



Absorber and stripper stack emission measurements during a carbon capture from flue gas using MEA solution test phase at the Technology Center Mongstad

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Overview

Quantitative real-time monitoring of atmospheric monoethanolamine and byproducts emissions from industrial-scale carbon capture at Mongstad are reported using Proton Transfer Reaction-Time of Flight-Mass Spectrometry.

Introduction

TCM recently began testing its industrial-size carbon capture facility. To meet the regulated emission criteria, it is of importance to qualitatively and quantitatively follow the discharge of amines and their degradation products to the atmosphere during operation. The real-time, online quantification of such volatile/semivolatile organic compounds from stack emission is feasible with the deployment of Proton Transfer Reaction-Time of Flight-Mass Spectrometry (PTR-ToF-MS) due to its fast response, high sensitivity in the sub ppb range, wide dynamic range, and its unique mass resolution allowing formula determination.^a The capabilities and uncertainties of the proposed method were determined using in-situ calibration data and by comparing with neighbouring FT-IR analyzer during Aker Clean Carbon's (ACC) plant commissioning phase using an aqueous monoethanolamine (MEA) solution. Thus, the measurements presented here represent results from an initial, non-optimized carbon capture testing phase in August 2012.

Methods

The inflow to the stack, outflow from the absorber, and the one from stripper column were periodically directed, through the heated (90 °C) and constantly flushed Teflon PFA lines, to a hot stainless steel manifold, to which both PTR-ToF-MS and FT-IR analyzer were connected (Fig. 1). The main running parameters of PTR-ToF-MS (Ionicon) were set by drift tube temperature (110 °C), drift voltage (500 V) and drift tube pressure (2.2 mbar), corresponding to an E/N value of ~125 Td.

