

Issued for information	01	28.06.2019	Shell	TS	ML
Reason for Issue	Client's Rev.	Rev. Date	Prep. By	Checked	Approved

Company: Fortum Oslo Varme AS Project: Project CCS Carbon Capture Oslo Document title: **Pilot Plant Final Test Report** Number of pages: Client's Document no: NC03-KEA-P-RA-0016 Contractor's Document no: N/A Rev: N/A 3 KI: CONFIDENTIAL Attachments: (113 pages) efortum 1. Shell Catalysts & Technologies "Fortum Oslo Varme CO2 capture pilot plant - final report" (41 page) Oslo Varme 2. Eurofins calibration - amines (2 pages) Burofins calibration - degradation products (3 pages)
Eurofins calibration - IC-ICP (4 pages) 5. Flowmeter validation (13 pages) 6. NOx assessment (38 pages) 7. Ramboll calibrations (7 pages) 8. UiO calibrations (3 pages) 9. Extractive Gas Sampling set-up (1 page) 10. Extractive sampling validation (1 page)



Project: Project CCS Carbon Capture Project no. NC03 Client's Document No: Rev: NC03-KEA-P-RA-0016 01 Document Title: Pilot Plant Final Test Report

Date: 28.06.2019



Revision History								
Reason for Issue	Rev.	Date	Change					
Issued for information	01	28.06.2019						

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Project: Project CCS Carbon Capture Project no. NC03 Client's Document No: Rev: NC03-KEA-P-RA-0016 01 Document Title: Pilot Plant Final Test Report

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### 1 CONTENT

This report contains:

- 1. Shell Catalysts & Technologies "Fortum Oslo Varme CO2 capture pilot plant final report"
- 2. Eurofins calibration amines
- 3. Eurofins calibration degradation products
- 4. Eurofins calibration IC-ICP
- 5. Flowmeter validation
- 6. NOx assessment
- 7. Ramboll calibrations
- 8. UiO calibrations
- 9. Extractive Gas Sampling set-up
- 10. Extractive sampling validation



# Fortum Oslo Varme CO<sub>2</sub> capture pilot plant

**Final Report** 



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Shell Catalysts and Technologies	
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# 1 Executive Summary

This report summarizes the main findings of the 2000 hours pilot campaign run from March to June 2019, to demonstrate amine emissions from CO<sub>2</sub> capture, using CANSOLV DC-103 absorbent, from the Klemetsrud incineration plant off-gas.

The main objective was to demonstrate low amine emissions - below a target of 0.4 ppmv, which constitutes the lower limit of the confidence interval established by the NILU and the University of Oslo to ensure ground level nitrosamine concentration limits are met.

Absorbent degradation was also monitored, as well as other performance parameters, in particular CO<sub>2</sub> product purity.

#### Amine emissions

During the 500 hours test, the amine emissions were on average of 155 ppbv and only very occasionally exceeded the target of 0.4 ppmv, in particular during a malfunction of the ESP (during which the BDU was brought online by the operator, but subsequently put back off-line).

The table below summarize the average emissions over the stable operation period starting April 5<sup>th</sup> and the 500 hours test period.

	units	Value <sup>(2)</sup>
Target	ppbv	< 400
Stable operation period <sup>(1)</sup>	ppbv	195
500h test period	ppbv	155
500h test period excluding ESP malfunction	ppbv	44

Table1: Amine emissions

Note 1: Operating period starting April 5<sup>th</sup> onwards

Note 2: All values calculated from PTR-TOF-MS measurements reported on one-minute time interval.

During the 500 hours test the BDU (Brownian Diffusion Unit) was only operated for a short period (less than two hours) at the end of the "ESP malfunction-peak".

#### Absorbent degradation

The total degradation rate was evaluated based on the evolution of relative concentrations of undegraded amines and degradation products.

The total degradation rate is calculated to be  $0.078 \text{ kg/tCO}_2$  (captured).

However, the total degradation rate result captures absorbent oxidative degradation and degradation to nitrosamine. The latter depends essentially on NO<sub>2</sub> concentration in the inlet gas, which in the pilot campaign has been different from the value used to design the full-scale plant (1.4 ppmv vs 0.8 ppmv).

Thus, most relevant is a comparison of the observed and predicted oxidative degradation rates, which are obtained by subtracting the nitrosamine degradation rate (calculated from inlet NO<sub>2</sub>) from the total degradation rate. Those rates also need to be reported to the rich amine inventory fraction, which is different in a pilot unit and a full-scale plant.

The observed oxidative degradation rate is 17 mg/h.L<sub>rich</sub>, 40% lower than the value predicted using the tools employed to design the full-scale unit.

In the flue gas, only the secondary volatile degradation product ammonia has been reported, at 1 ppmv level or lower.

#### <u>CO<sub>2</sub> product purity</u>

Contaminants have been either detected at very low levels or have been found to be below detection limits, as shown in the table below.

Component	Units	Average	Max measured	Method
Amine 1	ppbv	3 (1)	83	PTR-TOF
Amine 2	ppbv	n.d.	n.d.	PTR-TOF
Amine 3	ppbv	n.d.	n.d.	PTR-TOF
Deg 1	ppbv	n.d.	n.d.	PTR-TOF
Deg 2	ppbv	n.d.	n.d.	PTR-TOF
Deg 3	ppbv	n.d.	n.d.	PTR-TOF
Formaldehyde	ppbv	4	140	PTR-TOF
Acetaldehyde	ppbv	800	2,400	PTR-TOF
O <sub>2</sub>	ppbv	Note 2	Note 2	Bag Sample
NH <sub>3</sub>	ppbv		< 100	Extractive sampling + IC

Table 2: CO<sub>2</sub> product purity

Note 1: most values are close to or below sensibility limit

Note 2: bag sample results were not available at the conclusion of this report. However presence of O<sub>2</sub> in the CO<sub>2</sub> product results purely from physical solubility in the absorbent and is not expected to deviate from values reported in full-scale design.

#### Steam Consumption

Although the steam consumption observed on a pilot plant is typically not representative of a full-scale unit (in particular due to higher heat losses, and because of the uncertainty on steam flow measurement), it has been compared to values predicted by the tools used to design the full-scale plant.

The observed steam consumption as GJ per ton captured CO<sub>2</sub> is 4.1 GJ/t, while the predicted value is 4.3 GJ/t.

It is important to note that:

- The consumptions above are significantly higher than those used for the design of the full-scale unit as the pilot plant is not equipped with an MVR heat recovery system.
- The pilot unit operating conditions have not been optimized to minimize energy requirements, in particular for target lean loading. They have been maintained within the window of operation representative of the commercial plant, which are expected to be optimal in terms of energy requirements, however it is possible that a commercial plant will achieve lower steam consumption once its operating conditions are optimized.
- The reported energy consumption is directly dependent on the steam flow measurement, the reliability of which has not been thoroughly assessed as this was not one of the primary objectives of the pilot campaign.

# 2 Introduction

This report summarizes the main findings of the 2000 hours pilot campaign run from March to June 2019, to demonstrate emission performance of CANSOLV DC-103 technology at the Klemetsrud incineration plant off-gas.

It addresses aspects relevant to the pilot campaign objective (in particular the main objective of demonstrating low amine emissions). For more detailed accounts of pilot plant operation reference is made to the weekly reports issued by FOV team. For background information on the pilot campaign plan and objectives, reference is made to the test plan prepared by FOV (document NC03-KEA-Z-TB-2001).

A first section briefly summarizes high-level considerations on the campaign and pilot operation during this campaign; again, reference is made to FOV reports for details.

A second section addresses validation of the on-line analytical instruments' readings and offline analytical methods (based on Shell's experience with similar campaigns). Questions around other process-related instrumentation) are addressed in weekly reports issued by FOV (notably validation of gas flowmeters readings, for which an extensive analysis has been done by FOV, which has been extracted from weekly report of week 14 and is attached in appendix 10.1).

The following section addresses the main plant operating parameters, and is followed by two sections addressing respectively amine emissions – the campaign main objective, and absorbent degradation.

The last sections address respectively other process performance parameters / campaign objectives, and key take-aways for the design of the commercial unit.

# 3 General considerations on pilot plan campaign

The initial start-up / plant capability demonstration was followed by a period of familiarization, involving:

- Troubleshooting of hardware issues (in this case control of water wash drain and temperatures, location of the Absorber sump level control valve, as well as non-process related issues such as steam generator regular trips).
- Bringing operating parameters stably within the target window
- Validation of process instruments readings (and determination of systematic errors)

From Shell experience, this is to be expected in any new pilot unit (especially when the unit has been designed and built on a very accelerated schedule, as in this case). Credit is given to FOV team for very efficiently and diligently taking all required actions. As a result, a period of stable operation was achieved from the beginning of April onwards, i.e. about a month after initial start-up / plant capability demonstration which, based again on Shell experience, is a remarkable achievement.

It is important to note that based on Shell's design tools and experience, to identify optimal operating conditions (notably in terms of energy requirements and CO<sub>2</sub> capture cost), optimization is always required once units are in operation.

This optimization has not been performed for the pilot plant as the main objective was to demonstrate amine emissions in operating conditions matching the current design of the fullscale plant design.

# 4 Instruments and analytical methods

#### 4.1 Instruments

There are several key online instruments for the pilot plant which required accurate verifications. The following sections summarize the verifications which were performed.

#### 4.1.1 Gas Flowmeters

FOV has done an exhaustive analysis of flowmeter readings to qualify values reported and has proposed a necessary correction factor for the inlet gas flowmeter. This correction ensures that the CO2 removal efficiency is consistently measured by 2 methods; i) absorber side and ii) CO2 product side. The summary of the analysis done by FOV has been extracted from FOV weekly report for week 14 and is provided in appendix 10.1.

#### 4.1.2 Online Analysers

Appropriate calibration and validation have been performed and documented for the different gas analysers, as shown in the table below. Results obtained through those analysers are assumed to be reliable.

Instrument	Owner	Description
FT-IR	Ramboll	Ramboll has confirmed that the CO <sub>2</sub> concentration measured by FTIR is accurate. FTIR is calibrated daily by driving a reference spectrum with nitrogen. This includes a verification with span gas at 15 vol % CO <sub>2</sub> and zero with air. Gasmet FTIR does not drift. The background spectra have been valid all the weeks and the measurements have been valid. For most of the testing period the FTIR has been located at absorber inlet to ensure steady measurements at this location.
		Ramboll calibrations report is attached to this report in Appendix 10.1.
Rack	Ramboll	The rack analyser for CO <sub>2</sub> has been located at the outlet of the absorber to ensure consistent and reliable measurements at this location. Daily verifications are performed with a CO <sub>2</sub> span gas at 15 vol % and zero with air. It has been confirmed that there is no drift on the analyser; very few calibrations have been needed and typically daily verification are only needed.
PTR-TOF-MS	Univ. Oslo	Instrument calibrated by UiO for amine components and main degradation products.
	Univ Oslo	Two instruments were used to measure NO/NO2 an FTIR and a
$100_{x}$ / $100_{2}$	& Ramboll	Chemiluminescence instrument.
	C Kamboli	Results demonstrate good consistency between NOx for both analysers.
		However, the report by University of Oslo attached in appendix 10.1 shows NO2 cannot be accurately measured by FTIR, and from FTIR measurements is best estimated as 0.04 *(NO).

Table 3: Instrumentation calibration and validation

# 4.2 Analytical Methods

#### 4.2.1 Amine titration

Amine titrations have been performed on site to provide a quick turnaround measurement of amine concentrations in the lean amine and water wash sections. This is important to allow the operators to control the process at the desired amine concentrations. Several validations have been performed by Ramboll to confirm the good accuracy of this method for amine determination (see Tables below).

