21GRD06 MetCCUS

Literature survey on the influence of temperature, pressure, material, tubing length and of the specifications that are used for the sampling lines in the online measurement of the key impurities in CO2

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Lead partner: **DTU**

Other partners: VTT, Air Liquide, DNV

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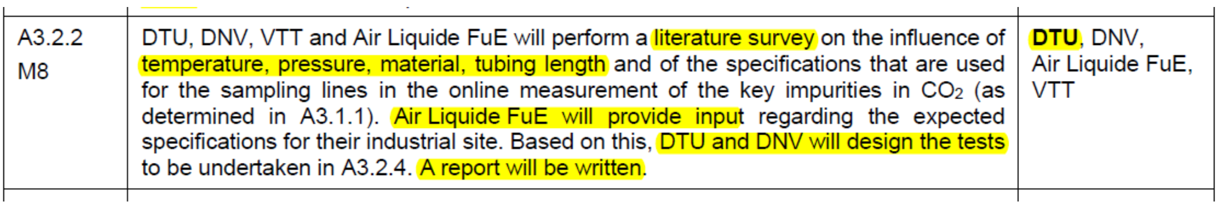

A3.2.2 M8	DTU, DNV, VTT and Air Liquide FuE will perform a literature survey on the influence of temperature, pressure, material, tubing length and of the specifications that are used for the sampling lines in the online measurement of the key impurities in CO_2 (as determined in A3.1.1). Air Liquide FuE will provide input regarding the expected specifications for their industrial site. Based on this, DTU and DNV will design the tests to be undertaken in A3.2.4. A report will be written.	**DTU**, DNV, Air Liquide FuE, VTT

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Contents

Summary

The Report has focus on CO2 sampling from high-pressure CO2 sources such as e.g. pipelines and gas cylinders. Influence of CO2 pressure, temperature, gas composition and sampling approach onto (impurities) measurements in CO2 is discussed. A role of coatings for impurities measurements has been described. A new sampling approach has been suggested for accurate impurities measurements in CO2 in high-pressure gas phase.

Introduction

CCUS is an old and new topic at the same time. Much research, developments and demonstrations have early been done regarding CO2 capture and storage from (oxyfuel) combustion processes where a cheap and affordable fuel like coal were frequently used. At that time the major focus was placed on industrial demonstrations about how various CO2 capture steps can be link in and implemented to reach a high CO2 capture efficiency. Various standard industrial analysers designed and made for flue gas measurements have been used in the process and product control and not much attention has been paid to discriminate differences between differences in the gas matrixes. Nowadays it is clear that various impurities in CCUS process chain can have various impacts on materials and quality (or purity) of the captured CO2. Impurities set varies from a CO2 capture and cleaning process in question and therefore it is important to have an unified approach for on-line gas analysis related to CCUS applications. The Report presents a literature review of specifications required for gas sampling lines used in the on-line measurements of key impurities in CO2.

At the present, based on the feedback from the project stakeholders and industrial partners, impurities measurements in CO2 are mainly of the interest in CO2 product streams where purity of the CO2 is about 95%.

For CO2 transportation in a pipeline (or by a transport) the CO2 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 [1] and temperature 5 -35°C [2]. A CO2 phase diagram is shown in Fig.1. Above 7.4 MPa CO2 exists as a single danse phase over a wide range of temperatures. The Fig. 1 shows also a typical p/T point for pipeline inlet and Fig. 2 shows visual pictures of CO2 in various physical sates.

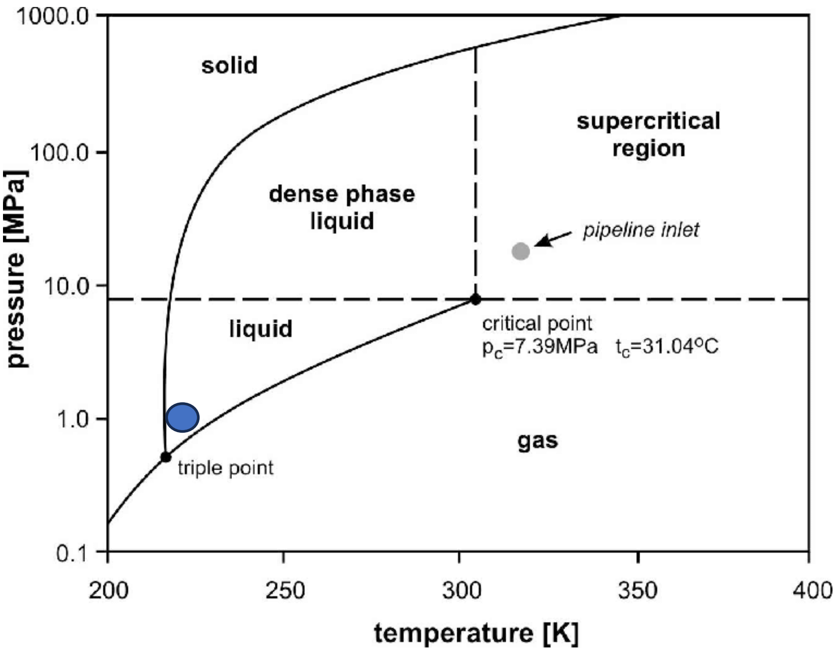


Figure 1: Phase diagram of CO2. Typical shipping range is giving by a blue oval in the triple point corner (10 bar/- 50°C).

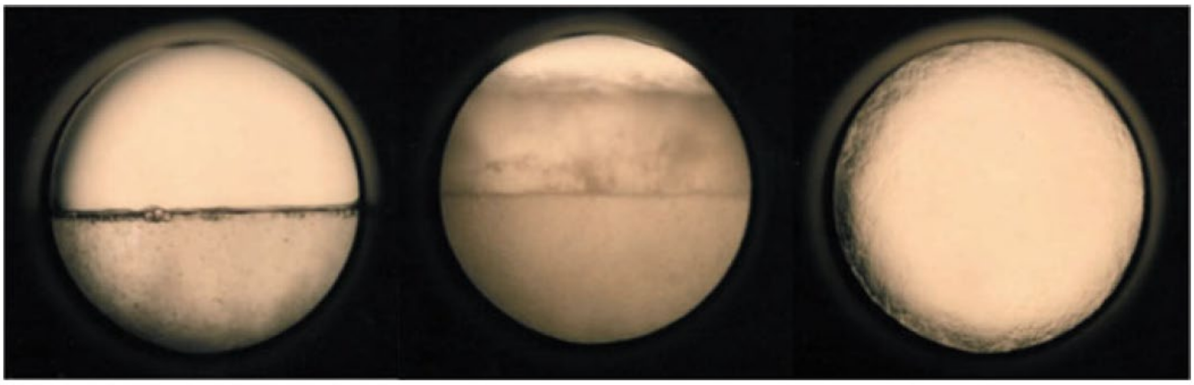


Figure 2: CO2 photographs: two-phase state liquid-gas system (left); meniscus less well-defined (middle) and homogeneous supercritical fluid (right) [3].

To our knowledge there are no yet commercial analysers for on-line analysis of CO2 impurities at such high pressures. Therefore, the CO2 should be taken out from an access point (pipe or gas storage) at transferred to an analyser in a *gaseous* form. There is a limited information about CO2 as a super-critical liquid/gas from physical and chemical points of view. Moreover, a behaviour of typical gas fittings such as valves, pressure regulators etc. is not well known/documented at these conditions. Therefore, any “transient” CO2 states should be avoided in regard to impurities analysis.

Impurities

Outcomes of the Task 3.1 activities led to a compilation of impurities most of interest for captured and cleaned CO2 (product gas), Table 1.

Table 1: Identified key impurities in CO2 and their upper concentration range.

Component	Amount fraction
Water (H2O)	≤ 50 ppm
Hydrogen (H2)	≤ 0.75 %
total sulphur-contained compounds (incl. mercaptans)	≤ 20 ppm
Hydrogen sulfide (H2S)	≤ 10 ppm
Sulphur oxide (SOx)	≤ 20 ppm
Total Nitrogen oxides (NOx =NO2+NO)	≤ 10 ppm
Total amine compounds (MEA)	≤ 1 ppm
Total glycol compounds (MEG/TEG)	≤ 0.025-0.5 ppm
Ammonia (NH3)	≤ 50 ppm

As one can see from the Table 1, there are several gas components known by their high reactivity (e.g. SOx, NOx, H2S and NH3). They are typically founded in relatively high concentrations. Among those, H2O is expected to be below 50 ppm. SO2, NO2 and H2O can cause at certain conditions acid formation (HNO3 and H2SO4) and H2S in a reaction with NO2 can be a source of additional H2O, SO2 and NO. However, this reaction is quite slow and may take hours to generate products (SO2, H2O and NO). In stagnated CO2 flows one can expect slow time variations in impurities concentrations which may indicate on other by-products formation. Therefore, it is necessary to do dynamic measurements for those five components at the same time.