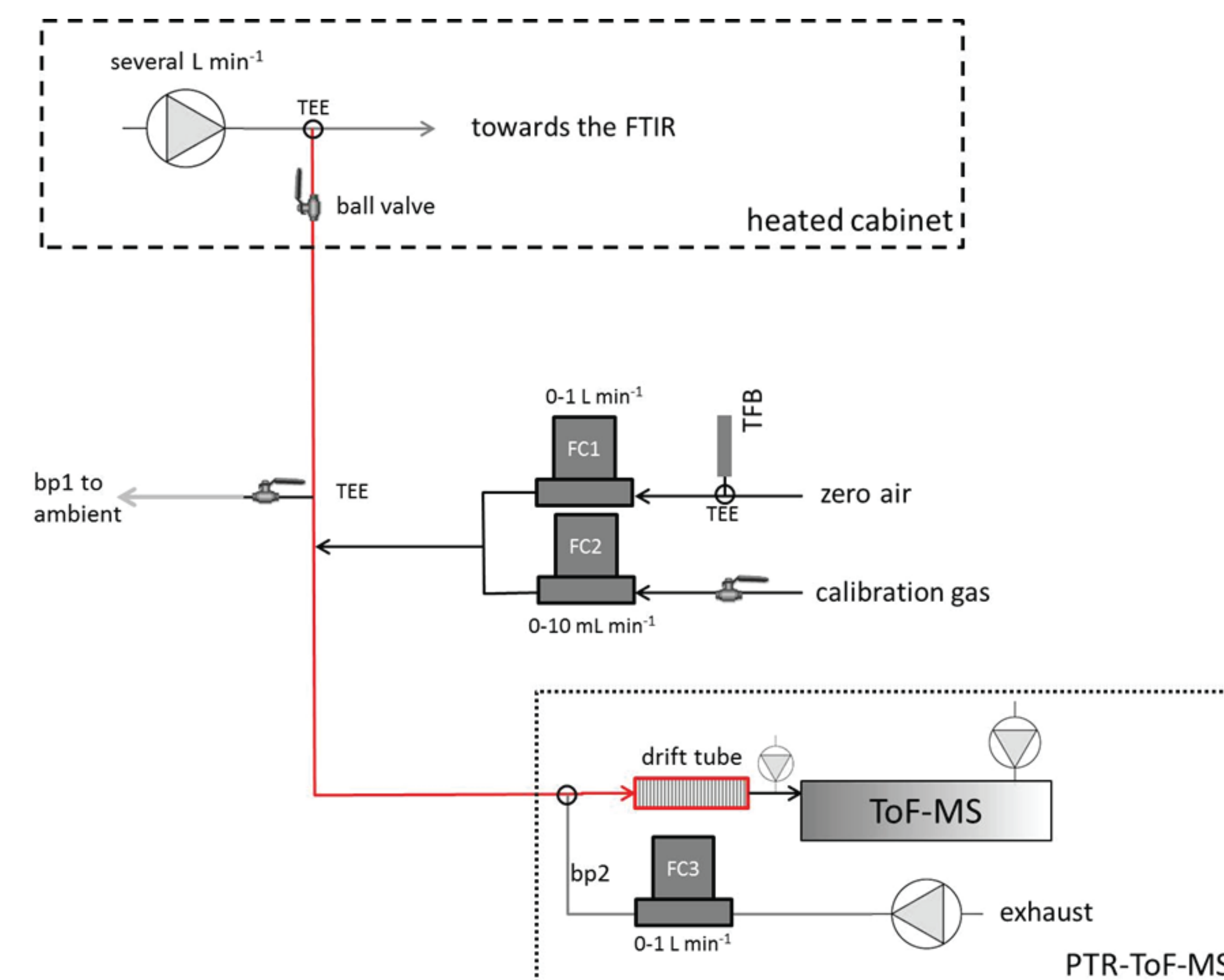
