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The applicability of proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) to the detection of nitramines in flue gas and air

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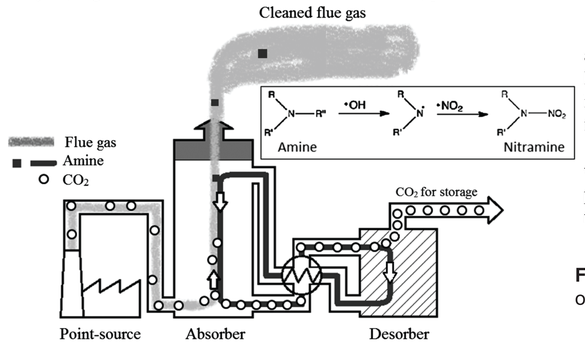
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Overview

The analytical performance of proton transfer reaction time-of-flight mass spectrometry was investigated on a suite of toxic nitramines ((R_1R_2)-N-NO_2) that are potentially present in industrial emissions and in ambient air.

Introduction

- Natural aliphatic amines and anthropogenic cyclic amines/alkanolamines produce toxic nitramines via *atmospheric photo-oxidation* in the presence of nitrogen oxides (NOx).[a] *Nitration* of amine-based solvents for CO_2 capture may cause nitramine emissions from post combustion carbon capture (PCCC) facilities.
- Detection of nitramines in air/flue gas is analytically challenging (low molecular weight and high polarity analytes, high water and ammonia levels in the matrix, potential artefact formation from amines and NOx).



- PTR-ToF-MS has been widely applied for *online* analysis of volatile organic compounds (VOCs) in the ambient environment and from industrial point-source.[b]
- The scope of the present work was to characterize the analytical performance of PTR-ToF-MS in the detection of nitramines.

Figure 1. Schematic illustration of amine-based CO_2 capture.[c]

Methods

- Aqueous nitramine standards were nebulized with high-purity nitrogen using a Liquid Calibration Unit (LCU; Ionicon Analytik GmbH, Austria) (Figure 2a).
- The LCU unit was connected to the PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH, Austria) using heated (100 °C) passivated stainless steel tubings (Restek, Bellefonte, MA, U.S.A)
- The PTR-ToF 8000 drift tube was operated at a temperature of 100 °C, a pressure of 2.20 mbar and a voltage of 500 V (corresponding to an E/N-value of 130 Td).
- Instrumental response factors for acetone (in ncps/ppbV) obtained with the LCU and with a certified gas standard (dynamically diluted in humidified synthetic air) were in excellent agreement (Figure 2b).

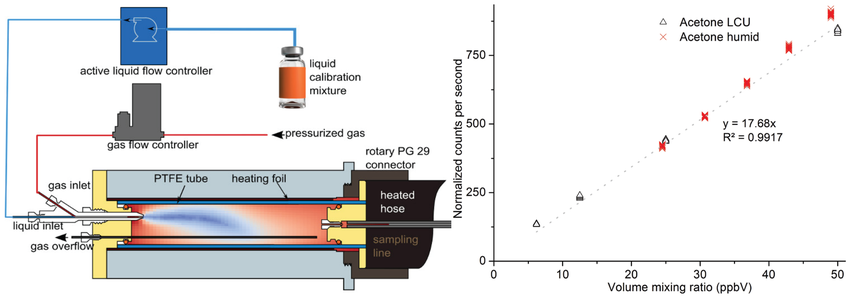


Figure 2. LCU unit coupled to a PTR-ToF 8000 instrument (left panel) and acetone calibration curves (right panel) obtained with the LCU (open black triangles) and with a certified gas standard (red crosses).

Results

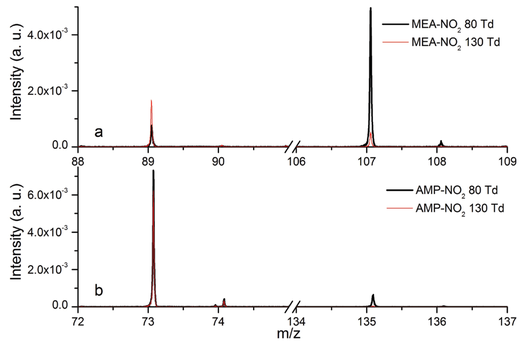


Figure 3. PTR-ToF 8000 mass spectra of MEA-NO_2 (upper panel) and AMP-NO_2 (lower panel) obtained at E/N=80 Td (black curve) and E/N=130 Td (red curve). Variation of E/N values can be used for compound identification.

