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Atmospheric Measurement Techniques Discussions

Interactive comment on "Determination of atmospheric organosulfates using HILIC chromatography with MS detection" *by* A. P. S. Hettiyadura et al.

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Anonymous referee #4 general comments: "This is an interesting piece of work focusing on analytical method optimization for atmospherically relevant organosulfates in ambient aerosols. The authors utilized a HILIC column to achieve a better separation of small organosulfates that mainly originate from isoprene oxidation. What is notable here is that the authors have synthesized a series of authentic standard compounds to optimize the separation and quantification of these compounds. The authors present their newly optimized method in a clear manner and it should be relatively easy to replicate the method for people who have been experienced in HPLC/MS techniques. I

recommend the paper be accepted subject to minor revisions. My more specific questions/comments are given below."

Response to referee #4 general comments: We agree with the referee about the scope of this manuscript. As the referee has stated, the purpose of this manuscript is to clearly communicate the sensitive and accurate quantification method that we developed using HILIC-MS/MS. Indeed the synthesis of organosulfates provides accurate quantification of organosulfates in atmospheric samples. We thank referee for their careful review of our manuscript. We have addressed the referee's specific questions and comments in the point-by-point response letter below.

Referee #4 comment 1 - Pp. 12590 line 4: "The detection of organosulfates is not analytical challenging. Do the authors mean 'quantify' rather than 'measure' here? Can the authors be more specific about the challenge in measuring organosulfates here (e.g. lack of authentic standard compounds)?"

Response to referee #4 comment 1: We agree with the referee that it should be corrected as "quantify" rather "measure" and we have revised this sentence to include why it is challenging to quantify organosulfates.

The text at line 4 Pp. 12590 previously read: "Organosulfates have, however, proved analytically challenging to measure. This study presents a sensitive new analytical method for the quantification of organosulfates based upon ultra-performance liquid chromatography with negative electrospray ionization mass spectrometry (UPLC-ESI-MS/MS)."

The text at line 4 Pp. 12590 has been revised to read: "Organosulfates have, however, proved analytically challenging to quantify, due to lack of authentic standards and the complex sample matrix in which organosulfates are observed. This study presents a sensitive and an accurate new analytical method for the quantification of organosulfates based upon ultra-performance liquid chromatography with negative electrospray ionization mass spectrometry (UPLC-ESI-MS/MS) with the aid of synthesized organosulfate standards."

Referee #4 comment 2 - Pp. 12590 line 17: "The authors may reconsider the use of 'superior' here. Is the ultrasonication really 'superior' when the difference between the two methods is so small? The authors may opt for the ultrasonication based on the result obtained in their study but the ultrasonication is certainly not superior to the rotary shaking considering the potential negative artifact formation from acoustic cavitation."

Response to referee #4 comment 2: We agree with the referee that the term "superior" may be replaced with "better" to more clearly convey the results of this study, as both methods were found to be equally efficient with a small difference in the precision. While ultrasonication can form negative artifacts due to acoustic cavitation the results of this study demonstrate that no such negative artifacts result for the target analytes in the organic-solvent rich extraction. The abstract and discussion in "3.4 optimization of extraction" have been revised accordingly: In the abstract, the text at line 17 Pp. 12590 has been removed: "Sonication was determined to be the superior method for its better precision."

The text at line 17 Pp. 1259 has been replaced with: "Sonication was determined to be a better method due to its higher precision with compared to rotary-shaking." The text at "3.4 optimization of extraction", line 10 Pp. 12602 previously read: "Extraction by sonication has previously been associated with negative artifacts, due to the formation of hydroxyl radicals and heat, which can degrade certain organic compounds (Mutzel et al., 2013; Riesz et al., 1985). Rotary shaking, on the other hand, is considered to be a milder method of extraction that is not subject to these potential problems."

The text at 3.4 optimization of extraction, line 10 Pp. 12602 have been revised to read: "Previous studies have observed formation of negative artifacts during sonication due to acoustic cavitation (Mutzel et al., 2013;Riesz et al., 1985). Rotary shaking, on the other hand is considered as a milder method of extraction."

