

Demonstrating a Refinery-adapted cluster-integrated strategy
to enable full-chain CCUS implementation - REALISE

D2.5 Quantification of emissions and CO₂ quality

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Executive summary

This report presents work related to REALISE project Task 2.3 and Task 2.4. It consists of two main parts:

- Quantification of potential emissions to the atmosphere of HS-3 solvent compounds and resulting degradation products from the CO₂ capture plant
- Qualitative analysis of captured CO₂ stream at different locations (leading to the liquefaction unit, along the liquefaction unit)

To fulfil this task, the gas phase of the system has been systematically analysed throughout the duration of the campaign using both online and offline methods. As an online method, FTIR instrument was used, whilst for more detailed and accurate analysis, gas has been sampled using a SINTEF developed technique and collected liquid samples have been subsequently analysed with a LC-MS scan.

Calculated results revealed systematic emission of solvent compounds (1- Pyrrolidineethanol, 3- Aminopropanol) and degradation compounds: Pyrrolidine and N-Nitrosopyrrolidine, although in very low concentrations.

In addition, the effectiveness of emission mitigation methods was investigated by studying the dynamic response of emissions to changes in the water-wash section conditions, as well as the efficiency of using multiple water-wash sections. It was observed that the temperature in the water wash section can have a significant impact on emissions. On the other hand, using all available water-wash sections made it possible to bring down the emissions to marginal levels.



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1 Introduction

1.1 Background

This report describes work related to the quantification of emissions and CO₂ quality based on the HS-3 test campaign reported in the deliverable: *D2.4. HS-3 Campaign at Tiller plant*. CO₂ quality related activities are part of Task 2.4 while quantification of emissions is an activity in Task 2.3.

Other activities in Task 2.4 are reported in three other deliverables. The overview of all activities in Task 2.4 and where these are reported can be found in the table below:

<ul style="list-style-type: none">• Possible degradation mechanisms and effect of impurities in the flue gases on solvent degradation will be identified using data from both WP1 and WP2. (NTNU, SINTEF, TNO)• Development of analytical methods for degradation components specific for HS-3 solvent (SINTEF)	<ul style="list-style-type: none">• Deliverable 1.1 discusses in detail the proposed degradation mechanisms and developed analytical methods.• Link to the journal publication.
<ul style="list-style-type: none">• Analysis of the samples from mini-pilot and Tiller pilot campaigns (SINTEF)	<ul style="list-style-type: none">• D2.3 HS-3 campaigns at the Irving refinery• D2.4 HS-3 campaign at Tiller pilot plant
<ul style="list-style-type: none">• Effect of impurities in the flue gases on CO₂ quality• Develop analytical methods for pressurised CO₂ samples (SINTEF)	This report

2 Emissions measurements

2.1 Motivation for emissions measurements

Emissions measurements are an important aspect of every experimental campaign at Tiller CO₂ capture plant to establish emission profile for environmental monitoring and assessment of an overall process performance. As described in more detail in the deliverable D2.4 (Chapter 5- Solvent analysis and degradation), amine solvents are prone to both thermal and oxidative degradation. Naturally, the volatile degradation products end up in the gas phase of the system, subsequently leading to unwanted emissions to the atmosphere. Since these compounds could be potentially harmful to the environment and human health, it is important to accurately measure their concentration in the CO₂ capture plant's exhaust gas.

Two main types of emissions from a CO₂ capture plant can be distinguished: gas phase emissions (due to volatility), and aerosols based emissions (known also as mist or fog). The chosen sampling method was designed to capture both gas and aerosol form emissions.

One must be aware that, the hazard assessment is solvent specific and there are usually no emission limits established, especially in the case of newly developed solvents. Therefore, the available data for similar compounds belonging to the same chemical group shall be evaluated.

Emission of these compounds is also undesired from the process performance point of view, as it indicates a loss of solvent which in turn can affect the capture efficiency, following a mechanism: emission of solvent = less and less solvent in the system over time -> less reactive species -> less potency to capture CO₂.

Performing such measurements at different points in the system allows tracking and quantifying the compounds in the gas phase and eventually contributes to verifying the mass balance of the whole system. Tiller plant is highly flexible, allowing to sample the gas phase from various points in the system depending on the specified research interests. Although usually, measurements are taken at the following points:

- **Exit to the atmosphere** – for environmental monitoring and assessment of the overall emissions from the CO₂ capture plant. Sampling the gas at this point also gives an indication of the efficiency of the preceding water wash/ acid wash sections or other equipment for emissions mitigation.
- **Top of the absorber** and downstream each water-wash section– depending on the process conditions and solvent used it can be of interest to analyze the gas phase profile based on water-wash applications.
- **Product CO₂ stream** – to assess the purity of the captured CO₂. Since the CO₂ product is later sent to the liquefaction unit and stored, this measurement should be treated as a qualitative analysis of the residual concentrations in the CO₂ stream rather than emissions as such.

Knowing the emission source and profile allows applying the correct mitigation measures such as the number of water washes, optimization of process conditions, and usage of other equipment (demisters, acid wash, etc.)

Finally, such measurements serve as a validation for model predictions. In theory and in a simplified approach, modeling of gas-phase emissions can be considered as a function of vapor pressure of the component in question and the temperature in the water wash. Although it is uncertain, how quickly the system reaches equilibrium and the degradation of the solvent over time provides additional complexity. Aerosol emissions are an even more intricate phenomenon, as they depend on the nature of condensation of different components, and temperature gradients in the system, yielding their varied susceptibility to create mist emissions. Therefore, it is crucial to perform emission measurements, especially in the case of newly developed solvents.

2.2 Methodology

Emissions measurements can be performed online and offline through manual sampling methods and subsequent analytical methods.



2.2.1 Manual sampling for offline analysis

SINTEF has developed sampling techniques based on modifying EPA method¹ 5 for the analysis of sweet gas exiting amine solvents based CO₂ capture plants. Depending on the nature of the solvent and analytes of interest, the method is adjusted and optimized to ensure efficient sampling, after which the components in question will be captured and subsequently sent for MS-analysis.

Two sets of impinger trains with acid solutions were utilized for gas sampling. The setup of the sampling train consists of 4 standard 250 mL impinger flasks in series. The first flask is empty to allow the aqueous condensate from the gas to accumulate, which is possible due to the fact that the flasks are immersed in a cold bath. The following three flasks are partially filled with predetermined amounts of the appropriate absorbent. To specifically target NH₃ (+also convenient for amine components), 0.1 N sulfuric acid (first set) was used, whereas for capturing nitrosamines, solution of 0.1 M sulfamic acid (second set) was found to be suitable. A suction pump is conveniently placed downstream to the impinger-set to provide the necessary driving force, nevertheless, without itself interfering with the sample. It is usually fitted with a flow-adjustment valve which enables control of the gas flow rate to suitable velocities that enable isokinetic sampling from the stack. The whole gas sampling equipment is shown on **Figure 2-1**.

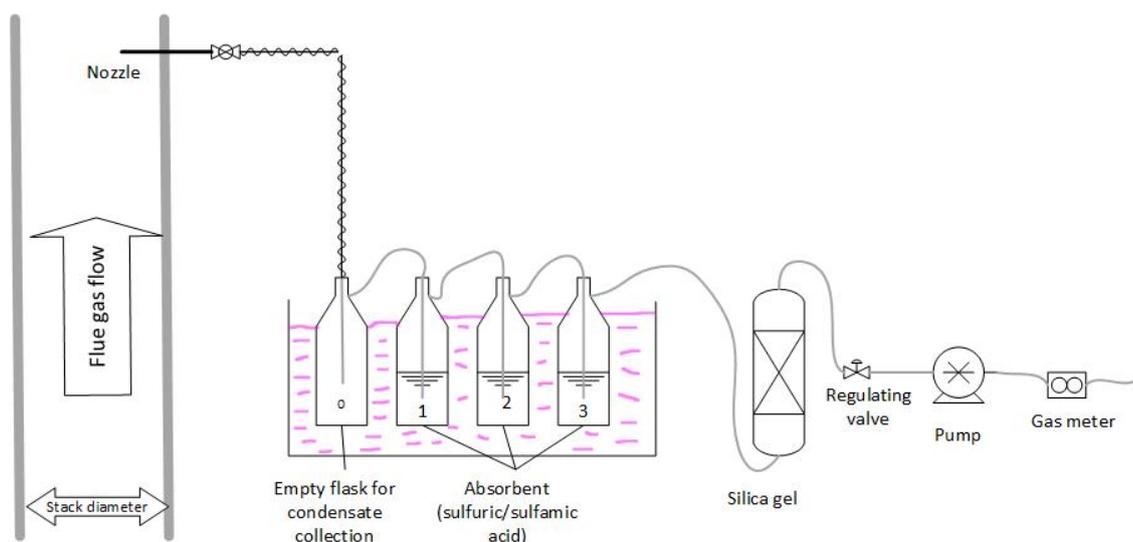


Figure 2-1: Schematic of the impinger train setup connected to the CO₂ capture plant's gas flow

An important criterion to evaluate the sampling absorption efficiency is based on comparison of relative analyte-recovery in the sequence of impinger flasks along the sampling train. The rule of thumb used for this type of sampling is that 90% (or more) of the captured component is to be found in the series preceding the last flask/bottle in the chain, ideally resulting in the last flask with no analyte found. This is considered as sufficient criteria for adequate capture efficiency for manual emissions sampling.