Gas Sampling

General sampling concept

A generic on-line gas measurement method consists of an analyser connected through an interface to a gas sampling point, Fig. 3.

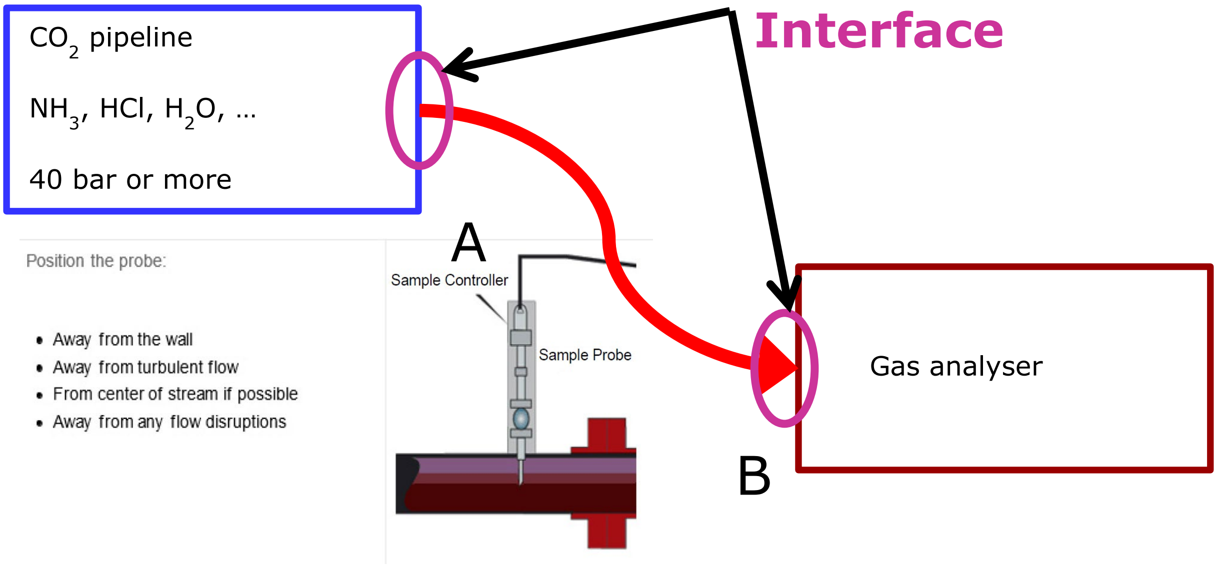


Figure 3: A generic on-line gas measurements method. The interface connects the analyser entrance point “B” to a “A” access point (port) on a CO2 gas line (storage).

The interface (gas sampling line) can be a polymer-based or SS steel tubes and can optionally be heated to the same temperature as a measurement volume in the gas analyser (e.g. a gas cell). The interface should, as much as possible, be inert to the sampled impurities in order to minimize their potential losses during “A” to “B” transport (e.g. during gas adsorption or chemical reactions on the walls of the sampling line.

The interface at the point “A” ends with a sampling probe which in its simplest realization might be a piece of a rugged (SS) tube (i.e. not influenced by any flow pattern changes). The end of the tube should have a cut at 45° angle facing downstream. This orientation reduces probability of line blocking by solid particles or liquid droplets.

The probe should be positioned:

- away from walls
- away from turbulent flows
- in the middle of the stream
- away from flow disruptions

CO2 throttling

CO2 is quite different compared to other commonly used gases such as Ar, N2 or O2: it has a large Joule-Thomson effect. The effect is caused by cooling of the gas when the gas is forced through a porous medium or an orifice (e.g. through a valve). Gas passing is called a throttling. Among other gases hydrogen, helium and neon has a minimum cooling because of throttling, while the CO2 has some of the largest.

Calculated pressure vs. enthalpy diagram for CO2 is shown in Fig. 4. Throttling is characterized by no changes in enthalpy, shown by vertical lines in the Fig. 4.

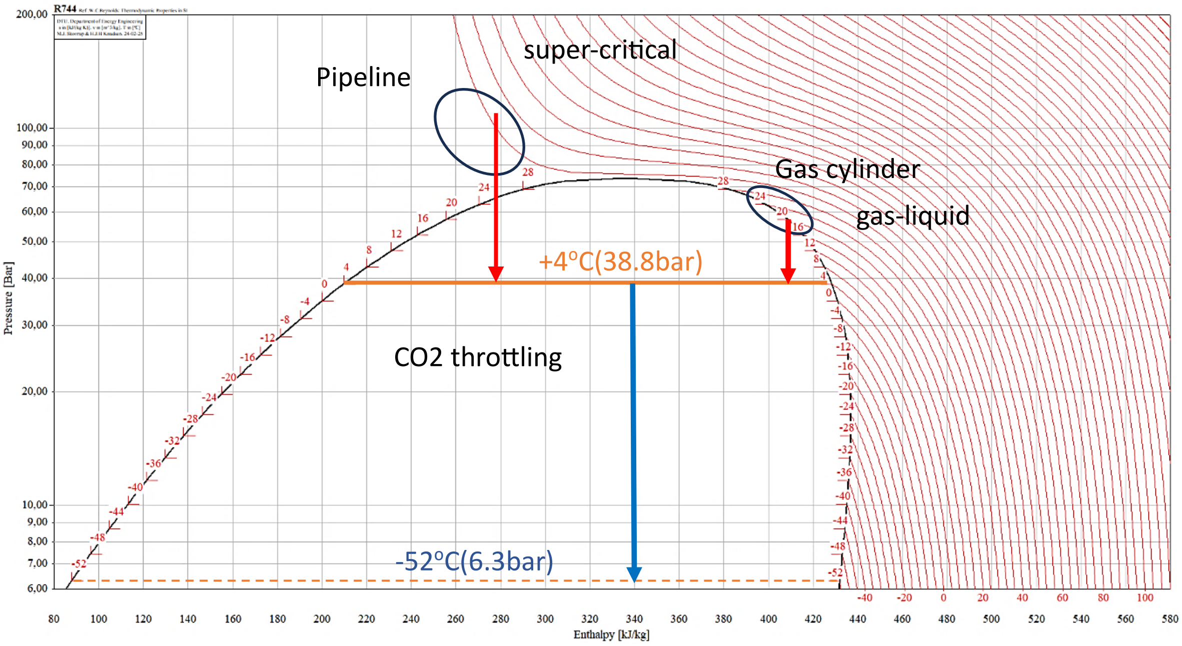


Figure 4: Calculated CO2 pressure-enthalpy diagram [4]. Red lines are isotherms. Ovals show CO2 pipeline and gas cylinder pressure/temperature ranges. Vertical lines show CO2 throttling. CO2 triple point: - 56°C/5.2 bar.

As one can see from the Fig. 4, CO2 expansion from e.g. 120 bar (pipeline domain) or CO2 gas cylinder (65 bar domain) to 38.8 bar (after the valve) will cause a CO2 cooling down to + 4°C with a two-phase CO2 formation (liquid-gas). However, at + 4°C ratio liquid density to gas density is very low. at Further expansion to e.g. 6.3 bar or even to 1 bar will lead to a significant temperature drop and dry ice (CO2) formation which will clog the sampling line.

Water in CO2

Water is most common impurity component in many process gases. Reactive molecules such as NH3 and SO2 tend to make a good bound with H2O ones in the stream. If H2O is present in CO2 (e.g. CO2(99.7%) purity from Air Liquide can contain up to 200 ppm of H2O at 5 bar), then a CO2 pressure reduction can cause realise of H2O from the liquid CO2 into the gas phase with followed H2O condensation as a liquid (free water), Fig. 5. Water can “capture” e.g. NH3 and form aerosols. A dew point of aerosols is typically higher as for the H2O, i.e. aerosols condensation can happen on a valve surface even at ambient conditions. In the Fig. 5, the olive line shows H2O solubility in CO2 at 20°C. There is a sharp change in H2O concentration when the pressure approaches about 57 bar. As one can see from Fig. 6 at 57.3 bar there is CO2 phase change (from dense liquid to gas-liquid). The latter is caused by enthalpy increase in the system. The Fig. 5 shows, if H2O content in the CO2 is below 200 ppm, no liquid water will be released with CO2 cooling to 0°C and de-pressurizing. Although there is no common agreement about to what extent the CO2 should be "H2O-free", a typical buried pipeline temperature on the European mainland will adopt the ambient ground temperature of 5-10°C over distance which gives upper limits for H2O concentrations, Fig. 5. At the same time, it was reported that H2O levels of 300-500 ppm (0.3-0.5 kg/m3) are accepted by industries for CO2 transmission pipelines [6]. Those levels are in a good agreement with the red line (+ 10°C) in the Fig. 5. According to the Table 1, the maximum expected H2O concentration is 50 ppm which approximately corresponds to - 15°C H2O dew point at 40 bar and - 52°C at 1 bar.

