

Demonstration of a novel instrument for online monitoring of absorber emissions to air

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ABSTRACT

A novel concept for online monitoring of nitrosamines, solvent amines and their degradation products in amine absorber emissions to air was demonstrated at the Tiller CO₂-lab pilot facility. The monitoring concept is based on SINTEF patent No. PCT/EP2011/073557. The measurement method applies gas sampling by capture of analytes in a condensate stream from a single stage condensate collector unit. An improved design for the SINTEF prototype for online gas and liquid measurements has been established as part of the CCUS-ALIGN project. The new design has low complexity and improved robustness, making it applicable as integrated part of industrial monitoring systems. The established prototype was successfully tested for monitoring of trace gas emission from a CO₂ capture pilot plant, demonstrating measurements of nitrosamines at levels far below the lower detection limits of commercial industrial online analyzers. Results from testing of a condensate collector prototype indicate high capture efficiency for analytes of interest, including analytes present in aerosols during operation conditions where the absorber emit mist to the atmosphere. The measurement concept has potential for significantly reducing the costs related to manual gas measurements for critical trace gas components in plant operation. Application of the concept can enable continuous measurements of nitrosamines and other critical trace gas analytes in the emissions to air not currently available in absorption-based CO₂ capture processes.

1. Introduction

Large scale CO₂ capture plants have a need for continuous chemical monitoring of the process, both related to process optimization, operational control, solvent degradation and for emission control and documentation of compliance to statutory regulations. Given the large flue gas volumes processed in CO₂ capture plants, analytes of sub-ppm concentrations in the emissions to air from the absorber outlet are of importance for monitoring, as mg/Nm³ per volume flue gas emitted converts to tons per year emitted to air from the plant. The potential for the presence of compounds hazardous to health and environment, like nitrosamines, nitramines, amines, and their degradation products further make emission monitoring a mandatory task from amine-based carbon capture plants (Gjernes et al., 2013; Helgesen and Gjernes, 2016; Karl et al., 2011; Nielsen et al., 2012; Reynolds et al., 2012; Silva et al., 2013).

1.1. Absorber emission gas sampling and analysis challenges

There are currently no existing commercially available industrial online analyzers fulfilling the needs for monitoring of gas trace analytes in the flue gas from amine-based CO₂ capture plants (Wittgens et al., 2010). Available industrial gas sensors, such as FTIR (Fourier Transform Infrared Spectroscopy), typically have lower limits of quantification (LOQ) down to 1 ppmv. For environmental adverse trace gas components, such as nitrosamines, are present in much lower concentrations at ppbv-levels. Given these low concentrations, there are currently no existing commercially available online analyzers fulfilling the needs for industrial continuous emission monitoring. Some industrial instrumentation is available for continuous monitoring of trace components in the solvent or water wash liquid, however no current products cover the full needs for monitoring of these gas trace analytes in the flue gas (Wittgens et al., 2010; Full-scale Mongstad CCM Technology Qualification Program, 2013).

Correct trace gas analysis from amine scrubbers is a challenging task due to the combination of low concentrations, number of analytes, high

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water content and formation of aerosols and droplets in the off-gas flow. Isokinetic sampling is mandatory to achieve representative measurements. Several options exist for dedicated ambient air trace gas analysis and monitoring, however the primary challenge for all available analyzers is that these require non-condensing and/or precipitating gas compounds in the measurement cell for reliable operation. Thus, the need for heating of the gas for analysis by heated sampling lines and measurement cells to ensure complete evaporation of the gas sample is evident. Applied continuous monitoring system as FTIR spectroscopy and proton-transfer-reaction mass spectrometry (PTR-TOF MS) use heated sampling lines and measurement cell to avoid water condensation, otherwise water soluble components will not be detected (Morken et al., 2017). PTR-TOF MS instruments have very good sensitivity (Zhu et al., 2018), however they have some limitations compared to traditional mass spectrometers; one limitation is that the analytes need to have a higher proton affinity than water. Although the use of other reagent ions than H_3O^+ can help to overcome this limitation. Another limitation is that the benefit of fragment ions and the generation of qualifier ions that makes it possible to use spectrum search the same way as for gas chromatography MS (GC-MS). Due to the high water-content and the presence of liquid aerosols and droplets in the gas emitted from a CO_2 scrubber, high temperature is needed in the sampling lines to avoid liquid residues entering the gas analyzer. Long sampling lines result in longer residence times of the sample at elevated temperature. Excessive heating accelerates nitrosamine artefact formation from reactions between flue gas NO_x and secondary amines. Elevated temperatures also have potential for degrading compounds of interest during gas sampling (Wittgens et al., 2010).

The emission monitoring task at hand requires reliable measurements of low- and sub-ppmv concentrations of analytes. Available analytical methods are mainly for laboratory purposes, and not for industrial online monitoring. The currently available instruments will need considerable improvements to achieve satisfactory continuous operation (24/7) with wet flue gas. labor-intensive manual isokinetic measurements with gas sampling in a cooled sampling train followed by laboratory analysis is the currently available approach to monitor harmful trace gas emissions from amine-based carbon capture processes. Manual isokinetic measurements are a cost- and manpower intensive procedure.