¹ <https://settek.com/documents/EPA-Methods/PDF/m-05.pdf>.



Glass equipment should be clean and if Teflon tubing is applied as the connecting line between successive flasks, it must be (preferably) new or thoroughly cleaned. A sample of the unused absorption solution should be collected to have a background/reference sample available.

Correct orientation/flow of the sampling equipment should be verified prior to sampling. The volume of the sampled gas basically depends on the desired limit of detection/quantification, which is correlated to the available analytical method and/ or equipment. The recommended flow rates for midjet impingers is in the range of 1-3 L/min with liquid absorbent volumes of ≈ 15 mL in each impinger bottle (used for the CO₂ stream purity measurements) whilst 14-16 L/min and 75 mL are recommended for standard impingers (used for sampling of the plant's exhaust gas). This implies that the sample flow rate should be sized appropriately in order to meet isokinetic requirements at the sampling nozzle inside the stack.

Before sampling starts, an air leakage test must be done to ensure that the sampling line and train are airtight. With the impinger sampling-train system installed and tested for leakages, the gas pump can be started. If leakages cannot be eliminated completely, they should not exceed 2% of the sample gas volume.

Figure 2-2 (an extract from the plant's P&I) shows the top of the absorber column (AC-4b) with the two water wash sections WW1 and WW2 as well as the external water wash columns, WW3 & WW4. The gas from the upper absorber section (AC-4b) flows through a demister (AC-D) and then through the two water wash sections, WW1 and WW2. At the top of the column, the gas flows through another demister (AW-D) before it flows through a horizontal channel out of the building. When water-wash sections are in use, the wash-water is re-circulated with a pump and cooled down by heat exchangers. As indicated on the Figure 2, two sampling points right before the exit to the atmosphere were used, together with an already existing line to the FTIR instrument, enabling simultaneous online measurement and connection of the two sets of the impinger trains.

Under normal operation, it is mainly WW2 that cools down the gas phase and provides condensed water for washing. The used water in WW2 is then directed to WW1 and used there before it is sent to the lean buffer tank (Tank2). This is the mode of operation followed during the REALISE HS-3 solvent campaign. During the last week of the campaign, the external water wash sections WW3 and WW4 were tested, and emission measurements were taken for each condition.

Also, liquid samples were collected from the points following each of the water wash sections, to serve as a reference and validate the efficiency of the water wash sections in 'cleaning' the absorber's gaseous emissions.

Following the sampling, the collected liquid samples are securely delivered to the analytical lab, where similarly to the solvent samples are analyzed with the LC-MS scan.



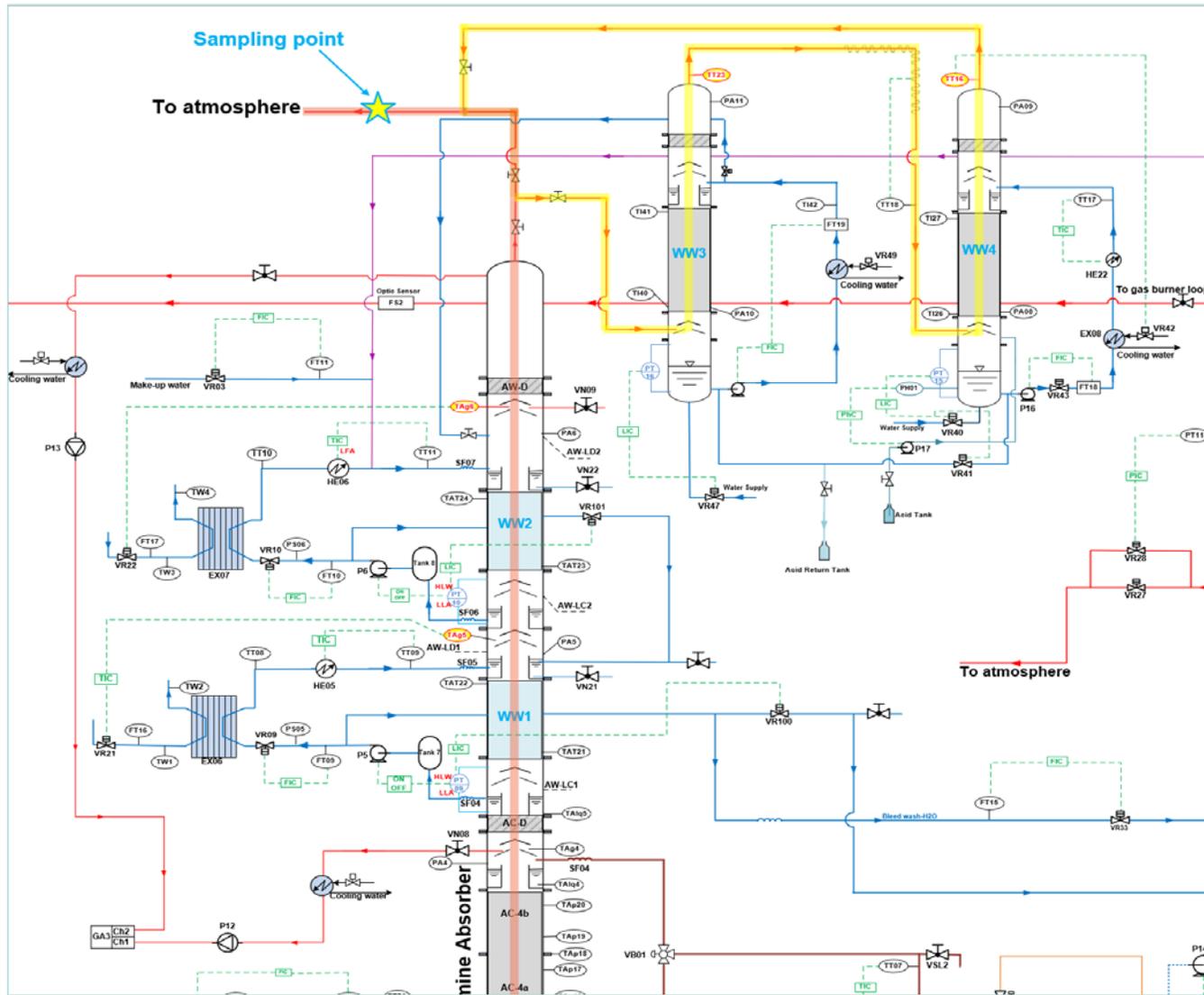


Figure 2-2: Extract from the P&ID illustrating location of the available gas paths: brown - for use with the internal water washes WW1 & WW2, giving flexibility to sideline the external water-washes WW3 & WW4 while the yellow path – incorporates WW3 & WW4 and that loop is inclusive

2.2.2 Numerical processing

Following the sampling procedure and analysis of the samples, numerical processing is necessary to calculate normalized concentrations of the analyte in the flue gas. This is based on the recorded data, such as:

- Sampling time
- Total gas volume passed through the impinger train
- Temperatures in the water bath and in the gas meter
- Atmospheric pressure
- Weights of the flasks and silica gel dryer before and after sampling

2.3 Results and discussion

Table 2-2 presents the main results from the emissions measurements during the REALISE campaign. In total 12 impinger train measurements were performed. Measurements number 1-10 were taken with the two water wash sections active, number 11 with three and number 12 with all four available. During measurements 6,7,8 & 9 deliberate temperature changes were conveniently introduced in the appropriate water-wash sections (see Figure 2-5). The purpose was to study the dynamic response of the emissions to any such changes. On these occasions, impinger train measurements were performed in parallel to FTIR, for three conditions: 1) steady state – high emission, 2) transient state emissions, 3) steady state- low emission. This means that the measured emissions don't reflect the standard steady- state operation of the CO₂ capture plant, but rather intermediate, extreme cases.