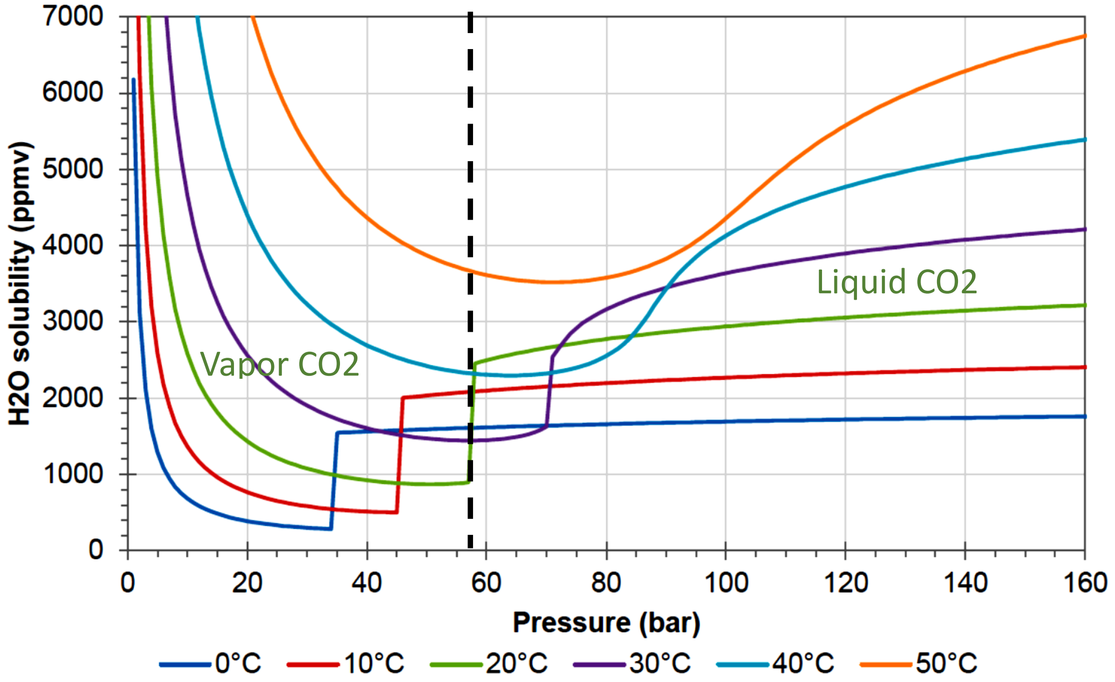


Figure 5: Calculated H2O solubility in CO2 at various temperatures and pressures [5]. Olive line: 20°C. Vertical dashed line shows two CO2 phases separation.

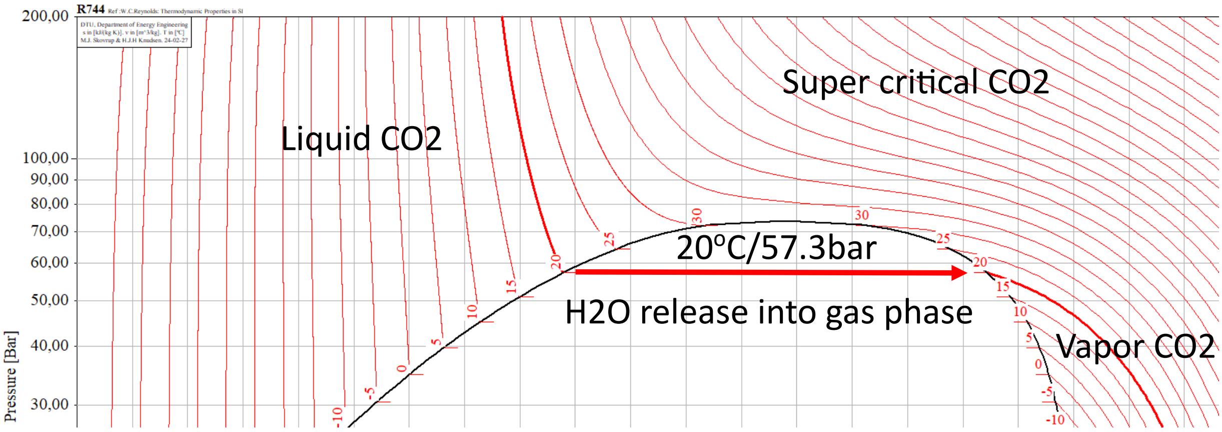


Figure 6: Calculated CO2 pressure-enthalpy diagram in 30-200 bar range [4]. Red lines are isotherms. Red horizontal arrow line shows CO2 phase change at 20°C which can cause H2O release in gas phase, Fig. 5.

Hydrates

Apart from H2O release with pressure reduction, there is a possibility of CO2 hydrate formation. As one can see from Fig. 7, the conditions in the pipeline and after the choke are inside the hydrate-stability zone for the water-saturated system but outside the hydrate-stability zone for the 250-ppm-water-content system [7]. The Fig. 7 shows that the risk of hydrate formation in a pure CO_2 stream at temperatures between -2 and 30°C and at pressures up to 200 bar is low if the water content is below 250 ppm. At even lower H2O concentrations the risk should be lower as well.

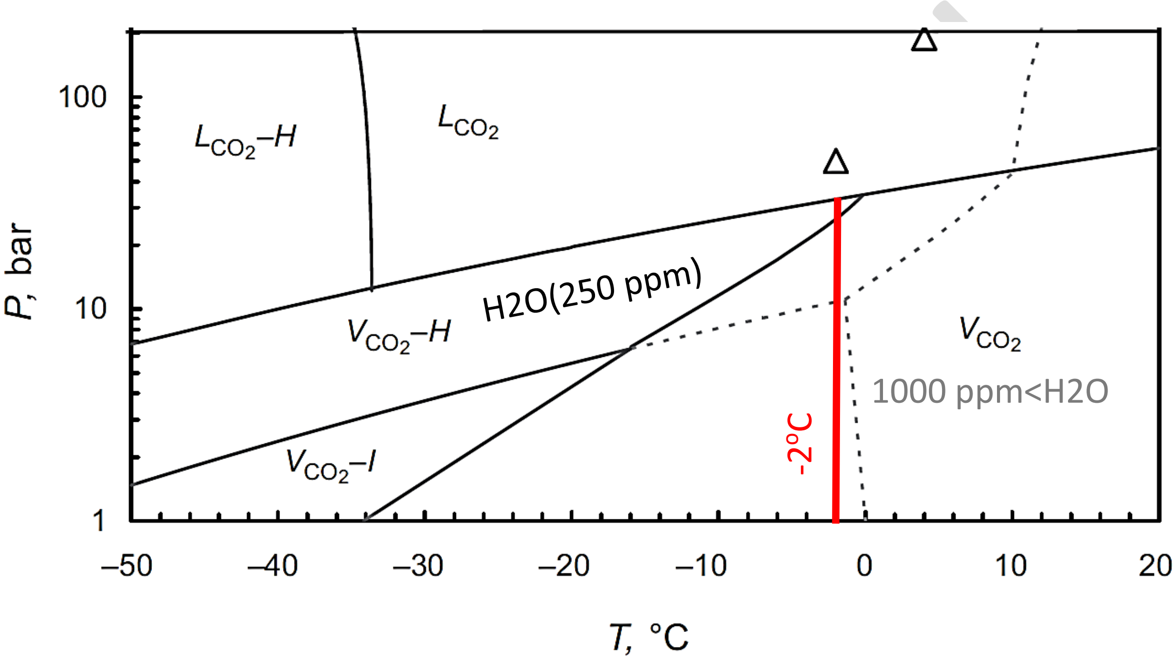


Figure 7: Pure CO2 hydrate-stability zone (black lines) for 250-ppm system (H: hydrate; V_{CO2}: CO2-rich vapor phase; L_{CO2}: CO2-rich liquid phase; I: ice). Gray dotted lines represent hydrate/ice-stability zone at saturated condition (i.e. in the presence of free water) [7]. Vertical red line shows low temperature limit for hydrate-free gaseous CO2 with H2O(250ppm).

CO2 mixtures

Final consideration for a sampling line design should account for mixtures. The presence of impurities alters the critical pressure of the CO2 stream due to the differences in the vapour pressure of various constituent species [8]. Fig. 8 shows few examples of calculated phase envelopes using the Peng-Robinson equation for pure CO2 and CO2 mixtures obtained from five industrial CO2 streams.