1.2. SINTEF concept for monitoring of absorber trace gas emissions

SINTEF has ownership to a patent (Einbu et al., 2012) for industrial online scrubber emission monitoring demonstrated with a prototype gas sampler in an in-house project in 2010 (Unpublished results). The proposed concept applies the same gas sampling principle as standard manual isokinetic gas sampling setups combined with automated continuous analysis of gas analytes by liquid analysis of impinger absorbent or condensate. A fluid transfer system or 'fast-loop' is provided for transferring the liquid sample from the gas sampler to a remote central liquid analyzer. SINTEF has successfully demonstrated the concept with integration of a liquid mass spectrometric (LC-MS) analysis to a series of sampling impingers for continuous gas sampling, the absorbent liquid hold-up in the impinger was automatically controlled. Proof-of-concept of the SINTEF patent has previously been performed for online gas emission monitoring in a pilot plant amine absorber, applying online analysis of amine in the gas phase by a remotely located MS analyzer (50 m away from the sampling point). MS analysis enables identification of compounds based on the molecular mass. A special auto-sampler vial was designed to enable sampling of liquid from the fast-loop circulating absorption medium from an operating gas sampling impinger. A special impinger was designed for liquid level control by an overflow mechanism, providing sampling of liquid free of bubbles (impinger gas sampling bottles have vigorous bubbling during operation, and continuous sampling from these is not trivial). Residence time of absorption medium in the gas sampling impinger was set by

controlling the addition of fresh absorbent to the system and balanced removal of used absorbent. This allowed for continuous operation of the gas sampling impinger and enables lowering the analytical detection limits by increasing exposure time of the absorbent to sampled gas, significantly longer than what is possible in conventional manual gas sampling. The method demonstrated similar or better LOQ (by increasing liquid residence time in the impingers) for trace gas analytes as for manual isokinetic gas sampling and analysis.

MS analysis enables identification of compounds by molecular mass of the analytes and reduces the issues of multi-compound calibration and its cross-sensitivity issues. Advantages of the concept compared to other available online analyzers are: 1) Access to sensitive high-resolution analysis of the liquid phase by MS. Low detection limits with similar lower limit of quantification as those found in manual sampling and analysis, 2) Representative isokinetic sampling of gas and droplets/mist and analysis without heated sampling lines and thermal degradation or accelerated artefact formation in the sample, 3) Option for parallel chemical analysis of solvent and water-wash liquid by MS in the same setup and 4) Option for historical collection of samples as a function of time, enabling later stage re-analysis or further investigation of gas- and liquid samples.

The demonstrated method of online liquid analysis of liquid from a continuous operated impinger sampling train involves a certain complexity which could be challenging in an industrial online monitoring application. A critical review of the prototype concluded that the setup demonstrated functioned as intended, but that the complexity of the gas sampling unit and liquid fast loop challenging for successful implementation as a robust instrumentation for 24/7 operation in an industrial environment.

Capturing the analytes directly in the condensate of a single stage cooler would simplify the setup by eliminating the need for an impinger train and the need for circulating the gas absorption medium between the analyzer and gas sampling bottles. Based on previous experience with manual gas sampling and analysis of emissions to air from amine-based CO_2 capture absorbers (Full-scale Mongstad (CCM) Technology Qualification Program, 2011), it is known that analytes of interest generally are water soluble and can in theory be captured in the condensate from the sampled gas only. Compared to sampling of gas in an absorption solution, where analytes are cumulated in the solutions over time, the analytes present in such condensates contain a representative composition of the emissions to air upon sampling. Sampling of condensate over time results in a condensate stream which is representative for the gas composition averaged over a given sampling time. Condensate mainly contains water, which is a good matrix for liquid analysis compared to absorption solutions like sulphuric acid, also enabling easier options for up-concentration of samples.

Given the robustness requirement for industrial applications, a revised design was proposed with significantly reduced complexity, involving a high efficiency single stage gas cooler tailored for maximum capture of absorber mist and with continuous collection and analysis of liquid condensate containing the captured analytes of interest.

2. Experimental

2.1. Gas sampler prototype design

A new instrument for continuous analysis of trace compounds in absorber emissions to air by condensate analysis was designed at SINTEF. The prototype of the design, hereby referred to as "ACEMS" (Absorber Continuous Emission Monitoring System), was built and successfully demonstrated for emission monitoring in a pilot plant absorber.

In the design, an isokinetic gas sampling setup is applied. The gas sampling pump is positioned upstream the condensation gas cooler to facilitate isokinetic withdrawal from a stack, enabling elevated pressure of about 100 mbar(g) in the gas cooler which is beneficial for

condensing and droplet growth in the condenser. Condensate and collected droplets and aerosols from the cooler are continuously collected and analyzed, with the liquid being driven out of the cooler by the pressure from the gas sampling pump. Integrated Peltier cooling elements in the gas cooler enables electrical power as the only utility needed for operation of the unit. The prototype design is compact enough to fit in a small gas sampling cabinet.

Fig. 1 shows the process flow diagram of the SINTEF ACEMS prototype.

Since a large portion of the analytes of the absorber emissions can be present in droplet form, satisfactory capture efficacy of analytes in a condensate setup relies on enough cooling and contact time for the collection of aerosols and droplets. Work was performed on designing a custom gas cooler and condensate collector aiming at near 100% capture efficiency of analytes of interest. Sintered metal blocks in the gas cooler inventory enables high specific surface heat-transfer area between the gas and the cooler internals and short gas residence time in the cooling stage. These porous metal bodies have a relatively dense mass with a high specific surface area for good heat transfer and with low liquid holdup volumes. Complete capture of sampled droplets and aerosols is enabled by the efficient cooling and droplet growth in the sintered metal structure of the cooler. The sintered metal block allows for coalescence of droplets in the structure and drainage of the liquid. The compact design of the cooler enables short residence time of the condensate collected, shortening the dead time in the measurement of collected condensate out of the unit. Fig. 2 depicts the designed custom gas cooler for the gas sampling prototype.

