Real-Time Monitoring of Emissions from Monoethanolamine-Based Industrial Scale Carbon Capture Facilities

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Supporting Information

ABSTRACT: We demonstrate the capabilities and properties of using Proton Transfer Reaction time-of-flight mass spectrometry (PTR-ToF-MS) to real-time monitor gaseous emissions from industrial scale amine-based carbon capture processes. The benchmark monoethanolamine (MEA) was used as an example of amines needing to be monitored from carbon capture facilities, and to describe how the measurements may be influenced by potentially interfering species in CO₂ absorber stack discharges. On the basis of known or expected emission compositions, we investigated the PTR-ToF-MS MEA response as a function of sample flow humidity, ammonia, and CO₂ abundances, and show that all can exhibit interferences, thus making accurate amine measurements difficult. This warrants a proper sample pretreatment, and we show an



example using a dilution with bottled zero air of 1:20 to 1:10 to monitor stack gas concentrations at the CO_2 Technology Center Mongstad (TCM), Norway. Observed emissions included many expected chemical species, dominantly ammonia and acetaldehyde, but also two new species previously not reported but emitted in significant quantities. With respect to concerns regarding amine emissions, we show that accurate amine quantifications in the presence of water vapor, ammonia, and CO_2 become feasible after proper sample dilution, thus making PTR-ToF-MS a viable technique to monitor future carbon capture facility emissions, without conventional laborious sample pretreatment.

1. INTRODUCTION

Carbon capture (CC) technology is widely regarded as a means to prevent carbon dioxide (CO₂) from anthropogenic fossil fuel combustion and other industrial activities from entering the atmosphere, provided sufficient financial incentive.^{1–7} To mitigate CO₂-driven global warming without a drastic reduction in fossil fuel combustion, removing most of the CO₂ emissions from stationary sources such as coal-fired power plants requires the application of CC technology. According to the IPCC ³ in 2005, a CC-based removal of 60–600 Gt-C of cumulative anthropogenic CO₂ emissions is possible worldwide by 2100 under least-cost assumptions and given scenarios for stabilization of atmospheric greenhouse gas concentrations between 450 and 750 ppm.

Currently, the use of postcombustion CC employing liquid absorbents, such as aqueous amine solutions, is most commonly used over alternative methods of absorbing CO_2 .^{5,6,8,9} In amine-based CC, the CO_2 -rich flue gas after combustion is introduced into an absorber tower and exposed to a low temperature counter-flow of lean aqueous amine solution. CO_2 absorbs forming a carbamate, which subsequently reacts with another base molecule to reversibly form a carbamate salt. The now CO_2 -enriched solution is pumped through a heat exchanger into a stripper tower, where it is heattreated, which decomposes the carbamate back to CO_2 and amine; the latter is then recirculated via the heat exchanger to the absorber tower.¹ During its use in the CO_2 capture process, the amine solution both slowly loses amine via evaporation and fugitive emissions, and ages via thermal and chemical degradation. The latter has been studied for over a decade^{10–29} and was recently reviewed.³⁰ Make-up amine solution thus has to be added to maintain the carbon capture capacity. Depending on the actual operation parameters and $SO_x & NO_x$ prescrubber settings, the estimated MEA makeup rate varies from 129 to 221 mmol/kmol CO_2 captured at coalfired power plants.³¹

Deploying amine-based CC technology may require large amine production facilities³² and will inevitably lead to significant new emissions to the atmosphere of both amines and their degradation products formed in the CC process. Interest and concern about such atmospheric emissions has been expressed due to the effectiveness of amines in the atmospheric particle nucleation process,^{33–45} a change in industrial emissions composition and amount,^{46,47} and the possibility of forming toxic nitrosamines and nitramines.^{29,48,49} To minimize such emissions, it is recommended to apply one or more water-wash stages downstream of the CO₂-absorption

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Figure 1. Sampling setup schematic for amine and other VOC monitoring at the TCM carbon capture test facility. The red flow path was largely made of Siltek tubing and heated to 100-130 °C to avoid condensation and minimize wall adsorption. The black flow paths were not heated but also consisted of Siltek tubing, and the gray flow paths were made of SS or Teflon PFA (bp1). Abbreviations: bp, bypass; FC, Flow Controller.