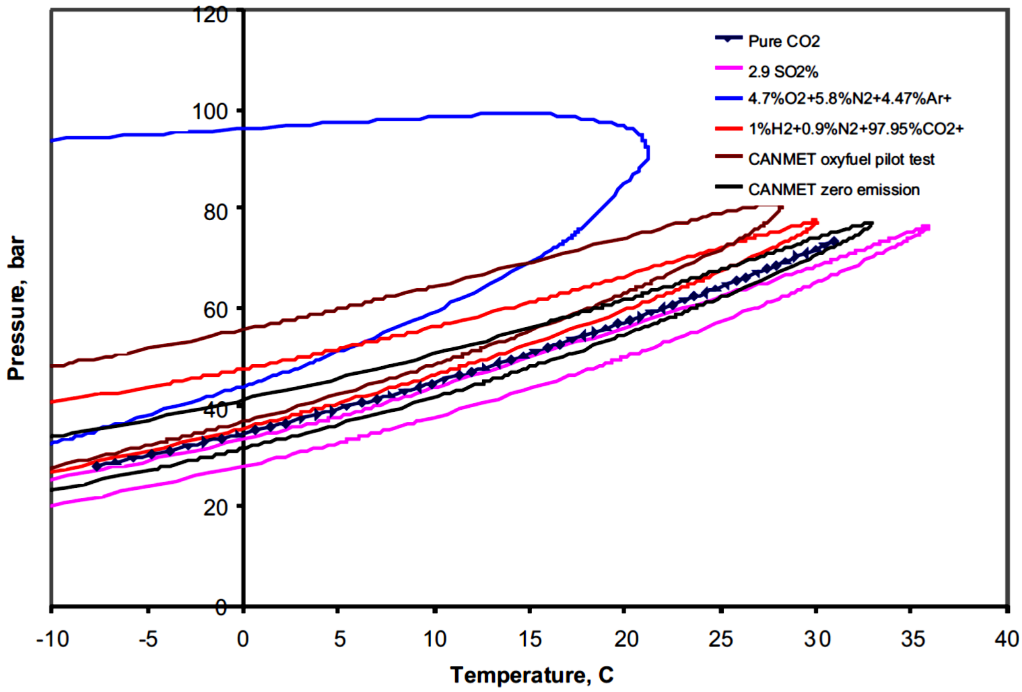


Figure 8: Calculated phase envelopes for pure CO2 and CO2 mixtures [9].

The black line with points in the Fig. 8 shows pure CO2 case. Other lines show CO2 mixtures with:

- magenta: SO2(2.9%)
- blue: **N2(5.8%)** + **O2(4.7%)** + **Ar(4.47%)** + NOx(100ppm) + SO2(50ppm) + CO(50ppm)
- red: **H2(1%)** + **N2(0.9%)** + **Ar(300ppm)** + H2S(100ppm) + COS and other (few ppm)
- wine: **O2(5.2%)** + CO(221ppm) + SO2(1431ppm) + NO(243ppm)
- black: CO(1.05%) + SO2(1.7%) + H2(0.32%) + H2S(690ppm).

As one can see from the Fig. 8, the critical temperature and pressure of the mixtures are quite different from that of pure CO2. N2, O2, Ar and H2 show the greatest effect of increasing the saturation pressure of the liquid and decreasing the critical temperature. One extreme case is the mixture from oxyfuel combustion (blue): the critical temperature decreases by about 10°C in comparison with that of pure CO2, and the liquefaction pressure increases by over 50 bar. On the other hand, SO2 (magenta) results in a decrease in the saturation pressure and an increase of the critical temperature, as is expected from the high critical temperature of pure SO2 (158°C). It can also be seen that low-concentration impurities, such as CO and NOx would not significantly affect the phase behaviour of CO2 [9].

According to the Task 3.1 results, expected CO2 concentration in the industrial (end product) CO2 streams will be above 95% while expected highest **N2** and **H2** concentrations are below **4%** and **2%** respectively, with **Ar(< 4%)**, CH4(< 4%), CO(< 0.2%) and **O2(< 20ppm)**. Therefore, a possible critical temperature and pressure for such mixtures will be somewhere in between the blue and red lines in the Fig. 8, i.e. a bit shifted towards a higher saturation pressure (ca. + 10 bar) and a lower critical temperature (ca. - 5°C). Therefore, the horizontal orange + 4°C/38.8 bar CO2 line in the Fig. 4 can potentially transform to a -1°C/49 bar line for CO2+H2+N2+... mixtures (see also Fig. 8).

Summarizing all above given discussions one can conclude that a first step pressure reduction from 70-200 bar to 40-70 bar will be quite safe in respect to impurities measurements at hydrate-free conditions.

Practical CO2 sampling
Because extensive CO2 throttling two possible CO2 sampling approaches are possible.

Sampling method 1

The first is shown in Fig. 5. The approach is based on a classical use of available commercial analysers which typically operate at about 1 bar (or lower) pressures.

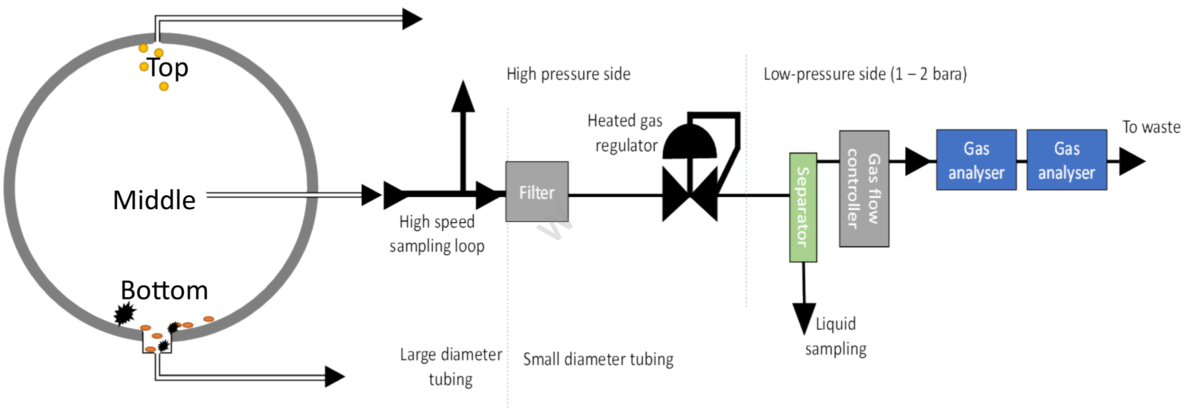


Figure 9: Possible CO2 sampling arrangement: from high (pipe) to low (analyser) pressures [5].

There are three possibilities for sampling: top position (light components), middle position (bulk phase), and bottom position (heavy components) Applying a large-diameter flange at the bottom would allow for accumulation of heavy components if the turbulence is not too high [5]. Alternatively, the sampling probe can be used from top position as shown in the Fig. 3 for mapping of the CO2 stream across.

The optional filter can be used to remove solid particulate and to avoid blocking of the small diameter tubing. According to the Task 3.1 solid particulate should not exceed 1 mg/m3 or 1 ppm. The filter will introduce an additional pressure drop in the system and a care should be taken for a safe depressurising and pressuring of it.

A (electrically) heated gas regulator is used to reduce pressure from 60 bar (or more) to about 1 bar. This is a significant drawback of the approach because throttling in the regulator initiates a strong and quick CO2 cooling down (to temperature below - 52°C, Fig. 4) and some components can be separated from the CO2 bulk phase, even if the regulator is heated because temperature non-uniformities in the regulator. This is because most of the impurities have a low CO2 solubility after liquid to gas phase transition, similar as shown in the Fig. 5 for H2O. Fig. 10 shows an example of condensate and particles accumulated inside the heated regulator.

Figure 10: Products precipitated inside the heated regulator body (left) and on regulators diaphragm (right) [5]. Green/yellow solids on the right is elemental sulphur.

It should be however noted that if H2O or other impurities concentrations are low (as in the Table 1), then the phase transition should not affect impurities in the CO2 and non if them will (theoretically) be separated from the CO2.

Other drawback of use the regulator in given geometry is local overheating of the gas in the regulator which can lead to a temperature-promoted reactions between impurities, heating element and the regulator body. To achieve maximum thermal efficiency a heating element of the regulator is normally in a direct contact with the process medium. The gas heating happens before gas throttling. Therefore, the gas composition measured at the end of the line may be biased.

Finally, a gas flow controller before the analysers can also influence on the impurities composition. It may have also a memory effect to e.g. NH3 or SO2 and therefore either a long purge time of the whole sampling line or coatings in the controller are required.

Sampling method 2

The second sampling approach is based on Fig. 4 and the Project activities in the Wp3. The sampling approach is based on a first step pressure reduction from e.g. 150 bar to 40-70 bar with use a (coated) reduction valve without electrical heating. Then the measurements with use e.g. far-UV/FTIR or TDLAS spectroscopy are performed in special (also coated) gas cells at up to about 40-70 bar pressures.

Gas flow inside the pressure regulator can be considered as a gas flow through an orifice of a certain length and diameter and therefore a gas cooling will depend on the orifice geometry, CO2 inlet/outlet pressures and flow. Results of a CFD modelling of CO2 flow through the orifice 4 mm length (L) and 10 mm diameter (D) is shown in Fig. 11 at inlet CO2 pressure 10 MPa and temperature 373 K. Three panels show calculated steady-state temperature fields from 4.3 MPa to 5.7 MPa outlet pressures. The length of a low-pressure section in the Fig. 11 (from orifice to the right side of the plots) is 75 mm.

