21GRD06 MetCCUS

Report A3.2.3: Experiments to test the sampling of impurities, against material, for key impurities and materials

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METROLOGY PARTNERSHIP | EURAMET

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Summary

This report was written as part of activity A3.2.3 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 present the results of storage stability studies performed in four different sampling bags for methanol, ethanol, acetaldehyde, acetone, benzene, and hydrogen sulphide at different amount fractions in CO_2 for a storage period of up to 50 days. The results of these investigations are compiled in a material compatibility table to assist industry/laboratories in selecting suitable materials for sampling bags.

Contents

1 Introduction

Due to the production methods or the origin of the carbon dioxide (CO2), it usually contains species in traces that can have a negative impact on the equipment they come into contact with. Several standards contain requirements for CO2 quality assessment for different applications. For example,
ISO27913:2016 [1] specifies additional requirements and recommendations not covered on existing pipeline standards for the transportation of CO_2 streams from the capture site to the storage facility where it is primarily stored in a geological formation or used for other purposes (e.g. EOR or CO_2 use). EN936:2013 [2] prepared by the technical committee CEN/TC164 "water supply" is applicable to carbon dioxide used for treatment of water intended for human consumption. Document 70-17 [3] from EIGA describes the specification requirements (Table 12) for liquid carbon dioxide in bulk production tanks or intermediate storage tanks at the gas supplier's depots for use in foods and beverages and is applicable to carbon dioxide used in beverage or in food when carbon dioxide is in direct contact with food or with beverage such as an ingredient or additive.These standards often require analysis in a laboratory and therefore require the collection and transport of a gas sample from the point of use. The sample taken must be **representative** of the gas supplied; this assumes that no compounds are added to or removed from the gas during sampling.

The main challenge is for species at trace levels for which the risk of loss of contaminants in the 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)

Other challenges arise from the need for flow measurement specifically for the enrichment methods, the exact composition of which may not be known until it has been fully analyzed in a laboratory.

For sampling, different types of vessels exist, e.g., gas cylinders, canisters, sampling bags, impingers or sorbent tubes.

Before choosing a vessel, some considerations must be taken into account:

1) The conditions at the sampling point must fit the requirement for the vessels and for example, if the pressure at the sampling point is low (less than 1 bar), it would be difficult to fill a cylinder. If the pressure is high (>3 bar), a reduction is needed for sorbents, impingers and bags. Bags and sorbent tubes have maximal operating temperature range. Gas permeability (mostly for bags) may compromise the sample by addition of some amount fraction of components which may permeate through the vessel (mostly O_2, H_2O and CO_2).

2) The requirement for the vessels must fit the conditions of the analytical instruments. Enough volume sampled to perform all analyses (all replicates) and serve all instruments, enough pressure if needed by the instruments which implies that pressure from the vessels may need to be reduced.

2 Material compatibility

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 [4].

The same considerations apply to all parts of the sampling line and especially to those parts where pressure reduction takes place.

Material compatibility issues are often not well demonstrated experimentally [5], so it is of great importance to increase the knowledge of adsorption effects of relevant species on different materials under relevant conditions (matrix, pressure, concentration). Therefore, there is a need for systematic recovery experiments and short-term stabilities at defined and relevant conditions in terms of pressure, matrix and concentration. The results of these investigations should be compiled in material compatibility tables to assist industry in selecting suitable materials for vessels and sampling lines.

3 Selection of vessels

For cylinders, new information will be obtained as the results of the activities performed in task 3.1. In this task, 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 [6] during the Decarb project already give a good overview about the suitability of these vessels for organic impurities to be analysed in CO_2 streams.

Finally, for sampling bags, only little information is available and new tests are needed in order to assess the suitability of different sampling bags for different impurities relevant for CO_2. To fill the gaps in knowledge of material compatibility, RISE performed 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.

Four different bags were selected based on previous experiences (mostly from previous biogas and biomethane projects) and on the literature review performed in the activity A3.2.1.

Cali5Bond bags from Calibrated Instruments inc. are multi-layer foil sampling bags used at RISE for biogas and biomethane sampling with regards to the main components (methane, carbon dioxide, oxygen and nitrogen but also ammonia and hydrogen sulphide.

Altef bags from Restek Inc. made of polyvinylidene fluoride (PVDF) film is an alternative to Tedlar recommended by the provider for VOCs. From the same provider, multi-layer foil sampling bags are

recommended for permanent gases. These two types of bags have been used at RISE for biogas and biomethane sampling.

Airborne Labs International Inc (ALI) [7] has developed sampling equipment specifically for beverage grade CO_2 (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.