Amine Concentration Uncertainty by Titration ~ 50 wt % ar						nine	
Amine Standard (wt %	6)	) Measured Results (wt %					
51		52.2	51.4	51.4	51.9	52.2	51.4
51		52.1	51.6	52.7	50.9	49.8	51.3
51		51.7	51.4	50.6			
Average Deviation		%			-1.0		
Amine Concentration	n Un	certainty b	y Titration	~ 3 wt % a	mine	]	
Amine Standard (wt %	6)	М	easured R	esults (wt	%)		
3		3.17	2.86				
Average Deviation		%		-0.5		]	
Amine Concentration	n Un	certainty b	y Titration	~ 1 wt % a	mine	]	
Amine Standard (wt %)		Mea	sured Resu	ults (wt %)			
1		1	1	1.3	1.2		
Average Deviation	age Deviation %			-12.5			
Amine Concentration Uncertainty by Titration ~ 0.2 wt % amine						]	
Amine Standard (wt %) Measured Results (wt %)							
0.2		0.2	0.26				
Average Deviation		%		-15.0			

Table 4: Validation of amine titration method

Good accuracy is achieved from 0.2 wt % amine up to 51 wt% amine, however the relative precision is lower at low concentrations (as the method was developed to measure amine concentrations in the operating absorbent)

It should be noted that the amine titration will account for all amines and non-ionic degradation products which are within the DC-103 solution. The comparison in Section 4.2.3 with LCMS analysis confirms the accuracy of the measurements.

#### 4.2.2 CO<sub>2</sub> Loading titration

CO<sub>2</sub> loading measurements are also important to ensure that the amine solvent has an appropriate amount of residual CO<sub>2</sub> remaining in the solvent after regeneration. Therefore, it was agreed to do several calibrations to ensure method accuracy.

Gravimetric standards were prepared at  $0.5 \text{ CO}_2$  wt % and  $3 \text{ CO}_2$  wt % and analysed. The results have an acceptable accuracy (10 to 20% deviation) – see table below.

The deviation at target CO<sub>2</sub> loadings (around 0.1 mol/mol) loading is estimated by interpolation based on deviations at 0.03 and 0.18 mol/mol.

Table 3	5: •	validation	of	CO2	loading	analysis
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CO <sub>2</sub> Loading Method Uncertainty							
CO <sub>2</sub> Loading Standard		Measured Results					
(mol/mol)		(mol/mol)					
0.18	0.17	0.16					8
0.1							14
0.03	0.02	0.04	0.02	0.02	0.022	0.021	21

#### 4.2.3 LCMS

The LCMS method for analysing DC-103 amine components and degradation products has been developed at Eurofins for this campaign.

Calibration results have been provided for the main components including degradation products and are attached in appendix 10.1.

To confirm acceptability of LCMS results, two other comparisons were made:

- Eurofins LCMS results for amines and degradation products versus amine titration results
- Eurofins LCMS results versus measurements from Shell Labs.

#### i) <u>LCMS results versus titration</u>

A comparison between LCMS and on-site titration is shown below.

The titration captures all amine components and main degradation products (DEG 1, 2 and 3), thus the values shown for LCMS are also the sum of both amines (Amines 1, 2, and 3) and main degradation products (DEG 1, 2 and 3).

Error bars are not shown for LCMS. The method precision has been estimated by Eurofins to be 5-10% of measured value, however the consistent good agreement between the two methods indicates a better precision is actually achieved: The average difference between the two methods is 0.09 %wt, and the standard deviation 1.7%wt<sup>1</sup>. The good agreement between the two methods also indicates that no significant (unknown) amine species have been omitted in the LCMS analysis.

<sup>&</sup>lt;sup>1</sup> : The results of first analysis on February 28<sup>th</sup> have been discarded as methods were still in development and difference is significantly larger than for subsequent samples.

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#### Figure 1 : Absorbent concentration – titration and LCMS results

#### ii) <u>Eurofins LCMS results versus Shell Laboratories</u>

One sample from April 16th, 2019 was sent for analysis at Eurofins, Shell lab in India (STCB) and Shell lab in Amsterdam (STCA). Overall the agreement between the 3 laboratories is deemed acceptable as shown in the table below.

Table 6	: LCMS	validation -	round	robin	analysis

Analysis fo	or sample	Amine 1	Amine 2	Amine 3	Deg Amine 1	Deg Amine 2	Deg Amine 3
16.4. 11:00		wt-%	wt-%	wt-%	wt-%	wt-%	wt-%
Eurofins	LCMS	48	0.13	N.D.	0.67	0.09	0.03
STCB	LCMS	49.8	0.16	N.D.	0.52	0.05	0.03
STCA	PTR-MS	47.8	N.A	N.A.	N.A.	N.A	N.A

Additional samples analysed by Eurofins have also be sent to STCB for analysis and comparison of the results with those obtained by STCB. The figures below compare values measured by the two laboratories for the low concentration components (Amines 2, and degradation products).

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The figure 2-c compares total degradation products concentration obtained by STCB and Eurofins.

Although the agreement is good, at higher concentrations the measured concentrations for degradation products are slightly higher at Eurofins as compared to STCB. Since the degradation rate calculations in section 7 are based on Eurofins results, this translates to a conservative case as these are the highest degradation product concentrations.





#### 4.2.4 Foaming Test

The foaming test gives an indication of the foaming tendency of the absorbent, but an observed foaming tendency does not automatically result in noticeable foaming in the operating unit.

Foaming tests conducted by Ramboll showed a foaming tendency, which has been confirmed by a test performed on a duplicate sample by Shell Laboratory in Bangalore, as shown in the table below.

Table 7:	validation	of	foaming	test
----------	------------	----	---------	------

		Threshold for foaming tendency	Ramboll Sample 16_04	STCB Sample 16_04	
Foam Height	ml	150	320	280	
Break Time	S	15	> 500 s	> 4 min	

However, no symptoms of foaming have been observed during the pilot campaign as there was no noticeable pressure drops in absorber and regenerator (see section 8.5).

#### 4.2.5 IC & ICP Measurements

Eurofins was responsible for performing IC and ICP analysis to determine ammonia, organic acids and other trace components within the Cansolv DC-103 solvent. The calibration reports are attached in appendix 10.1.

Some relevant Low levels organic acids (which are classified as ionic degradation products) not targeted in Eurofins analysis were analysed in samples sent to STCB.

#### 4.2.6 Extractive Gas Sampling

The setup for the extractive gas sampling, which was used by Ramboll for isokinetic gas measurements, is described in appendix 10.2.

The critical quality assurance requirement for extractive gas sampling is to ensure that the amount of water effectively collected in the condensate trap corresponds to the theoretical amount of water in the gas entering the sampling train. This evaluation is also shown in section 10.2. The 2.5 % difference between calculated and measured condensed water is a strong indication that the extractive setup is valid.

# 5 Pilot Main Operating Parameters

### 5.1 Absorbent concentration

The figure below shows the evolution of total absorbent concentration (measured by titration), which has been maintained within the design window during the whole campaign.

The concentration was initially on the low end of the targeted range, but progressively increased, due to a negative water balance. As it approached the high end of the targeted range the operations team adjusted the prescrubber outlet temperature to condense more water from the gas in the absorber to stabilize the concentration.



Figure 3: Evolution of lean absorbent concentration

# 5.2 Absorbent lean loading

The figure below shows the evolution of the absorbent lean loading (measured by titration) over the pilot campaign.

The loading has been maintained within the defined target range of 0.8 to 1.7%wt CO<sub>2</sub>.

No optimization has been done to determine if the target  $CO_2$  capture efficiency (90+ %) can be achieved with a higher lean loading (i.e. lower steam consumption), or to lower the

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operating lean loading to target a higher capture efficiency (95+ %) on a sustained basis. This is planned for the extended operation period, in which periods of operation at different capture efficiencies are targeted.





# 5.3 Absorber and stripper operating conditions

### 5.3.1 Absorber

The table below compares operating condition of the pilot plant absorber and the full-scale winter design case.

Although target operating conditions for the pilot plant were defined to match the full-scale design, variations of the inlet gas split between K1, K2 and K3 (due notably to outages of one or more of the units) resulted in inlet gas deviating from the full-scale design conditions – it should be noted that outages of trains would not have the same impact on the full scale, as the total flow would go down, whereas in the pilot plant it has been maintained constant.

The variations resulted in significant fluctuations in  $CO_2$  concentration in the flue gas sent to the pilot plant absorber. Since the operating conditions, and in particular the circulation rate, were maintained stable, the plant had to be operated at a high circulation to accommodate inlet  $CO_2$  concentrations ranging from 10 to 14%v (wet)  $CO_2$ , compared to a design of 11.1%v wet for the full-scale plant (at the inlet of the absorber). This results in a high Liquid to Gas ratio, on average 28% higher for the pilot plant.

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Process Parameter	Units	Pilot Plant - 500 hrs Test – Average	Full Scale - Winter Case	Difference
Lean Amine Flow sent to Absorber	kg/hr	3,000	854,191	N/A
Flue Gas Flow Rate sent To Absorber	kg/hr	936	339,855	N/A
Liquid to Gas Ratio	kg/kg	3.2	2.5	28%
Flue Gas Temperature sent to Absorber	°C	40.0	35.7	4.3
Absorber Bulge Temperature (Bed 2 to Bed 3)	°C	68.0	64.0	4.0
Flue Gas Temperature sent to Water Wash	°C	45.0	52.4	-7.4
Flue Gas Temperature sent to Atmosphere	°C	40.0	44.3	-4.3
Lean Amine Temperature to Absorber	°C	30 to 32	35.0	4.0
Intercooled Amine Temperature to Absorber	°C	32 to 33	35.0	2.5
Lean Amine CO <sub>2</sub> Loading	mol/mol	0.08	0.05	60%
Inlet Flue Gas CO <sub>2</sub> Concentration	mol% wet	10 to 14	11.1	N/A

Table 8: Absorber operating conditions

The higher  $CO_2$  concentration and higher (on average) L/G impact the temperature profile in the absorber:

- While the flue gas supplied to the absorber was in average 4.3°C colder than the winter design case, the absorber bulge temperature, measured between the second and third packing bed, was in average still 4°C warmer than the winter design case. This is results from higher CO<sub>2</sub> concentrations and therefore increased local exotherm.
- Despite the increased exotherm, the treated flue gas leaving the top CO<sub>2</sub> absorption section was in average 7.4°C colder than the winter design case. This can be explained first by the higher L/G, enabling further cooling of the flue gas exiting the absorber. Note that other factors can contribute to this difference:
  - higher lean amine loading in the pilot plant (as the targeted capture is 90%+ rather than 95%+) leads to slower mass transfer kinetics in the top section and therefore further cooling of the gas leaving the absorption section.
  - The lean amine temperature supplied to the absorber was supplied at a temperature in average 4°C cooler than the winter design case.
  - The discharge temperature of the absorber intercooler was in average 2.5°C cooler than the winter design case.

#### 5.3.2 Stripper

The Stripper operating conditions have been maintained constant and within the operating window during the campaign.

The temperature is at the high end of the operating window (around 124C), while the pressure has been constantly at the lower end (close to 0.9 barg). This can seem surprising as the operating temperature and pressure are linked by the absorbent boiling curve. However, it should be noted that the reported temperature is the reboiler temperature, while the reported pressure is measured at the reflux drum, and is thus lower than the reboiler pressure due to the pressure drop in the stripper packing and overheads packing and condenser.

### 5.4 Water Wash

#### 5.4.1 Temperatures

The table below shows a comparison of the water-wash operating temperatures for the pilot plant and the full-scale unit design.

Operation of the pilot plant has shown that a  $\Delta T$  of 5C in the water-wash provides enough condensation to limit amine emissions. The  $\Delta T$  in the summer case is also expected to be sufficient but can be adjusted if required (increased water condensation is then compensated by purging reflux form the system).

		Pilot (typical)	Full-scale winter	Full-scale summer
Water wash inlet	С	45	52.4	54.6
Water wash outlet	С	40	44.3	51.2
Water wash $\Delta T$	С	5	8.1	3.4

Table 9: Water Wash operating temperatures

### 5.4.2 Concentration

The chart below shows the evolution of the water wash concentration during the campaign, measured both by titration and LCMS. Error bars have been added based on reported analytical accuracies (usually +/- 0.1%wt for titration and +/- 20% of value measured for LCMS).

Although the values reported by titration and LCMS are in agreement when taking into account accuracies, the results from LCMS see consistently lower. This may be due to the fact that LCMS

specifically discriminates for the absorbent amine compounds, while titration will also account for alkaline other alkaline components that may be captured from the gas in the water-wash.

Values for the full-scale design summer and winter operation are also reported. The pilot operating concentration is in line with the full-scale winter case, and slightly lower than for the summer case.

The water-wash concentration is not a design parameter in itself, and usually results from the amount of water condensed from the gas, i.e. water-wash operating temperatures, as explained above. However, it can be adjusted (reduced) by sending CO<sub>2</sub> reflux to the water wash section (scheme included in the full-scale design).