As one can see from the Fig. 11, increasing of the outlet pressure from the 4.3 MPa to 5.7 MPa leads to a contraction and nearly disappearing of the coolest gas-liquid zone spots (blue colour) and their move towards the orifice's back side. The coolest zone at 5.7 bar is just after the back side of the orifice. At the same time the "jet"-like cold tails (green colour) become shorter and more homogeneous with the rise of the outlet pressure. The temperature contrast between the jet and the surroundings is more pronounced at 5.7 MPa than that at 4.4 MPa and the gas temperature at the end of the outlet section approaches to the surroundings temperature. A typical L/D ratio in e.g. Swagelok regulators is around 0.5 which is close to 0.4 used in the [10]. The L/D ratio is important to understand a gas expansion through an orifice.

Although the conditions in the [10] cannot exactly be the same as in a real regulator, the shown temperature patterns can, in general, be used to qualitatively understand a CO2 expansion in the reduction regulators. A low, step pressure reduction, will minimize the CO2 cooling effects and bring the CO2 to a gas phase.

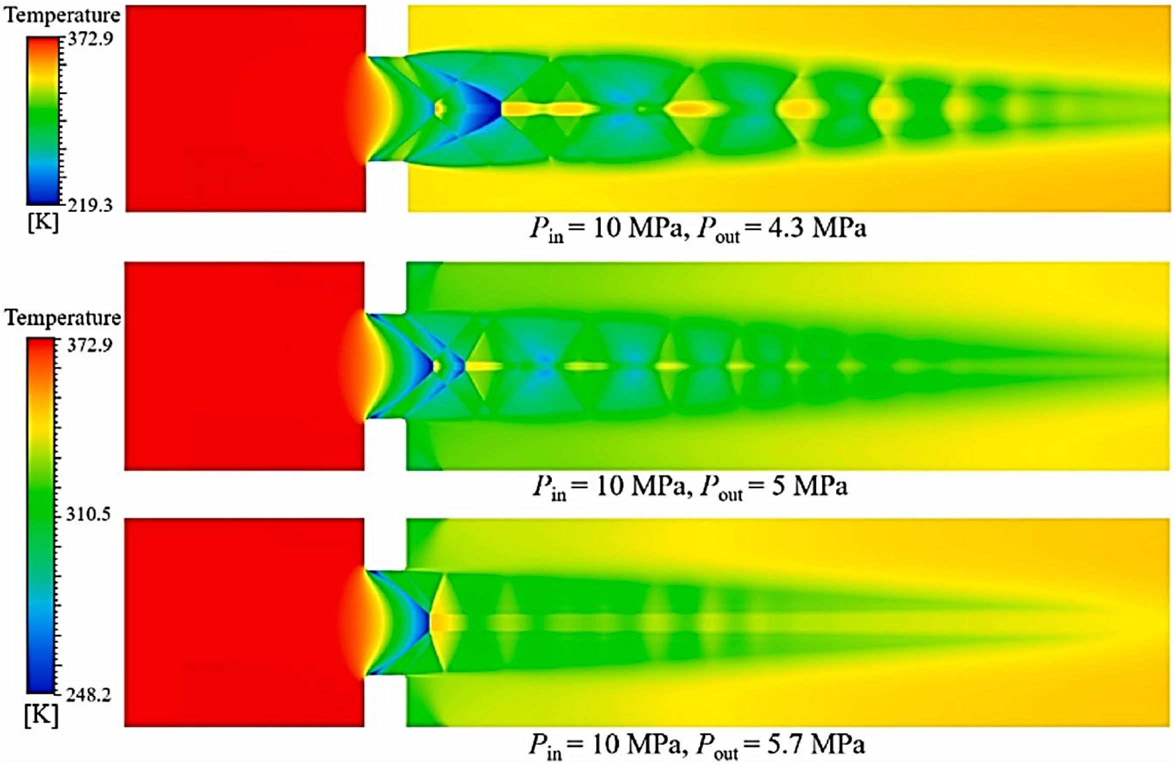


Figure 11: CFD steady-state temperature field modelling at different outlet pressures (T_{IN} = 373 K, D = 10 mm). Red: inlet gas section followed by orifice. Yellow-green: outlet gas section. L/D ratio is 0.4 [10].

After the first pressure reduction from e.g. 150 bar to 40-70 bar, the CO2 in the gas phase can be analysed in a gas cell with use of far-UV/IR or TDLAS spectroscopy techniques. After the cell the CO2 pressure shall be further reduced to a few bars pressure level. This second pressure reduction will initiate a strong CO2 cooling, Fig. 4. In order to avoid ice formation a heated pressure regulator should be used. Heating of the gas at this stage (after the gas cell) is not critical in respect to impurities because after the regulator the gas will be send to a vent.

A possible T-enthalpy diagram for the second method is shown in Fig. 12. CO2 (100 bar/+ 30°C) throttling to 40 bar initiates gas cooling to + 5°C along h = 270 blue line with gas-liquid phase formation. Then the gas flowing through the tube (after the regulator and towards the cell) at ambient conditions is heated back to + 18°C (h = 450, blue) that ultimately bring the CO2 to the gas phase. This is because the specific (subcritical) CO2 heat capacity (c_p) exponentially increases with temperature increase from 0°C to 30°C that further accelerates CO2 energy exchange with surroundings [11]. Further pressure reduction step (after the gas cell) towards 1 bar pressure in a heated regulator allows to avoid negative low temperatures and therefore ice formation on the downstream elements.

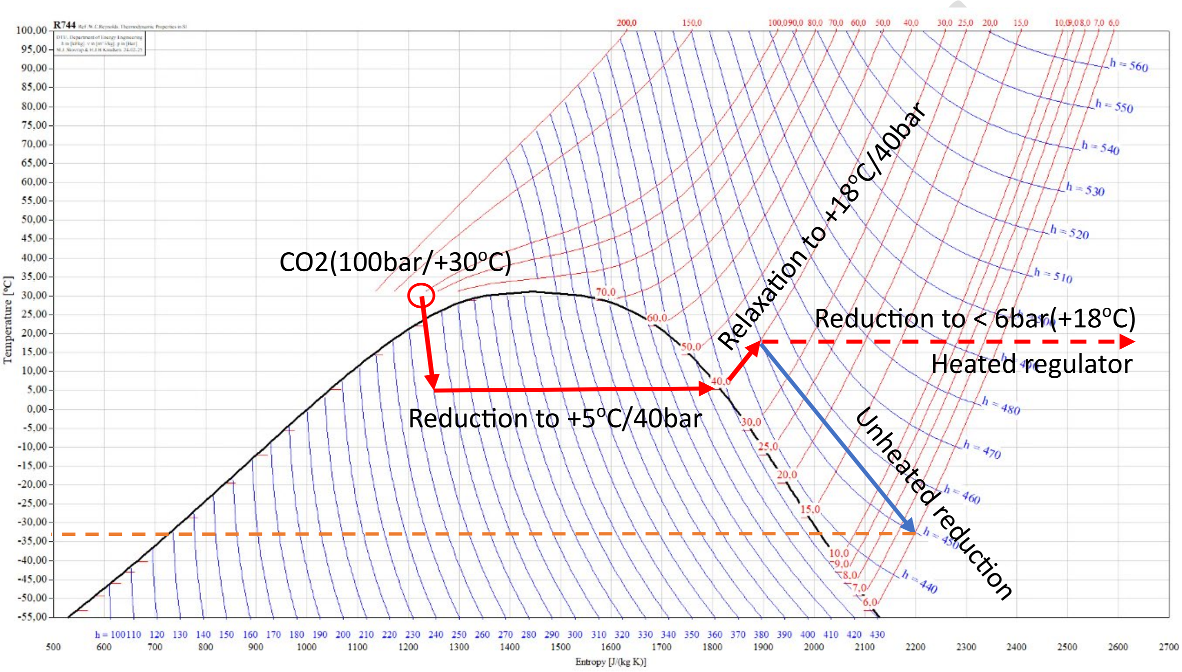


Figure 12: Calculated temperature-enthalpy diagram for CO2 [4]. Red and blue arrows show pathlengths for the method for 100bar/+30°C inlet condition. Red lines: isobars. Bue lines: isenthalps (lines of constant enthalpy). Enthalpy (blue) and pressure (red) numbers are given.

As one can see from the Fig. 12, without CO2 heating the CO2 temperature on a low-pressure side will drop below - 33°C at 6 bar (h = 450 line). In general, heating of the CO2 back to + 12°C (h = 440) is sufficient. It should be noted that above consideration is applied for a steady-state conditions. Preliminary measurements in the DTU’s lab with CO2(4.8) gas cylinder with a deep tube show the similar temperature patterns with temperature distribution across the sampling line elements.

A layout of the sampling system 2 is shown in Fig. 13. The CO2 can be taken as a dense or super-critical liquid to the sampling system. Sampling probe position in the pipe is variable.

