

REPORT

Measurement methods for selected emissions from amine-based carbon capture plants

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1 Introduction

To reduce CO₂ emissions from e.g. waste incineration and production plants, post combustion carbon capture with amine-based solvents is being tested in Denmark. Carbon capture with amine-solvents will lead to trace emissions from the absorber tower of amines and their degradation products to ambient air¹. Emissions of amines, and in particular their degradation products, including nitrosamines, nitramines, amides, and aldehydes may be harmful to human health and the environment. Hence, there is a need for applicable measurement methods to monitor and quantify such emissions. Emissions of amines and the degradation products takes place directly from the absorber tower. The degradation products are formed via thermal or chemical degradation of the solvent in the capture-stripping process where the solvent is recycled through repeated heating and cooling. Additionally, degradation products can be formed by subsequent atmospheric degradation of the "parent" amine². The Norwegian Institute of Public Health (NIPH) recommends that the sum of nitrosamines and nitramines should not exceed a concentration of 0.3 ng/m³ in ambient air to keep the lifetime cancer risk below 1:100.000.³

Monoethanolamine (MEA) is the benchmark solvent (30% in water solution) but other solvents like 2-amino-2-methyl-1-propanol (AMP), methyldiethanol amine (MDEA), and monoisopropanolamine (MIPA) can be applied as effective absorbents for CO₂ in mixtures with piperazine and water.

2 Measurement Methods

A recommended reference method will typically involve manual sampling using collection in a suitable absorbent that will be used for subsequent analysis. There are several manual methods that can be applied for measurement of amines and their degradation products. Some of these methods use solid absorbents for capturing the amines, and some use liquid absorbents. As we want to measure amines after a wet scrubber, the stack gas will have an increased temperature (e.g. 40-50 °C at the top of the scrubber), and a very high water content. Furthermore, it probably contains small aerosol droplets formed in the scrubber from the amine solution. Therefore, liquid absorbents in impingers are preferred to solid absorbents for emission measurements after wet scrubber systems.

Manual methods are labor-intensive and only provide information of the average concentration over the actual sampling period. Furthermore, the detection limit is strongly dependent on the sampled air volume, which depends on the sampling period and the flow. A higher time resolution can be achieved through online methods where concentrations are measured directly by means of automated analysis performed on site. Online methods have the advantage of providing time-resolved data providing results instantly. This is an advantage when measuring gases in dynamic systems, where gas concentrations can fluctuate strongly over short periods of time.

2.1 Online Measurements

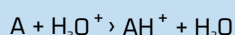
FTIR: Fourier transform infrared (FTIR) spectroscopy is based on gas molecules' absorption of infrared light. All gas-molecules with a permanent or induced dipole moment can be detected, which means diatomic molecules like O₂, N₂, and H₂ cannot be measured with this method. Each molecule has its own IR "fingerprint" in the obtained spectrum. The concentration is determined by the Lambert-Beer law:

$$A = c \cdot l \cdot \epsilon$$

Where A is the absorbance, c is the molar concentration of the analyte, l is the optical pathlength, and ϵ is the molar absorptivity of the analyte.

The detection limit of FTIR instruments typically applied for standard flue gas measurements is in the ppm range, which is insufficient for measurements of amine degradation products. Furthermore, identification and quantification of the analytes in complex mixtures may be difficult due to overlapping absorption bands.

PTR-ToF-MS/PTR-QMS: Proton transfer reaction mass spectrometry is an analytical technique where the analyte, A , is ionized by reaction with H₃O⁺ to form AH⁺, which is detected in a mass spectrometer.



The proton transfer reaction is a soft ionization technique, that leads to minimal fragmentation. Hence, most analytes will be detected at m/z corresponding to their molecular mass + 1. All volatile compounds with a proton affinity larger than the proton affinity of water can be detected, which includes a large variety of volatile organic compounds (VOCs) and inorganics.

