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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 #2

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The paper presents a detailed development of an analytical method for alkyl amines in aerosol particles based on ion chromatography. After a detailed optimization of several parameters, the method was applied to some field samples from biomass burning events. The topic is of high importance; selective and sensitive well-characterized analytical methods are strongly needed in atmospheric measurements. The paper is well written however, there are some points that need clarification before publishing:

Page 3, line 8: The authors point out, that the matrix of atmospheric samples can cause problems in the analytical measurements (which is true). Still I think that the problem of matrix effects is not too much discussed in the manuscript concerning this analytical method. For example on page 10, line 10/11 the authors write that using a

pre-concentration column, you can eliminate negative charged and neutral disturbing ions. Did you test this here? And still the separation of the amines from other dominating cations that are for example present in marine samples in high quantities (sodium, ammonium) would be a problem – they would be enriched using a pre-column. This could affect again the separation of the (lower concentrated) amines

Generally, I was wondering if you performed some further tests regarding matrix effects. Did you for example perform standard addition (to prove the accuracy of the method) with the field samples? This would be a high value in the method validation.

Page 6, Chapter 2.5 and 2.6. The authors use different types of field samples for the measurements of the amines with their method: nano Moudi aluminium foils and PM 2.5 filter samples. I was wondering if you considered measurements of field blanks, e.g. did the filter material and the sampling technique affect the sampling of the amines? Did you observe artifacts (e.g. from the gas phase) using the filter samples? This topic was addressed for example in Müller et al. (2009) in ACP that the authors cite here. Could you comment on this topic?

Page 8, line 13 and following: The authors report about the temperature effect in the IC separation. Also other authors have used temperatures above 50 °C e.g. van Pinxteren et al., (J Atmos Chem (2015) 72: 105, doi:10.1007/s10874-015-9307-3), have used a column temperature of 60°C in the IC separation of aliphatic amines. Maybe you can include previous publications that regard temperature effects in IC separation.

Page 8, line 32: "... have detected large quantities of MEA and DEA in ambient air..." do you refer to gas phase or aerosol measurements in the cited literature? Please specify.

Page 10, chapter 3.1.3 / Page 11, chapter 3.1.5: The authors discuss the problem of decreasing separation due to column instability. The authors mention that the high column temperature might accelerate this process. I am however sceptic if it is a good and practical solution to measure all samples at 30 °C and to repeat all measurements

that indicate the presence of DEA or TEA at higher temperatures. Do you have any marker for column stability that indicate when you should replace the column? As the column degradation occurs gradually you might lose peak information in your samples quite soon (especially regarding field samples).

Page 12: line 3 and following: The loss of calcium and magnesium. Could you speculate about the loss? Is it irreversible bound to the column surface? In the conclusion, you describe that ion chromatography methods often suffer from interferences with magnesium or calcium and the present work overcomes this problem. However, it can not be the solution to have an "unfortunate and unexplained" loss of these elements. Did you consult the manufactures about this problem? What is your future strategy here?

Page 12, line 37: unclear phase; did you mean "... in the size range of 100 to 560 nm"? Please clarify.

Page 13, line 21 and following: The high ratio of amines to ammonium is very surprising. As one explanation, the authors state that marine influences could be an explanation for this observation. While amines can indeed have significant marine sources (as also stated by the authors), also ammonium would be elevated then (as also shown in the cited literature, e.g. Gibb et al). So do you think that there could be a marine source producing so much more amines than ammonium? Is there any evidence in the literature?

Page 13, line 22: The authors might consider including the recent publication of van Pinxteren et al. 2015, as they reported high concentration of the amines in a marine region close to the Cape Verdean islands.

Page 13, line 28-31: Did you measure other marine tracers (like MSA) to test the hypothesis?

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