



## A compact and easy-to-use mass spectrometer for online monitoring of amines in the flue gas of a post-combustion carbon capture plant



Liang Zhu<sup>a</sup>, Tomáš Mikoviny<sup>a</sup>, Anne Kolstad Morken<sup>b</sup>, Wen Tan<sup>a</sup>, Armin Wisthaler<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of Oslo, P.O. Box 1033, 0315, Oslo, Norway

<sup>b</sup> Technology Centre Mongstad (TCM), 5954, Mongstad, Norway

### ARTICLE INFO

#### Keywords:

Carbon capture  
Amines  
Emission monitoring  
Technology Centre Mongstad  
Mass spectrometry  
PTR-MS

### ABSTRACT

We herein report on the adaptation and deployment of a compact and easy-to-use mass spectrometer for online monitoring of amines in industrial flue gas at ppb to ppm levels. The use of ammonia as a source gas in proton-transfer-reaction mass spectrometry (PTR-MS) greatly simplifies the detection of amines, making it possible to use a low-end commercial instrument version (PTR-QMS 300) for the measurements. We characterized the analytical performance of the instrument (sensitivity, limit of detection, precision, matrix effects) for nine solvent amines (monoethanolamine, dimethylaminoethanol, aminomethylpropanol, methyldiethanolamine, diglycolamine, piperazine, aminoethylpiperazine, methylpiperazine, N-(2-hydroxyethyl)piperazine) and three degradation amines (methylamine, dimethylamine, trimethylamine). The new analyzer was tested and validated in side-by-side measurements with established emission monitoring techniques at the Technology Centre Mongstad (TCM) in Norway. After validation, the instrument was permanently installed on top of the absorber tower to deliver real-time amine emission data to the plant information management system.

### 1. Introduction

As of 2018, the technologically most mature solution for removing carbon dioxide (CO<sub>2</sub>) from a fossil flue gas stream is to chemically absorb it into an aqueous amine solution. However, while CO<sub>2</sub> is efficiently captured as an amine carbamate salt, amines are partly volatilized and entrained into the flue gas stream. Amine-based post-combustion CO<sub>2</sub> capture (PCCC) plants thus emit amines to the atmosphere (SEPA, 2015). Atmospheric oxidation processes may partially transform the emitted amines into nitrosamines and nitramines (Nielsen et al., 2012), *i.e.* substances with known carcinogenic or potential carcinogenic properties. Based on a conservative risk analysis, inhalation exposure to the sum of PCCC-derived nitrosamines and nitramines should be kept below an annual average concentration of 0.3 ng m<sup>-3</sup> (Låg et al., 2011). Since it is not possible to monitor and surveil such low concentrations in the atmosphere, exposure to nitrosamines and nitramines is calculated taking into account dispersion and atmospheric processing of emitted amines. A key input parameter to such calculations is the emission rate of solvent amines and, importantly, also of common degradation amines such as dimethylamine. Accurate and continuous monitoring of amine emissions are thus a mandatory prerequisite for ensuring a safe operation of an amine-based PCCC plant.

The Technology Centre Mongstad (TCM) ([www.tcmda.com](http://www.tcmda.com)) in

Norway is the world's leading facility for testing and improving CO<sub>2</sub> capture technologies. Over the past five years, a variety of amine solvent technologies have been subjected to extensive testing, including the assessment of emissions to air. TCM has also undertaken significant efforts to validate and optimize emission sampling and measurement techniques. At present, TCM monitors amine emissions via i) manual impinger sampling and offline liquid chromatography mass spectrometry (LC-MS) analysis, ii) online Fourier Transform Infrared (FT-IR) spectroscopy analysis and iii) online Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-ToF-MS) analysis (Morken et al., 2017). Each of these methods has its drawbacks. Manual sampling is discontinuous and thus fails to catch the high variability of amine emissions. The FTIR analyzer suffers from a poor detection limit and detects amines only at ppm levels. The PTR-ToF-MS analyzer is expensive and requires full-time expert personnel for instrument operation and data analysis. In addition, considerable infrastructure and logistical support are required for installing this relatively large and heavy instrument at or close to the absorber stack. In the present work, we will demonstrate how a smaller, cheaper and easier to operate Proton-Transfer-Reaction Quadrupole Mass Spectrometer (PTR-QMS) can be used for online and real-time monitoring of amines in treated flue gas. We will also show how a modified mode of operation generates data that are easily interpretable by the non-expert. These data can be directly fed to the

\* Corresponding author.

