

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

Anonymous Referee #2

Received and published: 1 June 2019

Dovrou et al describe the laboratory measurement of HMS and sulfate by IC and AMS. A useful aspect of this work is the evaluation of the AMS measurement of HMS in the presence of other sulfur-containing species, which builds upon the work of Gilardoni et al (2016, PNAS), who showed the AMS mass spectrum of HMS only. Line numbers here refer to those in the tracked changes version of the manuscript.

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

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eluent and run conditions. I urge the authors to reconsider adding the AG18-AS18 column testing to their work here.

Major Comments:

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.

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.

Page 8, Lines 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).

Page 7, lines 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.

Page 11, Lines 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.

Page 11, lines 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.

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

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.

Additional Comments:

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.

Page 2, Line 16-20: Please provide references for these statements.

Page 6, Lines 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.

Page 6, Lines 30-32: This statement is confusing as written. Please clarify.

Please write out all acronyms used throughout the manuscript (as one example (there are others) – see use of RSMS and ATOFMS on Page 7, Line 7).

Page 7, Lines 29-30: Single-particle mass spectrometers have several lasers. Please correct “operating laser” to “desorption/ionization laser”.

Page 7, Line 35: 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.

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.

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.

Page 7, Line 29: Correct “AToFMS” to “ATOFMS”.

Page 8, Lines 5-6: Please move these sentences the first paragraph of Section 1.2, where ESI-MS is discussed.

Page 8, Lines 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.

Page 9, Line 17: Can you provide references here for the common use of this column?

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Page 10, Line 7: Please clarify “other species” here.

Page 10, Line 14: Fix reference formatting here.

Section 3.2: Some of this section repeats the methods and could be condensed.

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.

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