Figure 5: Water Wash amine concentration



## 5.5 Degradation products concentration

In a commercial plant in steady-state operation the total degradation products concentration is maintained constant by adjusting the TRU processing rate.

This pilot plant started with virgin DC-103 absorbent, but is not equipped with a TRU. Degradation products thus steadily increased over time, and it was expected that at the start of the 500h test period the degradation level would be close to that maintained in the full-scale plant.

Although degradation products do not affect process performance parameters (CO<sub>2</sub> capture efficiency, steam consumption), their concentration in the absorbent will impact potential presence and concentrations in the product gas streams (treated gas, CO<sub>2</sub> product), and may

accelerate degradation itself. The volatility of degradation products in the process gas streams also depends on their concentration in the absorbent.

Thus operating at a concentration close to the commercial plant is desirable.

The graph below shows that the 500h test was indeed run at degradation products concentration at or above the full-scale design value of 1%wt, and well within the typical design window.

Figure 6: Evolution of degradation products concentration



# 6 Pilot Plant Primary Objectives – Amine emissions

The amine emissions have been monitored continuously by PTR-TOF-MS (excluding periods when the instrument was used to analyse the  $CO_2$  product gas stream).

After the period of familiarization / troubleshooting, the amine emissions stabilized below the target of 0.4 ppmv on average.

During the 500 test the amine emissions were on average of 160 ppbv (based on PTR-TOF-MS data reported on a minute basis), and only exceeded the target of 0.4 ppmv on a few occasions, including a malfunction of the ESP (during which the BDU was brought online by the operator, but subsequently put back off-line).

The table below summarize the average emissions over the stable operation period starting April 5<sup>th</sup> (reference is made to the progress meeting minutes) and the 500h test period.

	units	Value <sup>(2)</sup>
Target	ppbv	< 400
Stable operation period <sup>(1)</sup>	ppbv	195
500h test period	ppbv	155
500h test period excluding ESP malfunction	ppbv	44

Table10: Amine emissions

Note 1: Operating period starting April 5<sup>th</sup> onwards

Note 2: All values calculated from PTR-TOF-measurements reported on one-minute time interval.

The graphs on next pages show the amine emissions for different moving time averages typical of emission permits (1h, 8h, 24h) over the stable operation period. Emissions shown are emissions for Amine 1, as Amine 2 and Amine 3 were consistently below detection limit of 5 ppbv (which is in agreement with expectations based on relative concentrations and volatilities of the different amines).

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Figure 7b: Amine emissions (8h rolling average)

Figure 7a: Amine emissions (1h rolling average)



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To confirm that there are not significant amine emissions due to mechanical entrainments (including aerosols), several extractive gas samples have been taken and analysed by LCMS.

The results are shown in the table below, against the emissions measured by the PTR-TOF instrument in the sample extraction period. The emissions measured by the extractive method are equivalent or lower than emissions measured by PTR-TOF-MS, which indicates that for the Oslo waste to energy plant emissions caused by aerosols or droplets are not a significant contributor (in which case the extractive sampling results would have been higher. The difference observed between the two methods is most probably due to uncertainty linked to extractive sampling).

Sampla	Extractive + LCMS	PTR-TOF-MS
Sample	(ppmv)	(ppmv)
1.5.2019 15:15-17:25	< 0.05	0.29
8.5.2019 14:15-16:15	0.06	0.12
15.5.2019 10:26-14:26	0.009	0.01
23.5.2019 08:55-12:55	0.005	~ 0.01 <sup>(1)</sup>
28.5.2019 10:30-15:30	0.004	<b>~</b> 0.03 <sup>(1)</sup>

Table 11: Amine emissions (Amine 1) measured by PTR-TOF-MS and extractive sampling

Note 1: Values are based on PTR-TOF-MS measurements around these hours due to lack of data at given time interval.

# 7 Absorbent Degradation

During operation, the absorbent can be degraded by oxidative degradation, and can also react with  $NO_2$  absorbed from the gas to form nitrosamines.

This results in a progressive accumulation of degradation products in the absorbent. In a commercial unit those degradation products are removed by thermal reclaiming to maintain their concentration at a design steady state concentration, typically 1-2%.

For the Klemetsrud pilot no thermal reclaimer was included in the unit as it was calculated that, at the expected degradation rates, the build-up of degradation products would be slow, and concentrations typical of steady state operation of a commercial unit would be reached only towards the end of the campaign.

The observed degradation products accumulation rate over the campaign can then be used to back-calculate absorbent degradation rate.

## 7.1 CANSOLV DC-103 degradation products

Oxidative degradation of the absorbent amines leads mainly to the formation of amide components, identified for the purpose of this campaign as DEG1 (DC-103 amide) and DEG2 (formamide).

Reaction with  $NO_2$  leads to the formation of a nitrosamine identified as DEG3.

To a lesser extent oxidative degradation leads to the formation of organic acids. Acetaldehyde and ammonia are also potential compounds generated by absorbent degradation, but at much lower levels.

All those components have been monitored during the pilot campaign, in process streams where they can be expected to be found based on their volatility. The table below provides a summary of the expected degradation products and detection methods.

Note that nitramines can be formed in the atmosphere after emission of amines at the stack, but are not expected to be formed in the process itself.

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Table12: Amine degradation products

	Volatility	Monitored by
DEG1	Low	Absorbent: LCMS Treated Gas: PTR-TOF-MS and extractive + LCMS CO <sub>2</sub> product: PTR-TOF-MS and extractive + LCMS
DEG2	Low	Absorbent: LCMS Treated Gas: PTR-TOF-MS and extractive + LCMS CO <sub>2</sub> product: PTR-TOF-MS and extractive + LCMS
DEG3	Low	Absorbent: LCMS Treated Gas: PTR-TOF-MS and extractive + LCMS CO <sub>2</sub> product: PTR-TOF-MS and extractive + LCMS
Organic acids	None	Absorbent: IC Treated Gas: Extractive + anionic IC CO <sub>2</sub> product: Extractive + anionic IC
Formaldehyde	High	Treated Gas: PTR-TOF-MS and FTIR CO <sub>2</sub> product: PTR-TOF-MS and FTIR
Acetaldehyde	High	Treated Gas: PTR-TOF-MS and FTIR CO <sub>2</sub> product: PTR-TOF-MS and FTIR
Ammonia	High	Treated Gas: FTIR and extractive + cationic IC CO <sub>2</sub> product: FTIR and extractive + cationic IC

## 7.2 Degradation products measured in pilot plant

#### 7.2.1 Main degradation products

#### <u>In Absorbent</u>

The graph in section 5.5 shows the evolution of the main degradation (DEG1, DEG2, DEG3) products concentration over the duration of the pilot campaign

It shows that DEG1 and DEG2 accumulate over time in the absorbent as they are continuously produced by amine degradation and have a low volatility.

DEG3 concentration on the other hand remains low, as this compound can degrade further and thus does not accumulate but reaches a steady sate concentration resulting from formation and destruction rates (and in the case of a commercial unit, removal in the thermal reclaimer).

The linear increase in concentration of DEG1 and DEG2 suggests that there is no promotion of further degradation by the degradation products themselves, at the observed concentrations. Should the pilot campaign be prolonged, it would be interesting to confirm if the same behaviour is observed at higher degradation products concentrations. This may allow to design the commercial unit to operate at higher degradation products concentration, and thus reduce the size of the TRU.

#### In treated gas and CO<sub>2</sub> product

Concentrations in the treated gas and CO<sub>2</sub> product, measured by PT-TOF-MS are below the detection limit of 5 ppbv.

LCMS performed on extractive gas samples have not detected any of the main degradation products above the detection limit of 0.01 mg/Nm<sup>3</sup> (corresponding to about 1.5 ppbv).

#### 7.2.2 Organic acids

#### <u>In Absorbent</u>

The figure below shows the concentrations, measured by Ionic Chromatography, of organic acids in lean absorbent samples analysed by Eurofins and Shell lab (STCB).

As expected, the accumulation rates of these compounds are orders of magnitude below the main degradation products accumulation rate. Even based on a conservative assumption of 1 mole of amine degraded for every mole of organic acid formed, the contribution to the total degradation rate is very low, within the uncertainty range of the calculated degradation rate.





#### In treated gas and CO<sub>2</sub> product

IC analysis performed by Eurofins on extractive samples from CO<sub>2</sub> and treated gas have not detected formate or acetate (detection limit 0.3 mg/Nm<sup>3</sup>), which is in line with expectations as those compounds are not volatile in the process operating conditions.

#### 7.2.3 Aldehydes and ammonia

Acetaldehyde, formaldehyde, and ammonia are highly volatile compounds (in the CO<sub>2</sub> capture plant operating conditions), and will be stripped from the absorbent, either in the absorber or in the stripper.

In CO<sub>2</sub> product

The PTR-TOF-MS has been used to analyze the trace components, including aldehydes, in the CO<sub>2</sub> product during the last 500 hours of testing. The table below shows the results for the aldehydes. Formaldehyde and Acetaldehyde are detected as expected, as well as another carbonyl in C3 (propionaldehyde or acetone).

Duration		Formaldeh	yde (ppbv)	opbv) Acetaldehyde (ppbv)		C3 Carbonyl (ppbv)	
Ddie	(h)	average	max	average	max	average	max
14-May	6	2	4	918	1148	15	18
16-May	6	2	57	857	1207	18	58
21-May	14	2	4	798	1302	15	26
23-May	6	2	3	553	644	13	17
28-May	6	15	145	913	2382	31	197

Table 13: CO<sub>2</sub> product measurements using PTR-TOF-MS.

Formaldehyde and C3 carbonyl concentration remain well below 1 ppmv, while acetaldehyde is detected at a few ppmv only. The graph below shows the average concentrations measured over the different periods and reported in the table above.

Ammonia has been detected in two extractive samples, at concentrations of respectively 0.06 and 0.02 mg/Nm3, i.e. 80 and 25 ppbv.

Simultaneous measurement results using FTIR at the CO<sub>2</sub> product outlet does not provide additional information as the detection limit for the FTIR is above 1,000 ppbv.

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#### <u>In treated gas</u>

Formaldehyde and acetaldehyde have been measured by PTR-TOF-MS in the treated gas. Average concentrations are respectively 4 ppbv for formaldehyde and 100-200 ppbv for acetaldehyde, with a max value of 400 ppbv for the later.

The graph below shows the ammonia concentration measured by cationic IC performed on treated gas extractive samples. The concentration is of the order of 1 ppmv or less. It is assumed the origin is the degradation of the amine, as the ammonia present in the flue gas is presumably captured entirely in the pre-scrubber. Compared to other amines such as MEA the ammonia emissions are quite low.

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# 7.3 Absorbent Losses and degradation rate

#### 7.3.1 Absorbent inventory

To estimate the degradation rate of the absorbent, the evolution of the absorbent inventory in the system needs to be accounted for (for example in case of very high mechanical entrainments at the stack, a gradual decrease in total amine mass in the system would result in an apparent reduction in degradation rate).

In the case of this pilot, since extremely low amine and degradation products concentrations have been measured in the treated gas and CO<sub>2</sub> product, the total mass of those components can be expected to be constant, once other mechanical losses are accounted for (due to liquid drained from the unit accidentally or on purpose, for example if large samples).

For a conservative estimate of potential losses, emissions of 200 ppbv over a period of 2,000 hours, assuming a (conservatively high) gas flowrate of 700 Nm3/h, would result in the loss at stack of less than 2 kg of absorbent, i.e. less than 0.3% of the initial 710 kg inventory.

As explained in section 4.2.3 the titration measures the amine components of the absorbent (Amines 1, 2 and 3) as well as the main degradation products (DEG 1, 2 and 3), so the absorbent concentration measured by titration multiplied by the total liquid volume in the system should remain constant. The graph below shows that this is indeed the case.

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Figure 11: Evolution of amine inventory



#### 7.3.2 Degradation rate

#### Degradation rate estimation

To calculate the degradation rate, the amine and main degradation products (DEG1, DEG2, DEG3) concentrations are converted to mol%, and are then reported as fraction of total concentration (amine + main degradation products).

The Graph below shows the evolution of fraction of amine and degradation products over time, as % of total amine + degradation products concentration.