stage, such as that accomplished at the Technology Center Mongstad (TCM) facility.^{50,51} Both the amines used in CC and some of their degradation products are removed efficiently via such washers. Nevertheless, since the presence of SO_{xy} NO_{xy} and fly ash in actual flue gas might introduce more complexities to the amine degradation pathways, it will be necessary to qualitatively and quantitatively monitor atmospheric emissions at the absorber tower under industrial operating conditions. For example, Norwegian authorities have set an annual cumulative amine discharge limit of 2800 kg for the TCM facility.⁵²

Due to the nature of the amines used in CC, and the particular sample gas composition likely to be encountered at CC facilities, new analytical methods for gas phase monitoring of amines and their degradation products are needed.⁵³ During the planning process for the currently largest CC testing facility at TCM in Norway, two analytical methodologies for emissions monitoring were selected: FT-IR spectroscopy and Proton-Transfer-Reaction Mass Spectrometry (PTR-MS). Both, in principle, allow measurement without sample preparation as required by conventional analytical methods, thus enabling realtime trace gas monitoring.^{54,55} Here, we describe our setup for emissions monitoring at TCM using a high resolving PTR-ToF-MS instrument, selected results from a testing period during summer 2012, and a more extensive laboratory evaluation of the instrument's response to the currently most used amine in CC, monoethanolamine (MEA). We show that PTR-ToF-MS can successfully be used to monitor stack emissions, but that either a series of corrections to the signal may be necessary depending on sample conditions under

industrial conditions, or, better, a dilution with dry zero air will provide acceptable sample conditions for long-term monitoring.

2. EXPERIMENTAL SECTION

2.1. Laboratory Setup. A commercial PTR-ToF-MS (Ionicon Analytik GmbH, Innsbruck, Austria) was employed for this study.⁵⁴ The response of the instrument's MEA signal to various gas compositions was tested in the laboratory using a combination of major gases present in typical exhaust gas from the absorber tower, particularly water vapor, ammonia, and carbon dioxide. A stream of low concentration MEA in air was produced from flowing zero air (synthetic air of 99.999% purity, AGA AS, Norway) over a G-Cal device with a nominal 82 ng min⁻¹ permeation rate (VICI Metronics, Switzerland). Water vapor was varied by bubbling mass flow controlled zero air through a wash bottle filled with distilled water at room temperature. Ammonia (103 ppm in high purity nitrogen, AGA AS, Norway) and carbon dioxide (99.995% purity, AGA AS, Norway) were introduced via mass flow controllers, and diluted into a stream of zero air or humidified zero air. All sample lines were made of either PFA Teflon or Siltek tubing. All tubing downstream of the bubbler and MEA permeation device was heated to 100 °C using a rope heater (Omega Engineering Inc., UK). The PTR-ToF-MS inlet line and drift tube were operated at 100 °C to minimize possible condensation of "sticky" substances in the sample stream (Figure S1 in the Supporting Information, SI). Drift tube pressure was fixed at 2.20 mbar, and drift tube voltage was set at 500 V, i.e., an operation at 120 Td (1 Td = 10^{-17} V cm²).

2.2. Field Setup. The PTR-ToF-MS was deployed into an instrument trailer at TCM in summer 2012. TCM officially opened in May 2012 and began operations a few months thereafter. To monitor absorber stack emissions, a heated PFA sample line (ca. 1/4 in. i.d., ca. 100 m long) had been installed to the top of the stack at 62 m, and filtered (stainless steel, SS, sinter filter) stack gas was pumped continuously to an SS manifold housed in a heated cabinet at the bottom of the stack. The manifold allows switching between different gas streams while maintaining continuous flows of 2 L min⁻¹ on all sample lines. TCM tested the sample line delay for MEA at different line temperatures using both onsite FT-IR and iso-kinetic sampling measurements, and found that maintaining 90 °C or higher temperatures allowed for quantitative transfer within several minutes.⁵⁶ A sample transfer pump installed inside the manifold cabinet pushes the sample toward the FT-IR. We installed a TEE junction into this line, which admits a small subsample flow through a valve toward the PTR-ToF-MS. Figure 1 shows the remaining setup: The sample flow is diluted with bottled zero air and a subsample flow is directly acquired by the PTR-ToF-MS. High precision mass flow controllers (Bronkhorst HT-MFC, Flow-Teknikk AS, Norway) were used to meter zero air, calibration mixture, and PTR-ToF-MS inflows. Total subsample flow downstream of the sample transfer pump was usually below 0.5 L min⁻¹, and dilution rates of 1:10 to 1:20 of sample-to-zero air were set such that a flow of at least 0.1 L min⁻¹ was maintained in the section between the sample overflow and the zero air dilution junction. Siltek (Restek Inc., U.S.) tubing, heated to 100-110 °C, was used for all transfer lines. Zero and calibration gas measurements were initiated by setting the zero air flow to several hundred mL min⁻¹ in excess of instrument inflow. A BTEX mix (Aromats Mix, cat. no. 34423, Restek Inc., U.S.) was used to calibrate the instrument using the toluene peak at m/z 93.03, and all peaks associated with the nine aromats in the mix were used to obtain mass spectrometer transmission curves. In addition, an internal mass standard (tetra-fluorobenzene, TFB, in form of a G-Cal permeation device, VICI Metronics, Switzerland) was installed into the zero air line.