4 Selection of components

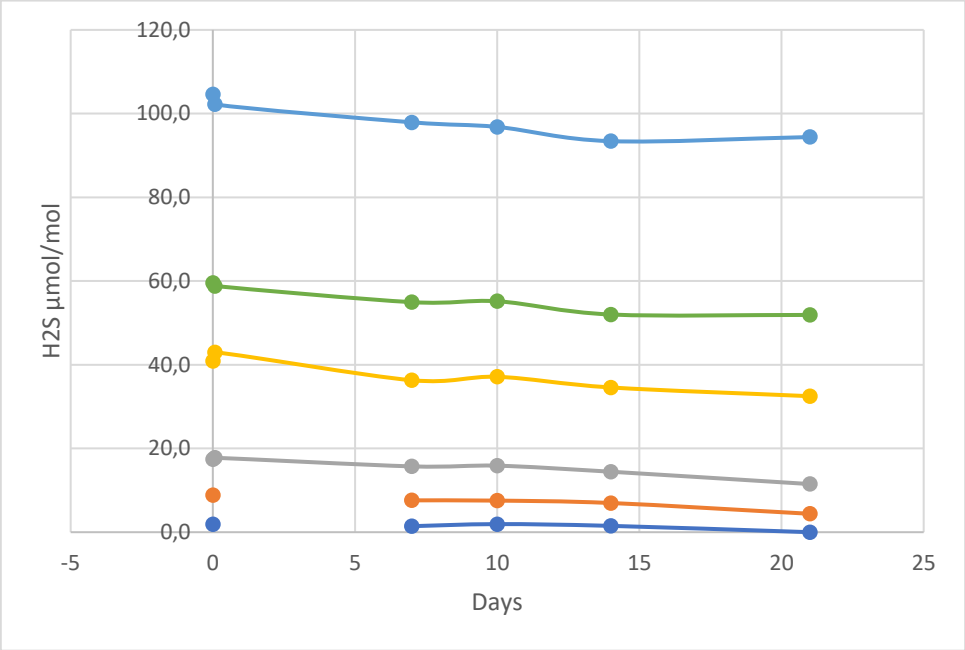
The components studied in this activity were chosen based on discussion with the Swedish industry (many plants require analysis according to EIGA doc 70/17 [8]) and included hydrogen sulphide, methanol, ethanol, acetaldehyde, acetone and benzene. Amount fractions for each component were selected based on the specification requirements for CO2 purity stated in e.g. EIGA doc 70/17.

5 Results

5.1 Hydrogen sulphide

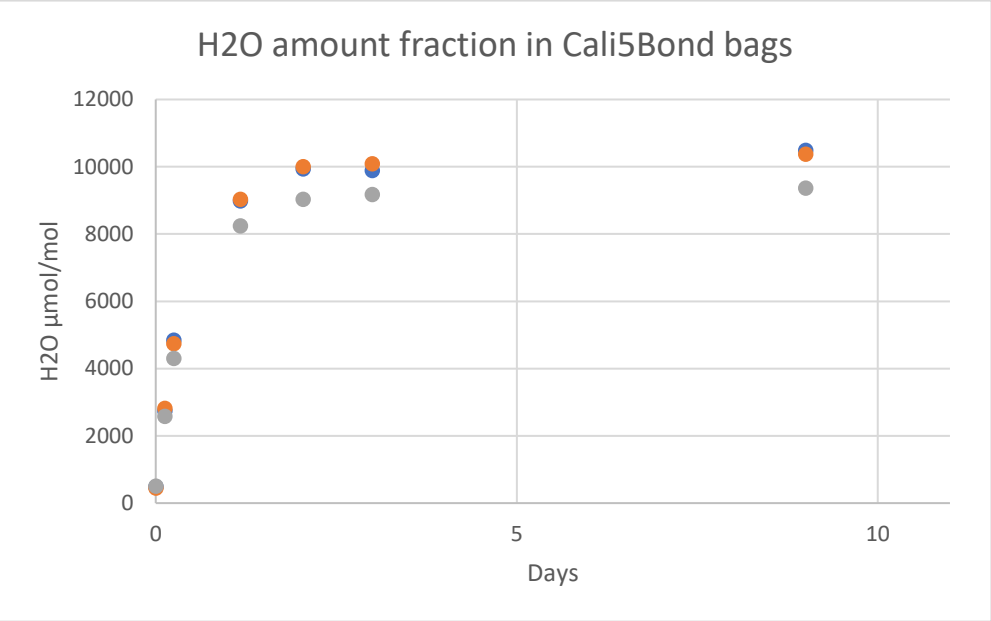
The stability of hydrogen sulphide amount fractions in carbon dioxide was tested in only one type of bags: Cali5Bond bags. Six different amount fractions were produced, from 2 to 100 µmol/mol. The results of the stability studies are presented in Figure 1.

Figure 1. Storage stability of hydrogen sulphide in CO_2 at amount fractions from 2 to 100 µmol/mol, duration 21 days



All amount fractions of H2S showed a slow decrease of response with time when stored in Cali5Bond bags. The decrease is depending on the amount fractions, more pronounced at low concentration (D21 loss of 100% at 2 µmol/mol and of 10% at 100 µmol/mol). It was observed that water from air quickly permeated through the walls of the bag as it can be seen in Figure 2 (less than 500 µmol/mol at the beginning of the study, around 2500 µmol/mol after 3 hours storage and quick increase up to around 10000 µmol/mol. Note that the amount fraction of water in ambient air during the duration of the stability tests was around 11000 µmol/mol). Oxygen only permeated to a limited extend (ca 300 µmol/mol of oxygen at the end of the test period).