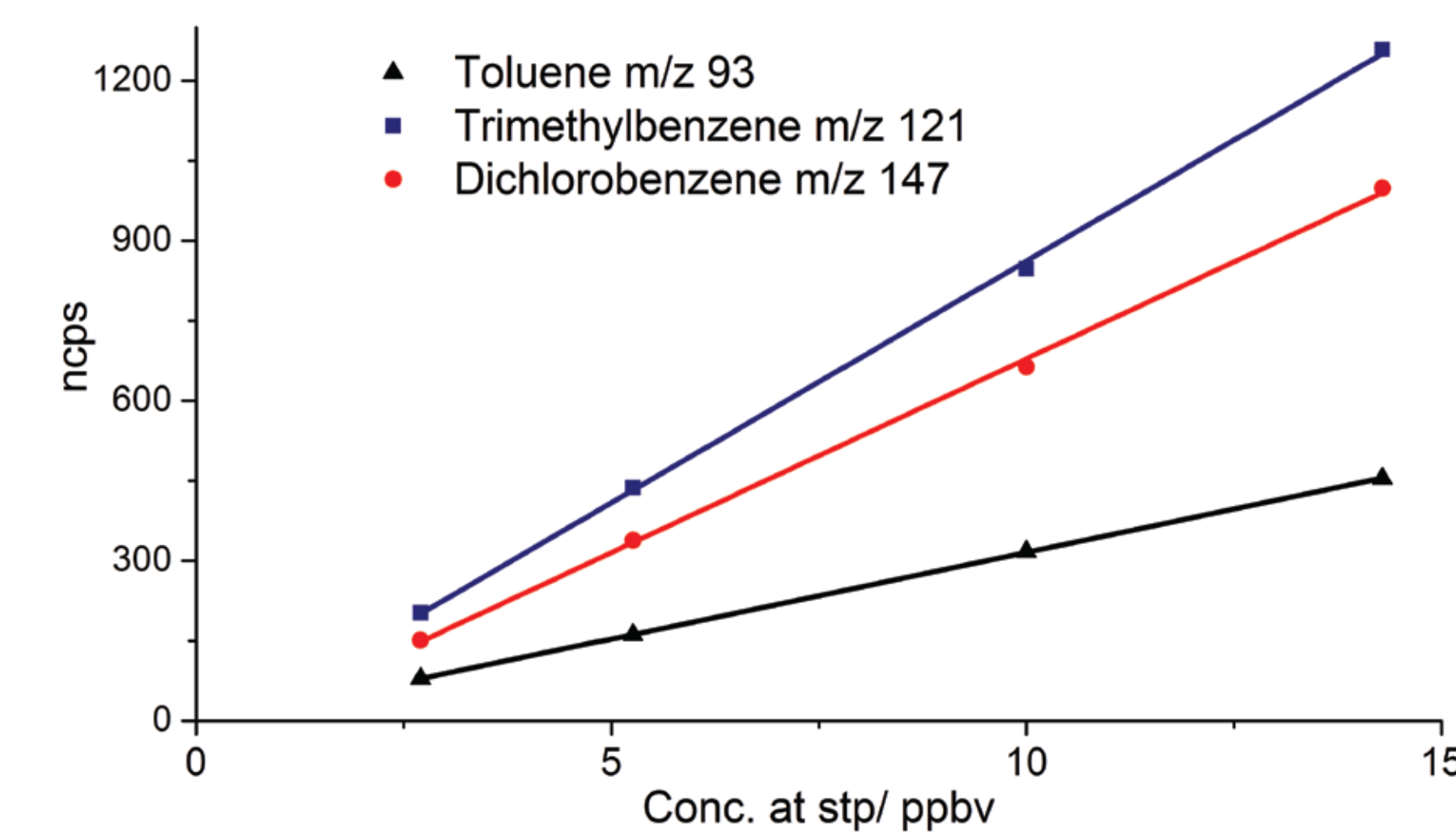


