

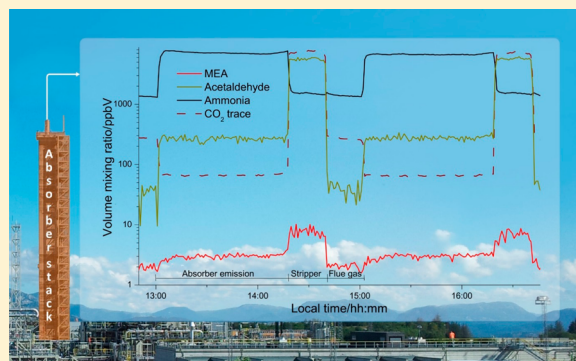
Real-Time Monitoring of Emissions from Monoethanolamine-Based Industrial Scale Carbon Capture Facilities

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S 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 CO₂ 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 CO₂ 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 IPCC³ 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 CO₂.^{5,6,8,9} In amine-based CC, the CO₂-rich flue gas after combustion is introduced into an absorber tower and exposed to a low temperature counter-flow of lean aqueous amine solution. CO₂ absorbs forming a carbamate, which subsequently reacts with another base molecule to reversibly form a carbamate salt. The now CO₂-enriched solution is pumped through a heat exchanger into a stripper tower, where it is heat-treated, which decomposes the carbamate back to CO₂ and amine; the latter is then recirculated via the heat exchanger to

the absorber tower.¹ During its use in the CO₂ 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 CO₂ captured at coal-fired 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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