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Atmospheric Measurement Techniques Discussions

Interactive comment on "Quantitation of nine alkyl amines in atmospheric samples: Separating structural isomers by ion chromatography" *by* Bryan K. Place et al.

Anonymous Referee #1

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This manuscript presents a method for quantification of atmospheric amines by ion chromatography. Detection and quantification of amines is an important area of research as few studies have focused on understand which amines are present beyond the methylamines. This is important work to publish to aid other in quantifying atmospheric amines. There are a few concerns about the manuscript in its current form. The loss of detection of magnesium and calcium during method testing suggests issues related to the IC method (improper suppressor current for eluent concentration) is concerning. As is the lack of blank filter samples analyzed to address potential issues in background especially since the glassware needed to be specially cleaned. Expanded comments on each of these issues and other areas are below.

Are there shifts in retention time in mixed cation-amine standards? Maybe cases where NH4+ or K+ are many times higher than the amine concentration? For your example chromatograms (not real samples) you are showing the amine and cations separately but I wonder if there are changes to retention time with increase cation concentration or differences in the peaks based on the matrix. And is it really appropriate to analyze the standards separately when determining concentrations in complex (real) samples. It seems that applications of this method might be in samples where the amine concentrations are much lower than other cation species. It would be helpful to address potential limitations, if they exist, for the upper end of cation to amine ratios.

Pg 4-5: optimized separation It would be helpful if you want others to use the method you've developed to include the text of the Chromeleon method file in the supplement. You are also missing important information including suppressor current, re-equilibration time, and injection volume. What is the typical pressure in the system?

Pg 5 Line 10-13: How much contamination do you see without the involved cleaning procedure? Do you see amines or just cations? Where could background amines be coming from?

Pg 5 Line 29: What is a calibration blank? The zero point in the calibration curve? Please explain in the manuscript. It might be nice to show an example in the supplement. This would also help to explain the peaks related to changes in the eluent.

Pg 6: BB samples Were blanks analyzed to determine background? Based on your thorough glassware and storage container cleaning procedure it seems like there might be background on your filters due to handling the filtering process. To report atmospheric concentrations without taking into account the filter/procedure blanks is concerning.

Pg 8: 35 Can you really separate Mg and Ca from the amines? In Fig 1 there appears to be a peak in amine trace at the same time Ca elutes. It is unclear to me what this peak is and where MBAH+ comes out relative to Mg and Ca. The loss of the ability to

detect Mg and Ca complicates this but it is an important consideration since Mg and Ca are commonly found in atmospheric aerosols. The change in the ability of detect Mg and Ca is very concerning will make it difficult for others to use your method.

Pg 9: 18 Could some range of variability be related to baseline noise from a failing/failed suppressor? See comment below related to loss of Mg and Ca detection.

Pg 10: 32 How long had the column been used when the degradation occurred? Is this method realistic to use for regular analysis if the column degrades with time. With so many peaks, often at low concentrations, it is critical to know when everything elutes.

Pg 12: 3-9 Loss of Mg and Ca is likely related to the suppressor no longer working as it should. In my experience Mg and Ca are the first to go when a suppressor stops working. Was it replaced with a new one (that worked with a traditional CS12 method)? There could be changes to the sensitivity of other species if the suppressor stopped working properly, especially those with the later retention times. We've observed that if you aren't controlling the current properly for the low concentration of MSA in the eluent you can go through a lot of suppressors. The manual for the SRS300 provides guidance for calculating the correct current setting. Please discuss the suppressor setting and potential implications if it wasn't working as expected.

Pg 13: 4 Please explain what the method blank is.

Comments on Figures:

Please include nominal concentrations of the cations and amines or someway to know if the change in peak height is a function of the method parameters or concentration. For example you suggest comparing Figure 3a and 1b (Pg 10 line 33) to see the shift in retention time - I can't help but notice the y-scales are very different. When you are losing peaks and seeing column degradation it is important to know if the peak height/area is also changing. The statements about the calibration curves suggest the areas didn't change over the course of your study but by including the concentration

information for each chromatogram/injection you would clearly show that.

In Figure 3b I like the separation of the types of amines. I think it would be helpful for the comparison between a and b to do the same for a, if possible. Or some type of color-coding by type.

Figure 5a: add a summation sign in y-axis label to clarify it is the sum of the amines. And add in the caption it is the sum of the methyl and ethyl amines as you state in the text. Also add what the error bars represent.

Figure 5 b: is this also ratio of the sum of the methyl and ethyl amines to ammonium?

Table 2 seems more appropriate for the supplement.

Minor Comments:

Pg 4: 9-11 Please define all amines here so the definitions are easily found in one place.

Pg 7:2 Remove therefore

Pg 10: 15 Please define ppqv

Pg 14: 1-2 Did the PM2.5 concentration need to be in excess of 200 ug/m3 for samples to be collected during the 8 hr period? Please clarify.

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