Figure 2. Water amount fractions in three different Cali5Bond bags measured during the stability studies for H2S in CO_2



5.2 Methanol

The stability of methanol amount fractions in carbon dioxide was tested in all four types of bags. Several different amount fractions were produced, from 3 to 25 µmol/mol. The results of the stability studies are presented in Figure 3 for Altef bags, Figure 4 for Cali5Bond bags and Figure 5 for True Blue and Multifoil bags.

Figure 3. Storage stability of methanol in CO_2 (amount fractions: 9 µmol/mol) in Altef bags

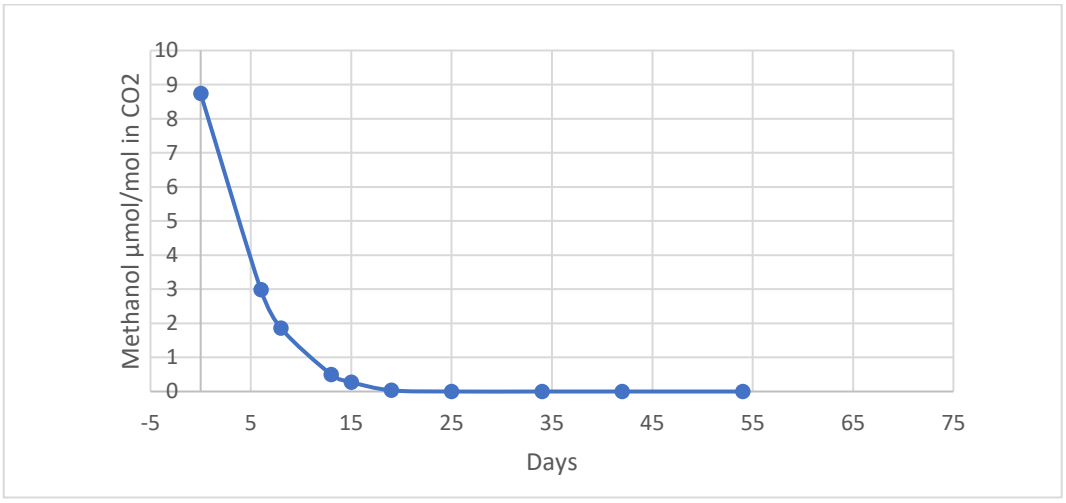


Figure 4. Storage stability of methanol in CO2 (amount fractions from 3 to 25 µmol/mol) in Cali5Bond bags

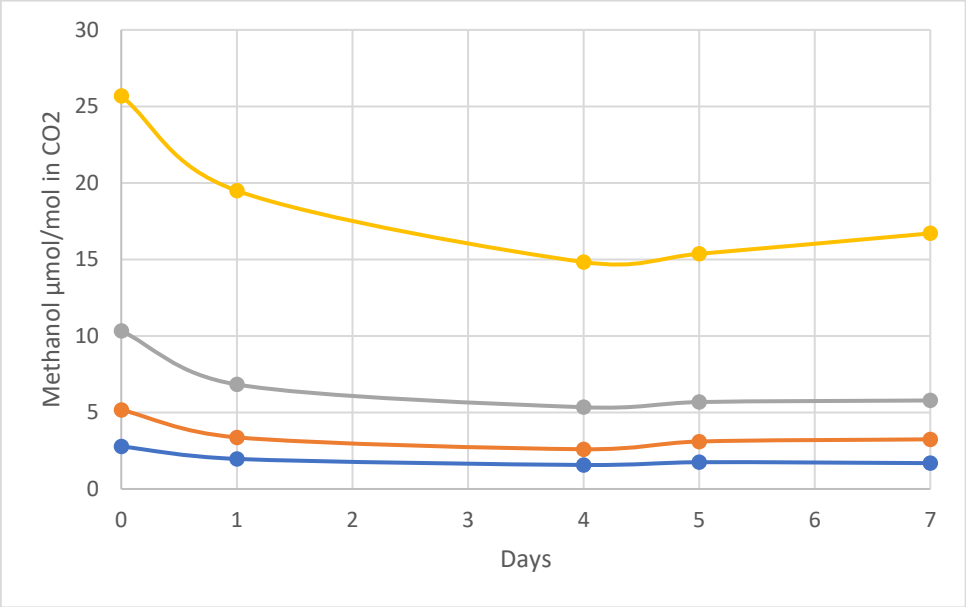
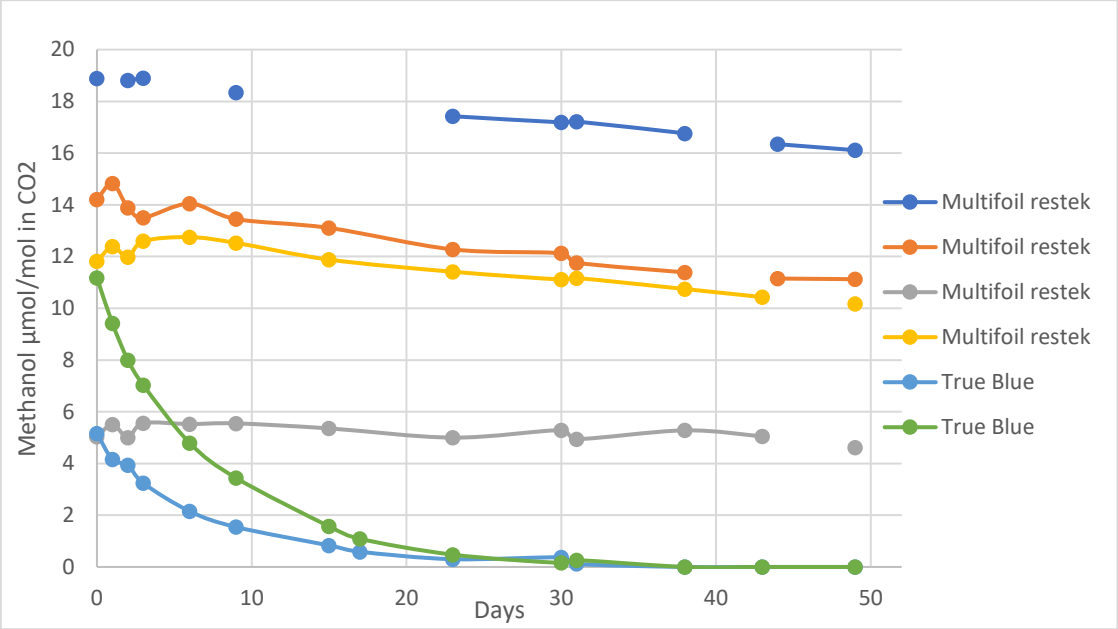


