

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 the Referee #2 for the comments that have helped improve the manuscript. The reviewer comments are in italics followed by our replies in normal text.

It is unfortunate that the authors decided not to test the AG18-AS18 columns used in the URG AIM-IC. I understand that testing a new column would require additional laboratory work, but I really believe it would significantly extend the usefulness of the manuscript, as the AIM-IC is being used by many researchers in China. In the reviewer response, the authors note that they expect that the columns “will not allow efficient separation of HMS and sulfate”, but this is highly qualitative and likely depends on the eluent and run conditions. I urge the authors to reconsider adding the AG18-AS18

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column testing to their work here.

Regarding the use of the AG18-AS18 columns: The separation efficiency of liquid chromatography columns is largely based on their functional groups. The conditions, temperature, sample volume and flow rate of the AG18-AS18 columns are the same as the AG22-AS22 columns according to technical specification of the AS18 column found in the manufacturer's website. Therefore, they will not affect the efficiency. Based on the functional groups of the AG18-AS18 columns we do not expect efficient separation due to the hydrophobicity of the analytical column and its functional group. In addition, the common eluent used is KOH. We chose the use of columns that require neutral eluent to avoid possible decomposition of HMS during the analysis which can be rapid at elevated pH.

Major comments:

Comment 1 ("Title"): The goal of this work, as stated through the paper, is to examine methods for the measurement of HMS in PM. Therefore, I suggest that the authors revise the title of their manuscript to specifically mention HMS and PM, rather than fog and cloud water.

The title has been revised to: "Measurement techniques of identifying and quantifying Hydroxymethanesulfonate in cloud water and particulate matter"

Comment 2 ("Page 7, Line 19 and Page 8, Lines 5-6"): The authors state "this method may result in noisy spectra for concentrations below 1 ppb" when discussing ESI-MS, but the paper cited (Chapman et al.) is from 1990. The signal/noise will depend on the mass analyzer used, in addition to the ionization method, and there have been great advances in mass analyzers and associated sensitivities over the past 30 years. Similarly, the LOD for the ESI-MS method is quoted as $\sim 100 \text{ ug/m}^3$, but again, I expect this would have changed significantly over the time since publication. Therefore, these statements should be qualified, and rather future work should be motivated here to examine current sensitivities on ESI-MS instruments.

We agree with the referee on the comment that there have been important advances in mass analyzers, and it is possible that the concentration and LOD mentioned might be improved. However, the Chapman et al. (1990) paper is, to our knowledge, the main study that describes the use of ESI-MS for the identification and quantification of HMS. Therefore, we believe that reporting lower LODs from more recent studies that do not consider HMS will not be accurate for the purpose of this study. We have included a statement emphasizing that due to improvements in the instrumentation over time such LODs might be improved.

The statement is in page 3 lines 29-33 on the revised manuscript: “Chapman et al. (1990) conducted an exploratory study reporting that the quantitative detection limit for HMS can be in the order of $100 \mu\text{g} \cdot \text{m}^{-3}$, for typical sampling conditions, using an ESI-MS. Since 1990 there have been advances in the ESI-MS technology that could possibly result in lower detection limits. However, to our knowledge, these technological changes have not yet provided quantitative evidence of lower detection limits with respect to HMS analysis.”

Comment 3 (“Page 8, Line 11-12”): In reviewing Whiteaker et al (2003, Atmos. Environ.) based on the reviewer response, this paper does not cite a lack of sensitivity by the ATOFMS for detecting HMS, making the statement on Line 11 misleading. Rather, Whiteaker et al. discuss the matrix effects of ammonium and sodium, which impact the peak area detected; I cannot find evidence in this manuscript that the LOD for HMS would be high, indicating a lack of sensitivity, and no comparison is provided to other techniques. Therefore, I suggest the authors remove the phrase “and lack of sensitivity” and instead suggest in the paper that a study of the sensitivity of single-particle mass spectrometry instruments to HMS is an area of future work needed (as eluded to now on Page 7, Lines 37-38).

