Atmos. Meas. Tech. Discuss., 7, C3999–C4001, 2014
www.atmos-meas-tech-discuss.net/7/C3999/2014/
© Author(s) 2014. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric Measurement Techniques Discussions

Interactive comment on "Measuring acetic and formic acid by proton transfer reaction-mass spectrometry: sensitivity, humidity dependence, and quantifying interferences" *by* M. Baasandorj et al.

Anonymous Referee #3

Received and published: 1 December 2014

The topic of online analysis of formic and acetic acid, being ubiquitously abundant in the atmosphere is well within the scope of AMT. The PTR-MS technique is nowadays widely used in atmospheric science, and the manuscript stresses the fact that PTR-MS data evaluation is susceptible to compound fragmentation patterns, interferences, sensitivities and hence respective instrument adjustments.

The authors describe isobaric interferences, fragmentation patterns and water vapor effects, and present respective corrections and recommendations for accurate inter-

pretation of the mass spectra with respect to sensitivities and E/N-dependencies.

Specifically the authors discuss the extent and variability of interferences for AA and FA measurements by PTR-MS in the lab and in ambient air in a representative urban region. The impact of humidity on the PTR-MS sensitivity (ncps) depends strongly on the collisional energy in the PTR-MS drift tube (i.e., E/N). The authors propose implied ion chemistry mechanisms occurring in the drift tube based on observed product ion distributions and humidity dependencies. They found opposing water-sensitivity relationships for different compounds (e.g. FA and Ethanol).

Furthermore they present an innovative acid trap method for separating FA and AA from various isobaric species. Some of the (isobaric) interferences can be resolved by applying the more recent high-resolution time-of-flight mass spectrometer, but some (isomeric) interference cannot even be separated based on exact mass.

The study is very well elaborated und the discussion well organized. I suggest publishing, after consideration of the following minor corrections:

Page 10902, line 24: The phrase "materials move upward with the flow and increase the exposure time" means that the absorber material is bouncing by a flow rate of only 35 sccm within the trap? They authors argue that loosely packing of the adsorber material led to increased exposure time (relative to what?). Why then was glycolaldehyde lost in a tightly packed trap and not in the loosely packed version? Did the flow restriction of the tightly packed material result in even longer exposure times? Please clarify.

Chapter 3.1 Trap performance: I got a bit confused about the phrases "background" "trap" and "no trap" of Figures 8 and 9 and "trap background" (Fig. 10) "PTR-MS background measurements" on page 10904, line 12, "trap background" on page 10904 in line 16 and "background acid trap measurements" in the text referring to Fig. 10 (page 10904 in line 21). Please check for consistency.

From the text I understood that Fig. 10 shows the “trap background” (i.e., “the trap background was monitored for 10 min by sending catalytically generated zero air through the acid trap and then to the PTR-MS”), followed by subsequent measurements of ambient air sent through the trap. It would be interesting to additionally plot the ambient air sampling data (bypassing the acid trap) in Fig. 10: on the one hand for better comprehension of the strategy applied, and on the other hand for information on the contribution of acids in the ambient air (i.e. difference between “trap signal” and “no trap” of ambient air showing the contribution of AA and FA, respectively)

Else: Does the used KOH-treated CarboBlack B packing material interact with water vapor at high ambient air relative humidity, leading to respective dependence of the trapping efficiency of (partly water soluble) glycolaldehyde, ethyl acetate and 2-propanol, ethanol and DME on the relative humidity of the sample air? Surface co-adsorption or capillary condensation could lead to increased uptake efficiency (negative effect on interfering species); occupation of active adsorption sites by water vapor could lead to even lower scrubbing efficiency (positive effect on interfering species).

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 10883, 2014.