several years for reference gas mixtures and only days or weeks for sampling). However, the table can help in selecting an appropriate cylinder. A cylinder which is suitable for preparing a PRM is automatically suitable for sampling. A cylinder not suitable for preparing PRMs may be suitable for sampling in some cases (no initial losses, acceptable losses the first weeks).

Impurities are classified as:

- non-critical: no specific issues are expected, and many cylinders and most available treatments are expected to perform fine.
- critical: adsorption and/or stability issues expected
- very critical: reactive impurities

Table 1. Summary of candidate cylinders and treatments [6]

| component  | CCUS Specifications Summary (NPL) | Classification | Candidate cylinders and treatments  |
|--|-----------------------------------|----------------|---|
| water (H <sub>2</sub> O)   | ≤20-50 ppm                        | critical       | DB Gold Performance (Effectech): NPL has reported stability for 5 ppm water in hydrogen. NPL says cylinders report slightly high, but due to the hydrophobic nature of the treatment may be a “truer” value due to lower adsorption losses<br><br>Water was found to be stable at around 5 μmol/mol in hydrogen in SPECTRA-SEAL and SGS cylinders for a few months.   |
| Sum [H <sub>2</sub> +N <sub>2</sub> +Ar+CH <sub>4</sub> +CO+O <sub>2</sub> ] |                                   |                |   |
| H <sub>2</sub>   | ≤0.005-2%                         | non-critical   | Experiments performed on aluminium and steel cylinders demonstrate that the aluminium cylinders are significantly more robust against adsorption/desorption processes for CO <sub>2</sub> (≈400 ppm), CO (10-200 ppb), CH <sub>4</sub> (≈2 ppm), and H <sub>2</sub> O (1-30 ppm) than steel cylinders<br><br>Concentration changes of CO in aluminum cylinders from 0.1 to 0.5 % depending on time (0.1 % for 6 months, 0.3 % for 12 months, 0.4 for 18 months, 0.5 % for 24 months). Mixtures were prepared in concentration range from 100 ppm to 1000 ppm. |
| N <sub>2</sub>   | ≤1-4%                             | non-critical   |   |
| Ar   | ≤1-4%                             | non-critical   |   |
| CH <sub>4</sub>  | ≤1-4%                             | non-critical   |   |
| CO   | ≤0.01-0.2%                        | non-critical   |   |
| O <sub>2</sub>   | ≤10-20 ppm                        | very critical  |   |
| total sulfur-contained compounds (incl. mercaptan)                           | ≤20 ppm                           | very critical  |   |
| COS  | ≤20 ppm                           | very critical  | Stability of COS would be similar to that of H <sub>2</sub> S within the DB gold effectech cylinders  |
| DMS  | ≤20 ppm                           | very critical  | DMS PRMs are projected to be stable for 9~12 years in aluminum cylinders with Performax, Aculife, and Experis surface treatments while, without the special surface treatments, the stability varies from 1.5 years to 3.5 years.<br><br>KRISS has developed DMS standards in Al-Experis cylinders, The DMS in the Al-Experis cylinder was projected to be stable for more than 4 years within an uncertainty of 3%   |
| H <sub>2</sub> S   | ≤5-20 ppm                         | very critical  | DB Gold Performance (Effectech): NPL has tested multisulphur mixtures at 5ppb in hydrogen as part of MetroHyve II. Coating performed well.  |