Quantification of an analyte requires that $[AH^+] < [H_3O^+]$, and quantification of A is given by:

$$[AH^+] = [H_3O^+]_0 (1 - e^{-k[A]t}) \approx [H_3O^+]_0 [A]kt$$

Where $[H_3O^+]_0$ is the initial concentration of H₃O⁺ before ionization of the analyte, A is the analyte concentration, k is the reaction rate coefficient of the proton transfer reaction between H₃O⁺ and the analyte of interest, and t is the reaction time in the drift tube.

The original version of the instrument was invented in the nineties by Lindinger et al.⁴ and was based on a quadrupole mass spectrometer (PTR-QMS), which only separates molecules by nominal mass. Hence, two isobars (molecules with different elemental composition but same nominal mass) cannot be distinguished. Examples are dimethylamine and formamide, which both would be detected at m/z 46, glycol aldehyde and acetic acid both detected at m/z 61, and xylene and 2-(nitroamino)ethanol both detected at m/z 107.

In newer versions of the instrument, a high resolution time-of-flight mass spectrometer (PTR-ToF-MS) is applied, which provides a higher mass resolution and a higher sensitivity, i.e. isobars can be separated and the detection limit is lower compared to PTR-QMS instruments.

FORCE Technology is now investing in a PTR-ToF-MS instrument, Ionicon, which provides real-time measurements in the ppt to sub ppm range with a high mass resolution. No sample preparation is needed, and the use of real-time data is advantageous, e.g. during the development phase when

implementing CC plants. PTR-ToF-MS enables the measurement of a wide range of organic and inorganic volatile compounds, including amines and their degradation products from carbon capture plants. PTR-ToF-MS is a well-established technique and has been applied for more than a decade for scientific applications.⁵ Zhu et al. described the measurement of MEA and its degradation products with PTR-ToF-MS in 2013 emitted from a post combustion carbon capture plant in Mongstad.⁶ But it has also been applied in a wide range of other applications like breath analysis in the food and medical industry.

2.2 Manual sampling and analysis

It is well-established in the scientific literature that amines, amides, nitrosamines, and nitramines can be collected in a sampling train consisting of two impingers placed in an ice bath, containing 0.1M sulfamic acid solution, see Figure 1. The analytes either condensate or are absorbed in the sulfamic acid solution and are subsequently analyzed with liquid chromatography triple quadrupole mass spectrometry (LC-MS/MS/MS).^{7,8,9} The quantification and limit of detection depends on the sampled air volume. The disadvantage of the method is the involvement of a lot of manual work and the delayed measurement results due to subsequent laboratory analysis.