The cooler is built in 316 steel consisting of two solid parts that are bolted together. The sampled gas enters the cooler from topside and then

passes through a series of sequential sintered metal block inserts (not shown in the mechanical drawings) and ribs. Condensate and collected droplets end up in a small volume sump with a liquid outlet. The exiting gas is turned upwards towards the gas outlet in a section with an increased cross-sectional area to create lower gas velocity to avoid droplets escaping the unit. Sections for micro Raschig metal rings (2 mm diameter) trapped between sintered metal plates was part of the design but testing showed there was no need for the additional Raschig rings, as the cooler operated sufficiently without these fillings with only sintered metal blocks present. The cooler has ports for temperature measurements in the inlet, in the rib section and in the outlet of the cooler. These measurements were important for temperature control and to avoid formation of potential ice in the cooler.

The prototype gas sampling unit was assembled in $40 \times 18 \times 75$ cm skid (width, depth, height) covered with aluminum sheets for protection and outdoors operation. Fig. 3 shows machine drawings and photos of the operational skid with the gas cooler.

The lower section of the skid houses the gas cooler with Peltier cooling elements. Two metal heat sinks with cooling ribs and fans for controlled air flow through the unit for removal of heat from the Peltier elements are clamped to each side of the cooling unit. The top section of the gas sampling unit contains power supply units and instrumentation for control (PID) and displays for temperatures and setpoints. A manual control valve on the gas outlet of the sampler enables regulation of pressure for controlled liquid flow for sampling out of the cooler sump.

2.2. Condensate analysis by mass spectrometry

In the current work, mass spectrometry (MS) was chosen for liquid

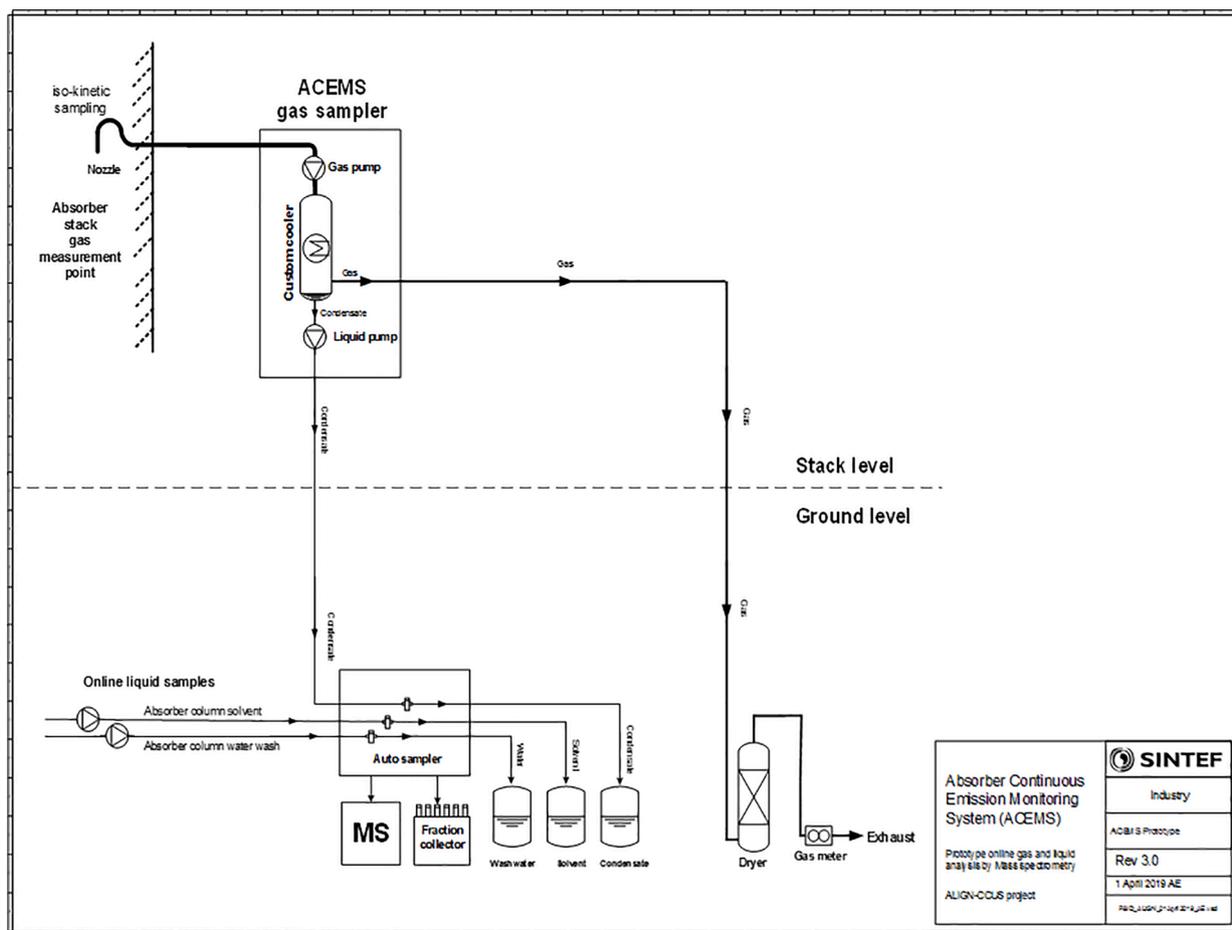


Fig. 1. Process flow diagram of prototype instrumentation of SINTEF patented concept for online monitoring of gas and liquids in a CO₂ capture absorber column.