The PTR-ToF-MS operational parameters were the same as in the laboratory. We worked dominantly in H_3O^+ ion mode and sensitivities of approximately 20 normalized counts per second per ppb (ncps ppb⁻¹) for toluene. Raw spectral data analysis, including dead time correction, mass calibration, peak fitting, area extraction, and signal averaging, were performed using the PTR-ToF data analyzer.⁵⁷ Averaged raw count rates, uncorrected for transmission efficiency, are reported here unless otherwise noted, because we are unsure of the accuracy of the MEA permeation device. Headers named VOC^{*n*=1}, and VOC^{*n*=1,2} stand for VOC raw count rates upon normalization with H_3O^+ only, and the sum of H_3O^+ and $H_3O^+(H_2O)$, respectively.

3. RESULTS

Laboratory and field experiments were conducted at analogous instrument settings, but room temperature was slightly higher and more stable in the laboratory than in the field. Background readings were obtained in both cases by admitting the dry zero air gas, which was the diluting gas in all cases and thus represented the appropriate background measurement. A zero measurement was commonly done for approximately 10 min corresponding to 3–4 residence times of MEA as determined from its exponential decay rate during the zero measurement.

MEA measurements were carried out only after a stable MEA signal was observed after installing the permeation source or after parameter changes were made. In dry conditions, observed mass peaks for MEA include the molecular mass +1 at m/z 62.06 with approximately 47% abundance, a molecular ion after water ejection at m/z 44.05 with 52% abundance, and a very small amount (<1%) of m/z 45.03 after ammonia ejection.

3.1. Laboratory Tests. *3.1.1. Water Vapor.* Water vapor mixing ratios were varied in stepwise fashion using mixtures of the same zero air with one branch routed through a wash bottle filled with distilled water at room temperature, while keeping the total flow and therefore MEA concentration constant. Relative humidity, as measured by a T-RH probe (model S-THB connected to U30 data logger, Onset Computer Corp., Cape Cod, U.S.) inside the overflow, was varied this way between near zero and ca. 88% relative humidity. The PTR-ToF-MS response to water vapor was followed on m/z 37, via the isotopic first water vapor cluster ion $H_3O^+(H_2^{-18}O)$, m/z 39. It produced a second order polynomial fit, with an $R^2 = 0.99$ (Figure 2), similar to previous work.⁵⁸ Under dry conditions,



Figure 2. Dependence of averaged m/z 37 ncps on relative humidity of sampling air. The normalized m/z 37 ncps values were derived from its isotopic peak at m/z 39. The dotted line is a second order polynomial fit, with an $R^2 > 0.99$.

the extrapolated value of m/z 37 was estimated to be approximately 6200 ncps, arising from residual water vapor diffusing out of the ion source, and consistent with previously reported values.^{59,60} However, the intensity of m/z 37 at highly humid conditions is subject to the working conditions of the individual PTR-MS instrument, and therefore might display a larger range. Higher water clusters such as H₃O⁺(H₂O)₂ (m/z55) and H₃O⁺(H₂O)₃ (m/z 73) were not taken into consideration due to their low abundances. Here, the good correlation between measured water cluster counts and humidity offers a reliable approach to estimate the relative humidity in the sample flow and thus apply corresponding corrections as necessary assuming the instrument's response is reasonably stable over time.