Figure 5. Storage stability of methanol in CO_2 (amount fractions from 5 to 18 µmol/mol) in True Blue and Multifoil bags

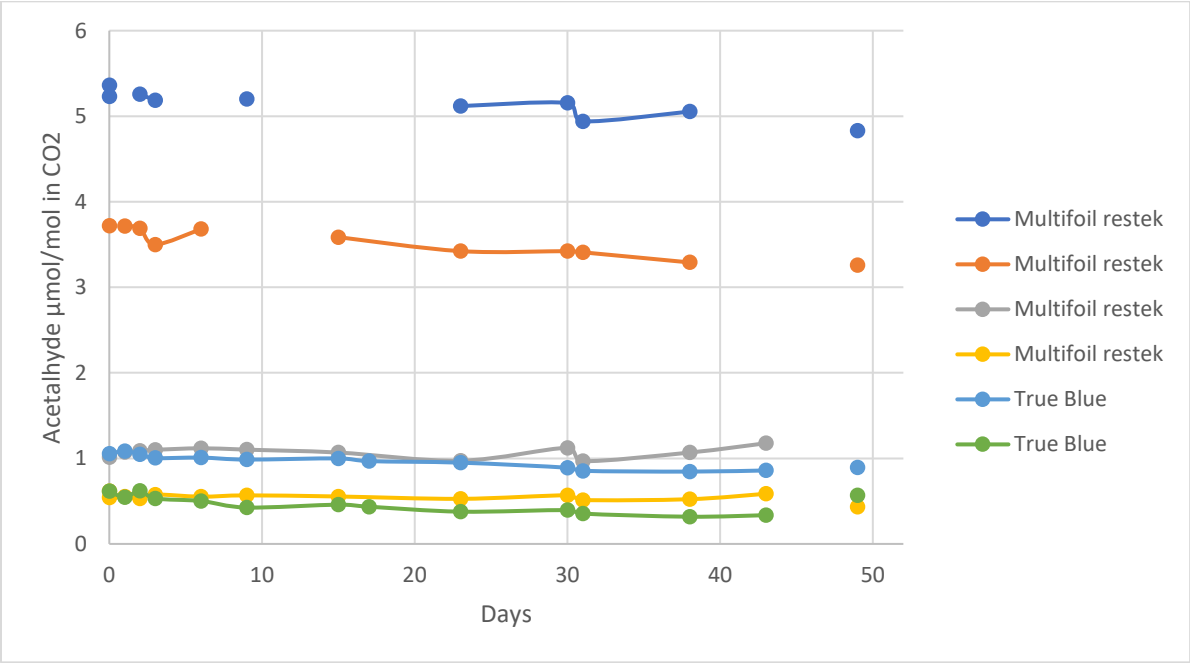


Low amount fractions of methanol in CO2 are not stable in either Altef or True Blue bags. Methanol showed a decrease of response with time when stored inCali5Bond bags, with a pronounced drop during the first days of storage and a more stable trend during the rest of the test duration. The best results were obtained when low amount fraction of methanol in CO2 were stored in Multifoil bags even if a slight decrease of concentration is 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.