We would like to thank the referee #2 for the comment. The sentence aims to provide a general statement for single-particle mass spectrometry and along with the work of Whiteaker and Prather (2003), the studies of Neubauer et al. (1996 and 1997) are

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cited. In the work of Neubauer et al. (1996 and 1997) it is stated that the assigned ion peak for HMS is “only observed from particles that contain a strong acid or proton donor” and that particles of a specific range were able to be examined. We have remove the statement “and lack of sensitivity” as we agree with the referee that these limitations can fall within the area matrix effects. We also agree on the necessity of stating that the sensitivity of these instruments with respect to HMS requires more detailed study in the future and we have included that statement on the revised manuscript.

The statement is in page 4 lines 26-27: “The sensitivity challenges of these methods with respect to HMS quantification yield the necessity of further study.”

Comment 4 (“Page 7, Line 6-8”): PALMS is a single-particle mass spectrometry instrument. Please correct here. Please also note that the single-particle mass spec papers listed here do not represent a complete list, as implied. Either include “e.g.” in front of the literature list, or conduct a more thorough literature search. Similarly, Section 1.2 describes each of the single-particle mass spectrometry studies listed here, but again, this is only a subset of published work on the subject, which is not reflected in the summaries presented. I’d encourage the authors to consider in Section 1.2 to conduct a more thorough literature search, and rather than describing each paper one-by-one, include a brief overview/summary of the observations.

We have corrected the phrase by including “single-particle”. We included the single-particle mass spectrometry papers that have been used for identification and/or quantification of HMS. We clarify that in the manuscript in the relevant section which is in page 3 line 11: “A variety of technical methods have been used to detect HMS, . . .”.

Comment 5 (“Page 11, Line 12-14”): The addition of the IC LODs and explanation of conversion to ambient mass concentration is very useful. However, please clarify how the LODs were determined and what they refer to, as there as multiple methods and definitions used in chromatography for LODs.

The LODs were determined by conducting sample runs of different concentrations.

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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 $n=0.2$ mM. 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. We wanted 99% confidence interval therefore we calculated the standard deviation to also determine the uncertainty. The uncertainty was very low $<1\%$ therefore we concluded that for our system the lowest corresponding concentration, for which a measurable peak was efficiently detected, is the LOD. We have added this information in pages 7 and 8 lines 38-39 and 1-3, 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 $n=0.2$ mM. 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 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."

Comment 6 ("Page 11, Line 24-27"): I am confused at why a significant underestimation occurred when the elevated baseline was used. How was this determined? Was a calibration curve obtained and then a known concentration run to check? What is "significant" in this case? Please clarify.

We have clarified this information in the manuscript in page 8 and lines 17-20: "When this was applied a significant underestimation of the concentration, $\geq 15\%$ of HMS with 4% uncertainty, of the compounds was observed, therefore the software automatic separation was selected to be used. The percentages of HMS and sulfate were obtained considering the software separation of the peaks and the underestimation was determined by obtaining the calibration curves for sulfate and HMS and examining known concentrations.". A calibration curve was obtained for all the examined compounds and

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a variety of known sample concentrations were tested. In all the cases we concluded that there was an underestimation of up to 15% of HMS, with 4% uncertainty, when the AS22 column was used, which is a significant underestimation.

Comment 7 ("Section 3.2"): What are the uncertainties in the percentages reported? Is reporting to one decimal place appropriate? Where the samples run in triplicate?

Each analysis was conducted 4 times with individual sample preparation before each analysis. For example, when we examined 2mM of HMS and 2mM of sulfate we prepared 4 different samples and analyzed them with IC. 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. Therefore, we concluded that it is accurate to report one decimal point.

Comment 8 ("Section 4"): Add a statement of the required concentration needed to distinguish HMS and sulfate (discussed on page 11), as this seems like it will significantly impact the recommendation of the necessary mass loading for ambient samples.