To explore this relationship further, we varied the drift tube voltage over its full range between 400 and 600 V (100–150 Td), resulting in large shifts of the mass 37/19 ratio at a given humidity level, summarized in Table 1. As expected, increasing the drift field strength led to more declustering and therefore the mass 37/19 ratio decreased substantially.⁶¹ Similarly, increasing drift field strength affected the MEA fragment at m/z 44, becoming more abundant relative to m/z 62 (Table 1). For the remaining experiments the drift tube voltage was kept at 500 V.

Table 1. Effect of Varying Drift Tube Voltage on Measured Water Cluster Abundance and MEA Fragmentation in Humid Ambient Air Compared to Dry Air

drift tube voltage (V)	m37/19 in dry air (%)	m37/19 in humid air (0.76% H ₂ O) (%)	m44/62 in humid air (0.76% H ₂ O)
400	3.2	9.3	0.41
450	1.3	3.8	0.85
500	0.7	2.0	0.99
550	0.5	1.4	2.14
600	0.5	1.2	4.96

In PTR-MS using hydronium ions, VOCs generally react with H_3O^+ but many low polarity VOCs do not react with the first or higher water clusters, $H_3O^+(H_2O)_n$, as their proton affinity does not exceed the one of the clusters, and the probability of ionization via ligand switching is low.⁶¹ In the case of MEA, which has a high polarity and a proton affinity of 930 kJ mol⁻¹, reactions with both H_3O^+ and the first water cluster are expected as their proton affinities are 690 and 808 kJ mol⁻¹, respectively.⁶² Somewhat unexpectedly, the PTR-ToF-MS parent-ion normalized response to MEA decreased with water vapor abundance regardless of whether only H_3O^+ or the sum of H_3O^+ and $H_3O^+(H_2O)$ were used in the normalization, shown in Figure 3 (raw data) and Table 2. While the sum of



Figure 3. Ion signal intensities of m/z 21 (H₃¹⁸O⁺), m/z 39 (H₃O⁺(H₂¹⁸O)), m/z 44 ((MEA-H₂O)·H⁺), m/z 62 (MEA·H⁺) and sum of raw data counts of m/z 44 and m/z 62 under different relative humidities in the MEA sampling flow. A constant E/N = 120 Td was kept during the measurement. Each scan is an average of two successive measurements of 10 s duration.

raw data counts was nearly constant (Figure 3), transmissioncorrected counts dropped slightly with increasing humidity. Thus, under the given instrument parameters, MEA undergoes protonation by both parent ions but seemingly less effectively by the first water cluster. Note that no hydrated MEA molecules were observed during this set of experiments.

In order to address the water vapor pressure dependence of a PTR-MS VOC signal, normalization is advised to follow the equation

$$[RH^{+}]_{norm} = [RH^{+}]/([H_{3}O^{+}] + Xr \times [H_{3}O^{+}(H_{2}O)])$$
(1)

in which the value of the compound-specific factor Xr has to be empirically determined.^{55,63,64} In the case of MEA using transmission-corrected data, we found that the least variability in the sum of mass 44 and mass 62 over the complete humidity range was achieved for Xr values between 0.5 and -1 with a best estimate of -0.3. The experiment was repeated using the aromats standard and Xr values for benzene and toluene were found to be -3.7 and -2.7, respectively, different from the values given by deGouw and Warnecke.⁵⁵ Larger values of Xr in our experiments can be understood as necessary to compensate for the heavily underestimated water cluster ions due to the declustering effect (see discussions below). It is worth noting that the benzene signal at m/z 79 is partially composed of a fragment from ethylbenzene, whose dissociation probability could also vary depending on humidity levels.

3.1.2. Ammonia. Ammonia mixing ratios were varied over a range of <1 ppm up to 13 ppm by diluting the ammonia standard into zero air. As exemplified in Table 3, ammonia

Table 3. Background-Subtracted Ammonia Counts and Corresponding MEA Results As a Function of Ammonia Mixing Ratios^a

