Atmos. Meas. Tech. Discuss., 5, C1045–C1047, 2012
www.atmos-meas-tech-discuss.net/5/C1045/2012/

Atmospheric Measurement Techniques Discussions

Interactive comment on "Dimethylamine and ammonia measurements with ion chromatography during the CLOUD4 campaign" *by* A. P. Praplan et al.

Anonymous Referee #1

Received and published: 18 May 2012

In this manuscript, the authors describe the application of ion chromatography to the measurement of ammonia and dimethylamine in an environmental chamber at CERN. The role of these constituents in the nucleation of atmospheric particles is not well-understood and motivates the need for high accuracy measurements at low mixing ratios (<tens of pptv). The subject matter is appropriate for publication in AMT, but issues related to uncertainty in the measurements should be more clearly addressed by the authors prior to publication.

The major objective for the development of the analytical procedure appears to be the

ability to provide high accuracy measurements of the analytes, yet there are several assumptions made in the approach that limit confidence in the results

1) In Figure 3, it appears that only one (or two) calibration standards other than the blank are in the range of the experimental data. Given that many ion chromatography systems are known to have non-linear responses to NH3 (e.g. Ullah et al., 2006), it may improve quantification to have additional standards in the calibration curve.

2) With regards to the selectivity of the technique, the authors indicate that their chromatography method allows for the resolution of NH3 and DMA, from each other and from Na and K. However later in the manuscript in Section 3.3, it is mentioned that NH3 values could not be obtained due to an interference in the chromatograms. To what do the authors attribute this interference, and how can they be confident that it does not affect the calculated mixing ratios at other times in the experiments? On a related note, what sort of problems would be encountered if other amines were present in the chamber?

3) In Section 3.1, the authors investigate the effect of the liquid-to-air-flow ratio on the sampling efficiency for DMA. The right-hand panel of Figure 4 would be more straightforward to interpret if the y-axis displayed the fractional or normalized signal, rather than the absolute mixing ratio. More importantly, the sensitivity of the sampling efficiency to the flow ratios is only tested for DMA and the results are applied to the scaling of the NH3 data. But as the authors describe in Section 3.1, the solubility and pKa of NH3 is quite different from DMA and this must introduce additional uncertainty to the calculation of the NH3 mixing ratios. This should be addressed in some quantitative way by the authors.

4) There is an important difference between the delivery of the analyte during calibration (direct injection without pre-concentration) and during sampling of the chamber. During each measurement interval, deionized water containing the soluble analytes is flowed over the concentrator column for a period varying between 70 and 210 minutes.

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The retention capacity of the concentrator columns can be influenced by injection flow rate and volume (e.g. Markovic et al., 2012). Given the large volumes of liquid passed through the concentrator columns in their method, the authors should assess whether there are any potential losses of analytes.

Technical comments

P2396, L11 ‘du’ should be ‘due’

P2397, L5, should read ‘...increasing a subject...’

References

S. M. R. Ullah, M. Takeuchi and P. K. Dasgupta, Environmental Science and Technology, 40, 962–968, 2006.

M.Z. Markovic., T.C. Vandenboer, J.G. Murphy, Journal of Environmental Monitoring, 2012. DOI: 10.1039/c2em00004k

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 2395, 2012.