We have added that the required concentration needed to distinguish HMS and sulfate under the described conditions is $>2 \mu\text{g}\cdot\text{m}^{-3}$ of HMS and that sulfate concentration has to be lower than HMS. The statement is in page 9 lines 25-26: "Using an IC system, the detection limit of quantifying HMS and sulfate is $0.8 \mu\text{M}$ and $0.2 \mu\text{M}$, respectively, and the required concentration needed to distinguish HMS and sulfate was determined to be $>2 \mu\text{g}\cdot\text{m}^{-3}$ of HMS and the sulfate concentration has to be lower concentration than that of HMS."

Additional comments:

Comment 1 ("Section 1.1"): While the pivotal work of Munger et al 1986 (Science) is cited later in the manuscript, it would be highly valuable and most appropriate for this to be cited in the first paragraph of Section 1.1, as it sets the stage for the entirety of this work.

In the revised manuscript we now cite Munger et al. (1986) in the first paragraph of the

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section where the HMS formation is mentioned. Page 1 line 29: “Hydroxymethanesulfonate (HMS; HOCH₂SO₃⁻) is the product of the aqueous-phase reaction between dissolved sulfur dioxide (SO₂) and formaldehyde (HCHO) and is considered an important compound in cloud and fog water (Munger et al., 1986; Dixon and Aasen, 1999; Whiteaker and Prather, 2003).”.

Comment 2 (“Page 2, Line 16-20”): Please provide references for these statements.

These statements refer to a response to a previous comment by the reviewer: “Metrohm MARGA uses a polystyrene/divinylbenzene copolymer with quaternary ammonium groups as functional group for separation of sulfite, sulfate and thiosulfate. Due to the fact that we are using the Dionex IC-5000+ IC model with adjustments in order to have a good separation of HMS and sulfate, compatibility issues might be encountered if we use a Metrohm column. It is possible that if the column used has polystyrene/divinylbenzene copolymer with alkyl quaternary ammonium group as functional group the separation of HMS and sulfate can be achieved, however we can not confidently make that statement. Unfortunately, we do not have access to this system for evaluation.”. The statements results of discussion with technicians from Thermo Scientific, technical documents provided from Metrohm and experimental observations we obtained from ongoing projects.

Comment 3 (“Page 6, Line 27-28”): Rephrase statement “...measurements of HMS have mainly been conducted of fog and cloud water only” as there have been many ambient PM measurements of HMS by single-particle mass spectrometry.

We have rephrased the sentence according to the reviewer’s recommendation. Page 2 lines 31-33: “Measurement of sulfate in ambient PM is common, whereas measurements of HMS have mainly been conducted for fog and cloud water. Studies reporting the presence of HMS in ambient PM using single-particle mass spectrometry have also been conducted (Neubauer et al., 1996; Neubauer et al., 1997; Whiteaker and Prather, 2003; Lee et al., 2003; Dall’Osto et al., 2009).”.

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Comment 4 (“Page 6, Line 30-32”): This statement is confusing as written. Please clarify.

We have clarified the statement in the revised manuscript. Page 2 lines 36-38: “Moreover, for MS, cations can be observed simultaneously in addition to sulfur-containing ions, whereas for IC a specified IC column with high sensitivity for sulfur-containing ions has to be used to identify them.”

All acronyms have been specified in the revised manuscript.

Comment 5 and 6 (“Page 7, Line 29-30” and “Page 7, Line 35”): Single-particle mass spectrometers have several lasers. Please correct “operating laser” to “desorption/ionization laser”. Matrix effects are inherent to the laser desorption/ionization process and have nothing to do with the inlet design, pump configuration, and reflectron. Rather matrix effects are associated with the competition in ion formation. Please correct here.

We have revised according to the reviewer’s recommendation. Page 4 line 4 and line 10: “desorption/ionization laser at 266 nm” and “have been optimized to overcome sensitivity issues by improving the inlet design”.

Comment 7 (“Section 1.2”): This section should describe the previous work of Gilardoni et al (2016, PNAS), who showed the AMS mass spectrum of HMS only. I realize that this paper is cited, but it would be useful for it to be described in the introduction to set the stage for how the current work builds upon this previous work.