The degradation rate is obtained from the slope of the amine fraction change over time. In principle the degradation rate can vary with the degradation products concentration, so it should be calculated in the range of degradation products concentration representative of full-scale operation, i.e. typically 0.5 - 1.5%. However it can be seen from the figure below that the slope has not changed over the course of the pilot operation, so estimation based on the 0.5 - 1.5% or over the whole operating period will give identical results.

The amine is degrading at a rate of 14.1E-08 /h of total inventory.

With a total inventory assumed to be constant at 710 kg, this represents a degradation rate of 10.0 g/h.

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Figure 12: Amine and degradation products relative to total absorbent

The commonly used basis to report degradation rate is kg/tCO<sub>2</sub> (captured). To this intent the degradation rate is reported to the average CO<sub>2</sub> production of 128 kg/h over the period considered, and a value of 0.078 kg/tCO<sub>2</sub> (captured) is obtained.

#### Comparison with predicted rates

For comparison with predicted rates and scale-up to commercial units, it is more relevant to consider separately:

- Oxidative degradation, which depends on the volume of rich amine inventory.
- Degradation to nitrosamine (DEG3), which depends on NO<sub>2</sub> ingress.

The degradation to Nitrosamine is calculated with Shell proprietary tools based on  $NO_2$  ingress and other plant design and operating parameters. In the case of this pilot, 90% of the  $NO_2$  is assumed to react with the absorbent amines, which is similar to the commercial plant design.

The average inlet NO<sub>2</sub> concentration over the operation period has been estimated based on NOx concentration measured by FTIR, as 0.04 times this concentration (see section 4.1.2). Using this method an average concentration of 1.4 ppmv has been is obtained.

This results in a degradation rate of 0.035 kg/tCO<sub>2</sub>. (captured)

It is important to note that the formed nitrosamine is also subject to further degradation, so that its concentration in the absorbent cannot be calculated based only on the degradation rate above.

The oxidative degradation rate is then obtained from the difference between total degradation rate and conversion to nitrosamines, i.e. 0.078-0.035 = 0.043 kg/tCO<sub>2</sub> (captured).

Since oxidative degradation depends on rich absorbent inventory, the basis for degradation rate is relative to the rich absorbent inventory, i.e. expressed in mg/h.L<sub>rich</sub>.

In commercial scale units the rich inventory is typically of the order of 30% of the total inventory. However, in pilot units it is usually lower. A rich inventory of 25% of total inventory had been assumed for the calculations presented in the progress meeting. For this final report the rich inventory has been confirmed to be around 25% of total inventory, based on the actual pilot unit construction drawings.

The oxidative degradation rate is thus calculated as:

0.043 kg/ton x 0.13 tons/hr x 1e6 mg/kg / (1,333 L x 25%) = 16.6 mg/h. L<sub>rich</sub>

The values obtained above are then compared with the values predicted by Shell proprietary tools, as shown in the table below. The observed oxidative degradation rate is 41% lower than the value predicted using the tools employed to design the full-scale unit (28 mg/h. L<sub>rich</sub>)

		FOV Pilot		FOV full-scale plant			
Process Parameter	Units			Winter	Summer	Max Cont.	Summer based on Pilot results
Rich Inventory	% of Total	25	5%		30%		
NO 2 in Flue Gas	ppmv wet	1	.4	0.86	0.83	7.81	1.40
		Measured	Predicted				
Oxidative	mg/L <sub>rich</sub> ∙hr	16.6	28.0	28.0	28.0	28.0	16.6
Degradation Rate	mg/L∙hr	4.1	7.0	8.4	8.4	8.4	5.0
	kg DC/ton CO 2 <sup>(1)</sup>	0.043	0.073	0.133	0.133	0.133	0.079
Degradation to Nitrosamine	kg DC/ton CO 2 <sup>(1)</sup>	0.035	0.035	0.021	0.022	0.202	0.036
Total Degradation Rate	kg DC/ton CO 2 <sup>(1)</sup>	0.078	0.11	0.154	0.155	0.335	0.11

Table14: Degradation rates

Note 1: unit is kg of 100% wt amine per metric ton of CO<sub>2</sub> captured.

# 8 Other performance parameters

### 8.1 CO<sub>2</sub> product purity

The FTIR analyser has been used to evaluate the presence of  $NH_3$ ,  $SO_2$ , aldehydes (formaldehyde and acetaldehyde), and  $O_2$  during week 14 (May 27<sup>th</sup> to June 6<sup>th</sup>). All were found to be below the detection limit, i.e. 0.2% for oxygen and 1 ppmv for the other components.

In addition, during the 500h test the presence and concentration of the absorbent amine components and degradation products have been measured by PTR-TOF-MS over periods of several hours, and two extractive gas samples analysed (by LCMS) for the same components.

All main amine and degradation products were found to be below detection limit, except for amine 1. Amine 1 was detected at 3 ppbv on average by PTR-TOF-MS, with a maximum value of 83 ppbv, while the two extractive samples led to concentrations of respectively around 0.5 and 10 ppbv.

The extractive samples were also analysed for ammonia and anions. All anions were below detection limit and NH<sub>3</sub> concentration was measured below 100 ppbv.

A bag sampling was also performed but results were not available at the time of completion of this report.

The table below summarizes the different results obtained to characterize CO<sub>2</sub> purity. For PTR-TOF -MS max and average values measured over the 500h test are reported. It is important to note that, as explained in section 5.2, during this period the degradation product concentration in the absorbent was similar to the commercial design, so the values obtained can be considered representative of the commercial plant operation.
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Component	Units	Average	Max measured	Method
Amine 1	ppbv	3 (1)	83	PTR-TOF
Amine 2	ppbv	n.d.	n.d.	PTR-TOF
Amine 3	ppbv	n.d.	n.d.	PTR-TOF
Deg 1	ppbv	n.d.	n.d.	PTR-TOF
Deg 2	ppbv	n.d.	n.d.	PTR-TOF
Deg 3	ppbv	n.d.	n.d.	PTR-TOF
Formaldehyde	ppbv	4	14	PTR-TOF
Acetaldehyde	ppbv	800	2,400	PTR-TOF
O <sub>2</sub>	ppbv	Note 2	Note 2	Bag Sample
NH <sub>3</sub>	ppbv		< 100	Extractive sampling + IC

Table 15: trace components in  $CO_2$  product (500h test period; n.d. = not detected above detection limit)

Note 1: most values are close to or below sensibility limit

Note 2: bag sample results not available at the conclusion of this report. However presence of O<sub>2</sub> in the CO2 product results purely from physical solubility in the absorbent and is not expected to deviate from values reported in full-scale design.

## 8.2 Absorbent loading capacity

The achieved rich absorbent loading was slightly lower than predicted. As explained in section 5.3.1, a high L/G was maintained during the pilot plant operation to ensure that more than 90%  $CO_2$  removal was achieved, even in periods of high inlet  $CO_2$  load.

The inlet  $CO_2$  concentration was variable, and despite the frequent excursions at high  $CO_2$  concentrations, there were many occasions when the inlet  $CO_2$  concentration was actually lower than design. Such lower inlet concentration (i.e.  $CO_2$  vapor pressure) results in lower maximum achievable equilibrium rich loading, and thus lower rich and delta loading.

Wall effects and liquid maldistribution are also expected to have a more pronounced impact on liquid channelling at pilot scale compared to large scale, and can lead to lower rich amine CO<sub>2</sub> loadings.

# 8.3 $CO_2$ capture efficiency

The CO<sub>2</sub> capture efficiency of a capture plant is normally limited by the mass transfer of CO<sub>2</sub> between the gas and the liquid, which depends both on:

- the mass transfer area available
- the absorption driving force, which depends in particular on the residual CO<sub>2</sub> of the lean absorbent.
- mass transfer coefficients on the gas and liquid sides, primarily on the liquid side of phase boundaries

However, if the absorbent circulation is too low, it can also be limited by the absorbent maximum loading capacity – which is determined by the temperature and  $CO_2$  vapor pressure at the bottom of the absorber.

During operation of the pilot plant, the gas flowrate was maintained as much as possible at the design value to ensure operating conditions representative of a commercial plant.

Depending on the relative K1/K2/K3 split of the inlet gas, the inlet  $CO_2$  concentration fluctuated, and frequently exceeded the maximum design concentration of the unit. With the unit operating at design gas flowrate, this means that the unit was operating above the maximum design  $CO_2$  load.

It should be noted that operation of the unit was not optimized, in particular the lean absorbent loading was kept within the initial target range, while lower lean loading (closer to the full-scale design of 0.05 mol/mol rather than 0.08 mol/mol) could have helped increase capture efficiency in periods of high inlet CO<sub>2</sub> concentration.

## 8.4 Steam consumption

The steam consumption in the pilot unit is not representative of the steam consumption of a commercial unit, due to:

- 1- The absence of energy recovery features of a commercial plant (lean absorbent and condensate flash system).
- 2- The potential discrepancies in performance of some secondary equipment like the leanrich exchangers
- 3- The higher heat losses in a pilot unit (even for a well insulated unit, due to higher external area / volume ratio).

The first two causes of discrepancies can be accounted for (and, for the second one, reduced by optimizing operating conditions), however the third one cannot be controlled and is difficult to estimate.

Nevertheless, the steam consumption of the pilot unit has been calculated and compared to the consumption predicted by Shell design tools (calibrated for commercial units) for the same operating conditions.

## 8.4.1 Pilot unit steam consumption

The steam consumption of a  $CO_2$  capture plant is most commonly evaluated in terms of t steam / t  $CO_2$ , or GJ/t  $CO_2$  (captured).

The pilot steam consumption is obtained simply by calculating the ratio of steam flow (or corresponding latent energy content) to pure CO<sub>2</sub> product flow (i.e. on a dry basis), the values being taken over a period of stable operation in conditions as representative as possible of the commercial plant.

Two stable operating periods are considered for this evaluation: April 14<sup>th</sup> to April 28<sup>th</sup>, 2019 and (during 500 hr test period) May 13<sup>th</sup> to June 4<sup>th</sup>, 2019. Those periods are identified in the graph below.



Figure 13: Periods considered for estimation of steam consumption

In the table below the observed steam consumption is compared with the consumption predicted by Shell design tools for the same operating conditions.

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Table16: Steam consumption

Process Parameter	Units	Period 1		Peri	od 2	
Avg Flue Gas Flow to Absorber	kg/hr	78	34	896		
Avg CO <sub>2</sub> Flow to Absorber	kg/hr	13	36	18	181	
Avg CO <sub>2</sub> Flow Captured	kg/hr	12	28	16	58	
Avg Removal	%	94.1%		93.0%		
Avg Lean Circulation	kg/hr	2,750		3000		
Avg Delta Loading	mol/mol	0.279		0.330		
Avg Rich Amine Loading	mol/mol	0.3	356	0.408		
Avg Lean Amine Loading	mol/mol	0.077		0.078		
		Observed	Predicted	Observed	Predicted	
Avg Steam Flow	kg/hr	250	262	289	305	
Specific Steam Consumption	GJ/ton	4.13	4.33	3.62	3.85	

It is important to note that:

- The consumptions above are significantly higher than those used for the design of the fullscale unit as the pilot plant is not equipped with an MVR heat recovery system.
- The pilot unit operating conditions have not been optimized to minimize steam consumption, in particular for target lean loading. They have been maintained within the window of operation representative of the commercial plant, which are expected to be optimal in terms of steam consumption, however it is possible that a commercial plant will achieve lower consumption once its operating conditions are optimized.
- The reported energy consumption is directly dependent on the steam flow measurement, the reliability of which has not been thoroughly assessed as this was not one of the primary objectives of the pilot campaign.

## 8.4 Contaminants ingress and pre-scrubber efficiency

The graph below shows the evolution of the concentration of inorganic anions and cations in the lean absorbent analysed by ionic chromatography (anions) and ICP-MS (cations) both by Eurofins and STCB.

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Anions and cations not shown on the graph have not been detected (detection limit is typically a few ppmvs for cations, refer to weekly reports by FOV).



Figure 14: Evolution of contaminants in absorbent

A linear fit can in theory be used to calculate an average ingress rate, based on total absorbent inventory of 1,335 L.

However, considering the uncertainty on the measured concentrations (as shown by difference between values obtained by STCB and Eurofins), the results would not be of significance at this point.

## 8.5 Absorbent foaming

Although foaming tests performed on absorbent samples indicate a high foaming tendency, no indicators of foaming within the units have been observed (typically high pressure drop in absorber and stripper). This is in agreement with Shell's experience as changes in foaming tendency are an indication of a plant that is more likely to foam than having a stable high foaming tendency result.