NH ₃ (ppmV)	m37/19 (%)	NH ₃ ncps	$\Delta m/z$ 21 + 37 (%)	$\begin{array}{c} \Delta \text{ MEA}^{n=1,2} \\ (\%) \end{array}$	m 44/62
0	0.7	0	-0.6	0.0	1.11
0.26	0.7	1147 ± 55	-2.9	-1.8	1.11
0.52	0.7	2899 ± 110	-4.6	0.0	1.12
0.78	0.7	4826 ± 90	-5.0	1.3	1.11
1.03	0.7	6602 ± 64	-5.3	1.5	1.11
1.29	0.7	8446 ± 42	-5.5	1.6	1.11
2.58	0.7	17428 ± 74	-7.7	7.0 ± 0.1	1.09
6.43	0.7	46942 ± 297	-11.1	14.9 ± 0.5	1.07
12.88	0.7	89680 ± 949	-15.7	21.5 ± 1.1	1.03
0	0.7	86	-3.5	-3.9 + 0.1	1.11

^{*a*}The " Δ m/z 21 + 37" column shows the percent of reagent ion consumption. Note that the mass 37/19 ratio did not change with varying ammonia concentrations.

Table 2. $H_3O^+(H_2O)/H_3O^+$ Ion Signal Ratio (m37/19), Variation of MEA Signal on Two Normalization Approaches ($\Delta MEA^{n=1,2}$, $\Delta MEA^{n=1}$), and MEA Fragmentation Ratio (m44/62) As a Function of Relative Humidity^{*a*}

rH @ 28.3 °C (%)	m37/19(%)	$\Delta \mathrm{MEA}^{n=1,2}$ (%)	Xr	$\Delta \mathrm{MEA}^{n=1}$ (%)	m44/62	predicted m37/19 (%)
0	0.6	0		0	1.12 ± 0.01	
24.70	2.4	-12.7 ± 0.2	-1.3	-11.1 ± 0.2	0.88 ± 0.01	16
37.80	3.8	-18.5 ± 0.3	-1.3	-15.9 ± 0.3	0.79 ± 0.01	25
51.40	5.5	-18.6 ± 0.4	0.3	-14.7 ± 0.4	0.71 ± 0.01	34.6
65.60	7.5	-21.9 ± 0.4	0.3	-16.6 ± 0.3	0.65 ± 0.01	42.9
88	11.2	-22.5 ± 1	0.3	-14.4 ± 0.8	0.57 ± 0.06	57.5
0	0.6	-7.2 ± 0.1	-1.3	-7.2 ± 0.1	1.13 ± 0.02	

"Here, a tailored Xr was calculated for the lower (0-40%) and upper (50-90%) humidity ranges, respectively. The "predicted m37/19 ratio" column is discussed in the SI.

initially had insignificant influence on the MEA ion abundance. However, at increasing ammonia mixing ratios its primary ion consumption becomes important (7.7% at 2.5 ppm), while at the same time the ammonium ion becomes a significant parent ion itself with faster proton transfer reactions from the ammonium to the amine. Thus, the observed amine ion abundance is actually increasing with increasing ammonia mixing ratios; we extended the aforementioned normalization formula to include ammonia such that,

$$[RH^{+}]_{norm} = [RH^{+}]/([H_{3}O^{+}] + [H_{3}O^{+}(H_{2}O)]) + Xr^{*} \times [NH_{4}^{+}])$$
(2)

It was found that an Xr^* value of 3 can be employed to correct the MEA signal dependence on ammonia. Furthermore, as the proton transfer reaction with ammonium is also softer, increasing ammonium mixing ratios led to a decreasing mass 44/62 ratio (Table 3) in addition to increasing signal abundance.

3.1.3. Carbon Dioxide. For comparison, CO_2 was introduced together with zero air at a low (<10%) relative humidity to achieve mixing ratios between 0.9 and 14.8%, enveloping typical flue gas CO_2 abundances. While parent ion H_3O^+ was hardly affected by large CO_2 abundances, CO_2 acts as a more efficient buffer gas than air.⁶⁵ We thus observed, summarized in Table 4, that with increasing CO_2 abundance

Table 4. Influence of Sample CO_2 Abundance on the $H_3O^+(H_2O)/H_3O^+$ Ion Signal Ratio and Relevant MEA measurements