Figure 2. Calibration curves for toluene, trimethylbenzenes and dichlorobenzenes, obtained from the measurements of a multi-component aromatics standard (Restek Inc., USA) with different dilution factors. The quantification of those uncalibrated VOCs in absolute concentrations as gas mixing ratios (parts per billion by volume, ppbv) was derived from data of calibrated VOCs (i.e., toluene), via application of transmission efficiency and reaction rate constant knowledge.^b



Results

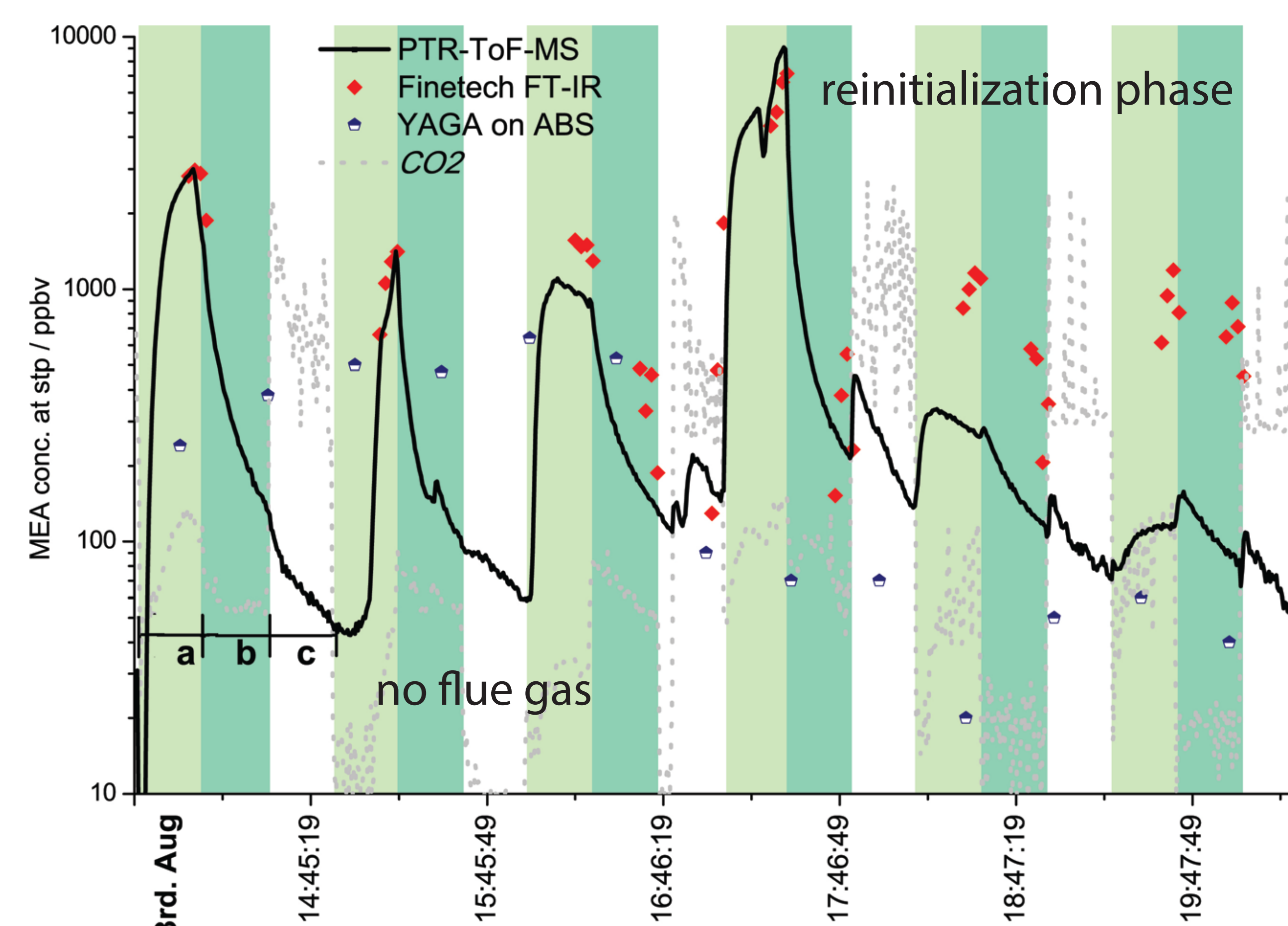


Figure 3: Monoethanolamine (MEA) measurements performed using PTR-ToF-MS, Finetech FT-IR, and YAGA Gasmet FT-IR on the top of the absorber tower. Sections “a, b, c” denote a periodic sampling sequence with a 45 min cycle: To Absorber, From Absorber, and Stripper, respectively. The non-quantitative CO_2 trace was plotted to guide the eye on the sampling cycles. Note that there was no flue gas entering the absorber before 17:30 h when the carbon capture processes were reinitialized. Thus, unrealistically high amine mixing ratios occurred prior to that time, which enabled instrument comparisons. In the first 4 hours, the MEA signal in the PTR-ToF-MS corresponded reasonably well to the Finetech FT-IR and at times the YAGA analyser. The much larger discrepancies at later stages could be due to the increased uncertainties of FT-IR measurements in the sub-ppm range, or sampling line and/or instrument surface contaminations.