The text at "3.4 optimization of extraction", line 19 Pp. 12602 has been removed: "Both methods were found to be accurate within 100±15% for 95th percentile values and did not introduce artifacts into extraction."

The text at "3.4 optimization of extraction", line 19 Pp. 12602 has been replaced with the following sentences: "Both methods were found to be accurate within 100±15% for 95th percentile values and did not introduce artifacts into extraction. Formation of negative artifacts during ultrasonication due to acoustic cavitation is found to be significant in highly aqueous extraction solvents (Riesz et al., 1985). Therefore the reason for negligible negative artifact during ultrasonication in this study may be attributed to use of an organic rich extraction solvent (acetonitrile: water, 95: 5)."

Referee #4 comment 3 - Pp. 12590 line 24: "I do not think this sentence belongs here. The abstract should highlight the most important results and conclusions of the manuscript. A vague future research plan does not add any useful information to the abstract."

Response to referee #4 comment 3: We agree with the referee and have removed this sentence, replacing it with a conclusion sentence.

The text at line 24 Pp. 12590 has been removed: "Future research will focus on the development of additional organosulfates standards, expansion of this UPLC-MS/MS to include more target molecules, and the application of this method to assess temporal variations in organosulfates in ambient environments."

In its place, the following text has been added at line 24 Pp. 12590: "The developed UPLC-MS/MS method is highly sensitive and accurate in quantification of smaller and highly polar organosulfates in the atmosphere and hold promise for extension to biogenically-derived organosulfates."

Referee #4 comment 4 - Pp. 12591 line 23 onwards: "I feel that the citations in the introduction are not very comprehensive and sloppy. I'd expect the authors to cite most of available papers at proper places, as there aren't hundreds of papers dealing with organosulfate analysis."

Response to referee #4 comment 4: We thank the referee for bringing this to our attention. While it is not our intention to review all manuscripts about the detection of organosulfates in ambient aerosol, agree that it is important to cite prior works in a clear and concise manner. In the revised manuscript, we have used the notation "e.g." as a means of indicating that we are providing key examples of prior detection methods and do not constitute a comprehensive review.

The following text at line 22 onwards Pp. 12591 has been removed: "Due to the atmospheric abundance of organosulfates and their importance in SOA formation, analytical methods have been developed to detect them in ambient aerosol by Fourier transform infrared spectroscopy (FTIR) (Hawkins et al., 2010; Maria et al., 2003), in-situ single particle mass spectrometry (Farmer et al., 2010; Froyd et al., 2010), and capillary electrophoresis (CE) and liquid chromatography (LC) coupled with negative electrospray ionization ((-)ESI) mass spectrometry (MS) (Olson et al., 2011; Surratt et al., 2008; Yassine et al., 2012)."

It has been replaced with: "Due to the atmospheric abundance of organosulfates and their importance in SOA formation, analytical methods have been developed to detect them in ambient aerosol by a range of off-line and on-line instrumentation, including Fourier transform infrared spectroscopy (FTIR) (e.g.(Hawkins and Russell, 2010;Maria et al., 2003)), in-situ single particle mass spectrometry (e.g. (Farmer et al., 2010;Froyd et al., 2010)), capillary electrophoresis (CE) (Yassine et al., 2012) and liquid chromatography (LC) coupled with negative electrospray ionization ((-)ESI) mass spectrometry (MS) (e.g. (Olson et al., 2011a;Surratt et al., 2008;Wang et al., 2013))."

Referee #4 comment 5 - Pp. 12599 lines 3-4: "Significant figures are not consistent in these numbers. Do the authors guarantee zero after a decimal point of 25.0, 50.0, 100.0, 300.0 and 500.0 μgL-1 standard solutions? Since the manuscript deals with a quantification method, I feel it is important to indicate the uncertainty properly."