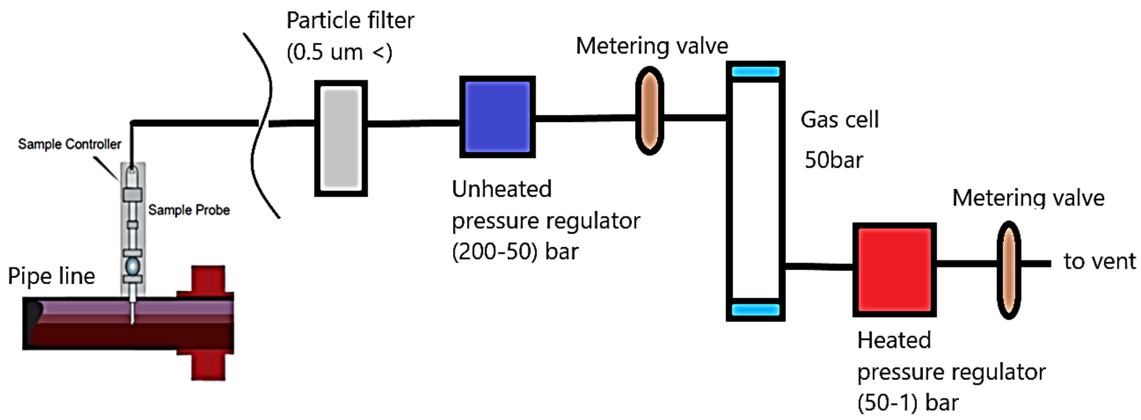


Figure 13: Sampling system 2 layout for impurities measurements in CO2 at high pressures. The measurements are performed in the gas cell at 40-70 bar. More than one gas cell can be used. All system components before and including the cell are coated.

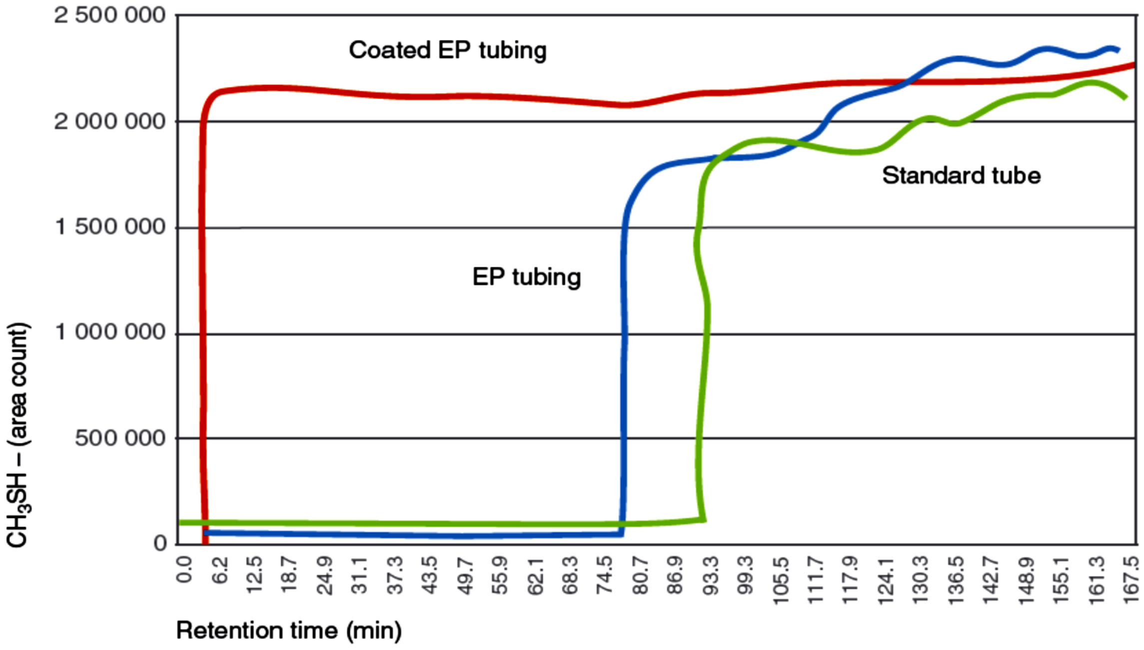
Apart from CO2 thermodynamics consideration with pressure and temperature variations, a special atention is required to sampling line materials.

Coatings

As a material for a gas sampling line, various (fluorinated) polymers (e.g. PFA, PTEF, FEP), or SS (non-coated, electro-polished, coated) tubes are used. Polymer tubes are flexible, rugged, and as e.g. in PTEF/FPA/FEP case are chemically inert and can be used at up to about + 200^{O}C in a continuous operation. However, the strength of the polymers is reduced with temperature. Thus e.g. the PFA tubing in Ø 4 mm (wall thickness 1 mm) size can be used up to 34.4 bar (+ 23^{O}C) and only up to 4.1 bar if it is heated to + 176^{O}C. For a comparison: the PTEF tubing with similar size can be used only up to 20 bar (+ 20^{O}C) and up to 10.6 bar at 150^{O}C. For the FEP, similar numbers are 17 bar (+ 20^{O}C) and 3.6 bar (150^{O}C). CO2 pressure reduction to 34.4 bar (or below) will lead to CO2 cooling down to about - 0.5^{O}C (or below), Fig. 4. Therefore, a sampling line configuration 1 will be required.

Besides of pressure/temperature limitations of polymers, a gas permeability though the polymers, has to be considered as well. Thus, the PTEF has a higher permeability than other thermoplastics and PFA has (at the same wall thickness) a lower permeability than PTEF. For purified and dry CO2, Air Liquid obtained a good experience with use PTEF tubing with/without a metallic braid protection. Various classical analysers (GC- and spectroscopy-based) working at about 1 bar inlet pressure were used.

For components and their respective concentrations listed in the Table 1 there are always adsorption issues for polar molecules such as H2O, H2S, mercaptans, ammonia or Hg vapor. An example of an analyser response on 0.5 ppm methyl mercaptan with use of different sampling line materials is shown in Fig. 14. As one can see it will take more then 2 hours to reach a steady state 0.5 ppm methyl mercaptan response in the analyser if a standard or electropolished tubes are used. Similar response time behaviour was observed for H2O traces [13]. For a shorter tube the response time will be shorter. However, for on-line measurements a response time about 1-2 min is frequently required (T0-90).



Response to 0.5 ppm methyl mercaptan into 30 m of 1/8 - inch tubing at room temperature with a flow rate of 40 mL min^{-1}.

Green	**Commercial grade stainless steel tubing**
Blue	**Untreated electropolished ss tubing**
Red	**Silicon coated electropolished ss tubing**

Figure 14: Response to 0.5 ppm methyl mercaptan for various 1/8” sampling lines of 30 m length [12].

Other example is ammonia sampling. Ammonia surface adsorption/desorption on various surface has been investigated in several studies (also in EUROMET-funded projects). Fig. 15 shows ammonia adsorption rates on several polymer and SS- coated, electropolished (EP) and raw tube surfaces. As one can see, a silicon-coatings (SilcoNert 2000) on a SS-tubes show lowest adsorption rate and have similar properties as PTEF. Those coatings can be applied on various object shapes and size and even elements of the sampling line such as valves, regulators etc. can also be coated and checked afterwards for a leak. Small size SS-tubes are flexible and can be used for pressures above 300 bar that is sufficient for most industrial applications.

For on-line impurities analysis it is important to have a fast analyser response and minimum impurities losses between A and B gas transport, Fig. 3. Response time (apart from analyser self-response) includes both: signal rise and signal fall times because A to B transport. An example of analyser response time on NH3(11.5ppm) in the gas stream is shown in Fig 16. Based line (dashed line) was measured with NH3 connection directly to the analyser inlet. The S200 coatings (= SilcoNert 2000) gives very close to the base line response.

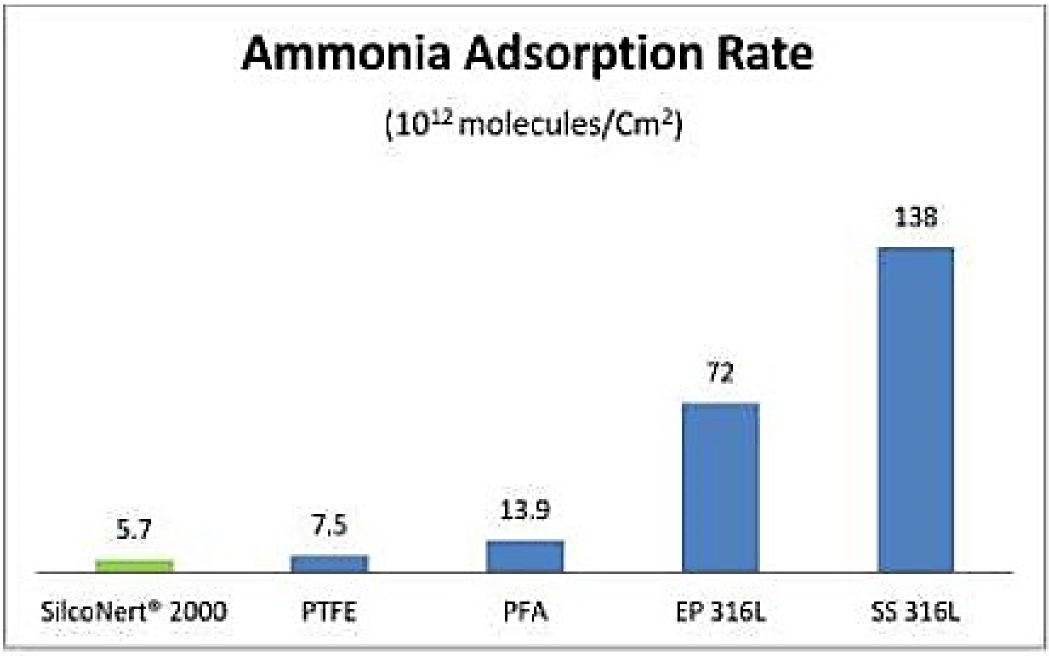


Figure 15: Ammonia adsorption rates on various materials surfaces [14].