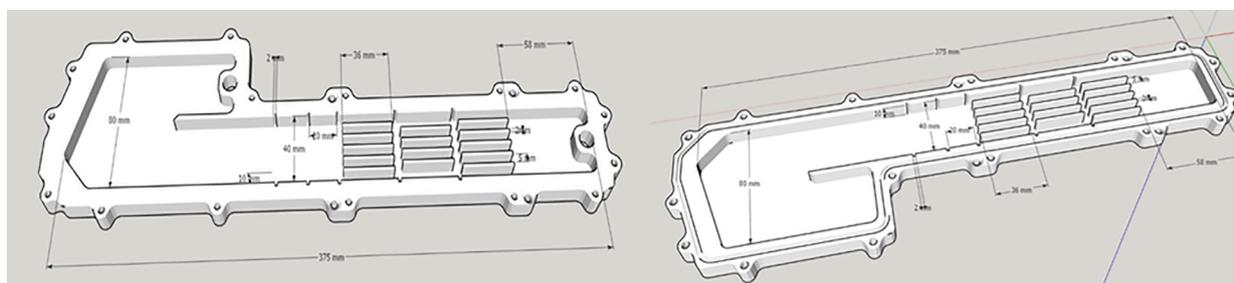


Fig. 2. Design of the custom gas cooler body developed (left and right part of metal block).

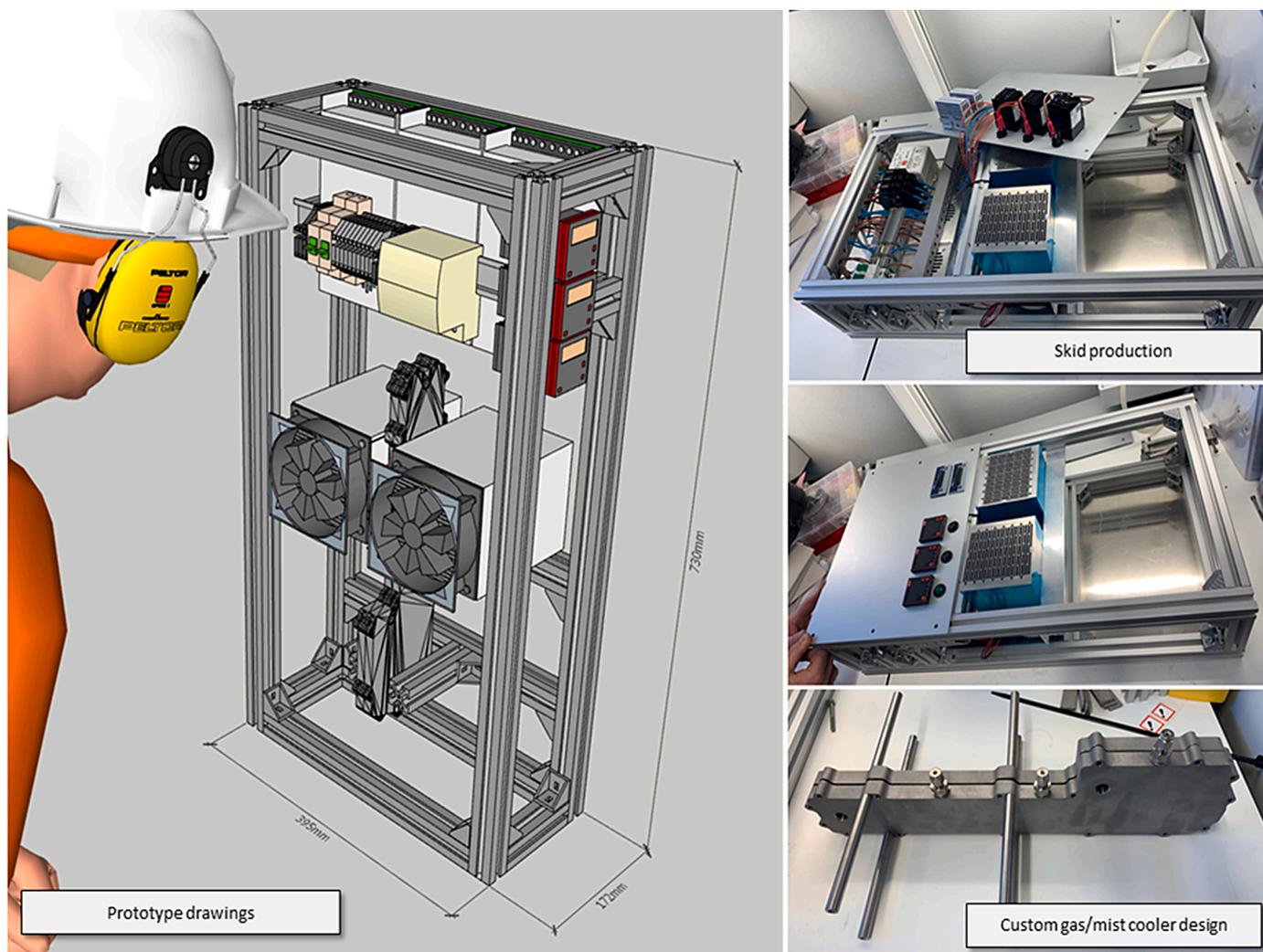


Fig. 3. Demonstration prototype gas sampler machine drawing and constructed skid.