[CO ₂] (%)	m37/19 (%)	Δ MEA ^{n=1,2} (%)	Δ MEA ⁿ⁼¹ (%)	m44/62
0	0.8	0	0	1.09
0.90	0.8	-0.1	0.1	1.09
2.22	0.9	1.4	1.8	1.01
4.44	1.1	4.2 ± 0.1	4.7 ± 0.1	0.93
7.40	1.4	10.1 ± 0.3	11.0 ± 0.3	0.83
11.80	2.1	15.4 ± 0.3	17.1 ± 0.3	0.72
14.80	2.6	18.6 ± 0.5	20.9 ± 0.6	0.65
0	0.7	6.8 ± 0.2	7.0 ± 0.2	1.09

water cluster abundance was increasing, the mass 44/62 ratio was decreasing, while overall MEA ion abundance was increasing. The increase of water cluster and MEA ncps signals can be attributed to the reduced mobility of the reaction products in the drift tube, while the better preservation of intact MEA molecules originated from the lower drift velocity of H_3O^+ ions and softer reactions with the more abundant water clusters relative to the hydronium ions. The MEA signal increase occurs despite an increase in water cluster abundance, meaning the boosting effect of CO_2 in the sample gas is much stronger than the water vapor effect.

3.2. Field Measurements. Due to the expected interferences from high ammonia, high humidity, CO_2 , and other degradation product abundances in the absorber stack samples, we provided the PTR-ToF-MS with a highly diluted sample stream, i.e., mostly bottled zero air. Observed mass abundances (in ncps) were converted to mixing ratios after (i) subtracting the background signals obtained under zero air flow only, (ii) applying the ratio of reaction rate constants between the compound to be quantified and toluene together with toluene's calibration factor during a recent dry air calibration measurement, (iii) applying the relative transmission efficiency between

toluene and the compound to be quantified using a recent transmission curve obtained from the same calibration, and (iv) applying the dilution factor. The accuracy of concentration determination following such procedure is often assumed to be approximately 30%, typically dominated by uncertainties in the employed reaction rate constants and transmission factor. Note that an external calibration curve for ammonia was established in order to eliminate the larger uncertainties at the low end of the mass transmission curve (Figure S4 in the SI). The simultaneous FT-IR measurements corroborated this approach.⁵⁶

The sample data shown here were obtained during a test operation of the absorber stack using a 30 wt-% aqueous MEA solution in August 2012 for treatment of flue gas from the nearby natural gas combined heat and power (CHP) plant. While likely not quantitatively representative of operative emissions under future energy and emissions optimized conditions, they are most likely qualitatively representative. During the period shown here, the plant achieved a 70% CO₂ absorption efficiency.⁵¹

To exemplify the capability of PTR-ToF-MS, Figure 4 shows the abundances of various masses, most of them found to be



Figure 4. Selected PTR-ToF-MS ion signal timelines, corrected with a dilution factor of 10, between approximately 12:30 and 17:00 h, 12 August 2012. Several permit-regulated compounds, including MEA, ammonia and acetaldehyde, are plotted. In addition, we show the mass 37/19 ratio measured in the 1:10 diluted flow, and a nonquantified CO₂ trace in gray shading to guide the eye with respect to the sample stream cycles indicated on the bottom.

elevated in the absorber stack exhaust over the incoming flue gas composition. The near stepwise behavior of all measured signals during sample stream changes gives confidence in the determination of stack emissions for the current sampling methodology.

MEA abundance was very low due to the water wash stages, and represented a minor component of emissions. Despite a very high humidity in the absorber sample, the diluted sample possesses only a relative humidity of approximately 33%, derived from the measured $H_3O^+(H_2O)/H_3O^+$ ratio. Dominant emissions, as expected, stemmed from the major MEA degradation products ammonia and acetaldehyde.^{12,20,30} Other dominant emissions included formaldehyde and formamide, also previously detected degradation products,²⁴ and two newly discovered compounds at m/z 81.044 and at m/z 62.024. The latter species were tentatively identified as pyrazine and nitromethane or methylnitrite (see SI), respectively, via their exact masses and subsequent laboratory testing with the authentic chemical (pyrazine). We also identified the intermediate species 2-amino-acetaldehyde at m/z 60.044, which, in addition to previously proposed mechanisms^{30,66} may not only be further oxidized, but also condense rapidly with excess MEA in the solution.⁶⁷ The resulting ethanol-imine product quickly oxidizes further only to subsequently condense internally to form pyrazine, which is pushed out of solution based on its lower pK_a and an approximately 100 times higher vapor pressure as compared to MEA. Lastly, among the minor compounds emitted were acetone and formic and acetic acids. No nitrosamines or nitramines were detected by the PTR-ToF-MS in the facility emissions.