## 8.6 BDU efficiency

Based on the incineration plant flue gas properties and gas cleaning system, it is expected that the target for amine emissions of 0.4 ppmv can be achieved without a BDU, and the main objective of the pilot campaign was to demonstrate amine emissions without the BDU in operation.

The BDU has thus been put in operation only for a short period prior to the 500h test to test its operation, and briefly during the 500h test as an upset in the upstream process caused a peak in amine emissions.

Further testing of the BDU is planned during the extended operation period to evaluate behaviour over a longer period (emissions, pressure drop).

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# 10 Appendices

10.1 Calibration and method validation reports

Fortum Oslo Varme CO<sub>2</sub> Capture Pilot Plant

10.2 Extractive gas sampling method and validation

🛟 eurofins

## Amine 1



Picture 1. Calibration curve for amine 1 (1-1000 µg/L)





## Amine 2

Compound name: AM 2 Correlation coefficient: r = 0.999708,  $t'^2 = 0.999415$ Calibration curve: 0.515159 \* x+-0.470024 Response type: Internal Std (Ref 7), Area \* (IS Conc. / IS Area ) Curve type: Linear, Origin: Include, Weighting: 1/x, Axis trans: None



Picture 3. Calibration curve for Amine 2 (5-1000  $\mu g/L)$ 



Picture 4. Chromatogram for Amine 2 (10 µg/L)

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## Degradation product 1

Compound name: Deg 1 Correlation coefficient: r = 0.998829, r'2 = 0.997659Calibration curve: 1186.72 \* x + .396.661Response type: External Std, Area Curve type: Linear, Origin: Include, Weighting: 1/x, Axis trans: None



Picture 1. Calibration curve for degradation product 1 (1-1000 µg/L)



Picture 2. Chromatogram for degradation 1 (5 µg/L, S/N 113)

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## Degradation product 2



Picture 3. Calibration curve for degradation product 2 (1-1000 µg/L)



Picture 4. Chromatogram for degradation 2 (1 µg/L, S/N 133)

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## Degradation product 3

Compound name: Deg 3 Correlation coefficient: r = 0.999268, r<sup>2</sup> = 0.998536 Calibration curve: 2042.17 \* x + 452.055 Response type: External Std, Area Curve type: Linear, Origin: Include, Weighting: 1/x, Axis trans: None



Picture 5. Calibration curve for degradation product 3 (1-1000 µg/L)



Picture 6. Chromatogram for degradation 2 (5 µg/L, S/N 145)



# 

Title: Pilot Plant Final Test Report, Attachment 4 - Eurofins calibration - IC-ICP

Date: 28.06.2019 Page: 1/4

## **CANCELS AND REPLACES\***

#### **Ramboll Finland Oy**

### Sauli Lundström

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#### Projekti Oslo

Sample number

#### 750-2019-00019965 750-2019-00019966

Sample reference			Lean amine 1.419	Water Wash 1.419
Sampling date and	time		01.04.2019	01.04.2019
General analyses of	f water			
Chloride (Cl)	RZB/6	mg/l	<100	<25
Fluoride	RZB83	mg/l	<20	<5,0
Sulphate (SO4)	RZB86	mg/l	150	<25
Ammonium (NH4)	RZC58	mg/l		0,020
Nitrate (as NO3)	RZB92	mg/l	<200	<50
Formiate	RZU01	mg/l	<100	<25
Acetate	RZU01	mg/l	<100	<25
Propionate	RZU01	mg/l	<100	<25
Butanoate	RZU01	mg/l	<100	<25
Lactate	RZU01	mg/l	<100	<25
Thiosulfates	RZB90	mg/l	<500	<25
Elements, solid ma	trix/dry w	eight, ICF	P-MS	
Microwave	RZE18	•	Done	
decomposition				
Elements, solid ma	trix/wet v	veight, ICF	P-MS	
Aluminium	RZ0Z3	mg/kg	<10	
Antimony (Sb)	RZ0YE	mg/kg	<0,50	
Arsenic (As)	RZ0Y8	mg/kg	<1,0	
Barium (Ba)	RZ0Y9	mg/kg	<1,0	
Mercury (Hg)	RZ0YG	mg/kg	<0,10	
Cadmium (Cd)	RZ0YI	mg/kg	<0,20	
Potassium (K)	RZ0YU	mg/kg	<100	
Calcium (Ca)	RZ0YJ	mg/kg	<100	
Cobalt (Co)	RZ0YK	mg/kg	<1,0	
Chromium (Cr)	RZ0YB	mg/kg	<1.0	
Copper (Cu)	RZ0YV	mg/kg	<5,0	
Lead (Pb)	RZ0YA	mg/kg	<1.0	
Magnesium (Mg)	RZ0YL	mg/kg	<100	
Manganese (Mn)	RZ0YW	mg/kg	<5.0	
Molvbdenum (Mo)	RZ0YM	ma/ka	<2.0	
Sodium (Na)	<b>RZ0YY</b>	ma/ka	<100	
Nickel (Ni)	RZ0YC	ma/ka	<2.0	
Iron (Fe)	RZ0YR	ma/ka	<10	
Zinc (Zn)	R7070	ma/ka	~5.0	
Thallium (TI)	R7071	ma/ka	~0,0	
		ma/ka	<1,0	
vandulutti (v)	RZUTD	mg/kg	<1,0	

#### **Eurofins Environment Testing Finland Oy**

Document no. NC03-KEA-P-RA-0016



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# **CANCELS AND REPLACES\***

			Analytical Report Nr. AR-19-RZ-013436-02 P Date 28.05.2019 Sample arrived 09.04.2019			
Sample number			750-2019-00019965	750-2019-00019966		
Sample reference		Lean amine 1.419	Water Wash 1.419			
Sample description	on		Liquid	Liquid		
Sampling date an	d time		01.04.2019	01.04.2019		
Vanadium (V)	RZ0YD	mg/kg	<1,0			
Specific analysis	RZPP0		Results as an attachment	Results as an attachment		
(*this report cance	els and repla	aces the pr	evious one, numbere	d AR-19-RZ-013436-01/750-2019-	00019965 dated 14/05/2019 whic	h must be

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## **CANCELS AND REPLACES\***

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## Analytical Report Nr. AR-19-RZ-013436-02 Date 28.05.2019 Sample arrived 09.04.2019

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#### Method information

I

Testcode	Parameter name, CAS	Default MU	Default LOQ	Accredited	Method	Laboratory
General a	nalyses of water	-				-
RZB76	Chloride (Cl), 16887-00-6	10%	0.5	Yes	Int. Method, IC, based on e.g. SFS-EN ISO 10304-1:2009, IC-EC	RZ T039
RZB83	Fluoride, 7782-41-4	15%	0.1	Yes	Int. Method, IC, based on e.g. SFS-EN ISO 10304-1:2009, IC-EC	RZ T039
RZB86	Sulphate (SO4), 18785-72-3	12%(<4mg/l) 10%(>4mg/l)	0.5	Yes	Int. Method, IC, based on e.g. SFS-EN ISO 10304-1:2009, IC-EC	RZ T039
RZC58	Ammonium (NH4), 14798-03-9	15%(>0,020mg/l) 25%(<0,020mg/l)	0.006	Yes	SFS 3032:1976, mod.	RZ T039
RZB92	Nitrate (as NO3), 84145-82-4	15%	1	Yes	Int. Method, IC, based on e.g. SFS-EN ISO 10304-1:2009, IC-EC	RZ T039
RZU01	Formiate		2	No	Internal Method EF2018, IC-EC	RZ
RZU01	Acetate, 71-50-1		2	Yes	Internal Method EF2018, IC-EC	RZ T039
RZU01	Propionate		2	No	Internal Method EF2018, IC-EC	RZ
RZU01	Butanoate		2	No	Internal Method EF2018, IC-EC	RZ
RZU01	Lactate, -		2	No	Internal Method EF2018, IC-EC	RZ
RZB90	Thiosulfates, 14383-50-7	20%	5	Yes	SFS-EN ISO 10304-3:1998, IC-technique	RZ T039
Elements,	solid matrix/dry weight, I	CP-MS				
RZE18	Microwave decomposition			No	SFS-EN 16174	RZ
Elements,	solid matrix/wet weight, I	CP-MS				
RZ0Z3	Aluminium, 7429-90-5	30%	10	No	SFS-EN 16171	RZ
RZ0YE	Antimony (Sb), 7440-36-0	25%	0.5	Yes	SFS-EN 16171	RZ T039
RZ0Y8	Arsenic (As), 7440-38-2	25%	1	Yes	SFS-EN 16171	RZ T039
RZ0Y9	Barium (Ba), 7440-39-3	20%	1	No	SFS-EN 16171	RZ
RZ0YG	Mercury (Hg), 7439-97-6	25%	0.1	Yes	SFS-EN 16171	RZ T039
RZ0YI	Cadmium (Cd), 7440-43-9	25%	0.2	Yes	SFS-EN 16171	RZ T039
RZ0YU	Potassium (K), 7440-09-7	25%	500	No	SFS-EN 16171	RZ
RZ0YJ	Calcium (Ca), 7440-70-2	25%	500	No	SFS-EN 16171	RZ
RZ0YK	Cobalt (Co), 7440-48-4	20%	1	Yes	SFS-EN 16171	RZ T039
RZ0YB	Chromium (Cr), 7440-47-3	25%	1	Yes	SFS-EN 16171	RZ T039
RZ0YV	Copper (Cu), 7440-50-8	25%	5	Yes	SFS-EN 16171	RZ T039
RZ0YA	Lead (Pb), 7439-92-1	25%	1	Yes	SFS-EN 16171	RZ T039
RZ0YL	Magnesium (Mg), 7439-95-4	25%	500	Yes	SFS-EN 16171	RZ T039
RZ0YW	Manganese (Mn), 7439-96-5	25%	5	Yes	SFS-EN 16171	RZ T039

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# **CANCELS AND REPLACES\***

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Elements,	solid matrix/wet weight,	CP-MS				
RZ0YW	Manganese (Mn), 7439-96-5	25%	5	Yes	SFS-EN 16171	RZ T039
RZ0YM	Molybdenum (Mo), 7439-98-7	20%	2	No	SFS-EN 16171	RZ
RZ0YY	Sodium (Na), 7440-23-5	25%	500	No	SFS-EN 16171	RZ
RZ0YC	Nickel (Ni), 7440-02-0	25%	2	Yes	SFS-EN 16171	RZ T039
RZ0YR	Iron (Fe), 7439-89-6	30%	10	Yes	SFS-EN 16171	RZ T039
RZ0Z0	Zinc (Zn), 7440-66-6	25%	5	Yes	SFS-EN 16171	RZ T039
RZ0Z1	Thallium (TI), 7440-28-0	25%	1	No	SFS-EN 16171	RZ
RZ0YD	Vanadium (V), 7440-62-2	25%	1	Yes	SFS-EN 16171	RZ T039
RZPP0	Specific analysis			No		RZ

Laboratory		
RZ	Eurofins Environment Testing Finland (Lahti)	(Not accredited)
RZ T039	Eurofins Environment Testing Finland (Lahti)	FINAS acc num. SFS-EN ISO/IEC 17025:2005 FINAS T039

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#### SIGNATURE

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Report electronically validated by

Additional information

New report version: Sulphate result of sample 750-2019-00019966 was corrected.

#### EXPLANATORY NOTE

This certificate may only be copied as whole. The results apply solely to the samples received and analyzed. Conclusion and other comments are not accredited.



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#### 5 **APPENDIX 1 - FLOW MEASUREMENT ANALYSIS**

#### 5.1 Purpose

The purpose of this Appendix is to provide an overview of the issues related to flow measurements at the pilot plant.

The purpose is also to evaluate which flow meter can be trusted (i.e. is reliable) and to what extent.

Finally, this Appendix also provides an evaluation of correction factors needed to improve the reliability of the readings.

#### 5.2 **Background / existing flow meters**

There are 3 flow meters for flue gas plus 1 for the  $CO_2$  product gas on the pilot plant that are relevant for this evaluation. In addition, there are 3 more flue gas flow meters upstream the pre-scrubber, measuring the amount of flue gas tapped from each incineration line located at the WtE plant. An overview of the locations for the 7 different flow meters has been provided in the Figure below.