5.3 Acetaldehyde

The stability of acetaldehyde amount fractions in carbon dioxide was tested in True Blue and Multifoil bags. Different amount fractions were produced, from 0.5 to 5 µmol/mol. The results of the stability studies are presented in Figure 6.

Figure 6. Storage stability of acetaldehyde in CO_2 (amount fractions from 0.5 to 5 µmol/mol) in True Blue and Multifoil bags



All amount fractions of acetaldehyde tested here are stable in Multifoil and True Blue bags even if the concentrations slightly decreased during the test period (the decrease is less than 10% of D0 concentration after 10 days of storage).

5.4 Ethanol

The stability of ethanol amount fractions in carbon dioxide was tested in all four types of bags. Different amount fractions were produced, from 3 to 25 µmol/mol. The results of the stability studies are presented in Figure 7 for Altef bags, Figure 8 for Cali5Bond bags and Figure 9 for True Blue and Multifoil bags.

Figure 7. Storage stability of ethanol in CO_2 (amount fractions 7 µmol/mol) in Altef bags

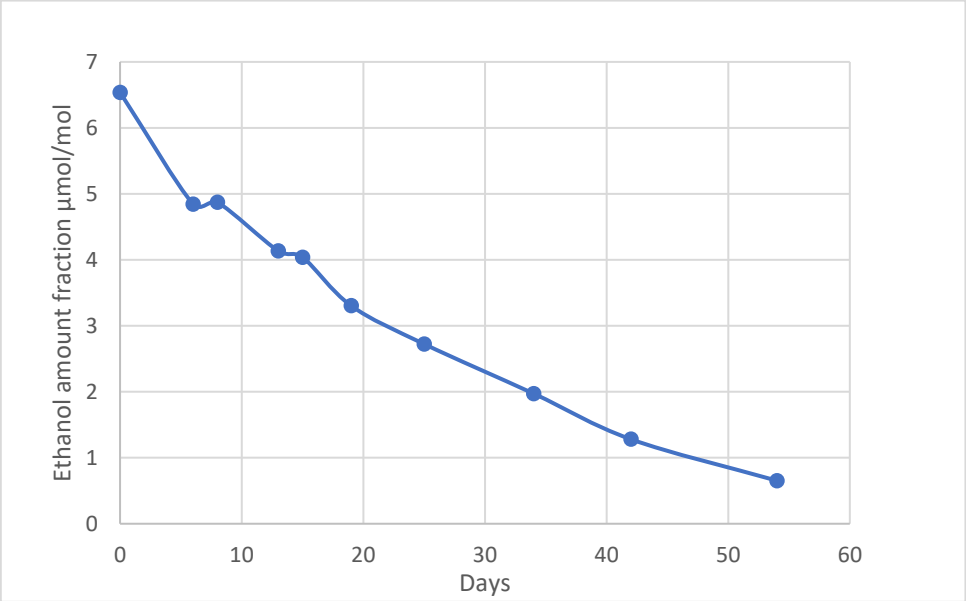


Figure 8. Storage stability of ethanol in CO_2 (amount fractions from 3 to 25 µmol/mol) in Cali5Bond bags