Response to referee #4 comment 5: We agree with the referee that the significant figures should be consistent (at three) and we thank the referee for bringing this to our attention. The text at line 3-4 Pp. 12599 has been removed: "The linear range of each authentic standard was determined using a series of standard solutions at 0.5, 1.0, 25.0, 50.0, 100.0, 300.0 and 500.0 μg L-1 that were prepared in organic mobile phase."

The text at line 3-4 Pp. 12599 have been revised to read: "The linear range of each authentic standard was determined using a series of standard solutions at 0.500, 1.00, 25.0, 50.0, 100., 300. and 500. μg L-1 that were prepared in organic mobile phase."

Referee #4 comment 6 - Pp. 12601 line 8 and corresponding references: "Gomez-Gonzalez should be Gómez-González."

Response to referee #4 comment 6: We thank the referee for bringing this to our attention. All occurrences of "Gomez-Gonzales" has been revised to "Gómez-González, " including p. 12601 lines 7-9, 17-20, p. 12605 17-20, p. 12608 lines 25-30.

Referee #4 comment 7 - 3.5 Application to ambient aerosol: "It is clear to readers that the separation is better with a HILIC column. How about the quantification? Have the authors compared the quantitative results from the HILIC and RP methods for atmospheric samples? I think the community likely adopts the authors' new method widely if the authors can add this information here to demonstrate the advantage of the HILIC method."

Response to referee #4 comment 7: We thank the referee for bringing this important point to our attention. This provides us with an opportunity to clarify the utility of reversed-phase (RP) and HILIC methods, which are complementary to one another, but are each better suited for different organosulfates. Moreover, the current HILIC method specifically targets carboxy and functionalized organosulfates that are not retained or separated from the sample matrix by RP methods. In addition, the comparisons we can make between the quantitative capabilities of HILIC and RP methods are limited, because an RP method has only been validated for of one of the target analytes in this study (benzyl sulfate). To the revised manuscript, we have added a discussion of the quantitative advantages of HILIC, guidance for others who may use this method, and a comparison of the quantitative results from our HILIC method to other methods.

Following paragraph is added to "3.3 Method validation" – Pp. 12602 line 4: The precision and the sensitivity of this method make it well suited for the quantification of organosulfates in ambient aerosol. The extracted filter samples from Centreville contained 18 – 48 μg organic carbon and yielded methyl sulfate, hydroxyacetone sulfate, lactic acid sulfate and glycolic acid sulfate concentrations within the linear ranges of their respective calibration curves. For accurate quantitation by LC-MS , organosuflates that utilize quantitation standards must be matched to the analyte (Staudt et al., 2014). When compared to prior studies that used authentic quantitation standards, the HILIC method proves to have comparable quantitative capabilities, with some notable differences. For example, the linear range obtained for lactic acid sulfate and glycolic acid sulfate in this HILIC method using a BEH amide column, ranges 25.0 – 300 μg L-1 compared to 5.0 – 500 μg L-1 reported by Olson et al., (2011) for their HILIC method which used an underivatized HILIC column (Olson et al., 2011b). While this HILIC-amide based method is well-suited for retention of small, polar organosulfates, it does not perform as well for less-polar organosulfates. For instance, benzyl sulfate retained 5.8 minutes on a reversed-phase UPLC column and when coupled with MS/MS detection has linear range of 0.1 – 150 μg L-1 and LOD 0.35 μg L-1 (Kundu et al., 2013;Staudt et al., 2014). Meanwhile, benzyl sulfate elutes in less than 1 minute from a BEH amide column, has a linear range of 25.0 – 300 μg L-1 and LOD of 3.9 μg L-1. The lower sensitivity for benzyl sulfate in thismethod is expected to be due to the use of acetonitrile (bp 82 °C) instead of methanol (bp 65 °C), which does not de-solvate as readily in the ESI source. Thus, the BEH amide method is complementary to reversed-phase methods, with reversed-phase chromatography is better suited for aromatic and higher-molecular weight organosulfates and HILIC is better for oxygenated and polar organosulfates."

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