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Atmospheric Measurement Techniques
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Discussions

Interactive comment on "Determination of alkyl amines in atmospheric aerosol particles: a comparison of gas chromatography-mass spectrometry and ion chromatography approaches" *by* R.-J. Huang et al.

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We thank the anonymous referee for his/her time to review our manuscript and particularly for his/her valuable comments and suggestions that have significantly improved the manuscript. We have made most of the changes suggested by the referee and have outlined these in detail below.

Anonymous Referee #1

The authors present a comparison of the two methods (GC/MS and IC) for the determination of alkyl amines in aerosol particles. They commented that the level of knowledge of amines in aerosol particles is weak due to lack of measurement data, which further is explained by difficulties in achieving accurate amine measurements.

I completely agree with the author's viewpoint. However, the rating is not top notch, because in my opinion, the authors fail to go in depth on matters of special importance for this compound class and in this type of measurements. I recommend substantial revision and major modifications, before it could be considered for publications.

1. Although the data are corrected for field blanks, the field blanks should be presented. This is of great importance for the GC/MS method due to the high sensitivity, but is also important for the IC method. Amines can be present in surprisingly many places with a great diversity of sources.

Response: We agree with the reviewer and have included the field blank values in the revised version. They are 0.04 ng m-3 of MA, 1.10 ng m-3 of DMA, <0.03 ng m-3 of EA, 1.22 ng m-3 of DEA, 0.29 ng m-3 of PA, and 0.28 ng m-3 of BA. The field blanks are below the limits of detection of the IC method.

2. The calibration principle is weak for the GC/MS method. If the reaction yield is low, you may have an unreacted amine residue in the discarded aqueous phase without knowing it. The only presented link to an independent measurement is one sample from Hong Kong. It is of critical importance to strengthen the calibration part by synthesizing the pure carbamate reference material and use the pure material for quantification.

Response: As shown in Figures 2-4, the peak areas are rather constant under optimized derivatization conditions. We therefore believe that the reaction yields are high and constant for all amines investigated in this study. This is also reflected in the good recoveries (84-99%) obtained by spiking known amounts of amine standard solutions onto the real ambient samples and then measuring the recoveries.

It is true that pure reference materials are often used for quantification. However, for quantifying analytes which need derivatization, it is accepted and often reported in the literature that the calibration curves are made following the same procedures used for real samples, especially in the case that standard reference materials are not commercially available. It can even minimize potential artifacts from the sample pretreatment steps, where both standard solutions and real samples are subjected to same artifacts (if any).

We have included the above discussion in the revised version of the manuscript.

3. A description is lacking of how the reproducibility and recovery data were obtained.

Response: The reproducibility was determined by calculating the relative standard deviation (RSD) of replicated measurements (n=5) of the identical filters that were subjected to the same pretreatment procedure. The recoveries were determined by the analysis of the spiked samples. We have added these in the revised manuscript.

4. The lack of measurement on real samples is in itself a weak point. One typical observation with amine measurements is how sample matrix constituents easily impair the measurement quality. Thus, a greater sample site diversity needs to be used for validation.

Response: We agree with the reviewer that influence from sample 'matrix effect' is often an issue to which one should pay special attention for the development of practical analytical methods. In this study, we examined the matrix effects by spiking the standard solutions of amines to the ambient PM2.5 samples. Our results show that the recoveries are 84-99%, which are considered to be acceptable. The use of selected ion monitoring (SIM) mode for the GC/MS measurements is an advantage for eliminating potential interference from sample matrix (or from the sample pretreatment steps) because it greatly enhances the selectivity (by monitoring the characteristic fragment ions selected) and sensitivity of the method. The analytes are identified when the following two criteria are met: (1) the chromatographic peaks for the unknown and standard

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samples coincide in retention time, and (2) the intensity ratios of the characteristic m/z of the unknown and standard peaks agree within ±15%. We have added these in the revised manuscript. We actually have applied this method to ambient PM2.5 samples collected in Hong Kong during an intensive field campaign. As pointed out at the end of this manuscript, we will present those data in a separate manuscript, discussing the seasonal variation, sources and atmospheric implications. However, we have added measurement results from additional five samples and compared between GC/MS and IC results in the revised manuscript (please see Figure 7 which replaces Table 3).

5. If possible, isotope labelled target amines should be used as internal standards for GC/MS to improve the quality control (is available for several of the target amines). In addition, techniques as standard addition quantification will improve the QA/QC part substantially, both for the GC/MS and the IC.

Response: We agree with the reviewer that the use of isotope labelled analytes as internal standards is always of advantage for accurate quantification. Unfortunately, we did not use the isotope labelled amines in this study because they are very expensive. However, we made very careful quality assurance for our measurements (e.g., analyzing samples spiked with amine standards and checking procedural blank). Please see the ‘Quality assurance’ part.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 2127, 2014.