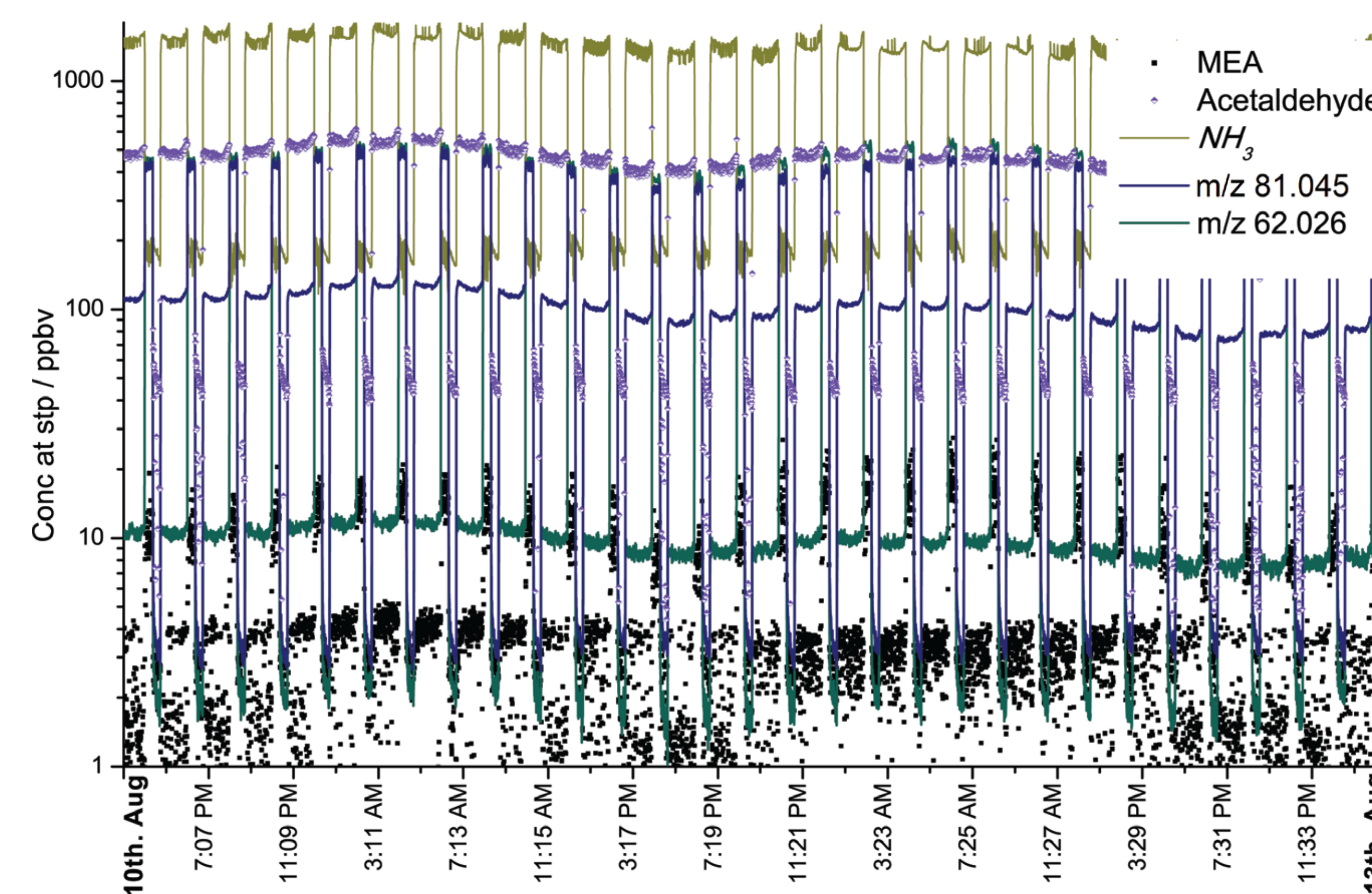


Figure 4: Prominent PTR-ToF-MS ion traces (MEA, acetaldehyde, *ammonia*, m/z 81.045 and one unknown peak at m/z 62.026) in the proton-transfer H_3O^+ mode for 3 days duration. The plateaued profiles of all selected peaks demonstrates the capability of the PTR-ToF-MS to quantitatively monitor industrial emissions over an extended period. It further suggests that significant by-products caused by thermal and, more likely, oxidative MEA degradation, either require more time (days to months) to accumulate before emission to the atmosphere may be observed, or are readily produced and efficiently emitted to the atmosphere based on their physical properties. Note that the prevailing *ammonia* signal is out of the linear response range of the PTR-ToF-MS.