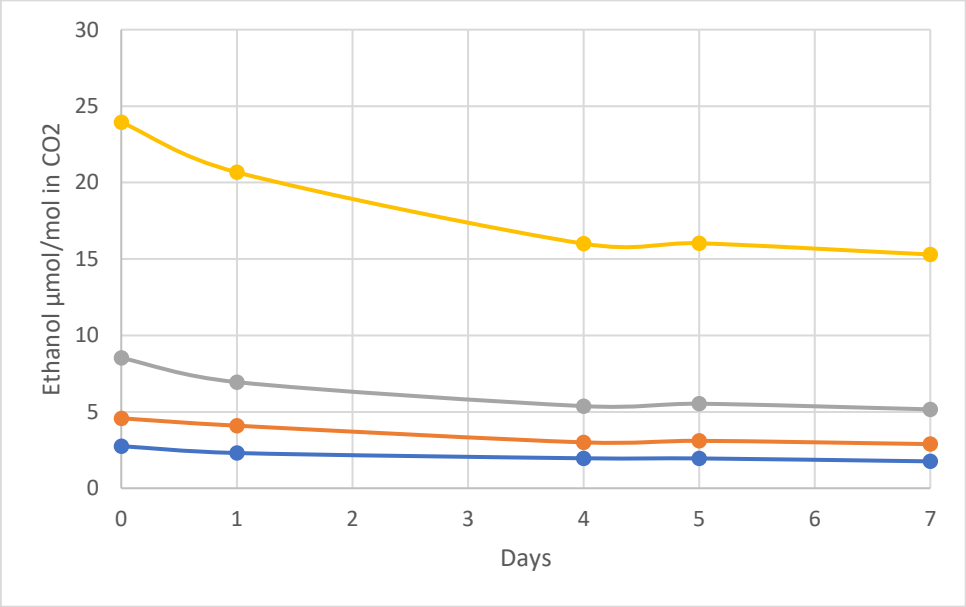
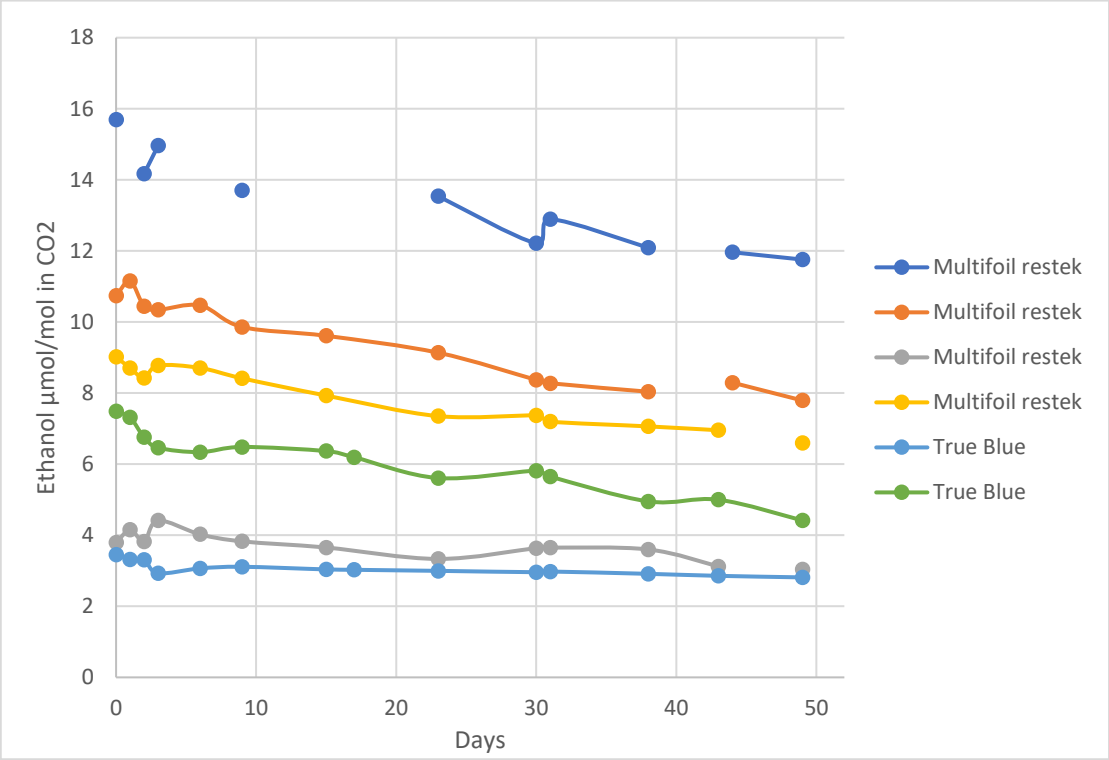


Figure 9. Storage stability of ethanol in CO_2 (amount fractions from 3 to 25 µmol/mol) in Multifoil and True Blue bags



Low amount fractions of ethanol in CO_2 are not stable in Altef bags. Ethanol 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

All amount fractions of ethanol tested here decreased slowly in Multifoil bags and in True Blue bags. The decrease is less than 10% of D0 concentration after 10 days of storage so these bags can be suitable if the analysis is done no less than 10 days after the sampling.

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5.5 Acetone

The stability of acetone amount fractions in carbon dioxide was tested in all four types of bags. Different amount fractions were produced, from 3 to 55 µmol/mol. The results of the stability studies are presented in Figure 10 for Altef bags, Figure 11 for Cali5Bond bags and Figure 12 for True Blue and Multifoil bags.

Figure 10. Storage stability of acetone in CO_2 (amount fractions 5 µmol/mol) in Altef bags