E-mail address: [armin.wisthaler@kjemi.uio.no](mailto:armin.wisthaler@kjemi.uio.no) (A. Wisthaler).

amine plant information management system, thus providing real-time amine emission information to the plant operators.

## 2. Material and methods

### 2.1. PTR-QMS 300 configuration and settings

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a well-established and well documented analytical method for online organic trace gas measurements (Lindinger et al., 1998). The gas to be analyzed is introduced into a low pressure reaction cell wherein organic molecules are softly ionized via gas-phase proton transfer reactions with  $\text{H}_3\text{O}^+$  ions. The latter are injected into the reaction cell from an external plasma ion source that is usually operated with pure water ( $\text{H}_2\text{O}$ ) vapor (Hansel et al., 1995). Instruments in the lower price category use quadrupole mass spectrometers (QMS) for mass analysis, while high-end instrument versions are based on orthogonal acceleration time-of-flight mass spectrometers (ToF-MS). For the measurements presented herein, we used a PTR-QMS 300 instrument (Ionicon Analytik GmbH, Innsbruck, Austria). This instrument is the smallest ( $56 \times 53 \times 61$  cm, 80 kg) and cheapest PTR-MS version currently on the market, making it the preferred choice for industrial monitoring applications. The instrument was modified in two ways:

- i) Diluted ammonia (1%  $\text{NH}_3$  in nitrogen, AGA AS, Oslo, Norway) was fed to the plasma ion source instead of pure  $\text{H}_2\text{O}$  vapor. By doing so,  $\text{NH}_4^+$  ions were formed as proton transfer reagent ions instead of  $\text{H}_3\text{O}^+$  ions. We denote this mode of operation as  $\text{NH}_3$  mode as opposed to the conventional  $\text{H}_2\text{O}$  mode.
- ii) A mass flow controller equipped with Kalrez® seals (0–10 sccm range, Bronkhorst High-Tech B.V., Netherland) was used for supplying diluted  $\text{NH}_3$  to the ion source. Viton® seals which are routinely used in mass flow controllers should not be used with  $\text{NH}_3$ -containing gases.

The operational settings of the PTR-QMS 300 operated in the  $\text{NH}_3$  mode for detecting amines in a humid flue gas matrix were as follows: drift tube voltage 300 V, drift tube pressure 2.20 mbar, drift tube temperature 100 °C, ion source flow 2.5 sccm, ion source valve (SV) aperture 23%. The resulting reduced electric field strength was 76 Td ( $1 \text{ Td} = 10^{-17} \text{ V cm}^2$ ). The inlet capillary of the PTR-QMS 300 was heated to 100 °C. The  $\text{NH}_4^+$  ion signal ( $m/z$  18) was measured with a dwell time of 10 ms to prevent the channeltron detector of the PTR-QMS 300 from saturating. The mass spectrum was scanned in the  $m/z$  20–200 range with a dwell time of 200 ms per  $m/z$ . A full mass spectrum (ion current as a function of  $m/z$ ) was thus recorded every 36 s. We note that the PTR-QMS 300 instrument does not include an ion pulse counting system. Ion signals are thus recorded and herein reported as ion currents ( $i$ , in pA) and not as counts per second (*cps*).

### 2.2. Calibration

Instrumental response factors (in pA/ppbV) were obtained in calibrations with external standards. Quantitative aqueous standards were prepared for twelve amines obtained from Sigma Aldrich: methylamine (MMA, 40% wt. in  $\text{H}_2\text{O}$ ), dimethylamine (DMA, 40% wt. in  $\text{H}_2\text{O}$ ), trimethylamine (TMA, 25% wt. in  $\text{H}_2\text{O}$ ), monoethanolamine (MEA, > 99%), dimethylaminoethanol (DMEA, > 99%), aminomethylpropanol (AMP, > 99%), methyldiethanolamine (MDEA, > 99%), diglycolamine (DGA, > 99%), piperazine (PZ, > 99%), aminoethylpiperazine (AEP, > 99%), methylpiperazine (MEP, > 99%), *N*-(2-hydroxyethyl)piperazine (HEP, > 99%). In the laboratory, we used a liquid standard nebulization device (LCU; Ionicon