Figure 1. Pilot plant flow meter locations

#### 5.2.1 Flow meter types

The 4 flow meters located at the pilot plant are all thermal mass flow meters of the type Sierra Mass Flow 640. The working principle of a mass flow meter is based on heating a sensor up to a certain degree above the gas temperature and calculating the flow based on the required energy to maintain this temperature as the gas will cool the sensor. To be able to calculate the exact flow, the composition of the gas is of utmost importance as the enthalpy for each gas component differs significantly. The electrical power needed is directly proportional to the gas mass flow rate.

The 3 flow meters located upstream the pilot plant are also thermal mass flow meters, but in this case by Endress+Hauser (type T-mass 65).

#### 5.2.2 Flow meter readings

All flow meters report mass flow values in the same units, i.e. kg/h. The flow accounts for the composition of the flue gas at each location.

Based on the different locations at the pilot plant it should be possible to match various flow meters with each other, i.e. make mass balance calculations. For example:



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- 3 x FT (WtE) = FT-0003
- On a dry basis: FT-0003 = FT-0007 = 3 x FT (WtE)
- On a dry basis: FT-0007 = FT-0011 + FT-0209 = FT-0003

In addition, it should be possible to check the mass balances based on partial balances, such as the CO<sub>2</sub> balance (around the absorber) and the H<sub>2</sub>O balance (around the pre-scrubber).

#### 5.3 The problem

Currently, despite various trouble-shooting efforts (involving flow meter vendors/experts), the raw flow meter data based mass balances (partial or otherwise) remain unsatisfactory.

Below is a Figure giving an overview of the situation as it is currently with raw data from all 4 flow meters located at the pilot plant, as well as the combined value for the three flow meters upstream of the pilot plant.



Figure 2. Flow measurement values from 4 flow meters located at the pilot plant together with a combined (sum) value for the 3 flow meters located upstream of the pilot plant.

Based on the above Figure, it is clear that at least some of the flow meters show erroneous values. For instance, FT-0007 should not be higher than FT-0003. In fact, FT-0007 should be less than FT-0003 by the amount of water vapor removed/condensed out of the FG in the prescrubber. Also, FT-0011 + FT-0209 should be close to FT-0007 on a wet basis and exactly the same if converted to a dry basis. In addition, FT-0003 and the combined value from the WtE plant should be equal. This is not the case, but the trend of the flow meters match fairly well.

### 5.4 Analyzing the problem

In order to determine which flow meters to trust it is essential to understand the working principle of the thermal mass flow meter. As noted, the thermal mass flow meter is highly dependent on the composition of the gas and based on that the most reliable source representing a stable gas composition is to be found at the CO<sub>2</sub> product outlet, FT-0209.

In addition to flow meters, the pilot plant is equipped with a number of other instruments, which have been independently calibrated and verified. In this respect, the CO<sub>2</sub> measurements at the treated flue gas outlet are also very important as will be discussed and shown below.





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#### 5.4.1 Assumptions

Thus, to proceed with the analysis, the following has been assumed:

- FT-0209 is accurate to +/-3%
- CO<sub>2</sub> measurements at the FG outlet are accurate (to a varying degree based on measured concentration)
- The FG in and out of the absorber is H<sub>2</sub>O saturated (verified by measurements)<sup>1</sup>
- The CO<sub>2</sub> product is saturated with H2O (as a function of measured temperature and pressure)
- Flue gas molar mass is based on measurements of  $H_2O$  (and saturation assumptions),  $O_2$ ,  $CO_2$ . Remaining fraction is assumed to be pure  $N_2$ .

For evidence to support the above assumptions, see the following chapters.

#### 5.4.1.1 FT-0209 - CO<sub>2</sub> product flow meter

As part of the 24 hour acceptance test for the pilot plant, the CO<sub>2</sub> product flow meter (FT-0209) reliability was evaluated (see NC03-KEA-P-RA-0013 for details).

The flow meter was checked against 1) simulated amounts, 2) the control valve (valve position and characteristics) downstream the flow meter as well as 3) the CO<sub>2</sub> loading in the rich and lean amine. The evaluation showed good correspondence between the measured quantity and the calculated quantity.

In addition, since the gas through FT-0209 is always pure CO<sub>2</sub> with small variations in composition, the flow composition parameters are easily well defined.

Based on the above, the vendor has claimed that the accuracy of this flow meter is +/- 3% (or better). In other words, if the flow meter is showing 100 kg/h, the actual value is within 97 and 103 kg/h.

#### 5.4.1.2 Treated FG CO<sub>2</sub> concentration

The measurements are made in accordance with the quality management system of Ramboll Finland. Ramboll measurement services are accredited by Finnish accreditation Service (FINAS), testing laboratory T302 according to ISO/IEC EN 17025:2005.

Calibrations (daily when Ramboll present) and tuning reference materials are as follows:

- CO<sub>2</sub>-gas 15.0 ± 1 % (of concentration) and 100.0 % purity grade 4.0 gas (>99.99 %)
- N<sub>2</sub>-gas 100.0% purity grade 5.0 (>99.999 %) used for zero-point calibration and FTIR reference spectrum
- Linearity check provided

Example of data for week 13 as follows with uncertainties provided as +/- range:

Date	25.3	26.3	27.3	28.3	29.3	30.3	31.3
CO <sub>2</sub> (vol%, wet)	$0.4 \pm 0.1$	$0.0 \pm 0.1$	$0.1 \pm 0.1$	$0.1 \pm 0.1$	0.2 ± 0.2	0.2 ± 0.2	0.2 ± 0.2

<sup>&</sup>lt;sup>1</sup> At times, this might not be true as the heat pump on WtE plant line 3 removes a significant amount of water from the flue gas during operation.

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#### 5.4.1.3 H<sub>2</sub>O measurements around the absorber

Measuring the water content of the flue gas around the absorber provides a good way to evaluate the accuracy of the H<sub>2</sub>O measurements as it is reasonable to assume that the flow after the pre-scrubber is saturated with water.

Below is a demonstration of humidity measurements before the absorber (i.e. after the prescrubber) compared to those based on assuming  $H_2O$  saturated FG at measured temperature and pressure conditions.



Figure 3. Comparison of H<sub>2</sub>O measurements and assumptions in FG into absorber

Data for the humidity out of the absorber is not collected continuously and therefore it is not possible to provide a similar graph as above. However, the location of the FTIR instrument is switched to the absorber outlet periodically. The Figure below is based on such information.



Figure 4. Comparison of  $H_2O$  measurements and assumptions in FG out of absorber. Notice the significantly different time scale (1 hour) compared to Figure 3.

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Based on the above (as well as quality assurance reports by Ramboll, can be provided separately upon request) the  $H_2O$  measurements can be trusted.

#### 5.4.2 Dry gas flows

Based on knowing the temperature and pressure conditions, as well as the composition of the gas around the absorber and after the  $CO_2$  reflux condenser and drum, i.e. at respective flow transmitter location, it is possible to convert all three streams to dry conditions.

In addition, the water content is also measured at the WtE plant providing information about the H<sub>2</sub>O content in all three FG supply lines into the pilot plant. However, it should be noted that before the WtE flow meters can be trusted, the resulting H<sub>2</sub>O fraction in the combined flow is somewhat uncertain (due to the considerable difference in FG humidity between the different lines).

The below Figure represents all flow measurements converted to dry conditions, i.e. it is the same as Figure 2 without H<sub>2</sub>O in the gas streams.



Figure 5. Calculated  $H_2O$  free (dry) flow measurement values from 4 flow meters located at the pilot plant together with a combined (FT WtE) value for the 3 flow meters located upstream of the pilot plant. The dotted line is the sum of dry  $CO_2$  product out and dry treated FG.

As mentioned, by removing water from the equation, all of the following flows should be (very close to) equal: FT WtE = FT-0003 = FT-0007. However, FT-WtE is around 80 kg/h lower than FT-0003, which in turn is around 110 kg/h lower than FT-0007.

However, there is another combination of flows that should also match the above flows and that is FT-0011 (treated FG) together with FT-0209 (CO<sub>2</sub> product). This combined flow matches well only with FT-0003, suggesting that both FT-0003 and FT-0011 are fairly accurate or at least more accurate than FT-0007 and FT-WtE.

Notice also that the fluctuating behavior for FT-WtE and FT-0003 seen in Figure 2 has been significantly reduced when accounting for the FG water content.

Thus, in conclusion so far:

- FT-0003, FT-0011 seem to be fairly accurate, but needs to be verified with a CO<sub>2</sub> mass balance (as both could also be equally wrong)
- FT-0007 is too high



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FT-WtE is too low

#### 5.4.3 Calculated FT-0007

The incoming flue gas contains CO<sub>2</sub> that is selectively removed in the absorber and released in the stripper. This fact provides an opportunity to analyze the flow meters based on the  $CO_2$ balance alone.

All of the CO<sub>2</sub> entering the pre-scrubber leaves either at the top of the absorber or after the stripper column. We assume that the product leaving the stripper downstream the reflux condenser is pure  $CO_2$  (only traces of other components) saturated with  $H_2O$ . We can determine the pure CO<sub>2</sub> amount based on FT-0209 and the saturated H<sub>2</sub>O amount at the measured conditions (p, T).

The volume fraction of  $CO_2$  in the treated FG is known with good accuracy and based on the above (Chapter 5.4.2) it seems as if FT-0011 is fairly accurate. This provides us with the amount of  $CO_2$  out (in e.g. kg/h).

Furthermore, we know the concentration of CO<sub>2</sub> into the absorber, but we do not have a direct measurement of the flow (since FT-0007 seems to show a too high value). Thus, the only unknown in the equation below is  $\dot{m}_{CO2,supply}$ :

(1)  $\dot{m}_{CO2,supply} \times c_{CO2,supply} = \dot{m}_{CO2,treatedFG} \times c_{CO2,treatedFG} + \dot{m}_{CO2,product} \times c_{CO2,product}$ 

It should be noted that the above equation is simplified from the fact that the concentrations in the gas streams are measured on a volumetric basis and needs to be converted (using measurement data) to mass basis before applying to the equation. Once done however, the above equation allows the estimation of FT-0007 and below is a graph showing the calculated FT-0007 vs. the measured FT-0007.



Figure 6. Calculated vs. measured mass flow rate into absorber (FT-0007) together with measured values for FT-0003 (into pre-scrubber) and FT-0011 (out of absorber).

From the above Figure it can be seen that the measured mass flow rate into the absorber is too low (by around 80 kg/h on average). It is also apparent that there is some discrepancy in the FT-0003 and in the calculated FT-0007 value, but that seems to be an artefact of the H<sub>2</sub>O





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measurements into the pilot plant which as mentioned cannot be very accurate due to uncertainty in flow measurements into the plant. To evaluate this another Figure with the calculated dry FT-0007 value has been provided.

From the below Figure it can be seen that the calculated FT-0007 (dry) value is matching relatively well (although somewhat too high) with the dry FT-0003 as well as the combined FT-0011 and FT-0209 values. The match would be improved if FT-0003 and FT-0011 are showing slightly too low values.



Figure 7. All data on a dry basis. Calculated mass flow rate into absorber (FT-0007) together with measured values for FT-0003 (into prescrubber), FT-0011 (out of absorber) and the combined line for FT-0011 + FT-0209 (CO<sub>2</sub> product).

### 5.4.4 CO<sub>2</sub> mass balance

Based on Equation 1 it is possible to present a mass balance around the absorber. Ideally both sides of the equation are equal at all times, but if FT-0007 is showing a too high value the mass balance will be off.

Below is a Figure showing the relative (to FT-0007) error of the equation as a function of time based on raw data for the three relevant flow meters, i.e. FT-0007 (absorber inlet), FT-0011 (absorber outlet) and FT-0209 (CO<sub>2</sub> product).



Figure 8.  $CO_2$  mass balance based on flow- and  $CO_2$  measurements around the absorber and on the  $CO_2$  product ( $H_2O$  saturated  $CO_2$ ).

From the above Figure it is clear that the left side of Equation 1 gives too high values or the right side gives too low. However, evidence suggests (foregoing discussions) that it is in fact the left side, i.e. the flow meter FT-0007 that is showing too high values. Further support to this claim can be provided by estimating the  $CO_2$  balance based on FT-0003 instead, as done in the Figure below.



