Atmos. Meas. Tech. Discuss., 8, C971–C975, 2015
www.atmos-meas-tech-discuss.net/8/C971/2015/

Atmospheric Measurement Techniques Discussions

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 #1

Received and published: 30 April 2015

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8, C971–C975, 2015

Interactive Comment

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, N. Sarnela, T. Jokinen, H. Junninen, J. Hakala, M. P. Rissanen, T. Petäjä, and D. R. Worsnop

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30 April 2015

1 General Comments

In the manuscript the authors present a technique to measure amines using stable ion-molecule clusters, the employed technique seems to have potential to reach high sensitivity.

Although the results of the lab measurements are promising, dealing with the ion-molecule clusters seems to increase the complexity of measurements compared to

sulfuric acid measurements. A chapter that deals with the thermodynamics of the ion-molecule clusters seems to be missing in the manuscript. Although the technique seems to work under lab conditions, it might fail if more stable ion-molecule clusters are formed. So a discussion of amine concentrations below the detection limit is a bit early before the characterization of the measurement technique is not finalized.

I would suggest to aim this manuscript to instrument characterization because the field measurements presented include only poor results.

2 Detailed Major Comments

general point: Collision induced dissociation provides energy to take apart ion molecule clusters, additionally the acidified walls are absorbing amines. It seems difficult to judge the nucleation by measurements with results below the detection limit because other effects may play a role and change the sensitivity of the instrument.

general point: You have calibrated the instrument by the measurements at the cloud chamber? How do you avoid effects that change the instrument performances during the field campaigns, e.g. MCP aging, temperature fluctuations or other chemical species present? Wouldn't an online calibration be more reliable? Permeation tubes for DMA are available by companies which are well known to sell permeation tubes (cf. Bertram et al. (2011)).

general point: Cross sensitivities might be caused by other species, e.g. nitric acid sulfuric acid ion clusters are be more stable, as discussed in Kurtén et al. (2011). So the sensitivity could also change with the nitric acid concentration in the reactant gas stream. High water concentrations might cause an exchange of the amine in the sulfuric acid amine ion cluster, depending on the stability of clusters with many water molecules.

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general point: Do you see any interaction of the ion clusters with aerosol particles or signals that are correlated to nucleation events?

p. 3669, l.12-14: It should be specified whether "minute signals" are above the SN ratio and which species are found.

p. 3671, last paragraph: Collisions induced by electrostatic fields used are increasing the temperature of the ion molecule cluster to a few 100 C, which is well below 1 eV. Typically energies around 1 eV are reached in transfer stages. Thereby the evaporation rate is higher in the transfer stage.

p. 3674, l.12-14: The temperature stability of the instrument is mentioned on this page, in the field the temperature stabilization is more problematic. How is it granted for the field instrument?

general point: I'm missing some remarks how the amine background had been reduced, are the acidified walls the only approach used?

general point: How did you get rid of wall effects in the cloud chamber?

3 Minor Comments/Corrections

general point: also often ppt or ppq is used as unit it is more precise to use pptV or ppqV

p. 3671, l.17: "chemical ionization by either protonated water clusters...", better known as proton transfer reaction MS using water or other species.

p. 3675, l.11: ...in the space between...

p. 3675, l.12: ...carries the ions produced downstream toward...

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p. 3681, l.7: ..., mass flow controller...

p. 3681, l.17: ...when the instrument worked stable...

p. 3683, l.4: "collision limited ionization detection" makes no sense for me

References

Bertram, T. H., Kimmel, J. R., Crisp, T. A., Ryder, O. S., Yatavelli, R. L. N., Thornton, J. A., Cubison, M. J., Gonin, M., and Worsnop, D. R.: A field-deployable, chemical ionization time-of-flight mass spectrometer, Atmospheric Measurement Techniques, 4, 1471–1479, doi:10.5194/amt-4-1471-2011, http://www.atmos-meas-tech.net/4/1471/2011/, 2011.

Kurtén, T., Petäjä, T., Smith, J., Ortega, I. K., Sipilä, M., Junninen, H., Ehn, M., Vehkamäki, H., Mauldin, L., Worsnop, D. R., and Kulmala, M.: The effect of H_2SO_4 - amine clustering on chemical ionization mass spectrometry (CIMS) measurements of gas-phase sulfuric acid, Atmospheric Chemistry and Physics, 11, 3007–3019, doi:10.5194/acp-11-3007-2011, http://www.atmos-chem-phys.net/11/3007/2011/, 2011.

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