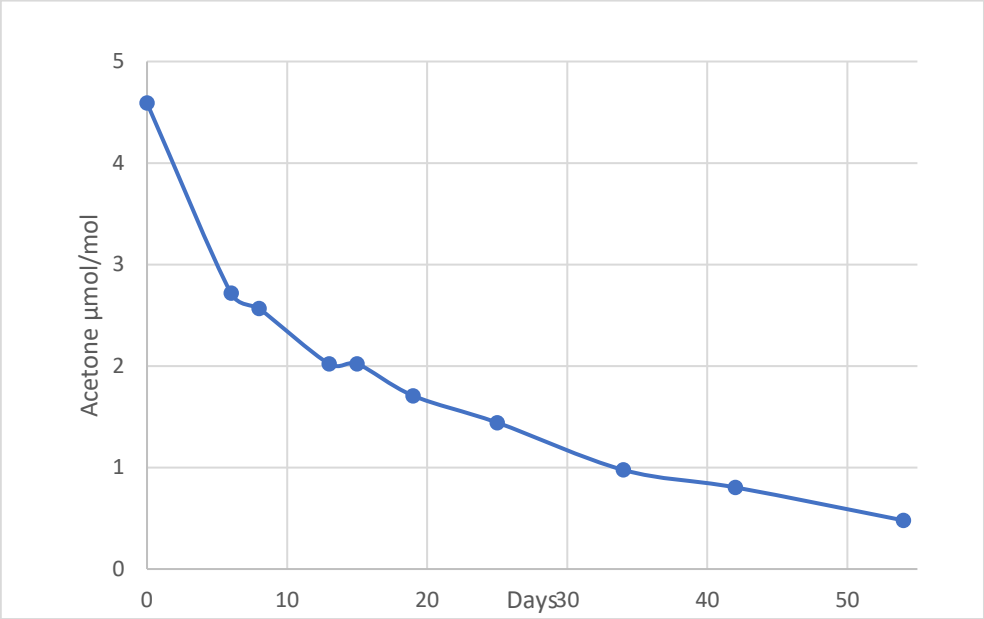


Figure 11. Storage stability of acetone in CO_2 (amount fractions from 3 to 25 µmol/mol) in Cali5Bond bags

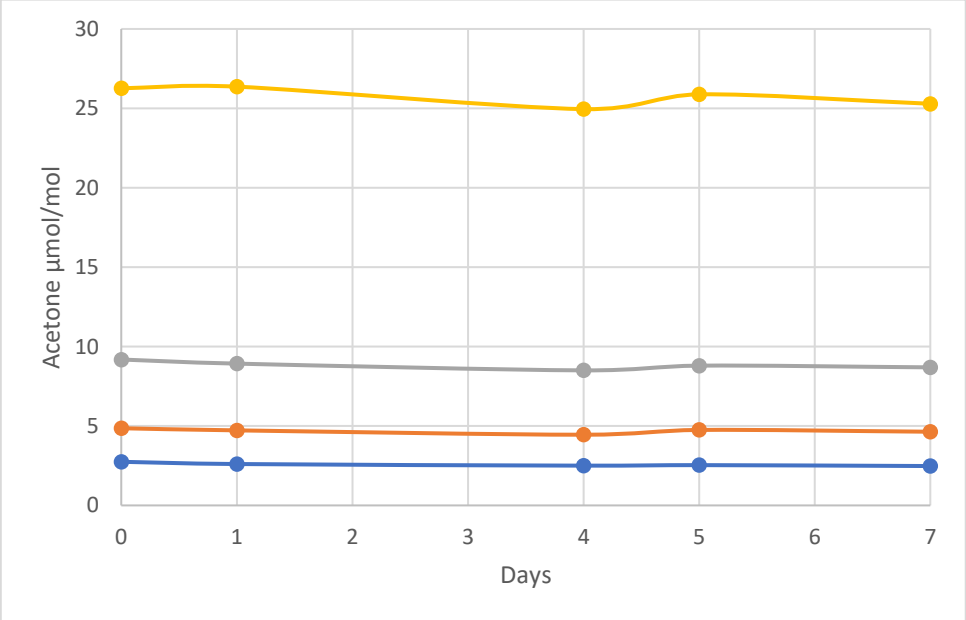
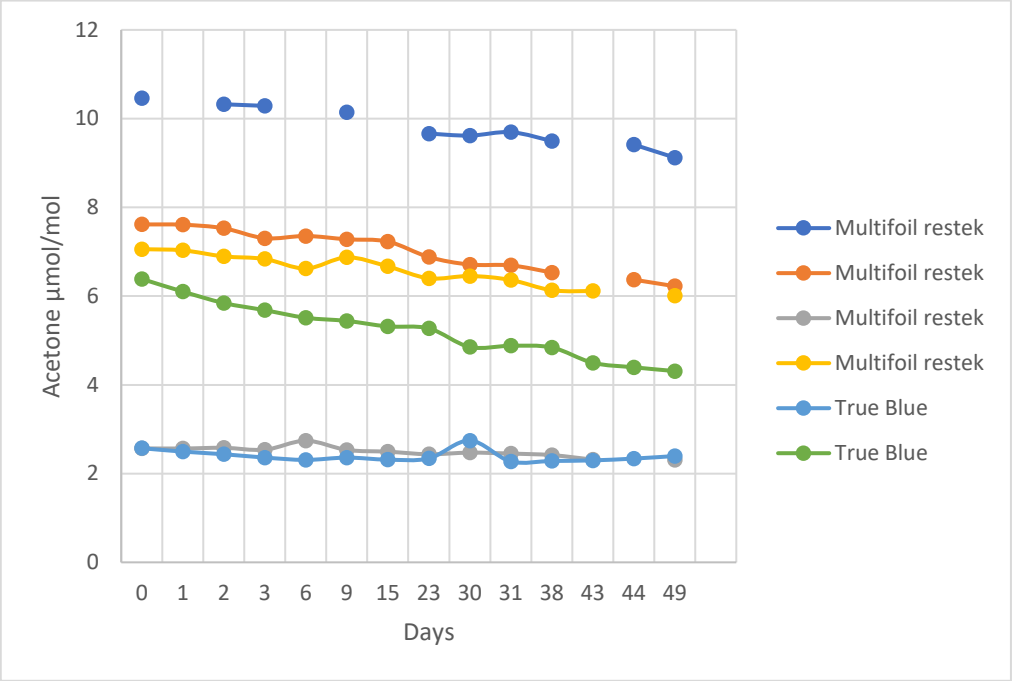