analysis. The general concept shown above is flexible regarding selection of method for liquid analysis. Other liquid analyzers could replace the MS in the flow diagram above. Automated pre-treatment procedures prior to analysis can also be part of the concept, such as dilution of the sample. Such operations can easily be automated by state-of-the art MS instruments. The option for continuous collection of samples for storage and later analysis is also an interesting feature; with the robust design of the current prototype, it can operate unmanned and continuously collecting gas samples as liquid samples at regular intervals, or samples can be collected manually at the same time as other liquid samples of solvent and water wash are sampled from the plant.

2.3. Water wash analysis by mass spectrometry

The prototype design included addition of online analysis of liquid sampled from the absorber solvent and water-wash liquid. Parallel measurements of analyte concentrations in solvent and water-wash for comparison with plant emissions to air can give valuable information for increased understanding of the water-wash operation and mist contribution to emissions. Online monitoring of solvent also has several advantages for optimizing plant operation and studying solvent degradation.

Implementation of online monitoring of liquid streams is a straightforward task, given the work on liquid fast-loop previously

demonstrated with the initial prototype. Continuous liquid sampling from the sump of the upper water wash of the absorption column was performed in parallel with the gas sampling in the pilot plant demonstration.

2.4. Pilot plant monitoring demonstration

The prototype skid was installed at the absorber column gas outlet at the SINTEF pilot plant at Tiller CO₂-lab. Sampling lines for gas samples from the pilot plant emissions to air and from water wash liquid from the upper water wash sump was connected to the prototype skid. A mass spectrometer setup was installed and connected to the prototype condensate outlet for continuous measurements. In addition, liquid sampling lines from the upper water wash sump were also connected to the mass spectrometer. Online monitoring was tested during the pilot plant test campaign in the ALIGN—CCUS project. Fig. 4 shows the installed prototype sampler at the absorber gas outlet.

As part of the tests, a Topaz aerosol generator was applied for dosing of aerosol kernels into the flue gas flow of the absorber inlet for creating high mist concentrations in the sampled gas out of the absorber. This was done in order to test the sampling efficiency of the prototype with the presence of high concentrations of aerosols in the sampled gas. Tests were performed with pilot plant operation without Topaz injection and different levels of absorber mist induced by the Topaz setup.

2.5. FTIR and manual reference measurements

A standard gas sampling impinger setup was mounted downstream the condenser unit to capture analytes escaping the condenser. In addition, an isokinetic manual impinger sampling train was installed in parallel to the online unit for comparison of measurement results. Iso-kinetic gas sampling to the prototype setup was performed and analyte capture efficiency was defined as amount of analyte captured in the condensate unit compared to the total analyte captured in the parallel

impinger train.

Pilot plant online FTIR gas measurements were also used as a reference for monitoring of water content and amines in the absorber emissions to air.

3. Results and discussion

3.1. Gas cooler gas sampling efficiency testing

Testing of analyte capture efficiency of the cooler in the presence of absorber mist was conducted at the Tiller pilot plant. A Topaz aerosol generator was applied for inducing high concentrations of absorber mist in the emissions from the pilot plant by dosing of aerosol kernels in the flue gas into the absorber. Standard gas sampling impinger setups were mounted in parallel and downstream the condenser unit to capture analytes escaping the condenser. Iso-kinetic gas sampling was performed, and analyte capture efficacy was defined as amount of analyte captured in the condensate unit compared to the total analyte captured including the impinger train. Table 1 shows the resulting analyte capture efficiencies obtained for MEA and ammonia.

The above results from testing of gas condensate sampling shows that the method had a high capture efficacy for amine of 99.8%. Ammonia capture efficiency is lower (69.8%) – this is as expected, due to its inherent high volatility of ammonia. Ammonia is regarded one of the

Table 1

Custom cold-trap proof-of-concept results.

	Manual emission measurement [ppmv]	FTIR measurement [ppmv]	Condensate unit capture efficiency[%]
2-ethanolamine (MEA)	118	120	99.8
Ammonia	25	32	69.8



Gas sampling prototype



Online liquid analysis by MS

Fig. 4. ACEMS prototype for online liquid and gas monitoring in operation at the SINTEF pilot plant (left picture). Right picture showing the mass spectrometer setup connected for analysing condensate from to the gas sampler.

most volatile analyte of interest, thus it is more challenging to efficiently capture by the condensation unit alone. However, this is not considered as a problem, since alternative online monitoring methods for ammonia exist, for example by FTIR. Based on previous experience with sampling in impinger trains with condensate collection, other amines, nitrosamines and nitramines are expected to have similar capture efficacy as MEA. The results demonstrate satisfactory capture efficiency for mist-related emissions, as aerosols are the major contribution to the high emissions measured in this specific case.