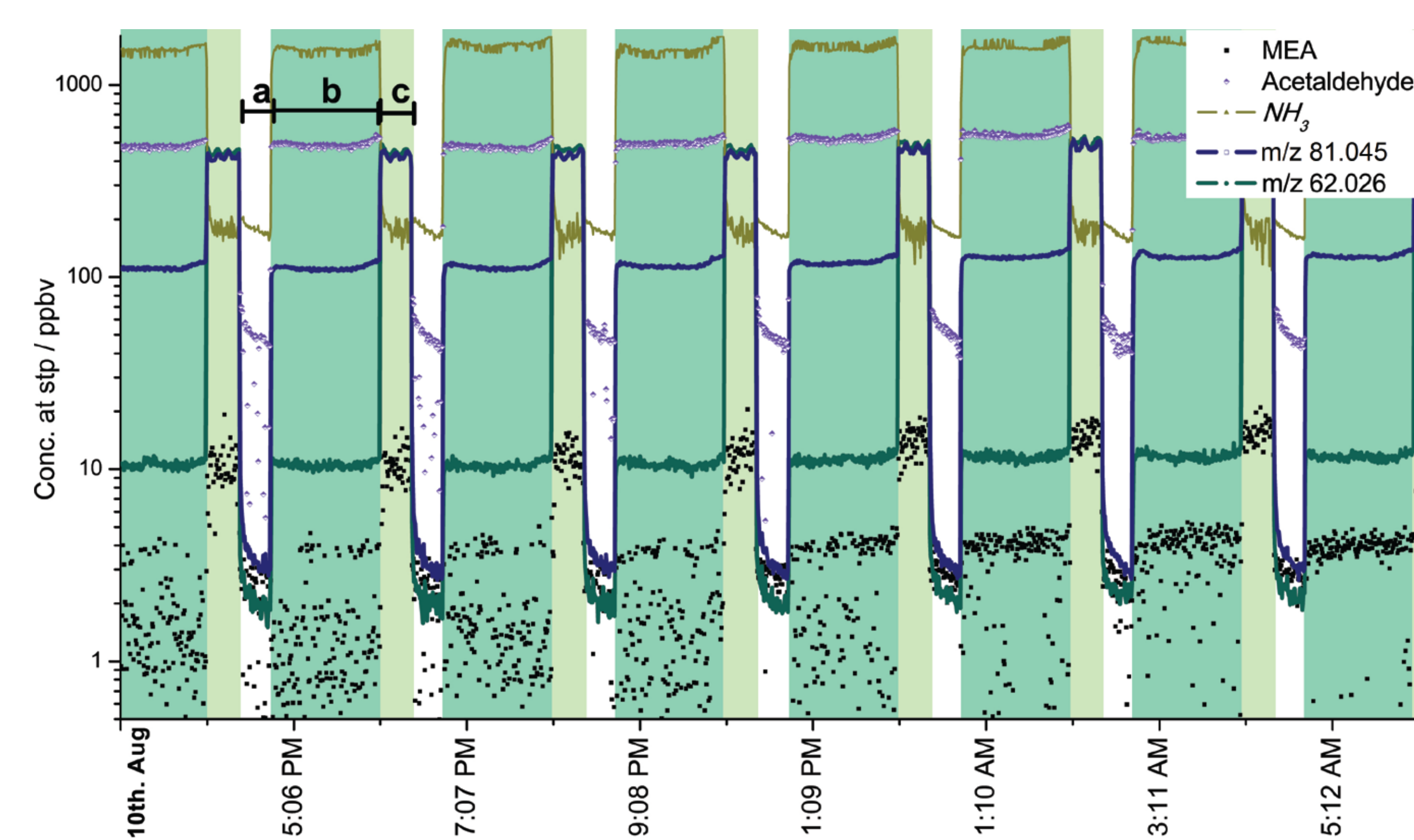


Figure 5: Zoomed time profile of PTR-ToF-MS measurements in the proton-transfer H_3O^+ mode. The oxidative MEA degradation products, *ammonia*, acetaldehyde and acetone, dominated emissions during stable operations. MEA was only emitted in significant amounts during the initiation phase, and later effectively removed by double water wash stages. Emissions were generally highest from the stripper column with exception of *ammonia*. Prominent emission of species at protonated mass 81.045 was observed ($C_4N_2H_5^+$, tentatively identified as pyrazine, which can form rapidly from oxidative MEA condensation^c, then azeotropically volatilize with water). A highly abundant ion at m/z 62.026 [$CH_4NO_2^+$] alongside the protonated MEA peak requires further identification.