In the meantime, FTIR instrument was running continuously. For those time windows corresponding to impinger measurements, the later will be used to validate performance of the instrument, whose main purpose is monitoring emissions trends online.

Once validated by the standard reference, the implication is that the FTIR can reliably be used to monitor emissions continuously with an appreciable degree of confidence. However, it is recommended, for long-term applications, to periodically perform impinger reference check tests (vs. FTIR) just in case the instrument experiences a drift.

2.3.1 Sampling efficiency

Sampling efficiency of the impinger train, defined as a percentage of analyte found in a particular flask appeared to be satisfactory, as in virtually all cases, no traces of analyte was recovered in the last flask. A typical sampling efficiency profile, visualizing the data from the 1st measurement is shown on Figure 2-3 and Figure 2-4, while data for all the rest measurements is given in Table 2-1. This data indicates that the sampling method was correctly chosen and the procedure was performed efficiently.

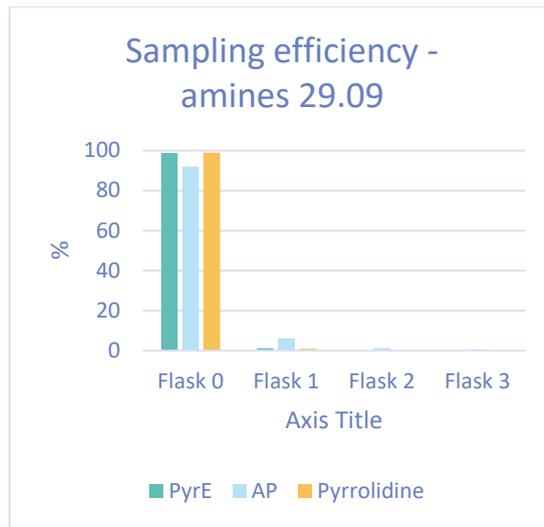


Figure 2-3: Sampling efficiency of the impinger trains for capturing amines

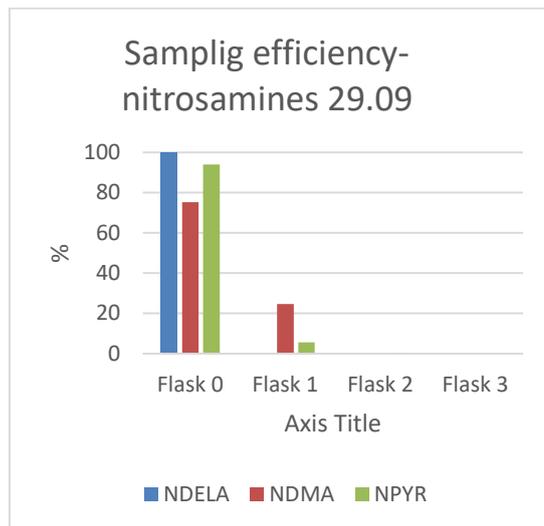
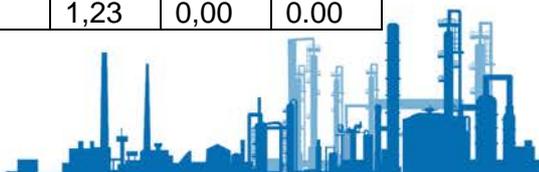


Figure 2-4: Sampling efficiency of the impinger trains for capturing nitrosoamines.



Table 2-1 Summary of the sampling efficiency data as the percentage of the recovered analyte in the sampling flasks.

Measurement	Date	Compound	Percentage of the recovered analyte in the sampling flasks			
			Flask 0 (condensate) [%]	Flask 1 [%]	Flask 2 [%]	Flask 3 [%]
1	29.09	PyrE	98,8	1,1	0,1	0,0
		AP	91,9	6,1	1,3	0,6
		Pyrrolidine	99,0	1,0	0,0	0,0
		NPYR	93,97	5,64	0,35	0,04
2	06.10	PyrE	98,41	1,48	0,10	0,01
		AP	90,58	8,09	1,05	0,28
		Pyrrolidine	98,88	1,08	0,04	0,00
		NPYR	93,14	6,32	0,50	0,04
3	13.10	PyrE	96,80	2,94	0,25	0,01
		AP	84,54	13,54	1,53	0,38
		Pyrrolidine	96,58	3,20	0,21	0,01
		NPYR	91,02	8,40	0,52	0,06
4	19.10	PyrE	99,07	0,86	0,07	0,01
		AP	92,07	6,42	1,37	0,14
		Pyrrolidine	97,46	2,44	0,11	0,00
		NPYR	79,56	18,75	1,46	0,22
5	14.11	PyrE	99,24	0,72	0,20	0,00
		AP	96,17	2,88	0,57	0,00
		Pyrrolidine	99,32	0,47	0,21	0,00
		NPYR	94,25	5,36	0,39	0,00
6a	16.11	PyrE	99,29	0,60	0,08	0,03
		AP	85,58	8,02	5,25	1,16
		Pyrrolidine	99,26	0,57	0,12	0,05
		NPYR	91,77	7,69	0,54	0,00
6b	16.11	PyrE	99,46	0,51	0,02	0,01
		AP	99,20	0,57	0,13	0,02
		Pyrrolidine	99,41	0,56	0,02	0,01
		NPYR	97,26	2,50	0,24	0,00
6c	16.11	PyrE	98,97	0,98	0,04	0,00
		AP	97,34	2,06	0,35	0,26
		Pyrrolidine	98,58	1,39	0,03	0,00
		NPYR	97,60	2,19	0,21	0,00
7a	17.11	PyrE	99,68	0,26	0,04	0,02
		AP	93,89	4,56	1,24	0,31
		Pyrrolidine	99,63	0,17	0,20	0,00
		NPYR	99,97	0,63	0,00	0,00
7b	17.11	PyrE	97,39	2,05	0,47	0,09
		AP	73,41	14,62	6,52	0,42
		Pyrrolidine	97,66	1,79	0,43	0,13
		NPYR	97,14	2,86	0,00	0,00
7c	17.11	PyrE	99,71	0,20	0,05	0,04
		AP	96,57	3,43	0,00	0,00
		Pyrrolidine	100,00	0,00	0,00	0,00
		NPYR	98,77	1,23	0,00	0,00



Measurement	Date	Compound	Percentage of the recovered analyte in the sampling flasks			
			Flask 0 (condensate) [%]	Flask 1 [%]	Flask 2 [%]	Flask 3 [%]
8a	01.12	PyrE	99,18	0,78	0,03	0,00
		AP	73,68	15,15	7,15	4,01
		Pyrrolidine	99,67	0,33	0,01	0,00
		NPYR	97,31	2,69	0,00	0,00
8b	01.12	PyrE	99,08	0,85	0,06	0,00
		AP	80,05	14,39	4,50	0,20
		Pyrrolidine	99,43	0,54	0,02	0,00
		NPYR	97,09	2,91	0,00	0,00
8c	01.12	PyrE	97,34	2,54	0,11	0,01
		AP	69,10	12,62	13,09	5,18
		Pyrrolidine	99,76	0,11	0,07	0,06
		NPYR	96,70	3,30	0,00	0,00
9a	02.12	PyrE	97,80	1,98	0,12	0,00
		AP	80,36	13,99	5,15	0,49
		Pyrrolidine	96,55	3,12	0,23	0,00
		NPYR	96,37	3,63	0,00	0,00
9b	02.12	PyrE	96,50	3,27	0,22	0,00
		AP	38,63	38,48	22,89	0,00
		Pyrrolidine	98,19	1,75	0,06	0,00
		NPYR	92,32	7,68	0,00	0,00
9c	02.12	PyrE	97,14	2,11	0,12	0,03
		AP	73,21	21,94	4,84	0,00
		Pyrrolidine	99,10	0,86	0,04	0,00
		NPYR	92,05	7,95	0,00	0,00
10	07.12	PyrE	98,70	1,20	0,09	0,02
		AP	88,62	9,81	0,99	0,47
		Pyrrolidine	99,03	0,90	0,06	0,01
		NPYR	90,53	8,78	0,65	0,04
11	08.12	PyrE	99,28	0,64	0,05	0,03
		AP	75,71	12,08	6,03	3,21
		Pyrrolidine	99,29	0,65	0,04	0,02
		NPYR	93,19	6,58	0,23	0,00
12	09.12	PyrE	97,05	2,00	0,55	0,41
		AP	89,48	7,72	1,50	0,99
		Pyrrolidine	98,20	1,48	0,17	0,15
		NPYR	88,07	11,33	0,60	0,00

2.3.2 Amines

The two solvent components: 1-Pyrrolidineethanol (PyrE) and 3-Amino-1-propanol (AP) were found consistently in the flue gas. Moreover, one degradation compound – Pyrrolidine, was also present.