On the basis of the results in Figure 4, an accurate determination of the MEA mixing ratio can be severely affected by the composition of the absorber emissions, i.e., high ppm ammonia content and oversaturated humidity, whereas other emissions and CO₂ likely pose negligible influences on the MEA signal. A correction may be derived as follows: The ammonia signal was insensitive to humidity level, guaranteeing an accurate derivation of ammonia concentration based on its external calibration curve (Figure S4 of the SI). While ammonia did not change the mass 37/19 ratio, abundant CO₂ does. Consequently, in a scenario of high carbon dioxide abundance, a careful deconvolution of individual impacts on the mass 37/ 19 ratio from both humidity and CO₂ should be performed in order to acquire an accurate estimation of the humidity level in the sampling flow. Relying on the results listed in section 3.1, 800 ppb ammonia increased the MEA signal by 1.3%, whereas a 33% relative humidity in the sample decreased the MEA peak by 16%, assuming a linear humidity dependence between the neighboring measured data points. Therefore, a correction factor of 1.17 should be applied to the calculated MEA values in the above diluted absorber emission data (Figure 4).

4. DISCUSSION

4.1. Water Vapor. Water vapor is a major component of flue gas. If PTR-MS is used in CC facility monitoring, then the potential dependence of observed ion abundances on water vapor abundance in the drift tube needs to be assessed. Several volatiles such as toluene, have been found to display a water cluster abundance dependence in PTR-MS.55 This occurs when said clusters do not transfer a proton upon collision with the same rate constant as the H₃O⁺ ion does. As clusters become more abundant at higher humidity, the protonated target compound changes disproportionately to the abundance of H_3O^+ or the sum of H_3O^+ and $H_3O^+(H_2O)$. In addition, a water vapor dependence may also be observed even when the reaction with the water cluster is as fast as with the hydronium ion, due to a declustering effect in the transition zone between the drift tube and the mass spectrometer,⁶³ which leads to an overestimation of hydronium ions in the drift tube relative to its clusters when observed at the detector.

Our MEA response data to water vapor can only be explained by assuming that a significant amount of $H_3O^+(H_2O)$ declustering occurs in the transition zone between the drift tube exit orifice and the ToF chamber nosecone, alongside a slower reaction of MEA with the water cluster as compared to the hydronium ion. The fact that the MEA response dropped less in the case of normalization to hydronium only compared to using both H_3O^+ and $H_3O^+(H_2O)$ to normalize, shows that MEA does react with the water cluster as expected, but at lower efficiency. On the basis of well-established quantum chemistry

calculation routes by Su and Chesnavich,⁶⁸ the reaction rate coefficients for MEA molecules reacting with H₃O⁺ and $\rm H_{3}O^{+}(\rm H_{2}O)$ were estimated to be 2.3 and 1.8 \times $10^{-9}~\rm cm^{3}$ molecule⁻¹ s⁻¹, respectively (Table S1 in the SI). Apparently, this small efficiency difference between the two reactions alone is not enough to quantitatively understand the MEA intensity drop under high humidity conditions. The raw MEA signals (Figure 3) gave a maximum loss of 8% under humid conditions, probably attributed to a less effective reaction of MEA with water clusters, and uncertainties of applying mass transmission factors. Thus, the stronger drop of the normalized MEA signals must be due to the fact that H_3O^+ as well as the first water cluster were rising with increasing humidity (Figure 3). As can be concluded from Table 2, the change from dry air to 24.7% relative humidity conditions generated the biggest drop in MEA ncps values, while there was a variation of only 9% in a broader range of higher humidity levels. This behavior is consistent with a significant difference between the measured and actual composition of ionizing species traveling in the drift tube due to the influence of the declustering effect.⁶¹ Although minimized in dry conditions and/or by applying high E/Nvalues, it still needs to be characterized and addressed when encountering highly humid sample flows.

The conventional normalization approach using the sum of $H_3O^+(H_2O)$ and H_3O^+ count rates should suffice in applications in which there is a narrow change of relative humidities over time. As previously reported, in varying humidity conditions, the empirically determined parameter Xr needs to be incorporated in order to correct for the humidity dependence of certain VOCs. The employment of Xr in the normalization equation also accounts for the aforementioned declustering effect and the relative transmission factor between m/z 19 and m/z 37. Alternatively, frequent external calibrations into humid air such as via routing the sample through a hot oxidation catalyst to create a zero reference instead of the bottled, dry zero air are necessary.