We have included more information of the work of Gilardoni et al (2016) in the section 1.2. Page 4 lines 8-9: “Gilardoni et al. (2016) provided the spectrum of HMS using standard samples. During that study HMS was used as a tracer of aqueous chemistry.”

Comment 8 (“Page 7, Line 13”): Consider replacing “RSMS, PALMS, AToFMS” with “Single-particle Mass Spectrometry” as these are simply three of many types of single-particle mass spectrometers.

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We have revised according to the reviewer's recommendation. Page 3 line 21: "1.2 Previous work identifying HMS using Single-particle Mass Spectrometry, Capillary Electrophoresis and reverse-phase HPLC".

Comment 10 ("Page 7, Line 29"): Correct "AToFMS" to "ATOFMS".

We have changed the "AToFMS" to "ATOFMS" in the manuscript.

Comment 11 ("Page 8, Line 5-6"): Please move these sentences the first paragraph of Section 1.2, where ESI-MS is discussed.

We have moved these sentences as suggested in page 3 lines 29-33 in the revised manuscript.

Comment 12 ("Page 8, Line 6-7"): Please clarify this sentence. Song et al. (2018) did detect HMS by SPAMS, even though the opposite seems to be stated in this sentence, with the opposite statement then in the following sentence.

We have clarified this sentence in the revised manuscript. The study by Song et al. 2019 (published) stated that the detection limit using AMS and SPMS could be lower than the detection limit reported by Chapman et al. (1990). In addition, the authors state that the SPMS data revealed that approximately 10% of HMS-containing particles in the total particles counts during haze events but they could not provide a quantitative measure particle as HMS, possibly due to fragmentation. Therefore, even though in that study HMS was able to be identified and it is stated that the detection limit could be lower than reported in the past, no quantitative information could be retrieved. Page 4 lines 20-21: "Although it was stated that the detection limit could possibly be lower using AMS and SPMS (Song et al., 2019) than the concentration reported by Chapman et al. (1990), $100 \mu\text{g} \cdot \text{m}^{-3}$ using ESI-MS,, such lower levels of HMS were not able to be detected using these methods. In their study, Song at al. (2019) were able to identify HMS as a component of SOA but they could not quantify it, likely for the reasons outlined below in this work."

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Comment 13 (“Page 9, Line 17”): Can you provide references here for the common use of this column?

The main reference is the technical report of the column provided by the manufacturer. The specific column, based on our experience, and the information provided by the manufacturer is the most common column for inorganic analysis.

Comment 14 (“Page 10, Line 7”): Please clarify “other species” here.

The phrase “the other species” refers to the other sulfur-containing compounds presented in Figure 1; sodium bisulfite, sodium sulfate and ammonium sulfate. We have clarified in the revised manuscript in page 6 lines 26-27 in the revised manuscript: “other species (sodium bisulfite, sodium sulfate and ammonium sulfate)”.

Comment 15 (“Page 10, Line 14”): Fix reference formatting here.

The reference formatting has been corrected in the revised manuscript.

Comment 16 (“Section 3.2”): Some of this section repeats the methods and could be condensed.

In the experimental section general information is provided however, in the section 3.2 we present more detailed information for each examined column pair.

Comment 17 (“Page 13, Line 1”): I’m confused by the statement “Applications of both IC and AMS methods to the same ambient samples in the future” as isn’t a finding of this work that the AMS is unable to distinguish between HMS and sulfate. Also, I’m confused because I thought these samples were not available for analysis based on the reviewer response. Please clarify.

We have clarified this sentence as our intent was to point out that it would be useful to use the methods we describe in this work to analyze the ambient samples, or similar samples from severe haze events and specifically samples from similar conditions of the work of Wang et al. (2014). Page 10 line 1 in the revised manuscript: “Applications

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of both IC and AMS methods to the same ambient samples from similar conditions of the January 2013 haze event”.

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