One must be aware that the emissions results shall always be interpreted in the relation to the plant operating conditions described in detail in deliverable D2.4 (HS-3 Campaign at Tiller plant). Therefore, results from one test to another can not necessarily be compared directly without



considering process parameters like temperature, solvent composition and loading, and to some extent the wash-water circulation rates. However, the results give a general impression of the emissions during different operating conditions. Note that there were no observation of aerosols during the campaign which would had a large impact on the emissions.

Nevertheless, throughout the planned campaign activities, emissions can be considered as rather low. PyrE is the most prevalent component in the gas phase. It seems logical, considering that it constitutes 40 wt.% of the initial solvent blend, although one must be aware that the mole fraction is just one factor influencing emissions, next to volatility and solubility in water. AP contribution was 15 % wt.%, and it appears to be even more stable, with concentrations in the gas phase between 0.02-0.17 ppm. Pyrrolidine was identified as the main degradation compound, although its concentration was below 1 ppm throughout the normal operation of the CO₂ plant. However, it can be seen from dynamic tests that under certain conditions (as those depicted in Figure 2-5), emissions for PyrE, AP and Pyrrolidine increased significantly while the corresponding values for AP were hardly changed.

To check the possible solvent degradation effect on emissions, during the last week of the campaign plant's conditions were set as they were shortly after the initial start-up. Therefore, a direct comparison can be made between measurements number 3 from the 13th of October and number 10 from the 7th of December. Apparently, solvent degradation was not significant enough to affect the emissions under normal operating conditions, whereas the effect of using additional water wash sections is clearly visible, resulting in very low emissions when using all four of them. However, concentration of AP during the last measurement seems not to follow this trend. Although, since it still remains in the very low concentration region it was identified as an outlier.



Table 2-2 Summary of the calculated emissions of the solvent components (PyrE, AP) and one amine degradation compound - Pyrrolidine. All concentrations in ppmv. Corresponding FTIR measurements are also shown. Measurements 1-10 performed with two water wash sections active. Note that a dry bed configuration was used in no 4 (Run 20). Measurement 11 performed with three water-wash sections active, measurement 12 performed with four water wash sections active.

Emission measurement	Run	Date	PyrE - impinger [ppmv]		PyrE-FTIR [ppm]	AP - impinger [ppmv]		AP- FTIR [ppm]	Pyrrolidine - impinger [ppmv]		
			SS- low	Trans	SS- high	SS- low	Trans	SS- high	SS- low	Trans	SS- high
1	5	29-Sep	6,47		-	0,02		-	0,72		
2	11	6-Oct	3,13		10,46	0,02		0,95	0,20		
3	16	13-Oct	5,83		12,56	0,02		0,81	0,91		
4	20	19-Oct	1,70		1,02	0,08		0,41	0,23		
5	35	14-Nov	3,21		5,77	0,05		0,36	0,44		
6	dynamic test	16-Nov	0,76	14,05	30,67	0,01	0,39	0,09	0,15	2,96	24,07
7	dynamic test	17-Nov	1,87	5,14	12,26	0,05	0,52	0,24	0,42	1,13	3,7
8	dynamic test	1-Dec	3,21	20,09	30,37	0,01	0,02	0,02	1,05	9,31	17,56
9	dynamic test	2-Dec	1,28	3,31	27,85	0,01	0,02	0,02	1,48	4,17	47,69
10	53	7-Dec	1,84		6,46	0,02		0,88	0,84		
11**	54	8-Dec	0,39		1,55	0,03		0,3	0,22		
12***	55	9-Dec	0,06		1,54	0,17		0,55	0,04		



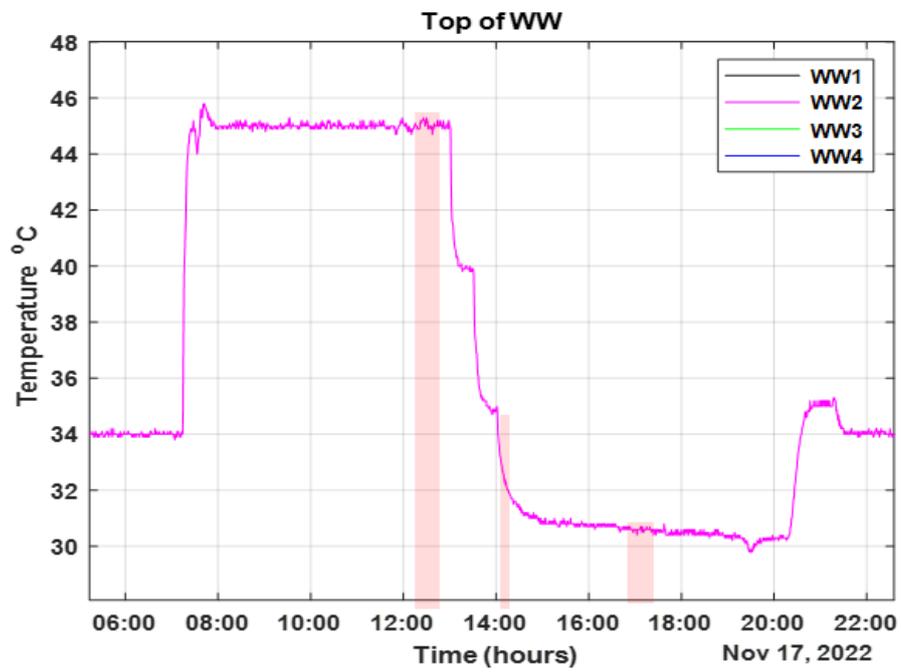
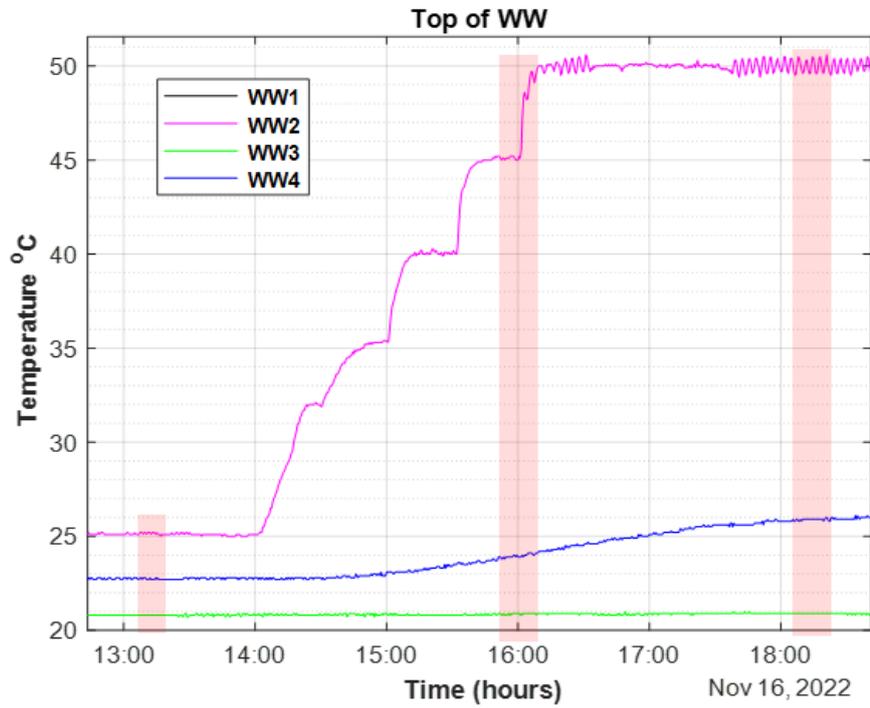


Figure 2-5: Plot illustrating how the temperature in the water-wash (WW2) section was manipulated in order to cause changes in emissions: on 16/Nov- the T was ramped up while on 17/Nov, the T was ramped down. It is important to note that only WW2 is shown because it is the one with pertinence to in this cases under study.



Deliberate arrangements were made to synchronize standard impinger measurements vs. the FTIR measurements. The objective was to compare/gauge FTIR performance against an established standard, in which case, the instrument was found to be moderately in good agreement with impinger values regarding PyrE emissions, whereas it exhibited significant deviation with respect to AP emission values. As a general comment, this deviation is understandable due to the fact that the FTIR instrument has no capacity (by design) for high accuracy for concentrations below 1 ppm. In cases where emission monitoring using the FTIR is required, corresponding values from manual sampling can then be used for re-adjustment of the FTIR model, after which it is possible to re-run the raw spectral data to obtain corrected values throughout the campaign. Doing this also allows to have a calibrated on-line measurement in case of using this solvent again.