Figure 12. Storage stability of acetone in CO_2 (amount fractions from 3 to 10 µmol/mol) in Multifoil and True Blue bags

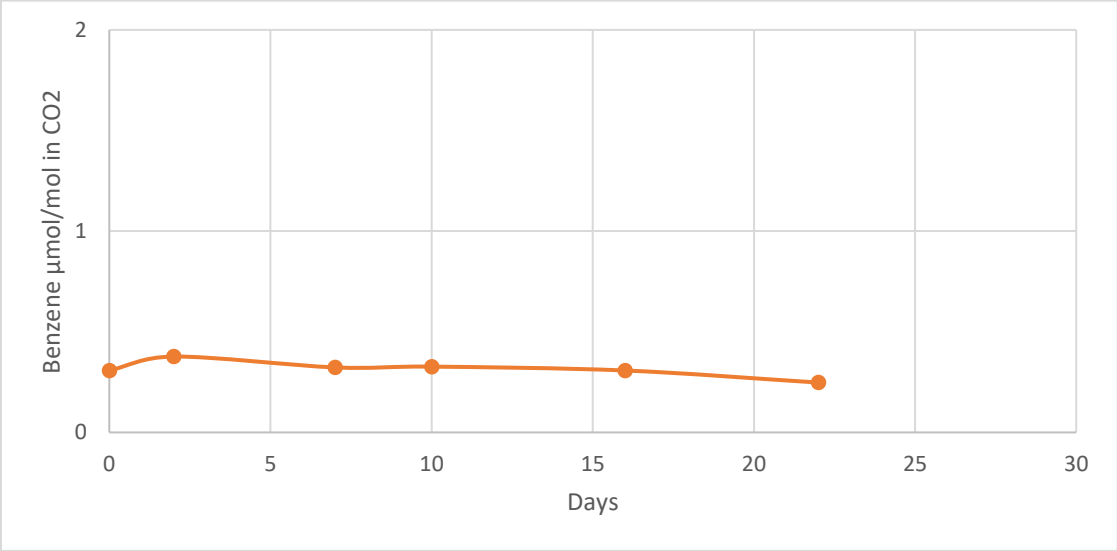


Low amount fractions of acetone in CO_2 are not stable in Altef bags. Amount fractions of acetone tested here are stable in Cali5Bond bags, Multifoil bags and True Blue even if the concentrations slightly decreased during the test period (the decrease is less than 10-15% of D0 concentration after 50 days of storage).

5.6 Benzene

Low amount of benzene could not be sampled nor stored in Multifoil bags as the concentration decreased directly probably through adsorption on the walls of the bags (tests done at different concentrations from 0.3 to 15 µmol/mol).
The same conclusion could be drawn for Cali5Bond bags but tests showing this trend were done at much higher concentration (ca 80 µmol/mol).
A stability test at 0.5 µmol/mol benzene in CO_2 in a Altef bag showed that the concentration remained stable for four days but due to problem with the instrument, the test was interrupted.
The stability of benzene amount fractions in carbon dioxide was tested in a True Blue bag at around 0.3-0.5 µmol/mol. The results of the stability studies are presented in Figure 13. However, this concentration was prepared by dilution of another gas and the concentration in the diluted bag is not accurately known so this test does not allow to conclude about the suitability of the True Blue bag at D0 for benzene.

Figure 13. Storage stability of bezene in CO_2 (amount fractions ca 0.3 µmol/mol) in a True Blue bag



The results of the tests performed are summarised in Table 1 and a conclusion about the suitability of the bag is given by using color codes together with comments:

- 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

6 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	

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7 Conclusions

Material compatibility issues are an important factor affecting the sampling of gases for purity analysis. In this project, we performed storage stability studies on four different sampling bags for methanol, ethanol, acetaldehyde, acetone, benzene, and hydrogen sulphide at different amount fractions in CO_2 for a storage period of up to 50 days.

The results clearly demonstrated that it is of great importance to increase the knowledge of adsorption effects of relevant species on different materials under relevant conditions (matrix, pressure, concentration) and confirmed that it is unlikely that one bag can be used for all impurities. The influence of concentration was demonstrated in only one case, for hydrogen sulphide.

The results of these investigations are compiled in a material compatibility table to assist industry in selecting suitable materials for sampling bags.
One bag performed clearly better than the three other options: Restek Multifoil which was found suitable for methanol, acetaldehyde, ethanol (limited suitability) and acetone but not for benzene. True Blue bags performed also well except for methanol.

8 References

[1] *ISO27913:2016 Carbon dioxide capture, transportation and geological storage — Pipeline transportation systems*, International Organization for Standardization, Geneva, Switzerland, 2016.

[2] *EN936:2013 Chemicals used for treatment of water intended for human consumption*, ,, Brussels, Belgium: European Committee on Standardization, 2013.

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