Figure 9.  $CO_2$  mass balance based on flow- and  $CO_2$  measurements before the pre-scrubber (FT-0003), after the absorber and on the  $CO_2$  product ( $H_2O$  saturated  $CO_2$ ).

Now (Figure 9) it can be seen that the left side (i.e. FT-0003) is providing too low values, indicating that the flow meter FT-0003 also is a little off. At this point it is important to note that previously (see Figure 5) it seemed as if FT-0003 and FT-0011 were showing fairly accurate results, but this needs to be re-evaluated based on the above. Due to the very low amounts of  $CO_2$  in the treated FG (FT-0011), the  $CO_2$  mass balance is currently (in the week used for analysis) dominated by the supply FG as well as the product  $CO_2$ . In other words, even if the

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treated FG would be much higher, the resulting impact on the CO<sub>2</sub> balance would be marginal; multiplying a high flow with a very low concentration is still a small number.

It can now be concluded that:

- FT-0007 confirmed too high
- FT-0003 is slightly too low, meaning that also FT-0011 is slightly too low (based on Figure 5).

### 5.4.5 H<sub>2</sub>O balance

Before the flue gas enters the absorber it goes through a pre-treatment step in the form of a pre-scrubber that cools down the flue gas. Because the flue gas contains a significant amount of water vapor as it enters the pre-scrubber, the cooler flue gas leaving the pre-scrubber becomes saturated with H<sub>2</sub>O. Based on the amount of FG entering and exiting the pre-scrubber together with H<sub>2</sub>O measurements it is possible to estimate how much H<sub>2</sub>O is condensed in the pre-scrubber. However, as FT-0007 is showing a too high value, the H2O out of the pre-scrubber is (without modifications) negative and obviously wrong.

Further evidence that FT-0007 is too high.

### 5.5 Implementing corrections

Based on the assumptions listed in Chapter 5.4.1 (particularly the accuracy of FT-0209) and the analysis in the foregoing chapters, the evidence suggest that:

- FT-0007 is too high
- FT-0003 and FT-0011 are somewhat too low

Applying simple constant correction factors provides good closure to the presented balances. However, it should be noted that the operation has been very steady (similar flow rate maintained) and therefore additional data needs to be analyzed in order to conclude this chapter.

For now, the following simple corrections have been implemented

- FT-0003 (corrected) = 1.08 \* FT-0003 (raw) into pre-scrubber
- FT-0007 (corrected) = 0.88 \* FT-0007 (raw) into absorber
- FT-0011 (corrected) = 1.11 \* FT-0011 (raw) after absorber

Applying the corrections to a few of the graphs provided above has been presented below.



Figure 10. Correction factors applied to Figure 8.



Figure 11. Correction factors applied to Figure 9.



Figure 12. Correction factors applied to Figure 5.

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#### 6 **APPENDIX 2 - APPLYING FLOW CORRECTIONS ON WEEK 14**

Applying the corrections discussed in Appendix 1 has been implemented on the data evaluated this week (14).







Figure 14. Correction factors applied to Figure 9.



Figure 15. Correction factors applied to Figure 5.

# Klemetsrud CCS Pilot

NOx-Intercomparison

Claus Nielsen Department of Chemistry University of Oslo June 10, 2019



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The data and results in this report has been quality controlled and verified according to generally accepted principles for publication in internationally recognised scientific journals.

Oslo, June 10, 2019

Clair Nicken

Claus Nielsen Department of Chemistry University of Oslo

## **Executive Summary**

The fluegas NO and NO<sub>2</sub> content was monitored by a Gasmet DX4000 FTIR and by a Teledyne T200 Chemiluminescence NO/NO<sub>2</sub>/NOx Analyzer. The NOx-levels were in general too high for the T200 analyzer and a provisional dilution system was employed during the final 500 hours of test campaign. A reliable dilution system was installed on May 20.

The NO-levels obtained by FTIR and T200 show a very high correlation,  $R^2 > 0.9$ , for all days. The NO<sub>2</sub>-levels obtained are associated with larger uncertainties and do not show the same degree of correlation.

In the lack of information on the mixing of the K1, K2 and K3 fluegas lines, it is suggested to use a simple linear relationship between the NO and NO<sub>2</sub> as a first approximation. The T200 data show a good correlation between the NO and NO<sub>2</sub> levels ( $R^2 = 0.94$ ; NO<sub>2</sub> = 0.04 × NO), whereas the FTIR data show much less correlation ( $R^2 = 0.65$ ; NO<sub>2</sub> = 0.006 × NO).

## 1 FTIR spectra of NO and NO2 in humid air

The standard Gasmet DX4000 FTIR<sup>1</sup> employs a multi-pass cell with a 5 m optical pathlength and operates at 180 °C with a spectral resolution of 8 or 4 cm<sup>-1</sup>. The sample pressure was fixed at 980 mbar in the FOV measurements.

The fluegas contains around 7% water vapour, 13% CO<sub>2</sub>, 10-100 ppm NOx of which NO<sub>2</sub> accounts for a few per cent. Figure 1 compares the theoretical spectra of air at 180 °C containing 7% water, 13% CO<sub>2</sub>, 100 ppm NO and 2 ppm NO<sub>2</sub>, to that of air at 180 °C containing only 7% water (it is assumed that the 2200 – 1400 cm<sup>-1</sup> region is used for retrieving the NO and NO<sub>2</sub> content). The figure illustrates that it is relatively easy to extract a ~100 ppm NO content (the blue and red curves differ visibly), whereas retrieval of ~2 ppm NO<sub>2</sub> is associated with a considerably larger uncertainty.



**Figure 1**. IR transmittance spectrum (blue curve) of air containing 7% water vapour, 13% CO<sub>2</sub>, 100 ppm NO and 2 ppm NO<sub>2</sub>. Optical pathlength 5 m, T = 180 °C, p = 980 mbar, res = 8 cm<sup>-1</sup>. The spectrum of 7% water is presented as the red curve.

 $<sup>^{1}\</sup> https://www.gasmet.com/de/wp-content/uploads/sites/6/2018/01/Gasmet-DX4000-Technical-Data-v1.10.pdf$ 

## 2 Comparison of NOx-data

The following pages show unbiased comparisons of the NO- and NO<sub>2</sub>-levels in the fluegas obtained by FT-IR and by a Teledyne T200 Chemiluminescence NO/NO<sub>2</sub>/NOx Analyzer.<sup>2</sup>



<sup>&</sup>lt;sup>2</sup> http://www.teledyne-api.com/products/nitrogen-compound-instruments/t200




















































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## 3 Data analysis

It is obvious from the figures in section 2 that the there is a strong correlation between the NO values reported from FTIR and from the NOx-monitor. The correlation between the reported NO<sub>2</sub> values is less obvious. The initial NOx-monitor dilution system was unstable and the FTIR data for NO have therefore been taken as reference. Table 1 summarises the slope of the coorrelation lines for NO<sub>monitor</sub> *vs*. NO<sub>FTIR</sub> and the square of the correlation coefficients ( $R^2$ ).

Table 1.	Summary of	the correlation	between H	FTIR and	T200	results	for NO,	the NO	mixing
ratio fron	n FTIR/T200	and the NO <sub>2</sub> m	ixing ratio	s from F	ΓIR an	d T200.			

Date	Slope of	R <sup>2</sup>	<no></no>	<no<sub>2&gt;<sub>FTIR</sub></no<sub>	<no2>T200</no2>
	correl. line		/ppm	/ppm	/ppm
2019.05.01 <sup>a</sup>			50.3	0.17	2.50
2019.05.02	0.931	0.973	41.7	0.25	2.50
2019.05.03 a			42.9	0.22	2.80
2019.05.04	0.975	0.986	51.2	0.02	3.30
2019.05.05	1.019	0.989	54.4	0.08	3.44
2019.05.06	1.241	0.971	79.5	0.37	4.48
2019.05.07	1.285	0.980	77.6	0.44	4.19
2019.05.08	1.301	0.971	68.4	0.54	3.30
2019.05.09	1.240	0.925	32.8	0.26	1.27
2019.05.10	1.203	0.953	39.2	0.59	1.57
2019.05.11	1.256	0.982	64.5	1.06	2.63
2019.05.12	1.271	0.987	65.2	0.88	2.71
2019.05.13	1.324	0.988	71.5	0.57	3.03
2019.05.14	1.391	0.910	71.2	0.21	2.97
2019.05.15	1.287	0.972	55.8	0.3	2.05
2019.05.16	1.254	0.944	42.0	0.26	1.33
2019.05.17	1.204	0.979	42.8	0.08	1.36
2019.05.18	1.196	0.978	43.7	0.09	1.40
2019.05.19	1.185	0.976	42.9	0.17	1.43
2019.05.20 <sup>b</sup>	1.198	0.980	64.6	0.21	2.04
2019.05.21 <sup>a</sup>			63.0	0.24	
2019.05.22 °	0.698	0.973	14.5	0.35	0.34
2019.05.23 °	0.730	0.981	16.7	0.31	0.39
2019.05.24 <sup>d</sup>			28.7	0.25	
2019.05.25 <sup>d</sup>			30.2	0.23	
2019.05.26 <sup>d</sup>			30.6	0.17	
2019.05.27 <sup>d</sup>			30.0	0.22	
2019.05.28 <sup>d</sup>			27.3	0.37	
2019.05.29 °	1.031	0.989	30.2	0.28	0.57
2019.05.30 °	1.025	0.984	29.9	0.17	0.61
2019.05.31 °	0.962	0.961	13.6	0.55	0.29

<sup>a</sup> Not analysed. <sup>b</sup> Data from the period  $0^{\underline{00}}$  to  $13^{\underline{00}}$  used. NOx-monitor near saturation in the period  $16^{\underline{00}}$  to  $24^{\underline{00}}$ . <sup>c</sup> Erroneous dilution employed in the raw data report. <sup>d</sup> Only FTIR data available. <sup>e</sup> New NOx-monitor dilution system installed.

There is insufficient information available to correlate the NO and NO<sub>2</sub> content in the fluegas to the blending of the K1, K2 and K3 lines. To a first approximation, a linear relationship between the NO and NO<sub>2</sub> content was assumed. Figure 2 shows a plot of the available data. It can be seen that the T200 NO and NO<sub>2</sub> data are reasonably correlated (slope 4 %,  $R^2 = 0.94$ ). The FTIR data are less correlated (slope 0.6 %,  $R^2 = 0.65$ ).



**Figure 2**. NO<sub>2</sub> content in fluegas versus the NO content. The dotted red line corresponds to NO<sub>2</sub> being 4 % of NO. The dotted blue line corresponds to NO<sub>2</sub> being 0.6 % of NO.

Intended for Fortum Oslo Varme AS

Document type
Calibration report

Date 6.6.2019

# FORTUM WARME OSLO, ANALYSER CALIBRATIONS



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Document no. NC03-KEA-P-RA-0016 Rev.01 Title: Pilot Plant Final Test Report, Attachment 7 - Ramboll calibrations

0	Accredited quant	tities and measuring	тос	1 – 1000 ppm <sub>propane ekv.</sub>
FINIAC	ranges		Humidity	1 vol% - saturated gas
FINAS	Particles	1-1000 mg/m <sup>3</sup> n	Flow rate	5 – 30 m/s
Finnish Accreditation Service	SO <sub>2</sub>	1 - 1000 ppm	HCI	0,1 – 50 ppm
T302 (EN ISO/IEC 17025)	NOx	1 – 1000 ppm	HF	0,1 – 15 ppm
	O <sub>2</sub>	0 - 21 vol%	Metals	0,05-0,5 mg/m³n
	СО	1 – 5000 ppm	PCDD/F-compounds and dioxin-like	
	CO <sub>2</sub>	0,5 - 20 vol%	PCB-compounds: >0,1 ng/m <sup>3</sup> (I-TEQ, su	

**Client:** 

Fortum Varme Oslo

Date of measurements: Authors of measurements: 25.2.2019-5.6.2019 Sauli Lundström, Janne Houni et al.

## **1. ABOUT CALIBRATIONS**

Calibration and tuning reference materials were as follows:

- $O_2$ -gas 5,0 with uncertainty of 1 % (of concentration). The first bottle used  $O_2$  was 5,1 %  $O_2$  and otherwise same concentrations.
- CO<sub>2</sub>-gas 15,0 with uncertainty of 1 % (of concentration) and 100,0 % purity grade 4.0 gas (>99,99 %)
- N<sub>2</sub>-gas 100,0% purity grade 5.0 (>99,999 %) used for zero-point calibration and FTIR reference spectrum.
- $SO_2$ -gas 10ppm with uncertainty of 2 % (of concentration). The second bottle is 20 ppm  $SO_2$ .