Analytik GmbH, Innsbruck, Austria) for generating gaseous standard atmospheres of the respective amines (Fischer et al., 2013). The nebulizer was supplied by two liquid flow controllers connected to the amine standard solution and ultra-pure water, respectively. During multi-point calibrations, an increase in the standard solution flow was compensated by a decrease in the water flow to keep the absolute humidity at a constant level ( $\sim 10 \text{ g m}^{-3}$ ). For varying humidity levels ( $5\text{--}40 \text{ g m}^{-3}$ ) while keeping the amine concentration constant, the flow of pure water was gradually increased with the standard solution flow being maintained at a constant level. The outlet of the LCU was directly connected to the PTR-QMS 300 instrument. A liquid standard evaporator (HovaCAL®; IAS GmbH, Oberursel, Germany; Vautz and Schmäh, 2009) was used for calibrations at TCM. We recommend performing calibrations on a monthly basis.

### 2.3. Validation measurements

The performance of the PTR-QMS 300 analyzer operated in the  $\text{NH}_3$  mode was validated at TCM during test campaigns with different solvents including MEA and proprietary amine solutions. The PTR-QMS 300 results were compared against data obtained with a PTR-TOF 8000 analyzer (Ionicon Analytik, Innsbruck, Austria) operated in the  $\text{H}_2\text{O}$  mode, with an Analect Anafin 2000 FTIR instrument (Applied Instrument Technologies, U.S.A.) and via impinger samples that were analyzed by LC-MS. More details on these techniques and the sampling set-up can be found in Morken et al. (2017).

## 3. Results and discussion

### 3.1. PTR-MS operation in the $\text{NH}_3$ mode

If amine-treated flue gas is measured by a PTR-MS analyzer operated in the  $\text{H}_2\text{O}$  mode, the resulting mass spectra are complex and difficult to interpret. This is owed to the fact that  $\text{H}_3\text{O}^+$  ions protonate all organic species in the flue gas, which typically contains not only amines, but also a variety of carbonyl, heterocyclic and other trace organic constituents (Morken et al., 2017). For selectively detecting the amines, we chose to operate the PTR-QMS 300 in the  $\text{NH}_3$  mode (Lindinger et al., 1998; Blake et al., 2006; Shen et al., 2009; Hansel et al., 2018).  $\text{NH}_3$  has a higher proton affinity than most organic species in the flue gas (Hunter and Lias, 1998), meaning that the analyzer will be blind to these compounds. The proton affinity of amines is, however, higher than the proton affinity of  $\text{NH}_3$  (Hunter and Lias, 1998) meaning that they will be selectively ionized.

Under the operating conditions detailed in the Materials and Methods section, the  $\text{NH}_3$  mode yielded  $\text{NH}_4^+$  ( $m/z$  18, 100%) and  $\text{NH}_4^+(\text{NH}_3)$  ( $m/z$  35) ions as the protonating agents. The relative abundance of  $\text{NH}_4^+(\text{NH}_3)$  ions was found to be humidity-dependent, increasing from 0.3% at an absolute humidity of  $5 \text{ g m}^{-3}$  to 4.1% at an absolute humidity of  $50 \text{ g m}^{-3}$ . We note that  $\text{NH}_4^+(\text{NH}_3)$  ions also act as proton donors to amines (via ligand-switching and internal proton transfer reactions). The ion currents at  $m/z$  18 and  $m/z$  35 thus need to be summed for correctly quantifying the total reagent ion current. In PTR-MS machines, analyte ion signals scale linearly with the reagent ion signal and thus need to be normalized to the latter for generating quantitative data. We normalized all analyte ion signals to a total ion current,  $i_{\text{tot}} = i(m/z 18) + i(m/z 35)$ , of  $10 \mu\text{A}$ . We note that high concentrations of  $\text{NH}_3$  in the flue gas did not affect the reagent ion signals. With 1% of  $\text{NH}_3$  being added to the ion source, the two reagent ion signals remained insensitive to tens of ppm of  $\text{NH}_3$  in the sample. It was thus not necessary to apply corrections as described by (Zhu et al., 2013) for PTR-ToF-MS measurements in the  $\text{H}_2\text{O}$  mode.

We note that  $\text{O}_2^+$  ( $m/z$  32) and  $\text{NO}_2^+$  ( $m/z$  46) ions are also formed

Download English Version:

<https://daneshyari.com/en/article/11007447>

Download Persian Version:

<https://daneshyari.com/article/11007447>

[Daneshyari.com](https://daneshyari.com)