Comparison between selected impinger measurements and FTIR is shown below (Figure 2-4). As indicated before, manual sampling and subsequent LC-MS analysis is a more accurate method than FTIR, especially in region of very low concentrations. Therefore it can be seen that FTIR consistently over-estimated the concentration of AP, whereas PyrE was in the same order of magnitude.



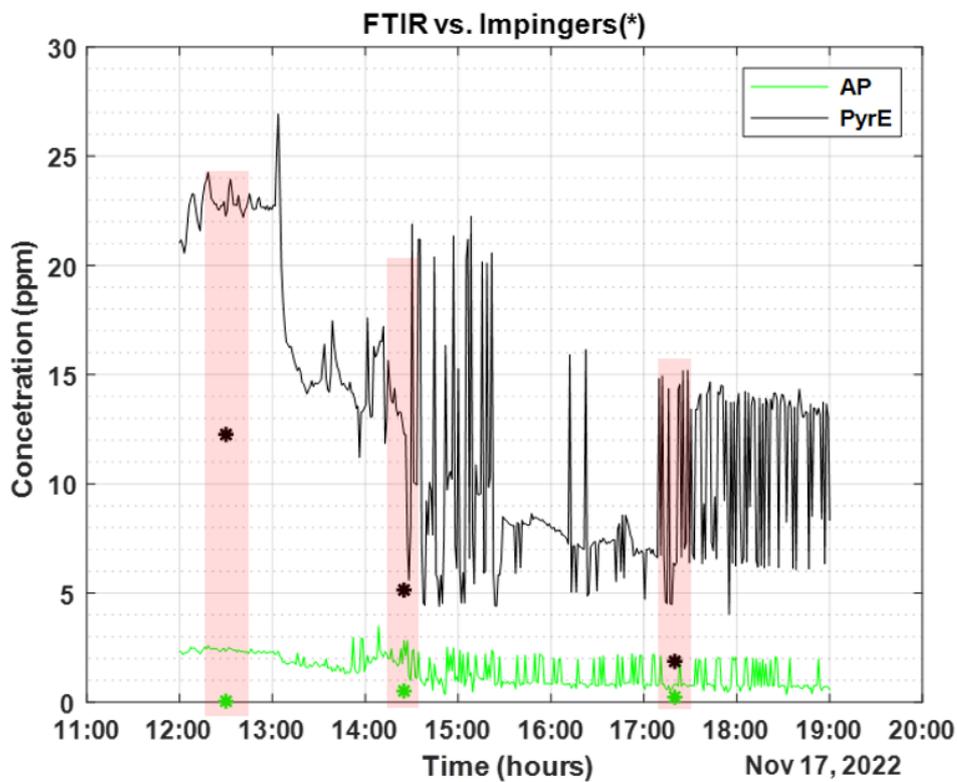
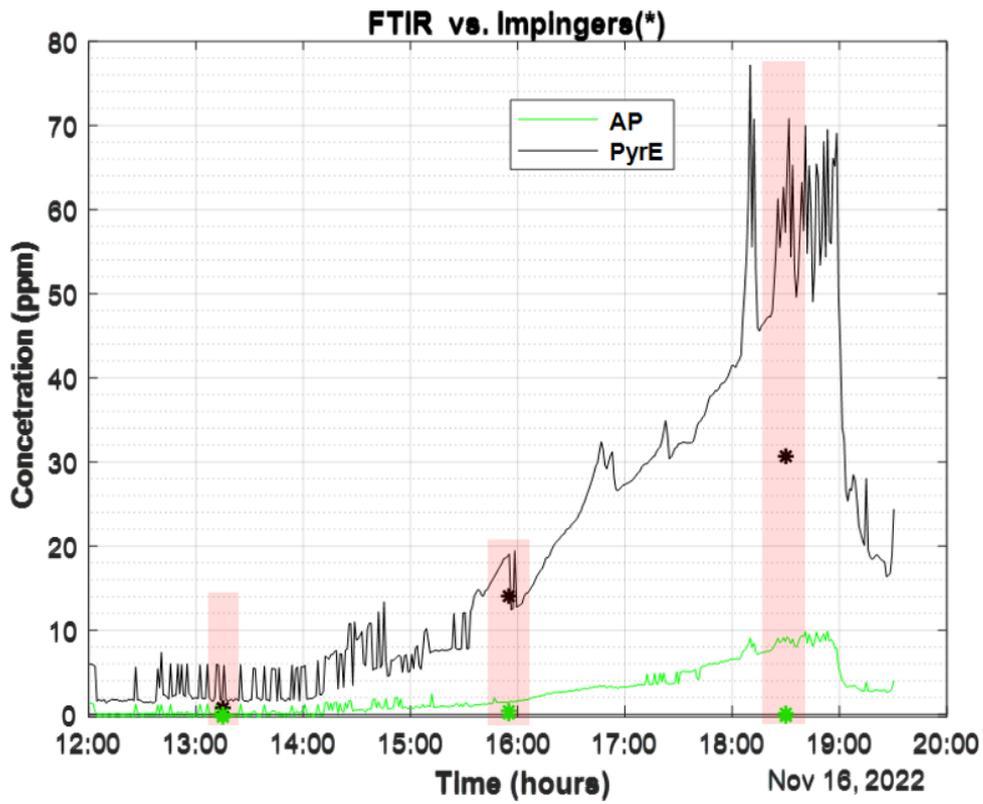


Figure 2-6: Plots illustrating FTIR performance vs. standard impinger measurements



2.3.3 Nitrosamines

Nitrosamines are a class of degradation products that are formed from the reaction of amines with nitrous oxide (NO_x) emissions. Initially, the presence of a number of different nitrosamines was investigated, however only three of them were found to be above the detection limit: N-Nitrosodiethanolamine (NDELA), N-Nitrosodimethylamine (NDMA) and N-Nitrosopyrrolidine (NPYR). Although despite being detected, the concentration of the first two appeared to be marginally low (1e-05 ppm), which is why later the focus was on NPYR only. Table 2-3 shows the calculated concentrations of nitrosamines from the sulfamic acid impinger train measurements.

Table 2-2: Summary of Nitrosamines emission measurements

Measurement no	Date	NPYR [ppmv]			NDELA [ppmv]			NDMA [ppmv]		
		SS-low	Trans	SS-high	SS-low	Trans	SS-high	SS-low	Trans	SS-high
1	29.09	0,00203			0,00043			0,00001		
2	06.10	0,00264			0,00006			0,00001		
3	13.10	0,00281			0,00008			0,00000		
4	19.10	0,00068			0,00000			0,00001		
5	14.11	0,00275			n/a			n/a		
6*	16.11	0,00114	0,00570	0,01223	n/a	n/a	n/a	n/a	n/a	n/a
7*	17.11	0,00273	0,00472	0,00915	n/a	n/a	n/a	n/a	n/a	n/a
8*	01.12	0,00281	0,01023	0,01318	n/a	n/a	n/a	n/a	n/a	n/a
9*	02.12	0,00131	0,00191	0,00849	n/a	n/a	n/a	n/a	n/a	n/a
10	07.12	0,00410			n/a			n/a		
11**	08.12	0,00101			n/a			n/a		
12***	09.12	0,00075			n/a			n/a		



3 Measuring impurities in the CO₂ product

3.1 The CO₂ compression and liquefaction unit (CCLU)

Quality of the CO₂ coming out from the capture unit can be crucial for transportation, storage and utilisation of CO₂. In REALISE, the CO₂Lab pilot is equipped with a compact CO₂ compression and liquefaction unit (CCLU), enabling liquefying the CO₂ produced in the capture process. The main objective is to identify and quantify expected impurities in the CO₂ product when using HS-3 solvent in the refinery industry. The focus is on HS-3 amines and amine degradation products in the CO₂.

For safety reasons the CCLU is built inside a cabinet with ventilation and CO₂ level alarm.

In the design of the CCLU, it has been an important issue to be as close to a large scale standard unit as possible such that the results at Tiller are relevant for industrial cases.

The compressor train design is based on three compression stages with cooling of the gas to 20 - 25 °C and water separation after each stage. The design compressor ratio for each stage is 2.8. Assuming 1.8 bara pressure for the CO₂ rich gas from the top of the desorber this will give pressures of about 5, 14, and 40 bara after each stage. The PI&D of the compression train is shown in the Figure 3-1.