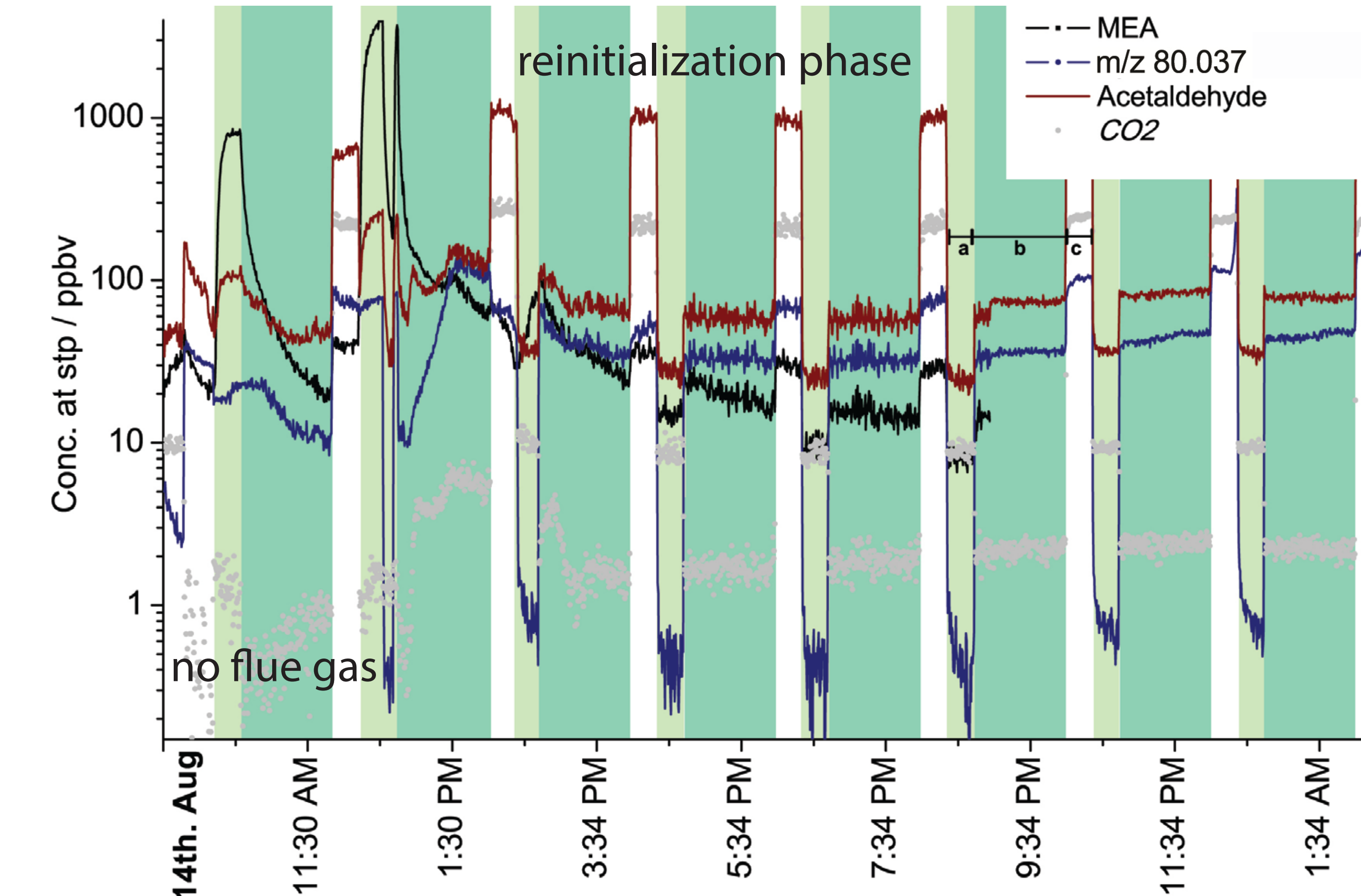


Figure 6: PTR-ToF-MS measurements performed in charge-transfer NO^+ mode, for identification of unknown molecules. Sections “a, b, c” denote the periodic sampling sequence within a 120 min cycle: To Abs, From Abs, and Stripper, respectively. The tentative identification of pyrazine was supported based on an observed molecular ion mass of 80.037 and its identical temporal pattern in the sampling cycles. In comparison, during the NO^+ ionisation mode measurements neither ions at m/z 60.01 ($[M-H]^+$, H-abstraction from the molecular ion) nor a molecular ion at m/z 61.02 (M^+) were observed, and this suggests that the aforementioned species [$CH_4NO_2^+$] did either not stem from CH_3NO_2 or, the ion formed underwent fragmentation under NO^+ ionisation conditions. Most likely, the detection of the ion at m/z 62.026 was due to an instrument artefact.

Conclusions

These initial results suggest that long-term emission monitoring from full-scale carbon capture facilities using PTR-ToF-MS is possible, reproducible, and quantitative within 10 to 30 percent. The amine (MEA) precursor and its major volatile degradation products were measured. Masses corresponding to potentially harmful minor byproduct emissions, e.g. nitrosamines and nitramines, were not detected above their detection limits (low ppb levels). Further testing will be necessary to determine whether measurement biases or artefacts exist due to the current instrument, sampling line, or gas composition parameters.

References

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