A sampling line artifact in stack emission measurement of alkanolamine-enabled carbon capture facility: surface reaction of amines with formaldehyde

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Liang Zhu[1], Tomas Mikoviny[1], Armin Wisthaler[1], and ***Claus Jørgen Nielsen***[1*]
[1] Department of Chemistry, University of Oslo, Norway
c.j.nielsen@kjemi.uio.no

UiO : Department of Chemistry
University of Oslo

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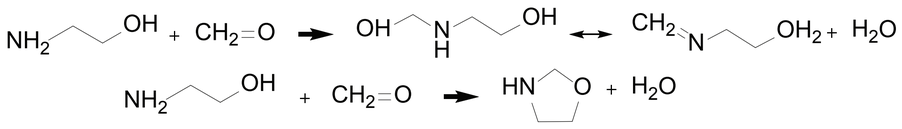
- Accurate measurement of amine emissions is essential for assessing environmental risks associated with industrial amine-based post combustion CO_2 capture facilities.
- Primary amines and formaldehyde condense in the sampling lines of measurement instruments, leading to potential underestimation of emission levels.

Background

Amine and formaldehyde emissions from the PCCC facility at Mongstad are continuously monitored by FT-IR and PTR-ToF-MS instruments. Both analyzers sample from the absorber stack through a shared 110 m long line. Different line materials and line temperatures have been tested at TCM for minimizing the surface adsorption of 'sticky' amines. Chemical losses have hitherto not been considered.

Concept

Formaldehyde, a common amine degradation product, reacts rapidly with primary amines. For instance, in reaction with MEA it forms either an imine or oxazolidine (Schiff-base condensation mechanism).



In this work, we report the results from laboratory studies on surface reactions between formaldehyde and a series of CCS-usable amines.

Methods

A flow of air containing an amine at variable mixing ratio (123-615 ppbV) was mixed with a flow containing formaldehyde at a constant mixing ratio (1230 ppbV). The mixture was flushed through a 2 m long, heated (100 °C), Silcosteel®-coated SS tube (1/8" OD) at a flow rate of 850 sccm. The residence time in the line is estimated to be ~5 s. The outflow was fed to a PTR-TOF 8000 instrument (Ionicon Analytik GmbH, Austria).

Results

Primary amines and formaldehyde react quickly on inlet surfaces. Equal amounts of amine and formaldehyde were lost in the sampling line. The fraction of amine lost is dependent upon the amount of amine. Secondary and tertiary amines were found not to react with formaldehyde in this test.

Amine	Condensation product	Amine lost
Methylamine	$C_2H_6N^+$, *m/z* 44.050	31.9%
Dimethylamine	-	0%
Ethylamine	$C_3H_8N^+$, *m/z* 58.067	22.5%
2-Amino-Ethanol	$C_3H_8NO^+$, *m/z* 74.063	65.4%
3-Amino-1-propanol	$C_4H_{10}NO^+$, *m/z* 88.076	93.1%
4-Amino-1-butanol	$C_5H_{12}NO^+$, *m/z* 102.092	66.5%
2-Amino-2-methyl-1-propanol	$C_5H_{12}NO^+$, *m/z* 102.092	67.2%
3-(Methylamino)-propylamine	$C_5H_{13}N_2^+$, *m/z* 101.108	99.8%
N-(2-Aminoethyl)-piperazine	$C_7H_{16}N_3^+$, *m/z* 142.134	74.8%
Ethylenediamine	$C_3H_9N_2^+$, *m/z* 73.076 (90%)	60.6%
	$C_4H_9N_2^+$, *m/z* 85.076 (10%)	

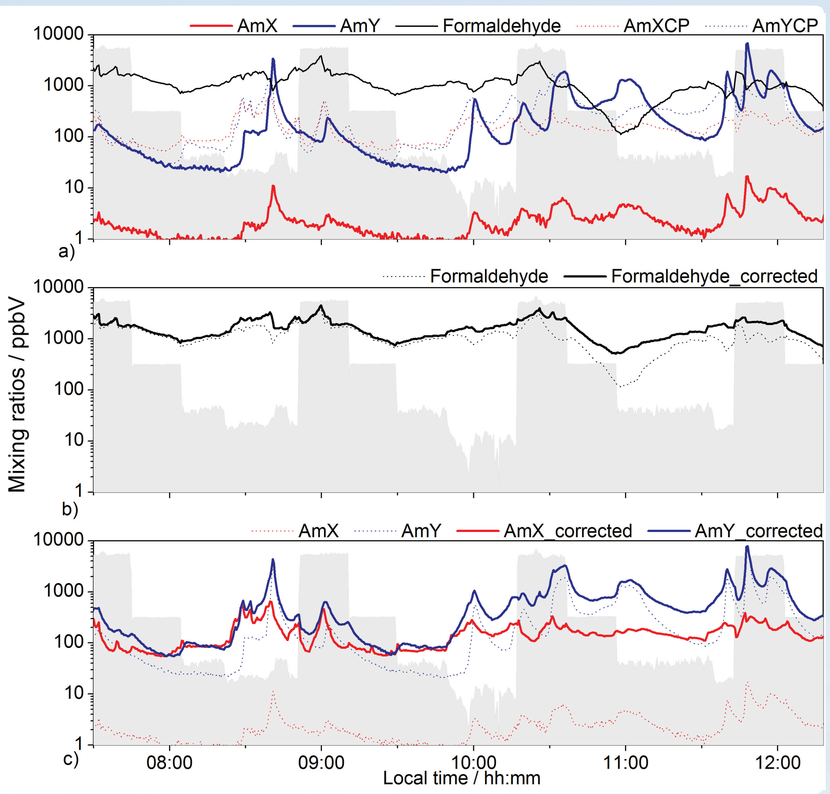
Table 1. List of amines, corresponding condensation products and the percentage of the injected amine lost in the inlet line. The values of 'Amine lost' were extracted from measurements with a 1:10 concentration ratio of amine:formaldehyde.

Nomenclature

m/z	mass number to charge number ratior ratio
ppbV	parts per billion by volume
VMR	Volume Mixing Ratio
PTR-ToF-MS	Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry
FT-IR	Fourier Transform Infrared Spectroscopy

Analysis

- Figure a shows the mixing ratios of two amines (AmX and AmY) and formaldehyde as measured at the end of the 110 m long sampling line.
- Amine emission spikes are accompanied by a drop in formaldehyde and a concurrent increase in the two respective amine-formaldehyde condensation products, AmXCP and AmYCP.
- It is possible to add the amount of condensed amine and formaldehyde to the measured amount of these species.
- Figures b and c show the time traces of the apparent (measured) and corrected mixing ratios of formaldehyde and amines, respectively.
- For the period shown, emissions of AmX, AmY and formaldehyde increase by a factor of 70, 2 and 1.3, respectively.



Conclusions

- Primary amines and formaldehyde condense quickly in the inlet lines of measurement instruments, leading to a significant underestimation of emission levels from amine-based PCCC facilities.
- PTR-ToF-MS detects respective condensation products, making it straightforward to derive the correct amine and formaldehyde concentrations in the amine wash gas.