|  |                               |               |   |
|--|-------------------------------|---------------|---|
|  |                               |               | IPQ uses cylinders with the special treatments Aculife III and IV and Megalife (Scott Specialty Gases).   |
| SO <sub>x</sub>  | ≤10-100 ppm                   | very critical | <p><i>Spectra-seal cylinders</i></p> <p>IPQ uses cylinders with the special treatments Aculife III and IV and Megalife (Scott Specialty Gases).</p> <p>Aluminum cylinders should be suitable for SO<sub>2</sub> according to review at the concentration from 9 to 100 ppm. Maximum change of the concentration 1 % in 24 month</p>   |
| Total NO <sub>x</sub>  | NO <sub>x</sub> : ≤10-100 ppm | very critical | <p>NO<sub>2</sub> in general is quite unstable instability will have little to do with the passivation treatment. NPL prepares NO<sub>2</sub> mixtures with an excess of oxygen to prevent instability, in Spectraseal coated cylinders, at 10ppm NPL can only guarantee about a year's stability</p> <p>Within framework of MetNO<sub>2</sub> project, NO<sub>2</sub> were prepared in Aluminum cylinders (sausage type) with a SilcoNert 2000 coating. <i>See table 2 below for other options</i></p> <p>IPQ uses cylinders with the special treatments Aculife III and IV and Megalife (Scott Specialty Gases).</p> <p>Concentration change of NO<sub>2</sub> in aluminum cylinders should be lower than 1 % at concentration 100 ppm.</p>   |
| Total aliphatic hydrocarbons (C2 to C10)   | ≤1.15-6%                      | non-critical  | aluminum cylinders internally passivated with either Spectraseal (BOC) or Experis (Air Products) treatments   |
| Total aromatic hydrocarbons (C6 to C10, incl. BTEX)  | ≤15 ppm                       | non-critical  | <p>Aluminum cylinders internally passivated with either Spectraseal (BOC) or Experis (Air Products) treatments</p> <p>NPL uses Experis coated cylinders (according to their experience, perform better than Spectraseal)</p> <p>NPL has tested DB Gold cylinders with a 30 component Ozone precursor mixture in nitrogen at 4 ppb. All were shown to be stable for a month. The components in the list were:</p> <p>ethane, ethene, propane, propene, i-butane, n-butane, ethyne, trans-2-butene, 1-butene, cis-2-butene, i-pentane, n-pentane, 1,3-butadiene, trans-2-pentene, 1-pentene, 2-methylpentane, n-hexane, isoprene, n-heptane, benzene, 2,2,4-trimethylpentane, n-octane, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene.</p> |
| Total volatile organic compounds (excl. methane, total aliphatic HC (C2 to C10), methanol, ethanol, and aldehydes) | ≤20-60 ppm                    | non-critical  | See above   |
| Total aldehyde compounds   |                               | critical      | Formaldehyde in nitrogen at nominal 2 ppm. Al-Acu-VIII cylinders appears to be suitable for use with formaldehyde in nitrogen   |

|   |                 |                       |   |
|---|-----------------|-----------------------|---|
|   |                 |                       | <p>mixtures, with a relative loss rate of &lt;1% yr<sup>-1</sup> or 1.2% a year, slow linear loss over 1 year (about 0.7% per month) in Luxfer (10L, SGS)</p> <p>10 ppm in N<sub>2</sub> in Spectraseal (10L, BOC): calculated decay rate of 1.6 ppb a day</p> <p>Experiments with Silconert 2000, Sulfinert and Performax showed with more than 80 % stability over 1 month at 1 μmol/mol formaldehyde in hydrogen</p>   |
| Ethanol                                   |                 | critical              | Ethanol tends to adsorb to cylinder inner wall<br>Based on CCQM-k93 report: Scott (Aculife IV) cylinders was mostly used for ethanol in nitrogen.   |
| Methanol                                  |                 | probably non-critical |   |
| Hydrogen cyanide (HCN)                    |                 | ?                     |   |
| Total amine compounds                     |                 | ?                     |   |
| Total glycol compounds                    | ≤0.08-10 ppm    | ?                     |   |
| Ammonia (NH <sub>3</sub> )                | ≤0.025-0.05 ppm | critical              | <p>10 ppm and 100 ppm NH<sub>3</sub> mixtures in nitrogen. No losses were observed with SilcoNert 2000 coated cylinders, relatively good performance for Spectraseal cylinders (BOC Linde) and cylinders from Takachiho.</p> <p>10 ppm in nitrogen was found stable in Aluminium SPectraseal (10 L, BOC), Aculife IV (Air Liquide), Takchiho, Stainless steel Silconert 2000 (1 L, Restek) for 12 month within 3% uncertainty</p> <p>Significant initial loss (&gt;50%) were observed for NH<sub>3</sub> at 0.2 ppm in hydrogen in Spectraseal (10 L, BOC) and Luxfer (10 L, SGS)</p> |
|   | ≤10-1500 ppm    |                       |   |
| Total carboxylic acid and amide compounds |                 | ?                     |   |
| Total phosphorus-contained compounds      |                 | ?                     |   |
| Ethylene (C <sub>2</sub> H <sub>4</sub> ) |                 | Non-critical          |   |
| Acid forming compounds                    | ≤10-70 ppm      | Very critical         |   |
| Nitrosamines and nitramines               |                 | ?                     |   |
| Dioxins and furans                        |                 | ?                     |   |