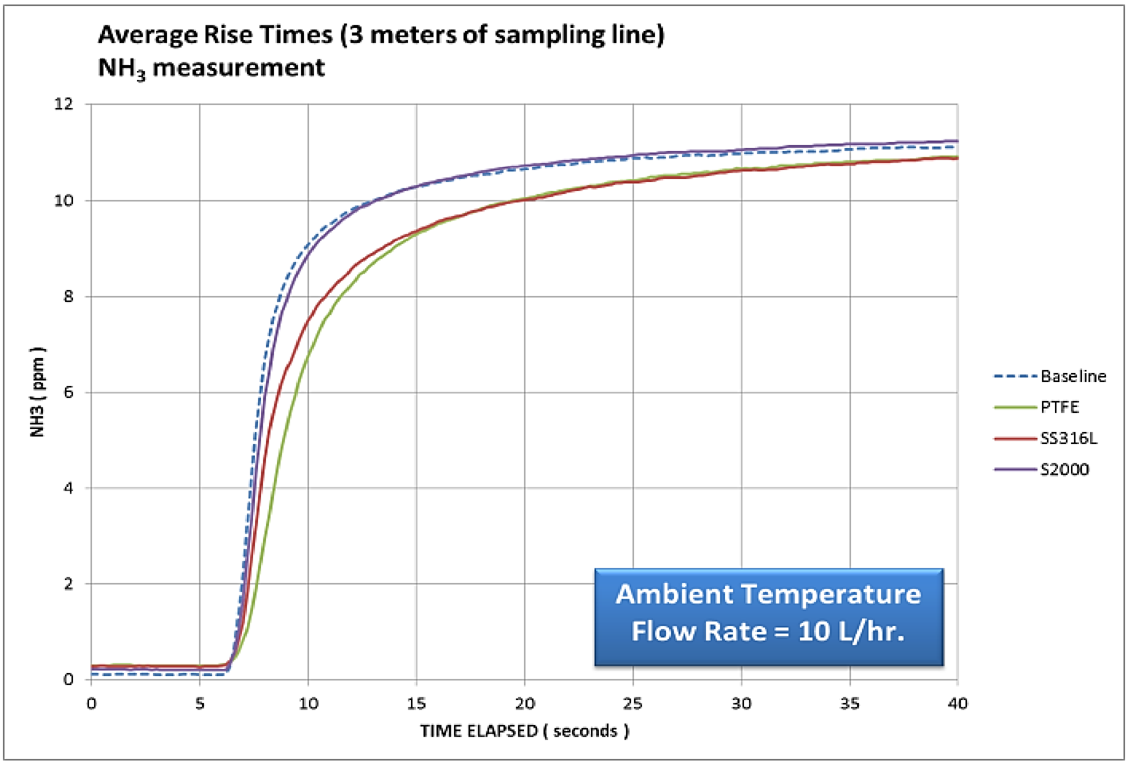


Figure 16: Response time (rise time) of various sampling line materials (PTEF, SS316L, SilcoNert 2000 coated SS316L) onto NH3(11.5ppm) at 10l/hr gas flow rate and 75mbar in ¼" tubes [15].

As one can see from the Fig. 16, the shortest response time of the analyser was achieved with use S2000 (= SilkoNert 2000) coatings on 3 m tubes. Average NH3 rise times ($T_{10\text{-}90}$) calculated from the Fig. 16 are [15]:

- none (intrinsic analyser response): 8.8 s
- PTEF: 16.2 s
- SS316L: 17s
- SilcoNert 2000 coated SS316L: 8.4s

Fig. 17 shows NH3(11.5ppm) fall times for the same sampling line materials as in the Fig. 16. The fall time shows how fast the analyser can see dynamical changes in concentrations.

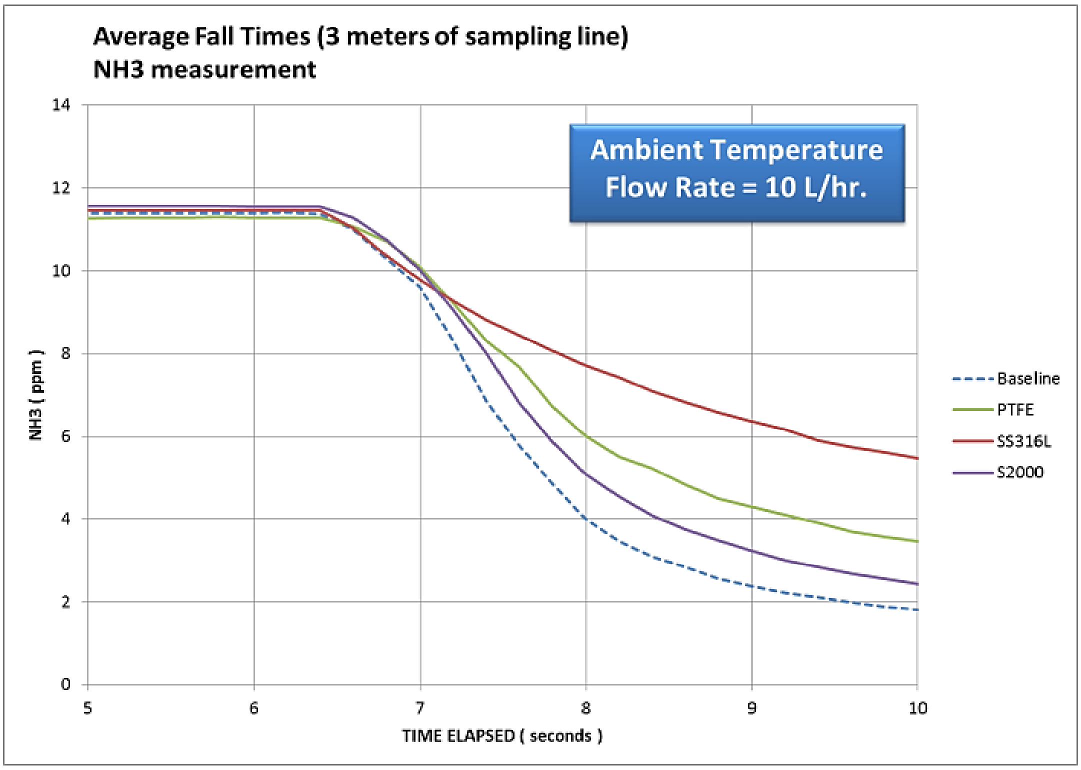


Figure 17: Response time (fall time) of various sampling line materials onto NH3(11.5ppm) at 10l/hr gas flow rate and 75mbar in ¼" tubes [15].