Calibrations are made when Ramboll personnel are present. Last two weeks calibrations were made during first and last on site -day of the week.

# 2. CALIBRATIONS

Here are described one calibration daily note every week.

2.1 Week 2: 25.23.3.2	2019
-----------------------	------

	Check values		Set values	
	zero	span	zero	span
02	0,0 (-)	5,0 (-0,1)	0,0	5,1
CO <sub>2</sub>	0,0 (-)	14,8 (-0,2)	0,0	15,0
SO <sub>2</sub>	-	-	-	-
FTIR (max/min)	-	-	-	-

#### 2.2 Week 2: 4.3.-10.3.2019

	Check values		Set values	
	zero	span	zero	span
02	0,0 (-)	5,2 (+0,1)	0,0	5,1
CO <sub>2</sub>	0,0 (-)	14,7 (-0,3)	0,0	15,0
CO <sub>2</sub>	0,0 (-)	100,0 (-)	0,0	99,9
SO <sub>2</sub>	-	-	-	-
FTIR (max/min)	-	-	-	-

#### 2.3 Week 3: 11.3.-17.3.2019

	Check values (drifts)		Set values (gases)	
	zero	span	zero	span
02	0,0 (-)	5,4 (+0,3)	0,0	5,1
CO <sub>2</sub>	0,0 (-)	14,8 (-0,2)	0,0	15,0
CO <sub>2</sub>	0,0 (-)	99,2 (-0,8)	0,0	99,9
SO <sub>2</sub>	0 (-)	10 (-)	0	10
FTIR (max/min)	59400 (max)	6800 (max)	-	-
2.4 Week 4: 18.3.-24.3.2019

	Check values (drifts)		Set values (gases)	
	zero	span	zero	span
02	0,0 (-)	5,3 (+0,3)	0,0	5,0
CO <sub>2</sub>	0,2 (+0,2)	101,1 (+1,1)	0,0	99,9
CO <sub>2</sub>	0,0 (-)	14,7 (-0,3)	0,0	15,0
SO <sub>2</sub>	0 (-)	10	0	10
FTIR (max/min)	60916 (max)	7388 (max)	-	-

### 2.5 Week 5: 25.3.-31.3.2019

	Check values (drifts)		Set values (gases)	
02	0,0 (-)	20,9	0,0	20,9
CO <sub>2</sub>	99,9 (-)	99,9	0,0	99,9
SO <sub>2</sub>	0 (-)	9 (-1)	0	10
FTIR (max/min)	59521 (max)	7272 (min)		

## 2.6 Week 6: 1.4.-7.4.2019

	Check values (drifts)		Set values (gases)	
02	0,1 (+0,1)	5,0 (-)	0,0	5,0
CO <sub>2</sub>	0,0 (-)	15,1 (+0,1)	0,0	15,0
SO <sub>2</sub>	0 (-)	10 (-)	0	10
FTIR (max/min)	58951 (max)	7175 (min)		

# 2.7 Week 7: 8.4.-14.4.2019

	Check values (drifts)		Set values (gases)	
0 <sub>2</sub>	0,0 (-)	5,0 (-)	0,0	5,0
CO <sub>2</sub>	0,0 (-)	15,0 (-)	0,0	15,0
SO <sub>2</sub>	0 (-)	10 (-)	0	10
O <sub>2</sub> (rack for FTIR)	-0,1 (-0,1)	5,0	0,0	5,0
FTIR (max/min)	58499 (max)	7014 (min)		

## 2.8 Week 8: 15.4.-21.4.2019

	Check values (drifts)		Set values (gases)	
02	0,0 (-)	5,0 (-)	0,0	5,0
CO <sub>2</sub>	0,0 (-)	15,0 (-)	0,0	15,0
SO <sub>2</sub>	0 (-)	10 (-)	0	10
CO <sub>2</sub> (FTIR test	0,0 (-)	15,5 (+0,5)	-	-
with gas)				
O <sub>2</sub> (FTIR test	0,0 (-)	5,1 (+0,1)	-	-
with gas)				
FTIR (max/min)	58464 (max)	7000 (min)		

# 2.9 Week 9: 22.4.-28.4.2019

Ramboll did not have  $SO_2$  -calibration gas this week.

	Check values (drifts)		Set values (gases)	
02	0,0 (-)	5,0 (-)	0,0	5,0
CO <sub>2</sub>	0,0 (-)	15,0 (-)	0,0	15,0
SO <sub>2</sub>	0 (-)	- (-)	0	- (-)
O <sub>2</sub> (FTIR test	-	20,5	-	20,6
with air)		(wet, ambient)		(wet, ambient)
FTIR (max/min)	58472 (max)	6980 (min)		

### 2.10 Week 10: 29.4.-5.5.2019

Ramboll did not have SO<sub>2</sub> -calibration gas this week.

	Check values (drifts)		Set values (gases)	
O <sub>2</sub>	0,0 (-)	5,0 (-)	0,0	5,0
CO <sub>2</sub>	0,0 (-)	15,0 (-)	0,0	15,0
SO <sub>2</sub>	0 (-)	- (-)	0	- (-)
O <sub>2</sub> (FTIR test	-	20,8	-	20,5
with air)		(wet, ambient)		(wet, ambient)
FTIR (max/min)	58638 (max)	6985 (min)		

## 2.11 Week 11: 6.5.-12.5.2019

New SO2 calibration gas has arrived by this week.

	Check values (drifts)		Set values (gases)	
02	0,0 (-)	5,0 (-)	0,0	5,0
CO <sub>2</sub>	0,0 (-)	15,0 (-)	0,0	15,0
SO <sub>2</sub>	0 (-)	20 (-)	0	20 (-)
O <sub>2</sub> (FTIR test	-	20,7	-	20,7
with air)		(wet, ambient)		(wet, ambient)
FTIR (max/min)	58357 (max)	6996 (min)		

## 2.12 Week 12: 13.5.-19.5.2019

	Check values (drifts)		Set values (gases)	
02	0,0 (-)	5,0 (-)	0,0	5,0
CO <sub>2</sub>	0,0 (-)	15,0 (-)	0,0	15,0
SO <sub>2</sub>	0 (-)	20 (-)	0	20 (-)
O <sub>2</sub> (FTIR test	-	20,65	-	20,65
with air)		(wet, ambient)		(wet, ambient)
FTIR (max/min)	58306 (max)	7013 (min)		

#### 2.13 Week 13: 20.5.-26.5.2019

	Check values (drifts)		Set values (gases)	
02	0,0 (-)	5,0 (-)	0,0	5,0
CO <sub>2</sub>	0,0 (-)	15,0 (-)	0,0	15,0
SO <sub>2</sub>	0 (-)	20 (-)	0	20 (-)
O <sub>2</sub> (FTIR test	-	20,6	-	20,6
with air)		(wet, ambient)		(wet, ambient)
FTIR (max/min)	58352 (max)	7027 (min)		

# 2.14 Week 14: 27.5.-2.6.2019

	Check values (drifts)		Set values (gases)	
02	0,0 (-)	5,0 (-)	0,0	5,0
CO <sub>2</sub>	0,0 (-)	15,0 (-)	0,0	15,0
SO <sub>2</sub>	0 (-)	20 (-)	0	20 (-)
O <sub>2</sub> (FTIR test	-	20,7	-	20,7
with air)		(wet, ambient)		(wet, ambient)
FTIR (max/min)	58377 (max)	7062 (min)		

### 2.15 Week 15: 3.5.-5.6.2019

	Check values (drifts)		Set values (gases)	
O <sub>2</sub>	-0,1 (-0,1)	5,1 (-)	0,0	5,0
CO <sub>2</sub>	-0,1 (-0,1)	15,0 (-)	0,0	15,0
SO <sub>2</sub>	0 (-)	19 (-1)	0	20 (-)
O <sub>2</sub> (FTIR test	-	20,6	-	20,6
with air)		(wet, ambient)		(wet, ambient)
FTIR (max/min)	58207 (max)	7091 (min)		

# PTR-ToF-MS Calibration

A commercial PTR-TOF 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) is used for measuring amines and degradation products in the absorber exhaust gas. The instrument was calibrated for Amine-1, Amine-2, Amine-1-nitrosamine, Amine-1-amide and Amine-1-formamide using a commercial liquid calibration unit (LCU; Ionicon Analytik GmbH, Innsbruck, Austria)<sup>#</sup> for evaporation of gravimetrically prepared aqueous standards in nitrogen.

The instrument sensitivity is calibrated against acetone and toluene employing cylinder D522190 from Apel-Riemer Environmental, Inc.

Stock solutions of Amine-1 (0.0180 M,  $\pm$  1%) and Amine-2 (0.020 M,  $\pm$  1%) were prepared gravimetrically and further diluted as the working solution for LCU measurements. Working solutions of Amine-1-nitrosamine, Amine-1-amide and Amine-1-formamide were prepared from the 0.01 M solutions received from Shell. The instrument has so far not been calibrated for Amine-2.

The compounds are generally sticky judging from the time it takes to plateau the ion signals; Amine-2 being the least and the Amine-1-nitrosamine being the most 'sticky.

The calibration factors (ncps/ppbV) for the aforementioned substances are listed below. The calibration factor of Amine-1-formamide is unreasonably high and the value is discarded for analysis (Two independent dilutions were carried out, and it is concluded that the received solution does not have the stated concentration). Until further the acetone response factor is used as a proxy for Amine-1-formamide.

Substances	calibration factor (ncps/ppbV)	Sum	Note
Acetone	19.9	19.9	New cylinder
Toluene	11.8	11.8	New cylinder
Amine-1	20.0	20.0	No fragments
Amine-2	20.8	20.8	No fragments
Amine-1-nitrosamine	12 for m/z [M+H] <sup>+</sup>	24.6	Major fragment [M-NO+H] <sup>+</sup>
	8.7 for [M-NO+H] <sup>+</sup>		
	4.0 for m/z 'xx'		
Amine-1-amide	14.9 for [M+H] <sup>+</sup>	19.1	Major fragment [M-CO+H] <sup>+</sup>
	4.2 for [M-CO+H] <sup>+</sup>		
Amine-1-formamide	57.1 [M+H]⁺	70.6	Major fragment [M-CO+H] <sup>+</sup>
	13.4 [M-CO+H] <sup>+</sup>		

The calibration is illustrated in the figures below.

<sup>&</sup>lt;sup>#</sup> LCU – Liquid Calibration Unit, see https://www.ionicon.com/product/trace-calibration-systems/liquid-calibration-unit-lcu

Title: Pilot Plant Final Test Report, Attachment 8 - UiO calibrations











Ramboll

# **Ramboll – extractive sampling**

Janne Houni



### 1. Probe

2.

- o 4 mm diameter titanium pipe
- towards gas flow, isokinetic sampling
- Titanium pipe is short and isolated before the T-piece
- 3. PTFE lines
  - one for amines, full sampling time
  - o one for NH3 / IC (anions), ½ sampling time for each line

### 4. Sampling bottles with absorption liquids

- 3 bottles + color changing siliga for amines
- 2 bottles + color changing siliga for IC (anions)
- 2 bottles + color changing siliga for NH3 (anions)
- Lines scaled for water content calculation
- o Ice is used to keep siliga dry

## 5. Sampling pumps with gas volume meters

- $\circ \quad \text{Sampling flow adjusted for isokinetic sampling} \\$
- $\circ$  ~ (velocity and temperature of the gas are measured)



# 8.5.2019 Janne Houni

# 1.5.2019 15:15-17:25 Treated flue gas sample Extractive sampling gas humidity calculation - treated flue gas

### **Measured values**

	condensed mass to	condensed water		
H2O, vol-%	sample (g)	mass (g/m3, pipe)	Temperature (C)	
7,3	58,3	54,5		42

## Saturated gas - calculation

	condensed mass to	condensed water		
H2O, vol-%	sample(g)	mass (g/m3, pipe)	Temperature (C)	
7,5	59,8	55,9		42

## Sample details

gas flow rate (m/s)	gas flow (duct) m/s	Isokinetic factor
9,9	11,7	1,19