

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 #2

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General comments

This paper reports the evaluation of two different analytical methods (i.e., GC/MS and IC) for determination of low-molecular-weight alkyl amines in atmospheric aerosols. Because low-molecular-weight aliphatic amines is likely involved with particle nucleation as well as chemical transformation of particles, measurements of alkyl amines in various ambient environments are valuable in providing information on origins of organic aerosols. In this paper, the procedures for evaluation and optimization of the amine analysis are well organized. In my opinion, however, the manuscript lacks the analysis using the ambient aerosol samples in the evaluation and optimization of the methods. This is an important point because the analytical result from ambient aerosol samples is expected to be different in chemical mixture from that with authentic standards in laboratory experiments. Moreover, descriptions on IC peak assignments include much ambiguity and need to be clarified. I recommend its publication in AMT after some revisions raised below.

Specific comments

(1) P.2134, L.17-20: I cannot understand what “a spiked sample” is. The authors state that “real samples are spiked with known amounts of amine standard.” Is that a sample with internal standard? Doesn't this mean that individual amines in ambient aerosols are mixed with corresponding amine standards? Please clarify this.

Response: We first measured a filter punch without spike, and then measured the second punch from the identical filter that was spiked with known amounts of amine standards. The differences between these two measurements were divided by amounts of amines spiked to calculate the recoveries for individual amines. We have clarified this point in the revised manuscript.

(2) Fig. 2: To investigate the effect of pH, did the authors use the amine standards? How did they control or change pH? Is the dependence on pH applicable to any cases with various concentration ranges of each amine? The authors should clarify these

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points.

Response: We used the standard solution of amines to investigate the effect of pH on derivatization efficiency. The pH of the standard amine solution was adjusted with 1 M HCl or 1 M NaOH and measured with a pH meter. If the concentrations of amines are higher, the reaction solution is more alkaline, which actually favors the completeness of the reaction as shown in Fig. 2.

(3) P.2139, L.6-11: Based on the analytical result from one sample (Table 3), the authors state that the concentrations of amines measured by the GC/MS are higher than those measured by the IC. They attributed this difference to evaporation losses of amines during the sample concentration and SPE separation procedures. However, this result is true for just one sample, and is this applicable to the other 23 samples which the authors obtained in this study? The authors should show how representative the analytical result is.

Response: We have measured additional five samples. The results are rather consistent with those already shown in Table 3 in the AMTD version of this paper, showing that the concentrations of amines measured by the GC/MS method are higher than those measured by the IC method. We have included the results from these 5 samples in the revised manuscript. Note that Table 3 is now replaced by Figure 7, showing the comparison of GC-MS method with IC method for the determination of ambient alkyl amines in PM_{2.5} samples. Unfortunately, we do not have enough materials left for IC analysis of the other 18 samples because they were used for other analysis.

(4) Table 2: The authors should add LOD in ng m⁻³ under the sampling condition of the ambient aerosol.

Response: Following the reviewer's suggestion, we have added the LOD in ng m⁻³ in Table 2 in the revised manuscript.

(5) Fig. 6: The authors state that they used the cation-exchange cartridges to remove

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the interfering cations. Even if 85% of TMA was lost by evaporation, the remaining 15% TMA peak should appear in the IC chromatogram (Fig. 6b). Where can we see the TMA peak in the chromatogram after the SPE pre-separation? Or if it is absent, then how did the authors estimate that "85%" of TMA was lost?

Response: To explore the absence of TMA in Fig. 6b, we tested 10-factor, 20-factor and 30-factor concentrated TMA standard solutions, which enables the determination of remaining ~15% of TMA. We have clarified this point in the revised manuscript.

(6) Fig. 6(b): How did the authors assign peaks after the pre-separation? Did they use amine standards to assign each of them? I would like to point out that on the lower left side of the peak 9 in Fig. 6(b), there seems to be another peak overlapped with peak 9. All of these points should be clarified.

Response: The peaks were identified by matching the retention times with measurements from individual amine standards. The reviewer is right that there is a small peak on the lower left side of peak 9, which is peak 8 (Ca²⁺). We apologize for this oversight and the mistake made on the shift of retention time. We have corrected the peak number and the retention time in Fig 6(b) in the revised manuscript.

(7) Introduction: I suggest the authors to add the following references regarding aliphatic amines in the Introduction section. (On atmospheric reactions of aliphatic amines) Angelino et al., *Environ. Sci. Technol.*, 35, 3130-3138, 2001. Murphy et al., *Atmos. Chem. Phys.*, 7, 2313-2337, 2007. (On marine sources of DEA and ON) Miyazaki et al., *Atmos. Chem. Phys.*, 11, 3037-3049, 2011.

Response: In the revised manuscript we have added the references suggested by the reviewer.

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