The S2000 coatings shows the fastest response to NH3 flow abruption. Calculated averaged NH3 fall times ($T_{100\text{-}10}$) from the Fig. 17 are [15]:

- none (intrinsic analyser response): 6.0 s
- PTEF: 18.2 s
- SS316L: 33 s
- SilcoNert 2000 coated SS316L: 9.4s

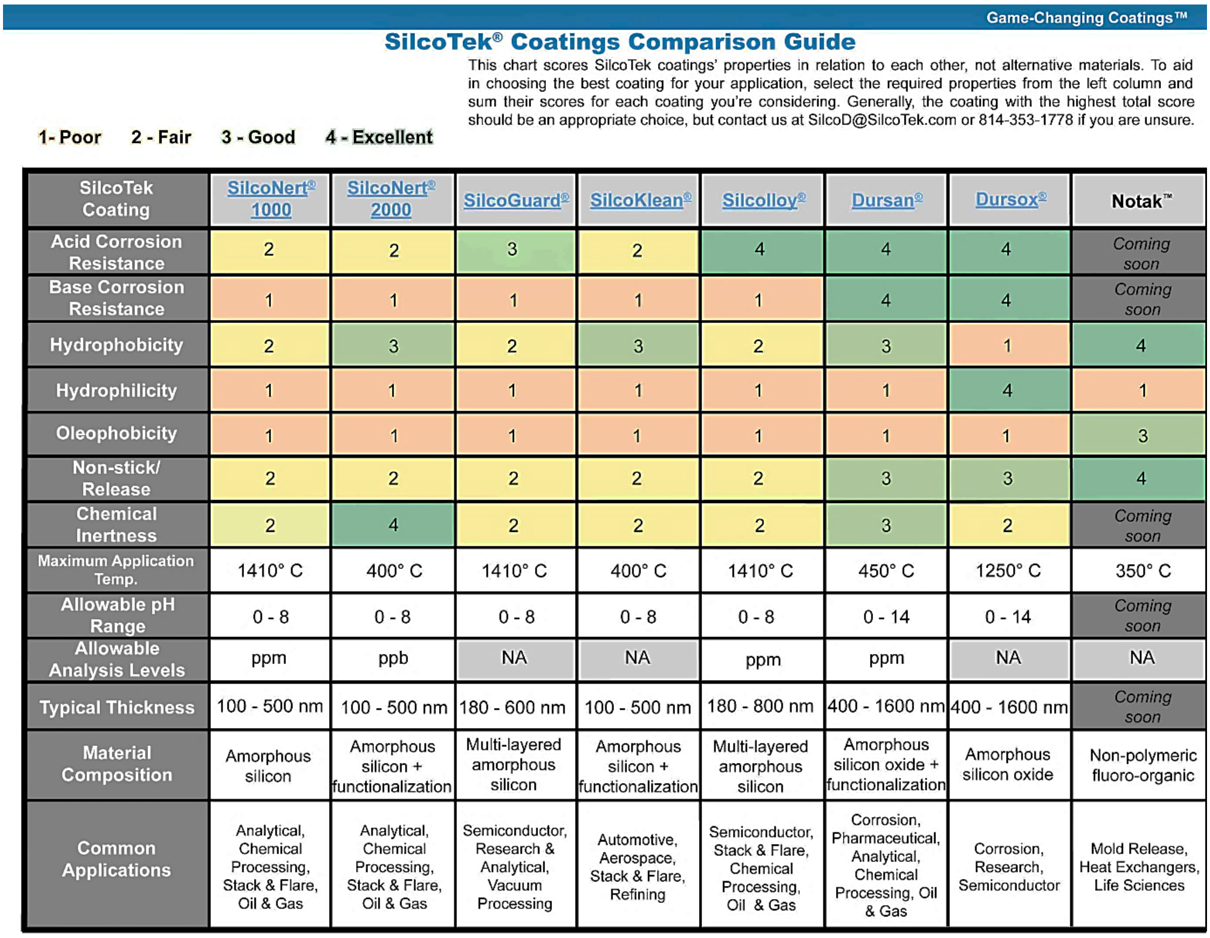
While the PTEF/ SilcoNert2000 shows similar rise/fall numbers, the SS316L has much longer (about two times) fall time compared to the rise one.

It should be noted that the SilcoNert 2000 coating is not an absolute solution and some retention of NH3 still occurs, albeit much less than with the other two types of lines.

In general use of any polymer tubing is not recommended for low concentration measurements (ppm-level or below) because possible gas permeation through the tubing wall. This is especially relevant to the measurements of humidity and oxygen in the gas on ppm/sub-ppm levels. Even for measurements at higher pressures (1 bar <) in the tubing ambient water vapours and oxygen can be drugged into the sampling line under high pressure flow conditions.

In overall in the measurements with corrosive gases and water on low ppm-levels a silicone-based coatings are recommended on all elements of the interface from the gas intake to the analyser. All elements of the analyser and the sampling probe those are in contact with the gas must also to be coated. In general, a short as possible tubing length between A and B is recommended for a shortest response time in on-line measurements. This is particularly important for high-pressure sampling because low gas velocity in the tubing (for the same throughput in the system).

A compilation of various industrial coatings available from SilkoTek company [14] is given in Fig. 18. Coatings such as SilkoNert 1000/2000 and DURSAN have been extensively tested in various EUROMET projects.



Game-Changing Coatings™

SilcoTek® Coatings Comparison Guide

This chart scores SilcoTek coatings' properties in relation to each other, not alternative materials. To aid in choosing the best coating for your application, select the required properties from the left column and sum their scores for each coating you're considering. Generally, the coating with the highest total score should be an appropriate choice, but contact us at SilcoD@SilcoTek.com or 814-353-1778 if you are unsure.

1- Poor 2 - Fair 3 - Good 4 - Excellent

SilcoTek Coating	SilcoNert® 1000	SilcoNert® 2000	SilcoGuard®	SilcoKlean®	Silcolloy®	Dursan®	Dursox®	Notak™
Acid Corrosion Resistance	2	2	3	2	4	4	4	Coming soon
Base Corrosion Resistance	1	1	1	1	1	4	4	Coming soon
Hydrophobicity	2	3	2	3	2	3	1	4
Hydrophilicity	1	1	1	1	1	1	4	1
Oleophobicity	1	1	1	1	1	1	1	3
Non-stick/ Release	2	2	2	2	2	3	3	4
Chemical Inertness	2	4	2	2	2	3	2	Coming soon
Maximum Application Temp.	1410° C	400° C	1410° C	400° C	1410° C	450° C	1250° C	350° C
Allowable pH Range	0 - 8	0 - 8	0 - 8	0 - 8	0 - 8	0 - 14	0 - 14	Coming soon
Allowable Analysis Levels	ppm	ppb	NA	NA	ppm	ppm	NA	NA
Typical Thickness	100 - 500 nm	100 - 500 nm	180 - 600 nm	100 - 500 nm	180 - 800 nm	400 - 1600 nm	400 - 1600 nm	Coming soon
Material Composition	Amorphous silicon	Amorphous silicon + functionalization	Multi-layered amorphous silicon	Amorphous silicon + functionalization	Multi-layered amorphous silicon	Amorphous silicon oxide + functionalization	Amorphous silicon oxide	Non-polymeric fluoro-organic
Common Applications	Analytical, Chemical Processing, Stack & Flare, Oil & Gas	Analytical, Chemical Processing, Stack & Flare, Oil & Gas	Semiconductor, Research & Analytical, Vacuum Processing	Automotive, Aerospace, Stack & Flare, Refining	Semiconductor, Stack & Flare, Chemical Processing, Oil & Gas	Corrosion, Pharmaceutical, Analytical, Chemical Processing, Oil & Gas	Corrosion, Research, Semiconductor	Mold Release, Heat Exchangers, Life Sciences

Figure 18: SilkoTek coatings comparison chat [14].

It should be noted that there is no single universal coating which can fit all applications. Some coating can be better for one set of gases, the other for another. For example for H2O trace measurements in ultra-pure gases such as Ar(99.9999%) or N2(99.9999%), the DURSAN coatings are recommended. Therefore, the choice of the coating depends on an application.

Conclusions

In the Report various practical aspects of CO2 sampling from e.g. pipelines or gas cylinders have been considered. In respect to analysis of purified and dry CO2 streams, optional particle filter can be removed from the sampling line if particle contamination risk is low.

A traditional sampling scheme when there is only a single pressure reduction step from e.g. 60-200 bar to 1 bar requires a heated gas regulator before the analyser. The pros of this approach are that a wide range of commercial analysers working at around 1 bar inlet pressures can be used at the end of the line. The cons are that in the heated regulator some chemical transformation of (reactive) impurities can happened because local temperature nonuniformities and direct contact of the heating element in the regulator with the flow. Moreover, the flow controller before that analyser can bias the measurements because of its memory effect, especially if the flow controller is not coated. Water enhancement factors for CO2 are not well known, and H2O measurements in an amount fraction at 1 bar might be difficult to translate to the H2O amount fraction in CO2 at high pressures.

The second sampling approach has been proposed. The approach is based on two stages pressure reduction which should reduce a risk of impurities loss: from 100-200 bar to 40-70 bar and then from 40-70 bar to 1-2 bar. The CO2 gas-phase analysis is made in a gas cell under high pressure conditions, below super-critical conditions (40-70 bar) after the first pressure reduction step. Then the gas is further de-pressurized in a heated pressure regulator and finally released to a vent. The benefit of this approach is that there is no extensive heating of the CO2 before the measurements take place. By-products formation such as e.g. hydrates is negligible (or at least minimized) with the proposed approach. At the same time, measurements at high pressures increase sensitivity for impurities detection while keeping measurement system relatively compact and simple in terms of overall coasts. The proposed approach can also be used for on-line measurements on CO2 steams with high H2O amount fractions as e.g. H2O(250 ppm) at 40 bar. For CO2 sampling from cryogenic sources an optional moderate CO2 heating can be applied.

CO2 sampling from high-pressure sources should be done with use silicon-based coatings on all the way through the CO2 intake to CO2 analyser. The SilcoNert 2000 or DURSAN coatings are best suitable for impurities (Table 1) sensing.

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