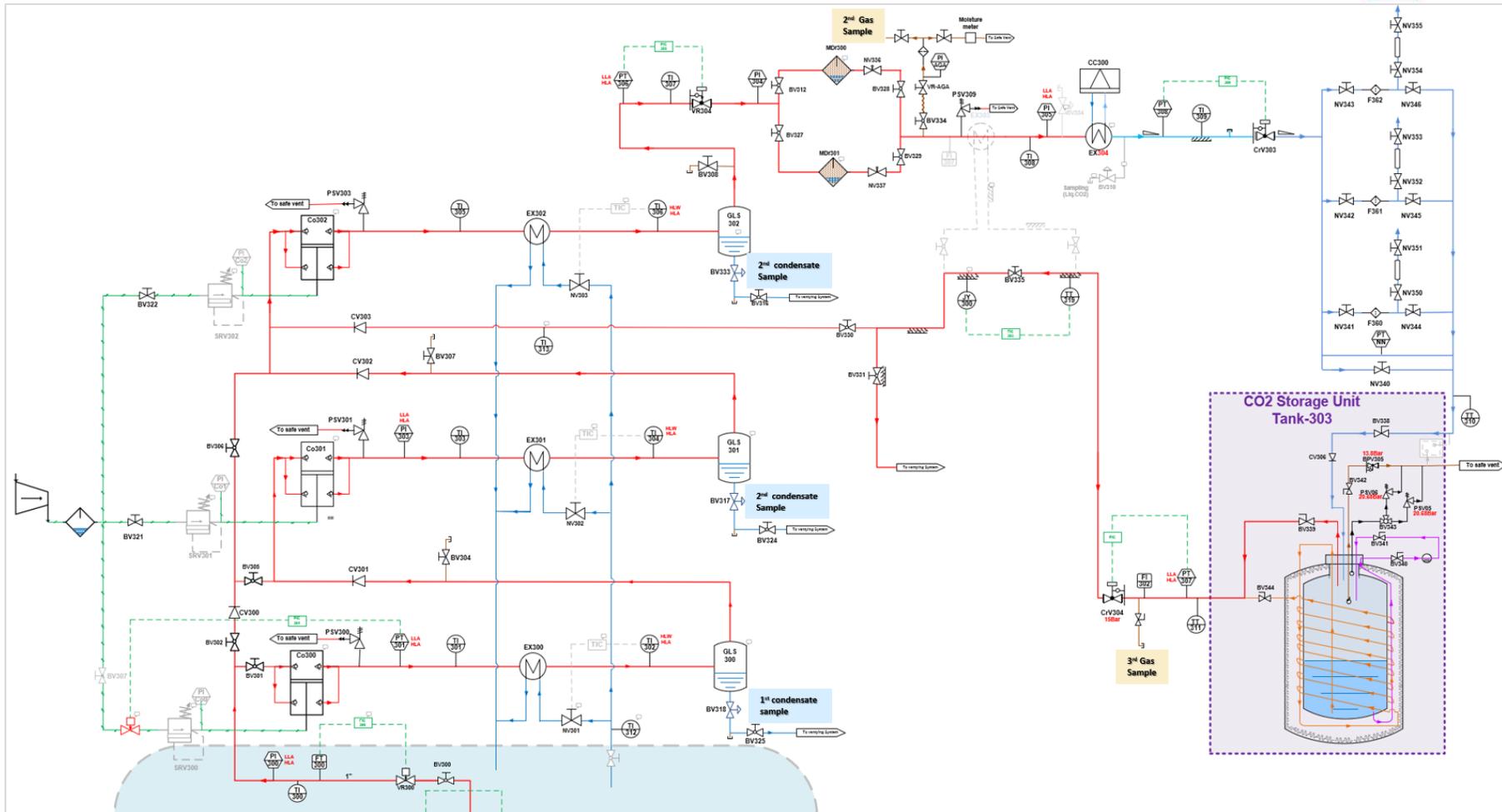


Figure 3-1: P&ID of the CCLU illustrating the sampling points for both the condensate and the gas phase. 1st gas sampling point exists but not shown in this diagram because it belongs to the main process further upstream.



The compressor stages are implemented using Haskel gasboosters from Proserv. These use compressed air to drive the piston in the boosters. At SINTEF Tiller such air is available for the whole area from a central compressor. Even if the design compression ratio is 2.8 they have some flexibility for increasing/decreasing this ratio.

The amount of CO₂ taken from the stripper CO₂ product stream is measured by a Coriolis flow meter (FT300). Also, the inlet temperature is measured (TI300). The gas then enters the first compression stage at approximately 1.5-1.8 bar and leave it at approximately 5 bars by using the first Haskel gas booster. The gas is then cooled down to 15-20 °C and the condensed water is separated out in a knockout drum. The gas is then sent to a second Haskel booster which increases the pressure to about 14 bar and then to the third booster which gives about 35-40 bar. There are knock-out drums after each of these two compressors as well. It is possible to take liquid samples from the drums.

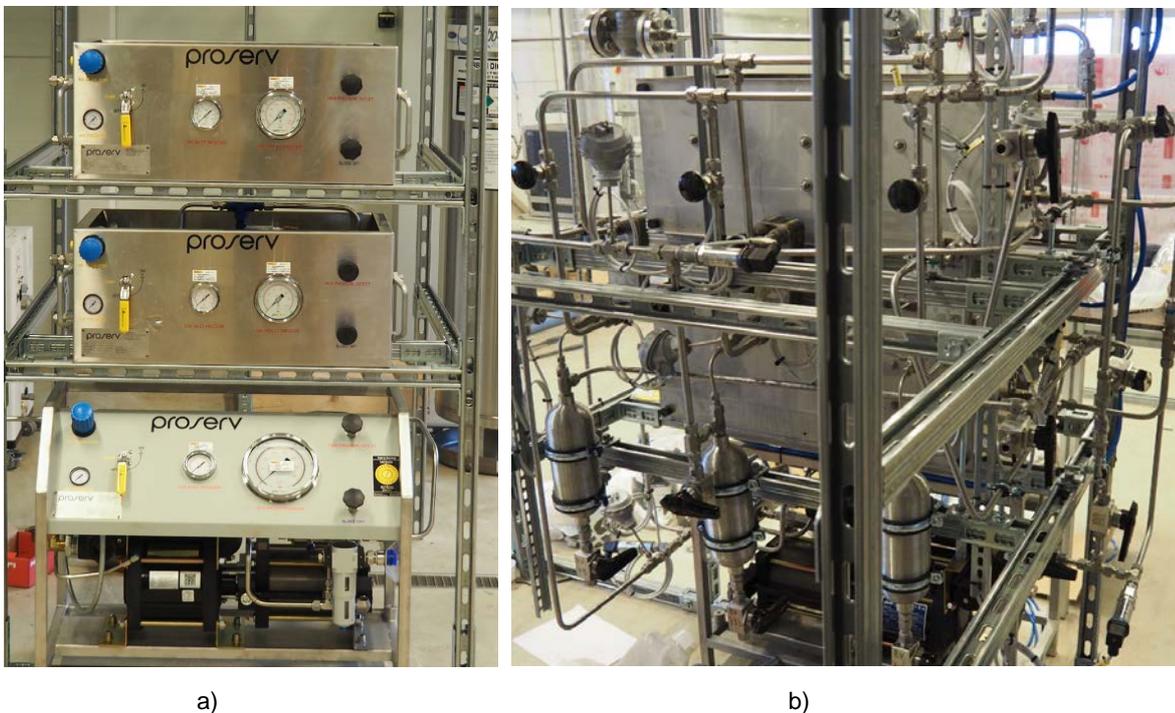


Figure 3-2. The three compressors a) Front view b) back view with pipes, valves and knock out drums

After the third knock out drum the compressed CO₂ gas is at 35 - 40 bar and 15 - 25 °C. The pressure is controlled by a control valve. The gas at this stage will have 400 – 600 ppm of water. To get down to 20 – 30 ppm that is often required, the gas is dried in a cylinder filled with molecular sieve 3Å beads. Two such cylinders are mounted in parallel (see Figure 3-4.) to increase the flexibility of the system.