### 6.3 Sampling bags

To help selecting an appropriate sampling bag, stability studies have been conducted as part of the activity A3.2.3 of the MetCCUS project [7].

Table 2 below summarizes the outcomes of these studies for four different bags.

- Grey: no test done
- Green: suitability demonstrated at D30 at least
- Orange: Limited suitability but acceptable in some conditions (for example analysis before D10)
- Red: the bag is not suitable (immediate losses or quick decrease of concentration with time)
- Purple: test not conclusive

## Summary of material compatibility of bags

| Component         | Amount fraction (μmol/mol) | Restek Multifoil                               | Restek Altef                              | Calibrated Instruments Inc Cali5Bond | Airborne Labs True Blue 2LT                    |
|-------------------|----------------------------|--|---|--------------------------------------|--|
| Methanol          | 4-8                        | Stable at least 30 days (loss < 20% after D50) | Concentration decreases quickly with time | 25-35% loss D1, then stable          | Concentration decreases with time              |
|                   | 10-15                      | Stable at least 30 days (loss < 20% after D50) | Concentration decreases quickly with time | 25-35% loss D1, then stable          | Concentration decreases with time              |
| Acetaldehyde      | 0.5                        | Stable at least D30                            |   |                                      | More than 20% loss D30                         |
|                   | 1                          | Stable at least D30                            |   |                                      | 15% loss D30                                   |
|                   | 4-8                        | Stable at least D30                            |   |                                      |  |
|                   | 10-15                      | Stable at least D30                            |   |                                      |  |
| Ethanol           | 4-8                        | 20-25% loss D50. Analysis before D10           | Concentration decreases quickly with time | 35% loss D4, then stable             | 20-25% loss D50. Analysis before D10           |
|                   | 10-15                      | 20-25% loss D50. Analysis before D10           |   | 35% loss D4, then stable             |  |
| Acetone           | 4-8                        | Max 15% loss D50                               | Concentration decreases quickly with time | Stable at least D7                   | Max 15% loss D50                               |
|                   | 10-20                      | Max 15% loss D50                               |   | Stable at least D7                   | Max 15% loss D50                               |
| Benzene           | 0.3 – 2                    | Not compatible as benzene adsorbs on the walls | Stable at least D4                        |                                      | Stable at least D20 but recovery at D0 unknown |
|                   | 7                          | Not compatible as benzene adsorbs on the walls |   |                                      |  |
| Hydrogen sulphide | Ca 2                       |  |   | 100% loss D30. Analysis before D5    |  |
|                   | Ca 10                      |  |   | 50% loss D30. Analysis before D5     |  |
|                   | Ca 20                      |  |   | 35% loss D30. Analysis before D5     |  |
|                   | Ca 40                      |  |   | 20% loss D30                         |  |
|                   | Ca 60                      |  |   | 15% loss D30                         |  |
|                   | Ca 100                     |  |   | Less than 10% loss D30               |  |

