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Atmospheric Measurement Techniques
Discussions
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Interactive comment on “Bisulphate-cluster based atmospheric pressure chemical ionization mass spectrometer for ultra-high sensitivity (10 ppq) detection of atmospheric amines: proof-of-concept and first ambient data from boreal forest” *by* M. Sipilä et al.

Anonymous Referee #2

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This paper presents the adaptation of an existing APi-TOF-MS utilizing a modified inlet for the detection of amines. Detection limits down to 8 ppq are reported for a 15-minute integration time under chamber conditions. The authors conclude based on the first field deployment following calibration and characterization experiments at CLOUD that atmospheric amines, specifically DMA was never present above the detection limit of 20 ppq at the SMEAR II research station in rural Finland.

This work merits publication in AMT as part of a growing number of time of flight mass spectrometers utilized for ultra low concentration detection of atmospheric gases after a few comments are addressed.

General Comments: The instrument appears to operate as intended during the chamber work where an independent calibrated instrument is available for confirmation/calibration. How might the instrument sensitivity change during deployment at other locations? Is no calibration standard available for in field calibrations to ensure the instrument is operating in a stable state?

The instrument appears to function well at the chamber, however the atmospheric measurements do little to prove the instrument is applicable to the atmosphere for detection of DMA.

Specific Comments: pg. 3671 26-30: It might help readers follow this section by separating out more clearly the issues common to all techniques for amine measurements (backgrounds etc), and then mass-spectrometer related issues (eg. resolution, mass accuracy, etc).

pg. 3673 20-23: How does the effective declustering strength change the cluster stability? Presumably the fields in the APi region of the mass spectrometer could de-cluster ions significantly – how are these set, controlled, optimized?

pg. 3674 13-20 and Generally: If the cluster distribution and ionized products are sensitive to operation temperature – how does atmospheric temperature changes effect the stability (and therefore sensitivity, detection limits) of this technique?

Given that there is a high laminar sample flow rate does the incoming air equilibrate with the trailer temperature? Or instead is the effective ionization temperature a function of ambient temperature? How would these types of temperature changes influence measurements under atmospheric conditions?

pg. 3676 15-16: Does this introduction of an orthogonal saturator flow influence the inlet transmission of amines as it seems likely it disrupts the laminar flow developed during transit down the inlet tube? How would this effect the transmission of amines down the inlet through the saturator to the chemical ionization region?

pg. 3677: 1-2: What is the material of the 40 cm long inlet tube? If metal (for example stainless steel) could that not introduce significant memory or equilibration effects? Would amines be better transmitted via Teflon tube?

pg. 3677 3-6: Is the charging efficiency always the collision limit? Other chemical ionization techniques are sensitive to (for example) water vapor, which is often present in high concentrations as well as functional groups present. Have there been any experiments that show this ionization method to be sensitive or insensitive to the water vapor concentration (under atmospherically relevant concentrations)?

pg 3678 10-15: Is this type of unambiguity true for the other masses as well – it would seem likely that at lower masses the probability of chemical and ion source related backgrounds would be higher? It would be nice to show the actual high-resolution fit, with all the isotopes constrained (Figure 5) as discussed in the text.

pg. 3681 7: mass slow → mass flow

pg. 3681 10-18: Was the zero gas ever humidified to match ambient air? Could the increases during the zero for DMA be re-equilibration of the walls of the inlet tube when a clean zero air flow is introduced? Where is the zero gas delivered? Similarly does the presence of O2 (from air instead of cryogenic N2) effect the zero determination or the ion chemistry at all?

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 3667, 2015.