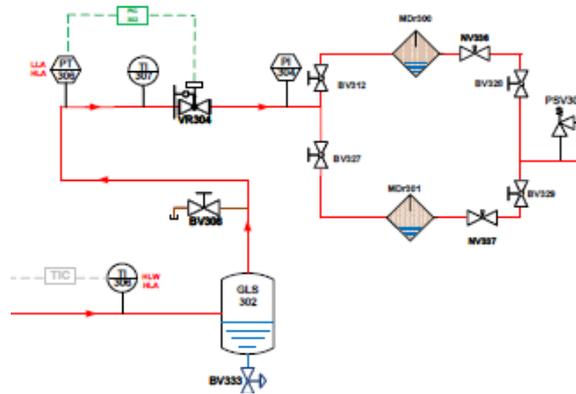


Figure 3-3. The drying system of the CCLU

An external Lauda Integral IN 250XTW cooler (See Figure 3-5.) provides a cooling medium (ethanol) at typically -5 to -15 °C. The CO₂ gas is liquified with this ethanol inside a plate-and-frame heat exchanger. The temperature of the liquid CO₂ is typically -5 to -10 °C.

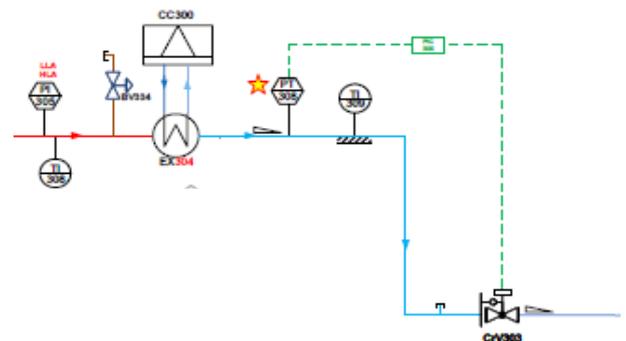


Figure 3-4. a) The external cooler Lauda.

b) Cooling and expansion of CO₂

Afterwards the liquid is expanded through an expansion valve CrV303 to the desired pressure (15-16 bar). This will produce a two-phase stream at about -26 °C that enters a CO₂ storage tank (Carbo-Max450) produced by Linde (Figure 3-6.) .



The gas phase will leave the tank through a control valve that keeps the pressure at 15 -16 bar. The liquid will be stored in the tank. The tank is well insulated, and any heat loss will be compensated by evaporation of liquid CO₂, which is then released through the control valve.

The gas out of the tank may either leave the unit to ventilation or be led back to the last stage compressor.

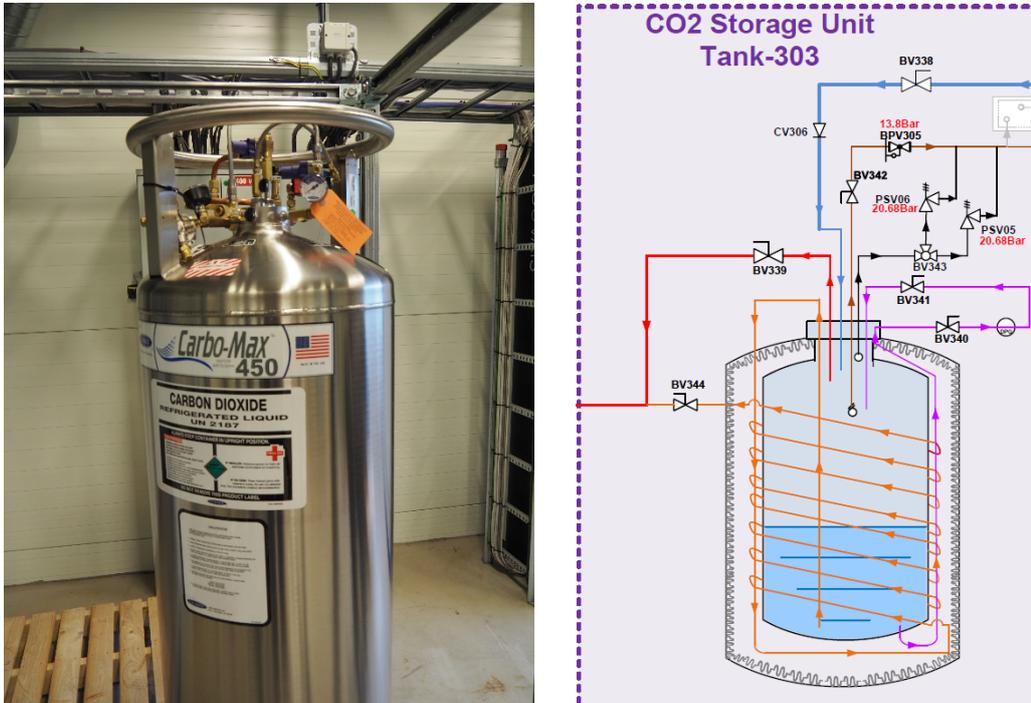


Figure 3-5. CO₂ storage tank CCLU.

Sensors and control loops are implemented into the Siemens PC7 system of the pilot plant. It is possible to take a sample of the gas after the dryers and of the gas stream out of the storage tank. Liquid samples can be taken from the knockout drums.

3.2 Instruments and analysis of N₂ and O₂

To analyse the CO₂ stream for Nitrogen and Oxygen, a pressurised (approximately 20 bar) sample was collected in an appropriate cylinder. The following sections discuss the used instruments and methods for the analysis along with the results.

3.2.1 Micro GC

Micro GC is a fast and convenient method for analysis of gas samples. For this purpose Agilent 990 Gas Chromatography was used with Soprane II software (SRA Instrument Analytical Solutions)

The Micro GC is equipped with two separate columns and thermal conductivity detectors (TCD). Channel 1 with a 3m + 10m MS5A, RTS column (Serial Nr CM20511010). Channel 1 is operated with Argon 5.0 carrier gas at a pressure of 22 psi and a temperature of 110 °C. Backflash time 40 sec. Channel 2 with a 10 m PPQ column (Serial No: CM21011005) and is operated with Helium 6.0 carrier gas at 22 psi and a temperature of 70 °C. The inlet, injectors and backflash module



are kept at 90 °C. The injection time was 50 ms for both channels. The run time for the gas analysis was set to 110 seconds.

3.2.2 Span gas

Span gas was used for calibration assuming linear response in the desired concentration range. The AGA Cylinder Nr: 7523112710536 / Certificate No.: 100673050, contained 308 mol-ppm ($\pm 2\%$) N₂ and 74.5 mol-ppm ($\pm 2\%$) O₂ in carbon dioxide (balance).

3.2.3 Sampling system

The gas cylinder was connected the analyser with standard Swagelok tube connectors. A Linde pressure regulator Type C300/1A-10B (No 10) in combination with flow meters are used to control the sample gas flow through sintered metal filter (pore size 5 μ m) and over the Geni A separation membrane. The sampling system was purged for 20 minutes with sample gas at 100 ml /min before sample was injected for analysis. The sample flow rate was adjusted to 50 ml/min vented to ventilation system while the GC internal sample pump extract with 5 ml min over 8 sec into the sampling loop and injected the sample gas into columns.

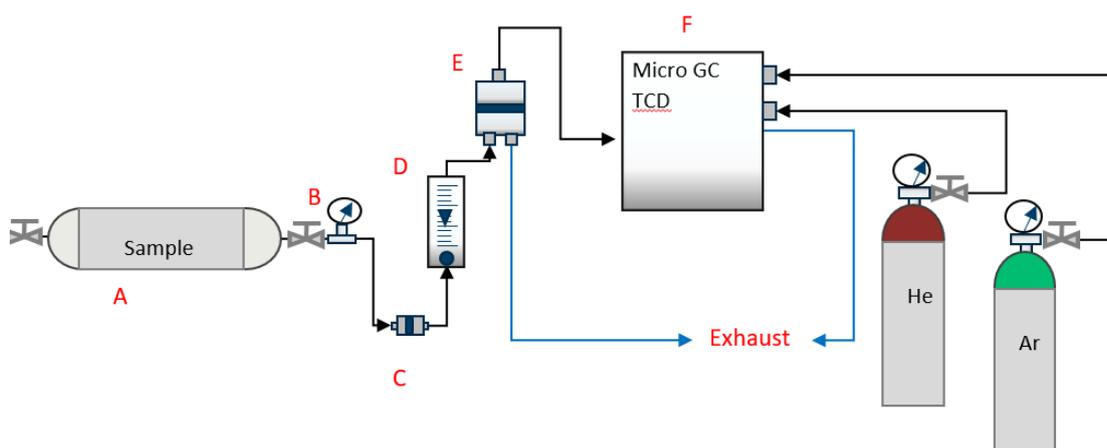


Figure 3-6: Sketch of sampling setup

Table 3-1: Components

Component ID	Description	Supplier
(A)	Gas cylinder	Swagelok
(B)	Pressure Regulator	Linde HiQ type C300/1A-10B (No 10)
(C)	External filter unit	Agilent
(D)	Flowmeter Type RMA- 150-SSV	Dwyer Instruments Inc., Mich. City, Indiana, USA
(E)	Genie® 170 membrane separator	A+ Genie Filters.com
(F)	990 Micro GC	Agilent