## 7 Preparation of the sampling vessels prior sampling

Any vessel used for sampling needs to be prepared before sampling:

- 1) Sorbent tubes must be cleaned by conditioning at relevant temperatures (different depending on the sorbent material) and stored at (typically) -4°C before utilization
- 2) Gas bags are usually only used one time, but they need to be cleaned from impurities that may have diffused in the bag while on a shelf. The bags should be flushed three times with an inert gas
- 3) Cylinders are usually used several times and may contain some traces from the previous sampling. Before the sampling (before traveling to the CO<sub>2</sub> site): flush the vessel several times with (ultra) clear gases such as e.g. N<sub>2</sub> (6.0) or Ar (6.0). One of the possible approaches can be as a “filling” and “pumping” loop for the vessel with clean gases. Pre-filling by very ultra-clean gases, e.g. Ar(6.0), before traveling to the site is also recommended. On-site vessel pressurizing -depressurizing steps can be performed several times

## 8 Step-by-step procedures for sampling

- 1) For offline sampling

Select the adequate vessels for each impurity to analyse

Prepare the documentation for the transportation of the sampling vessels back to the laboratory beforehand (to reduce the time between sampling and analysis). Sampling of liquid CO<sub>2</sub> require special handling

Prepare the sampling vessels prior sampling (see section 7)

Check compatibility between sampling point conditions and sampling vessels

If necessary, condition the gas at the sampling point (regarding temperature, pressure and flow)

Use most cost-effective chemically inert materials for sampling line such as e.g. high-grade PTFE tubing (e.g. a Ø6 mm PTFE FDA-approved tubing can be used between -60 °C till +250 °C and up 84 bar (burst pressure) operation conditions).

Flush the sampling line with the gas to avoid ingress of air in the sampling vessels

Fill the sampling vessels

- 2) For online analysers

Check compatibility between sampling point conditions and the analysers

If possible, evaluate the analyzer’s response time beforehand (response time depends on the conditions, for example pressure, temperature and flow rate) but also on the property of the compound to be analysed

If necessary, condition the gas at the sampling point (regarding temperature, pressure and flow)



Use most cost-effective chemically inert materials for sampling line such as e.g. high-grade PTEF tubing (e.g. a  $\varnothing 6$  mm PTEF FDA-approved tubing can be used between  $-60$  °C till  $+250$  °C and up 84 bar (burst pressure) operation conditions). The sampling is preferably as short as possible. For practical examples, see the results from activity A3.2.4 of the MetCCUS project.

Flush the sampling line with the gas to sample to avoid ingress of air in the sampling vessels (if necessary)

## 9 Conclusions

This report is a good practice guide intended to support the laboratories and industrials in charge of performing sampling for analysis of CO<sub>2</sub> samples in the CCUS field both onsite and offsite. The conditions at the sampling point must be known and eventual challenges due to the conditions must be solved before sampling by adding the necessary components to the sampling line. The guide also discusses material compatibility for sampling lines (relevant to both online and offline analytical methods) and sampling vessels (specifically relevant to offline methods) which is critical to keep the integrity of the sample. Example of material for vessels are shown both for sampling bags and sorbent tubes. Based on the outcomes of the stability studies, it is very improbable that one vessel will be adequate to store all impurities long enough to account for the time between the sampling and the analysis (mostly transport time but also if lead time due to instruments malfunction once the sample is in the laboratory). The sampling plan must include a selection of proper vessels. Step-by-step procedures for sampling is given at the end of the good practice guide.

Numerous challenges still need to be solved in order to ensure that the integrity of the sample is kept until analysis is performed. More stability tests are needed to guide in the selection of vessels. These tests must also take into account the fact that several impurities may be present simultaneously in the gas and possibly at different levels of concentration.

## 10 References

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