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Atmospheric Measurement Techniques Discussions

Interactive comment on "Measurement techniques of identifying and quantifying sulfur compounds in fog and cloud water" *by* Eleni Dovrou et al.

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We would like to thank Referee #1 for the comments that have helped improve the manuscript. The reviewer comments are in italic followed by our replies in normal text.

Major comments:

Comment 1 ("Title"): First of all, the title of the paper needs to be revised to better represent the main contents of the manuscript. For example, this work focuses exclusively on the AMS and IC methods, although there are other techniques available for HMS quantification. Also, the current title reads as if the method targets a range of sulfur containing compounds, but in reality it is primarily for HMS.

The title has been revised to: "Measurement techniques of identifying and quantifying

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Discussion paper

Hydroxymethanesulfonate in cloud water and particulate matter”

Comment 2 (“IC method information”): Secondary, more analytical details on the IC method are necessary. Information such as eluent composition, flow rate, column length, column temperature etc should be reported. For the quotation of detection limit in uM (e.g. page 7, line 14), the injection volume also matters. As this paper intends to present an improved IC method for HMS quantification, general aspects for evaluating and QA/QC an analytical method, such as calibrations curve, method precision (through repetitive analysis) and accuracy (through e.g. recovery analysis), and method robustness are important to be presented and discussed. It is also necessary to discuss the limitations and potential artifacts with the improved IC methods more thoroughly. For example, the stability of HMS is pH dependent. Loss of HMS is more severe at higher pH. The pH of the IC mobile phase is basic for eluent using sodium carbonate. The effect of HMS destruction during IC separating should be evaluated. Other issues such as the stability of the standard solution and potential loss of HMS in samples during storage are also important to discuss.

The eluent composition and flow rate are presented in Section 2.2.2 page 6 lines 1-2 of the revised manuscript. We have added the column and compartment temperature, delivery speed and delivery sample volume on page 6 lines 2-3: “The column and compartment temperatures were both 25oC and the delivery speed and delivery sample volume for the analysis were 4 mL/min and 4 mL.” Information regarding the calibration curves, detection limit, accuracy, precision and robustness of our method have been added in the revised manuscript on page 7 and 8 lines 37-39 and 1-5, respectively: “The detection limits were determined by conducting sample runs of different concentrations. The concentration, C, for which the IC could not provide a clear peak was identified and samples runs were conducted for concentrations C+n, where n=0.2 mÎIJ. The concentration for which the baseline and the peak were clearly distinguishable was defined and 6 runs were conducted for this specific concentration to verify it. The uncertainty was determined, <1%, considering 99% confidence interval therefore

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it was concluded that for the system used in this work the lowest corresponding concentration, for which a measurable peak was efficiently detected, is the detection limit. Standards were prepared before each experiment to ensure their stability and avoid possible decomposition if stored for a prolonged period of time.", page 7 lines 23-24: "Each sample analysis was conducted 4 times with individual sample preparation before each analysis. The area of the peaks was almost identical for sulfate and HMS in all 4 runs, with a difference only of 0.06 and 0.08 mM, respectively.", page 9 lines 3-8: "The eluent is also a technical aspect that differs between the two columns. The AS12A is an anion carbonate column, thus the eluent is neutral with respect to the pH, whereas the AS22 column is an anion hydroxide column, thus the eluent is basic with respect to pH. The stability of HMS has a strong pH dependence as it dissociates at high pH. The use of a neutral pH eluent avoids HMS decomposition during analysis. The majority of columns with alkyl quaternary ammonium functional group require neutral pH eluent, which also results in efficient separation of sulfur species." The pH of the eluent used for the AS12A was measured $\sim$7. The limitations of the method are presented in page 7 lines 30-32: "HMS and bisulfite/sulfite were not able to be separated as they had the same retention time in this case as well (Fig. 4). The efficiency and the clear separation of the peaks that the column provides allows for quantification of HMS when bisulfite/sulfite are not present." and page 8 lines 20-24: "If the concentrations are at lower levels, corresponding to <=30 μM of HMS, value experimentally estimated under laboratory conditions, which is equivalent to <=2 μg·mˆ(-3), assuming filter collection of ambient samples with sampling rate of $\sim$80 L·min, sampling time of $\sim$6 hr and extraction volume of 20 mL, an aliquot of which, 4mL, is used for sample analysis, and sulfate is of equal or higher concentration, the peaks corresponding to HMS and sulfate have lower area signals and will be treated as one peak. For pH=12 the peaks could not be distinguished."

Minor comments:

Comment 1 ("Page 2 line 2"): HSO3- can dissociate at pH < 6.

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We have clarified our statement on the revised manuscript in page 2 line 3: “In cloud and fog water, SO_2 reacts with water producing bisulfite (HSO_3ˆ-), when 3<pH<6, which further dissociates to form sulfite (SO_3ˆ(2-)) when pH>6.”

Comment 2 (“Page 3 line 12”): define RSMS and ATOFMS.

We have defined the acronyms RSMS and ATOFMS in the revised manuscript in page 3 lines 15-16: “(rapid single-particle mass spectrometer: RSMS, aerosol time-of-flight mass spectrometer: ATOFMS)”

Comment 3 (“Page 7 line 6”): what is 4x200nm corresponding to?

The statement 4x200 nm has a typo, it should be mm, and corresponds to diameter and length of the column. It has been corrected in all parts of the revised manuscript that it is mentioned. Page 7 lines 14 and 27: “(diameter=4 mm and length=250 mm of the column)” and “(diameter=4 mm and length=200 mm of the column)”.

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