3.2. Online FTIR reference measurements

Figure Fig. 5 shows online FTIR measurements during testing of the Figure prototype for continuous sampling. The figure shows concentrations of amines in the gas flow out of the pilot plant upper water wash section during three different Topaz settings applied: first (time 6:00 to 10:00 hr) no Topaz (and low mist), then medium (time 10:00 to 12:15 hr) and high settings Figure (time 12:15 to 16:00 hr) of the Topaz resulting in increased levels of absorber mist and amine emissions.

The upper graph in the figure shows AMP gas concentration [ppmv] in the gas phase, and the lower shows piperazine gas concentration [ppmv] measured by means of an FTIR. The FTIR measurements above show that concentrations of piperazine and AMP were around 1 ppmv with no operation of Topaz aerosol dosing. Upon starting the Topaz on the first setpoint at around 10 o'clock, levels of amines in the emissions increased to around 7 and 5 ppmv for piperazine and AMP respectively. With a increased setpoint of the Topaz, just after 12 o'clock, levels increase to around 13 and 9 ppmv for piperazine and AMP respectively. Topaz operation with aerosol dosing was shut off just after 15:30 (Note: there is a lack between start/shut down of the Topaz and the detected aerosols). Prototype measurements were performed for a period of about 2 h with the Topaz operating on its second setpoint. The Peltier elements was set to 4 °C, achieving a wall temperature of 4.2 °C in the condenser

of the ACEMS. The gas exiting from the prototype was measured to 8.5 °C. The exiting gas flow rate was measured using a Ritter gas meter.

3.3. Prototype demonstration measurements

Fig. 6 shows the results from MS analysis of condensate sampled by ACEMS system and water wash liquid in the same period.

As expected, concentrations of piperazine, AMP and nitroso-piperazine shows a steady increase in the water sampled from the upper water wash sump during the period. This is as expected since the analytes are building up in the water wash upon switching from low- to high concentrations of mist in the absorber outlet. Note that the levels of nitrosamine are about 3 orders of magnitude lower than the main amines, making it impossible to detect with the online FTIR-system installed.

Similar, for the gas sampling, the concentrations of the same analytes show a gradual increase in the concentrations of the condensate exiting the ACEMS sampler. This reflects the residence time of the condensate in the ACEMS gas cooler and the time for reaching steady state operation of the unit. The increasing levels in the condensate start to flatten out at the end of the test, as the gas cooler condensate inventory approached steady state.

Fig. 7 shows a comparison of different emission measurements as a function of time from FTIR, ACEMS condensate measurements and manual impinger measurements. FTIR and ACEMS measurements are continuous measurements, whereas the impinger measurements represent individual discrete measurements which are the average over the impinger sampling period indicated by the dashed lines.

Due to the condensate residence time in the gas cooler, the ACEMS sampler has a slower response time for its measurements compared to the FTIR (which has a response time of about one minute). For the measurement time interval above, the ACEMS system was at steady-state for the low-mist operation at the start, and a new steady-state is established upon the increased level of emissions in the mist. Based on

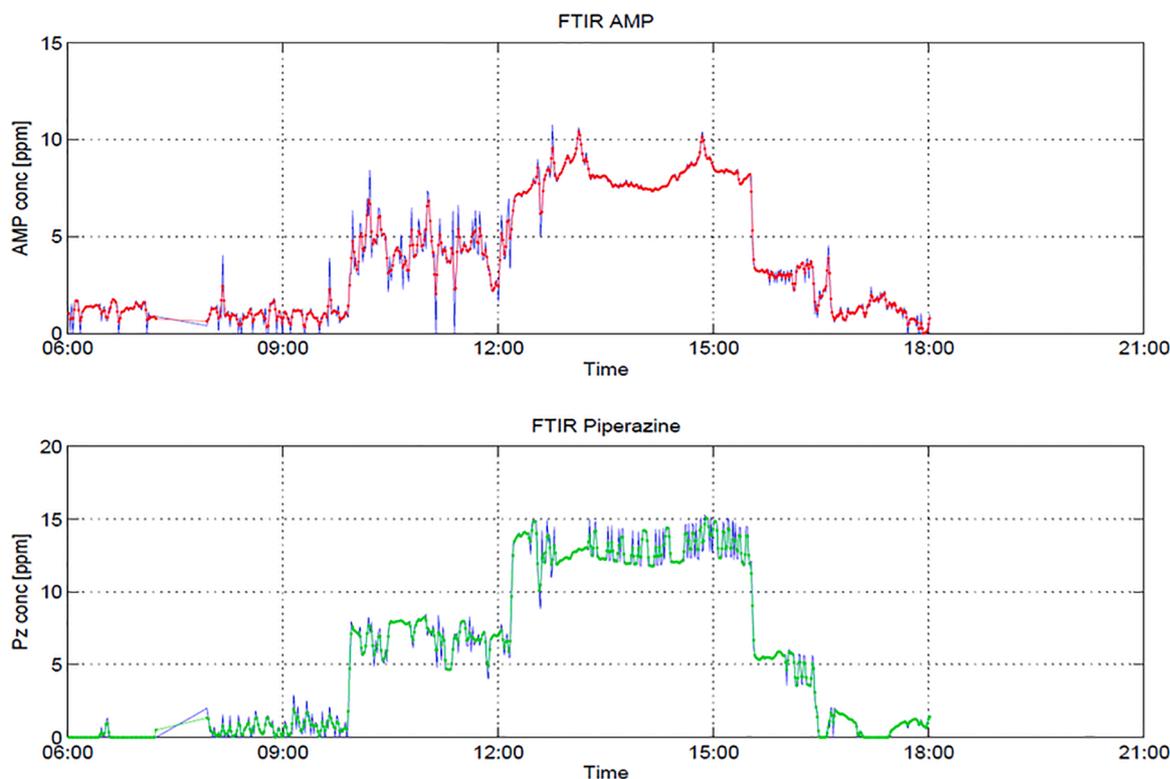


Fig. 5. Online FTIR gas measurements of the two main solvent components (AMP and piperazine) in the emissions to air from the pilot plant as a function of time during prototype testing.