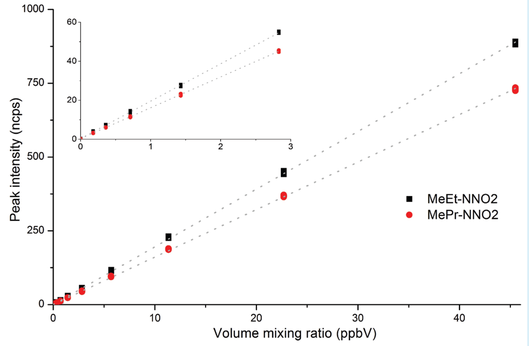


Figure 4. Calibration curves of two secondary nitramines demonstrating the linearity in instrumental response from 0.1 ppbV to 50 ppbV. The day-to-day reproducibility of instrumental response factors was better than 3 %.

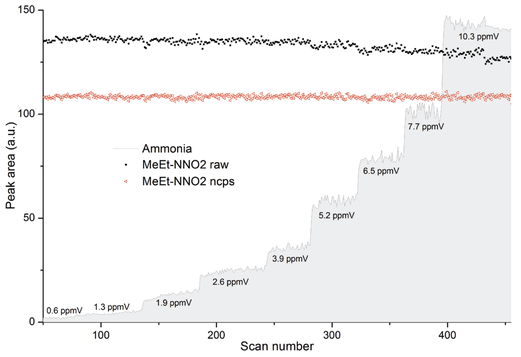
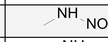
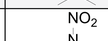
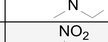
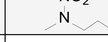
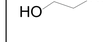


Figure 5. Protonated MeEt-NNO_2 signal (black: raw signal, red: normalized signal) as a function of variable ammonia mixing ratios (0.6-10.3 ppmV). Normalization (H_3O^+ and $H_2O{\bullet}H_3O^+$) corrects for the negative bias caused by high ammonia levels.

Table 1. Chemical abbreviation, structure, detected m/z signal (rel. abundance), decay response time, calculated H_3O^+ collision rate coefficient, measured instrumental sensitivity*, calculated sensitivity#, limit of detection (LoD) (S/N=3, 10s), E/N value and vapor pressure[c] of nine investigated nitramines.

chemical abbreviation	structure	detected m/z signal	decay response time	collision rate coefficient	measured instrumental sensitivity*	calculated sensitivity#	LOD (pptV)	E/N (Td)	Vapor pressure (mmHg)
Me-$NHNO_2$		77.032 (100%)	17.3	2.72	16.8	*16.6*	45	130	19.5
Et-$NHNO_2$		91.049 (100%)	12.8	2.79	16.4	*18.0*	28	130	8.45
DiMe-NNO_2		91.049 (100%)	4.6	2.89	20.0	*18.7*	23	130	0.88
MeEt-NNO_2		105.067 (100%)	4.3	2.99	19.6	*20.3*	16	130	0.61
MePr-NNO_2		119.080 (100%)	4.2	3.07	16.1	*21.8*	28	130	
MEA-NO_2		89.036 (7%), 107.046 (100%)	105.5	4.01	24.6	*n. a.*	17	80	1.22E-3
		61.055 (14%), 89.036 (100%), 107.046 (31%)		3.09	8.0 (12.8*)	*19.2*	60	130	
AMP-NO_2		73.068 (100%), 135.077 (6%)	22.2	3.66	18.8	*n. a.*	54	80	5.91E-3
		73.068 (100%), 135.077 (1%)		2.95	17.2 (17.3*)	*17.7*	59	130	
PZ-NO_2		85.076 (13%), 86.083 (83%), 132.076 (100%)	57.9	3.76	5.3	*n. a.*	62	80	6.68E-4
		85.076 (100%), 86.083 (46%), 132.076 (15%)		3.02	6.4 (10.1*)	*18.9*	202	130	
MOR-NO_2		87.068 (13%), 133.061 (100%)	5.0	2.99	12.6	*n. a.*	25	80	1.07E-3
		86.061 (84%), 87.068 (100%), 133.061 (65%)		2.45	5.3 (12.6*)	*15.6*	280	130	

* Total sensitivity including fragments

\# based on the calculated collision rate coefficient, mass-discrimination corrected.

Conclusions

- A high mass resolution spectrum library including data from nine nitramines has been established.
- Similar instrumental response factors were observed for nine different nitramines.
- PTR-ToF 8000 detection of nitramines exhibited good linearity, good reproducibility and low detection limits (double-digit pptV levels).
- High humidity or ammonia levels did not affect accurate quantification of nitramines.
- The use of a PTR-Qi-TOF[d] will allow to detect nitramines in real-time at single-digit pptV levels.

References

a. Nielsen, C. et al. Chemical Society Reviews, *2012*, **41**, (19), 6684 - 6704.

b. Zhu, L. et al. Environmental Science and Technology, *2013*, **47**, (24), 14306 - 14314.

c. Lindahl, S. et al. Environmntal Science: Processes Impacts, *2014*, **16**, 1825 - 1840.

d. Sulzer P. et al. International Journal of Mass Spectrometry, *2014*, **368**, 1 - 5.

Acknowledgements

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