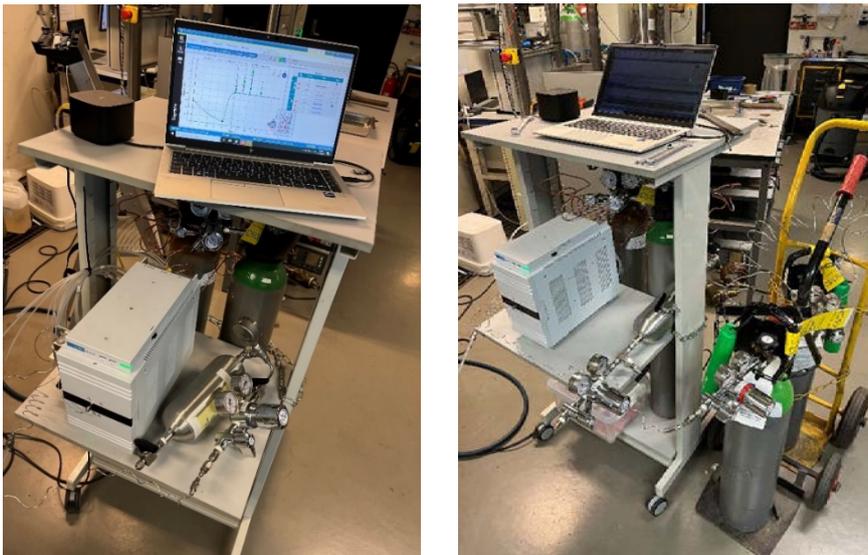


Figure 3-7: Agilent 990 Micro GC – Sampling setup

Sample was injected and analysed repeatedly until concentration reached stable level.

3.2.4 Results

Figure 3-9 and Table 3.2 present the results for the oxygen and nitrogen concentration in the CO₂ gas.



Figure 3-8: Cal gas injection and sample analysis



Table 3.2 Results for oxygen and nitrogen analysis. Results normalized- traces of other components not included.

	Sample 1 2022_12_01	Sample 2 2022_12_09
O ₂ [%]	0.006	n/d
N ₂ [%]	0.058	0.019
CO ₂ [%]	99.936	99.981

3.3 Measurement of amine and amine degradation products

To assess the purity of the product CO₂ stream and along the liquefaction unit a similar sampling procedure as for the main plant was utilized.

Measurements have been performed simultaneously at three points (also indicated on **Figure 3-1**):

- CO₂ stream from the main plant- exit from the desorber – 9th floor (1st gas sample)
- CCLU-1: After compression and prior to the liquid CO₂ tank (2nd gas sample)
- CCLU-2: After the liquid CO₂ tank (3rd gas sample)

Sampling at these points was performed on two occasions. First on the 11th of November and later by the end of campaign on the 9th of December. Samples were primarily analysed for the same components as for the emissions measurements (PyrE, AP, Pyrrolidine and NPYR), but also traces of other degradation products (NH₃, Methyl-AP) were found. As an addition to standard impinger measurements with an acidic solvent (sulfuric and sulfamic acid for each point), one additional set consisting of a flask with demineralised water and a DNPH cartridge was used, targeting carbonyls and ketones (Formaldehyde, Acetaldehyde, Acetone).

The calculated concentrations are given in Table 3-2 and Table 3-3.

Table 3-2 Calculated data for the CO₂ stream gas measurements. First test – 11th November

Compound	1- 11 November			Absorbent
	Point			
	CO ₂ stream – 9 th floor (1 st gas sample) [ppmv]	CCLU-1 (2 nd gas sample) [ppmv]	CCLU-2 (3 rd gas sample) [ppmv]	Acid / water/ cartridge
PyrE	0,22	0,0009	0,0017	Sulfuric
AP	0,1096	0,0022	0,0045	Sulfuric
Pyrrolidine	0,0317	n/d	n/d	Sulfuric
NH ₃	0,0019	n/d	n/d	Sulfuric
Methyl- AP	0,0004	n/d	n/d	Sulfuric
NPYR	0,0018	n/d	n/d	Sulfamic



Table 3-3 Calculated data for the CO₂ stream gas measurements. Second test – 9th December

2- 9 December				
Compound	Point			Absorbent
	CO ₂ stream – 9 th floor (1 st gas sample) [ppmv]	CCLU-1 (2 nd gas sample) [ppmv]	CCLU-2 (3 rd gas sample) [ppmv]	Acid / water/ DNPH cartridge
PyrE	0,72	0,0025	0,0007	Sulfuric
AP	0,0113	0,0016	0,0019	Sulfuric
Pyrrolidine	0,0152	n/d	n/d	Sulfuric
NH ₃	0,0293	n/d	n/d	Sulfuric
Methyl- AP	n/d	n/d	n/d	Sulfuric
NPYR	0,0003	n/d	n/d	Sulfamic
Acetone	0,66	1,13	0,04	Water+ DNPH
Acetaldehyde	18,5554	17,89	4,06	Water+ DNPH
Formaldehyde	0,0015	0,01	n/d	Water + DNPH



4 Summary

Emissions related to the Tiller CO₂ capture pilot plant operation with HS-3 solvents were systematically measured during the HS-3 experimental campaign, together with the quality of the resulting CO₂ gas stream.

A manual sampling method based on a modification of EPA method² 5 using standard impinger was used. Implementation ensured to meet sampling efficiency criteria. This is supported by the fact that results show that practically all analytes of interest were captured by the sampling impinger trains.

An online FTIR instrument was also used in parallel for continuous emission monitoring. Values from the standard impinger method could then be used to validate the performance of the FTIR model. For the components under discussion, comparison of the corresponding measurements (impingers vs. FTIR model) revealed that FTIR model performed fairly well for low emissions (<10 ppm PyrE), while it needs improvement for higher values and its accuracy is also limited by design in the very low concentration region (<1 ppm AP). Collected data from manual sampling can be used to enhance the FTIR model accuracy, in case of any future operation with HS-3 solvent. Notwithstanding, the FTIR managed to follow the emission trends during dynamic scenarios.

Of these two, it was observed that AP had virtually very low emissions irrespective of the temperature changes in the water-wash sections. PyrE had higher emissions relative to AP values and reacted to perturbations in the water-wash section immediately upstream. Nevertheless both components showed low emissions under normal operation, in which case implementation of the water-wash abatement techniques effectively lowered the emissions to <1ppm.

As a general comment, measured values indicate that the emission of solvent and degradation compounds during a standard plant operation can be considered as low (<10 ppm PyrE, <1 ppm AP, Pyrrolidine, < 4e-03 ppm NPYR). For normal operation, it was observed that there were no signs of a significant increase in emissions with respect to degradation components (Pyrrolidine & NPYR). This was achieved by performing emission measurements in the late part of the 12 week campaign vs. measurements performed for the same plant operating conditions in the first and last week of the campaign.

Such low emissions were also due to the application of plant's emission mitigation equipment (demisters, water-wash sections). By default, usage of two water-wash section was sufficient to keep the emissions at the aforementioned levels, whilst increasing the number of water-wash sections (up to four available) allows to bring down emissions to marginal levels (< 0.5 ppm). It was also found that the operating conditions of the water-wash section (mainly the temperature) can have a significant impact on emissions.

Since the CO₂ product is of great interest with respect to CO₂ transport and or CO₂ utilization, it is important to know the constituent components. This is not trivial since most components in this case will be in the ppb level. SINTEF's CO₂ capture facility at Tiller now includes a CO₂ liquification

² <https://settek.com/documents/EPA-Methods/PDF/m-05.pdf>.



unit. Effort was therefore made to measure (components in CO₂ product in the liquification loop/unit) what's possible within the technical means at SINTEF's disposal:

- CO₂ product sampling using Midget impingers with appropriate absorbents: sample analysis using MS-methods: Traces of the solvent amines and degradation were found at liquification point
- a pressurized CO₂ sample cylinder (from the CO₂ liquification unit) taken just before liquification point: analysis using micro GC, in which case traces of O₂ and N₂ were found in the sample

The results showed that amines and ammonia were far below the limit requirements set in the Northern Light project. The only component that was close to the limit was acetaldehyde (≤ 20 ppm).