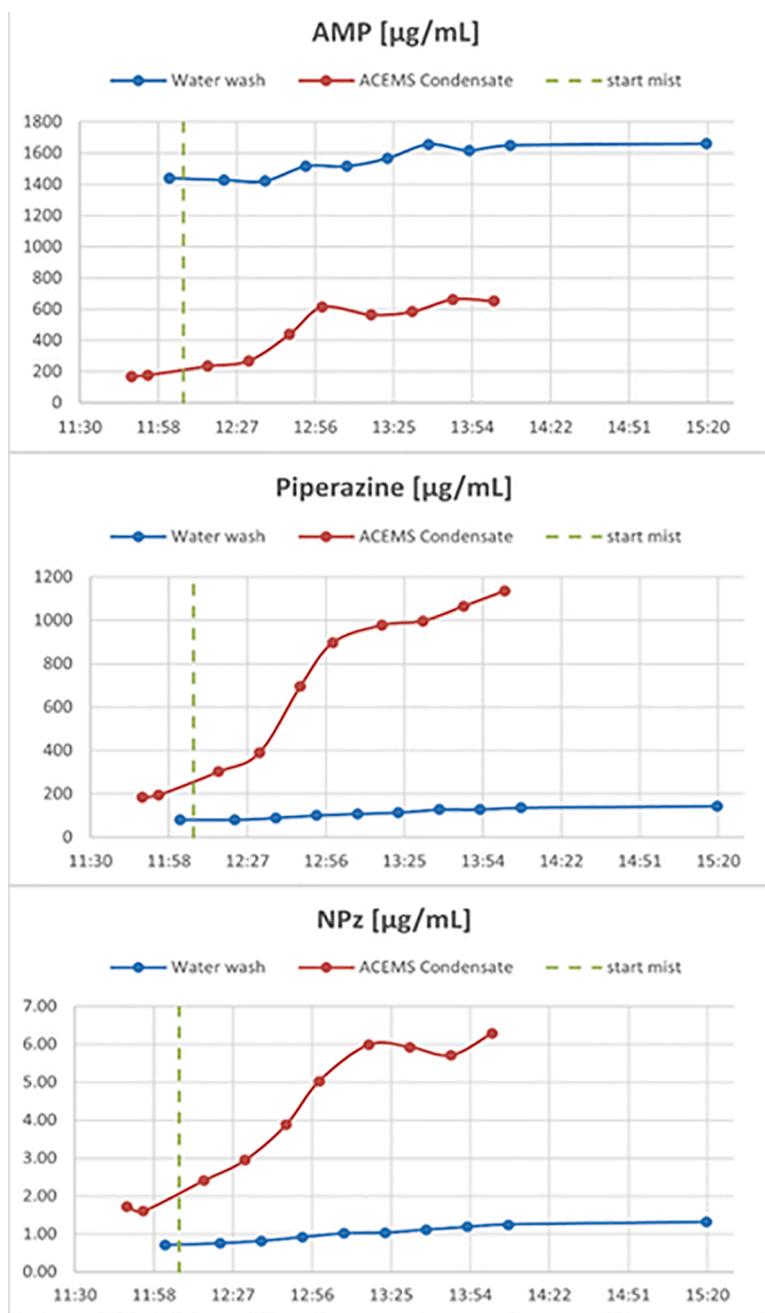


Fig. 6. Online analysis of sampled wash water and condensate from ACEMS system (emissions to air) during pilot plant operation. Concentrations of the main solvent amines (piperazine and AMP) and the main nitrosamine (Nitroso-piperazine, NPz) measured by mass spectrometry.

the results, this corresponds to about three hours with the current condensate inventory of the present gas cooler design. However, for measurement of overall emissions and for continuous confirmation of statutory regulations, this is a sufficient measurement time.

The results indicate that the ACEMS unit did not fully reach steady state during the above transitional measurements; comparison of amine measurements show the ACEMS measurements are lower than the FTIR and are still increasing when the measurements stopped. Considering the lag (residence time estimated to 3 h), the results indicate that the ACEMS measure concentrations of the main amines very much like what is measured by the FTIR. The same is the case for the nitrosamine measurements, showing the prototype measures lower concentrations than for the impingers, but is still in the process of reaching steady state upon termination of the MS measurements. These results indicate the prototype instrumentation can measure amines and nitrosamines like

what can be performed with a manual impinger train.