4.2. Ammonia. Ammonia is likely to be emitted in copious amounts from CC facilities as it is a major decomposition product of MEA and other primary amines used in the CC process.³⁰ Monitoring amine emissions therefore may require that the analytical technique used exhibits little to no interference from ammonia. Our results show that ammonia present in typical ppm amounts is likely to boost the PTR-MS amine signal. In fact, if simultaneous ammonia measurements by PTR-MS are not needed or desired, then the instrument could be run using ammonium as the parent ion for proton transfer, because the ammonium ion is more selective toward amines and other nitrogen-bearing compounds, and will provide for a higher sensitivity.⁶⁹

If simultaneous ammonia measurements are desired, then the expectedly high humidity, high abundance of ammonia, and other MEA degradation compounds, such as acetaldehyde, will require proper sample dilution, as was done in this study, to (i) avoid parent ion consumption, (ii) minimize the humidity effect, (iii) apply an ammonia calibration curve with confidence, and (iv) avoid other interferences.

4.3. Carbon Dioxide. As summarized in Table 4, the total MEA ion signal was increasing while the mass 44/62 ratio was decreasing with increasing CO₂ abundance. Moreover, a strong dependence of m/z 62 ncps values on CO₂ mixing ratio was observed (Figure S3 in the SI). This observation can be explained by the larger degrees of freedom of carbon dioxide relative to air, depositing less energy available for dissociation

upon collision, and the reduced mobility of the reaction products in the drift tube under high CO_2 content. Carbon dioxide is naturally in much lower abundance in exiting stack gas as compared to the incoming flue gas. However, the CO_2 · H⁺ peak at m/z 44.997 can interfere with acetaldehyde detection at m/z 45.033 rendering its quantification questionable under high CO_2 abundance conditions, such as during a situation of significant breakthrough due to nonoptimal operating conditions or in the flue gas itself. Under field conditions, a 1:10 dilution of the sample gas was generally sufficient to obtain a small enough CO_2 ·H⁺ peak to quantify acetaldehyde. However, at >5% of CO_2 in the sample gas, direct acetaldehyde quantification becomes questionable and quantification of MEA and other compounds will need to be corrected.

4.4. Field Data. The above results show that a proper sample dilution with dry zero air provides a sufficient methodology to eliminate or at least minimize corrections to the data otherwise necessary. While the sample is diluted, which leads to higher detection limits, all major MEA-related stack emissions can be and were monitored successfully. As previously described, uncertainties of quantitative measurements can be further reduced by studying and establishing corresponding correction approaches to the compound of interest in diluted yet interfering matrixes. Our results also demonstrate the necessity of making compound-specific humidity-dependent calibration series, especially for fragile substances, whose fragmentation profile at various humidity levels is desired.

Interestingly, no previous studies on MEA degradation have determined pyrazine or nitromethane/methylnitrite as a product. We attribute this finding to the fact that older studies have focused on the liquid phase composition, and both these species likely largely or completely escape the liquid before its analysis. A recent evaluation of gas phase MEA oxidation using PTR-MS⁴⁵ also reported the observation of $C_4H_5N_2^+$, protonated pyrazine, as a byproduct. While its formation and emission is straightforwardly explained, the formation of nitromethane/methylnitrite is not. We observed that nitromethane/methylnitrite was not initially present in the stack gas, but evolved after several hours of carbon capture operation. It is therefore more likely that it is a secondary degradation product. Its origin is possibly a result of a build-up of nitrite and nitrate in the solution from absorption of NO_x from the flue gas, and thus the compound would not have been detected in earlier studies because of a lack of NO_x in the tested air- CO_2 mixtures.

Equally interesting is the finding that we did not detect any of the larger molecular weight degradation products identified in partially degraded aqueous MEA solutions.²³ This is likely an effect of their low vapor pressure alongside high water solubility, which makes these compounds irrelevant with respect to gas phase emissions from future CC facilities. It may be more important for environmental impacts evaluations of future CC to consider the emissions of ammonia, acetaldehyde, and other gaseous emissions, such as the amines, assuming carbon capture is deployed globally at a larger scale.^{32,47,48}

ASSOCIATED CONTENT

Supporting Information

MEA signal as a function of drift tube temperature, quantum chemistry calculations, and theoretical MEA rate coefficients, MEA vs carbon dioxide gradient, and external ammonia calibration curve. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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