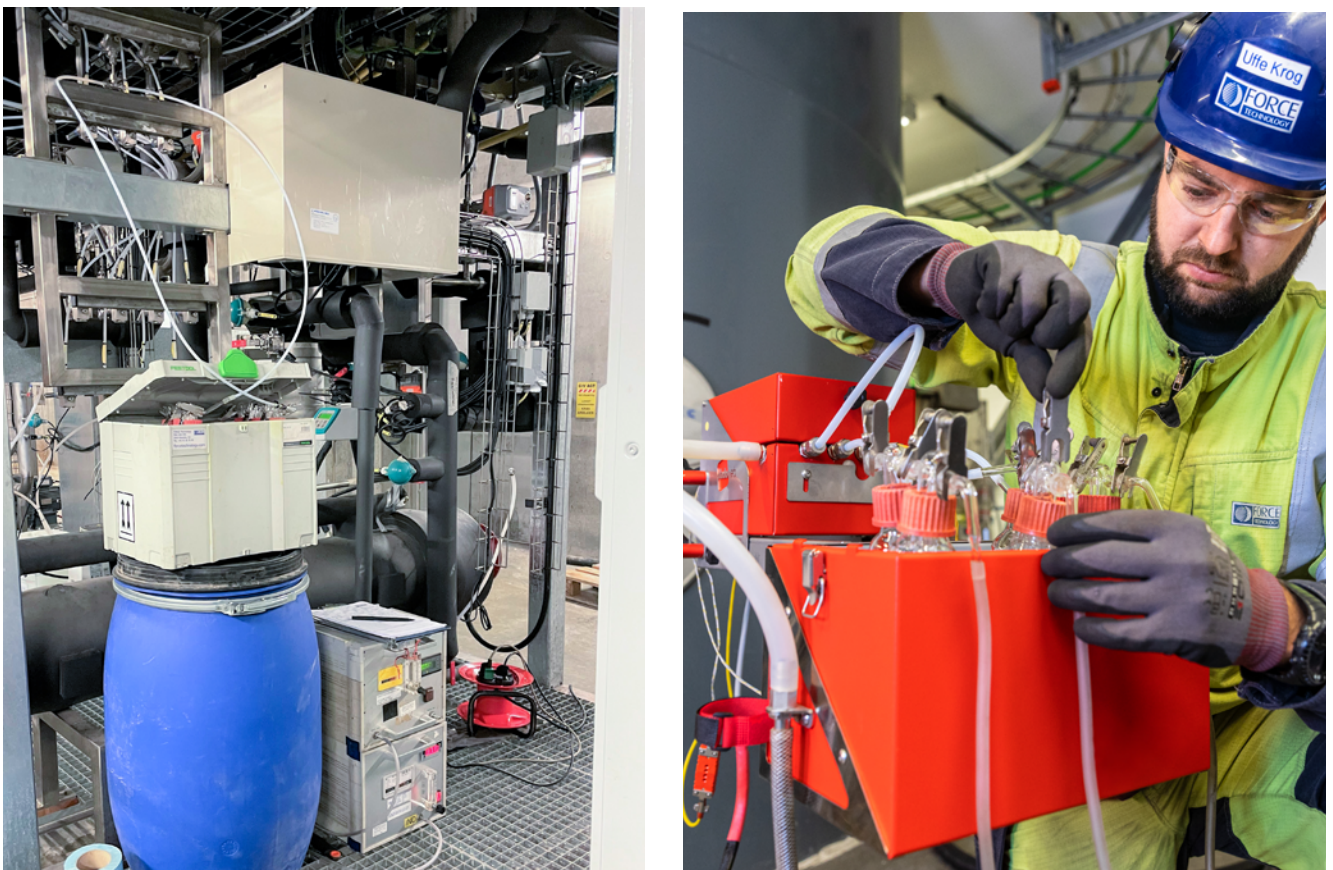


Figure 1 Example of impinger sampling of monoethanolamine and its degradation products at a carbon capture test plant.

Because of the sticky properties of amines and many nitrogen-containing compounds, heated inlets are always recommended for sampling of amines both for online and offline methods, to minimize the deposition of amines on surfaces in the inlet system. For offline methods with sampling in absorption liquid, the inlet should be flushed with absorption “cleaning” liquid after sampling, to wash out any deposited amines from the inlet, to further minimize this effect.

Impinger sampling captures the entire aerosol i.e. both the gas-phase and the aerosol particles. However, there may be uncertainties related to the sampling of aerosol particles in impingers e.g. as a consequence of difficulties in performing isokinetic sampling and possibly limited retention of aerosols in the absorption liquid, depending on the sampling flow rate and aerosol size^{8,9}. When heated inlets are applied in front of FTIR and PTR-ToF-MS, the measured concentration is the sum of the gas-phase amines and amines evaporated from aerosol particles. However, complete evaporation of aerosol particles is not given, and the extent of evaporation depends on the temperature of the sampling inlet, and on the amine properties and actual aerosol composition⁸.

FORCE Technology has wide experience in conducting measurements with FTIR and sampling with impinger trains. We are now expanding our instrumentation by investing in an PTR-ToF-MS instrument, which enables real-time measurements in the ppt to sub ppm range of volatile compounds including amines, amides, nitrosamines, and nitramines.

3 References

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