The results also confirms that the current ACEMS systems measurements averages gas samples of approximately the last three hours of gas sampling. This time can be reduced by a more compact design of the gas cooler inventory and increased gas flow through the system. A three-hour average for measurements of emissions to air is still sufficient for the application at hand (a stable operation of a CO₂-capture plant and monitoring of statutory regulations). The results indicate the ACEMS prototype unit has a high potential to replace work-intensive manual impinger sampling and sub-sequent off-line analysis for trace gas compounds. Further, whereas typical manual gas emission measurements are not performed frequently, a continuous operating prototype can always produce continuous results of 3-hour average samples during plant operation. In addition, a dilution of the condensate in the ACEMS prototype will increase the throughput and thus reduce the residence

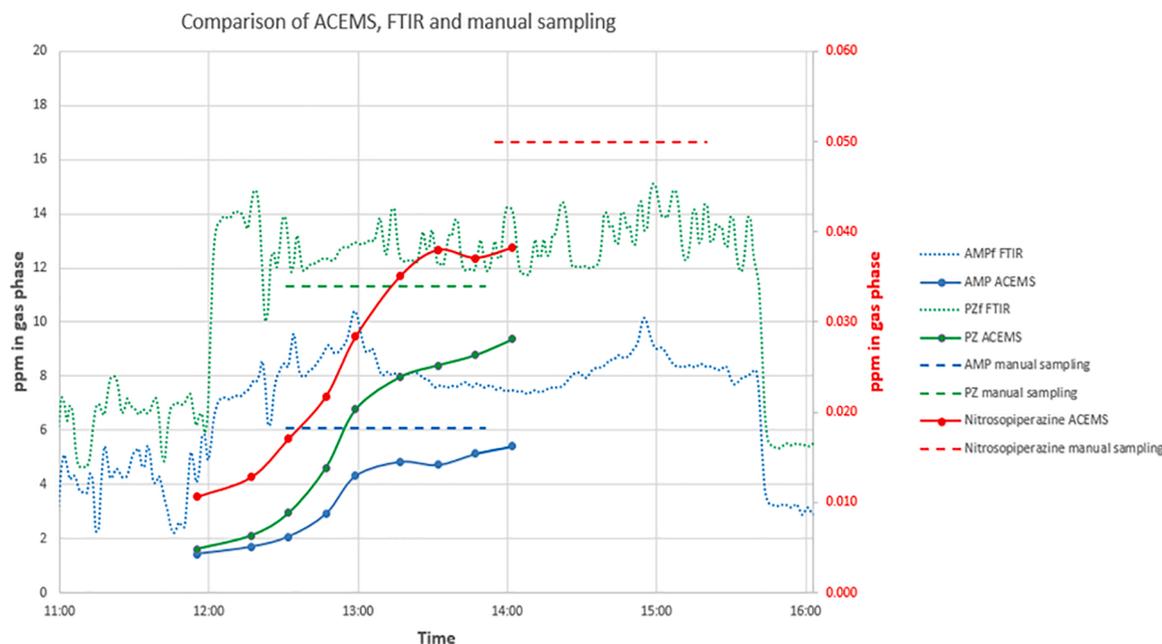


Fig. 7. Example of results from online monitoring of solvent amines and nitrosamines in the emissions to air from a CO₂ capture pilot plant absorber. Measured concentrations of the main solvent amines (piperazine and AMP) and the main nitrosamine (Nitroso-piperazine, NPz) from the ACEMS system measured by mass spectrometry (thick solid lines) compared to manual impinger measurements (dashed lines). The thin dotted lines represent the FTIR measurements of piperazine and AMP. Left axis represents solvent amines (AMP & Piperazine in gas phase [ppmv]), right axis represents nitrosamine concentration in the gas phase [ppmv].

time.

4. Conclusions

A novel design for online gas and liquid measurements of absorber emission trace gas analysis has been demonstrated. The design has low complexity and improved robustness suited for continuous industrial online monitoring applications. The presented methodology is generic and therefore allows for a wide range of applications covering analytes that demands complex work-up and derivatization of samples collected automatically by the autosampler functions of the mass spectrometer. The concept demonstrated can reduce the manual labor-intensive isokinetic sampling procedures with an automated operation. The method is useful for trace pollutants such as nitrosamines which cannot be measured by conventional gas analysis like FTIR due to lower detection limit. The system avoids heated transfer lines which could decompose some components.

Online sampling and analysis of a nitrosamine present in ppbv-levels in the emissions to air from an amine absorber was successfully demonstrated with good agreement with manual impinger gas washing bottle measurements. The method demonstrates monitoring of trace gas emission from a CO₂ capture pilot plant, quantifying nitrosamines at levels not detectable by commercial industrial online analyzers.

The results show amine and trace gas analytes from the emissions to air from a CO₂ capture absorber can be captured with high efficiency in the condensate from sampled wet gasses. Results from testing of a condensate collector prototype indicate high capture efficiency for analytes of interest, including analytes present in aerosols.

Without the presence of an online MS-analyzer, the unit allows for recovery of frequent condensate samples which can be analyzed in the same manner as plant liquid samples for analysis. This give relevant information about plant emissions to air that are not available from other online industrial analyzers.

More work needs to be invested in order to commercialize the unit, particularly establish the online condensate sampling and measurement concept as a viable alternative to manual sampling in industries. The current ACEMS system has been in operation for a limited time,

evaluation of long-term performance and replicability of the set-up is ongoing. The setup is regarded a valuable tool for emission monitoring activities in CO₂ capture pilot plants, enabling continuous measurements of emissions linked to analysis of liquid inventory of the plant.

The measurement concept significantly reduces the costs related to current manual gas measurements of critical trace gas components in plant operation and compliance with regulations. Application of the concept enable near continuous measurements of nitrosamines and other trace gas analytes in the emissions to air.

Declaration of Competing Interest

None.

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