

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

**Anonymous Referee #1**

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General comments:

This manuscript reports the development of an analytical procedure for organosulfates, which holds promise for the measurement of polar organosulfates in ambient fine aerosol samples. It also includes an attractive procedure for the preparation of organosulfate standards. The chromatographic method is based on the use of hydrophilic interaction chromatography (HILIC) with an amide column. As argued below I am missing some discussion why this column is superior to a bare silica column for HILIC. In addition, the results should be better compared with results obtained in previous studies.

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Specific comments:

Page 12592 - Introduction – line 14: Attempts other than those mentioned in the manuscript have been made in the past to resolve polar organosulfates, such as the MW 216 organosulfates that are related to isoprene. I specifically refer here to the study by Wang et al. (2013) where use is made of ion-pairing chromatography with dibutylammonium acetate as ion-pairing reagent. For completeness, it would be appropriate to also mention this study in the introduction, where other modes of LC separation based on reversed-phase chromatography are treated.

Ref.: Wang, W., Shalamzari, M. S., Maenhaut, W., Claeys, M. Ion-pairing liquid chromatography/negative ion mass spectrometry for improved analysis of polar isoprene-related organosulfates, *Rapid Commun. Mass Spectrom.* 27, 1585-1589, 2013.

Page 12592 – Introduction – line 26: HILIC has been used in prior work to resolve polar organosulfates but not with as much success as in the present study. I specifically refer here to the study by Olson et al. (2011), where use is made of another type of column, i.e., a bare silica column. It would be useful that the authors also discuss why the amide column is an improvement compared to the bare silica column.

Page 12599 – line 16: I am not sure that the bisulfate  $m/z$  97 anion ( $\text{HSO}_4^-$ ) is formed by a cyclic syn-elimination pathway, suggested by Attygale et al. (2001). Another pathway, involving a hydroxylic hydrogen atom and discussed in Wang et al. (2013) has also been suggested.

Page 12601 – line 7: I am confused about the presence of six methyltetrol sulfate isomers and suspect that only the two compounds eluting between 1 and 2 min correspond to methyltetrol sulfate isomers. Can the authors provide accurate mass data and product ion spectra for the  $m/z$  215 compounds eluting between 3 and 4 min to support their claim? Nevertheless, the baseline separation between the two first-eluting isomers is an improvement compared to regular C18 reversed-phase chromatography and compares quite well with that achieved with ion-pairing reversed-phase chromatog-

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raphy, reported in Wang et al. (2013).

Page 12602 – line 5: Acetonitrile has also been shown to give advantages for the extraction of compounds other than organosulfates such as carboxylic acid group-containing secondary organic aerosol compounds (e.g., pinonic acid, pinic acid, etc.) in that methyl ester formation can be prevented. It would be appropriate to also cite the following study by Kristensen and Glasius (2011) here.

Ref.: Kristensen, K.; Glasius, M. Organosulfates and oxidation products from biogenic hydrocarbons in fine aerosols from a forest in North West Europe during spring. *Atmos. Environ.* 45, 4546-4556, 2011.

Page 12601 – line 17 and Figure 3: The m/z 213 organosulfates do have volatile organic compound precursors other than isoprene, including 2-E-pentenal, a photolysis product of the green leaf volatile 3-Z-hexenal. See Gómez-González et al. (2008). No evidence could be found in the latter study for their relationship with isoprene.

Page 12614 – Figure 3: It would be relevant (perhaps more relevant than the m/z 213 organosulfates) to include the m/z 199 and m/z 183 traces, as the MW 200 and 184 organosulfates are polar and known to be related to isoprene. See Shalamzari et al. (2013).

Page 12603 – Conclusions – line 16: I suggest to keep the conclusions more general and write: “. . . . holds promise for the separation of other isoprene-derived and polar organosulfates.”

Technical corrections:

Page 12598 – line 23: replace “molecular ion” by “deprotonated molecule”. The term “molecular ion” is reserved for molecular ions formed by electron ionization. See IUPAC guidelines for terms relating to mass spectrometry by Murray et al. (2013).

Ref.: Murray, K. K., Boyd, R. K., Eberlin, M. N., Langley, G. J., Li, L., Naito, Y. Definitions of terms relating to mass spectrometry (IUPAC Recommendations 2013). *Pure Appl.*

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*Chem.* 85, 1515-1609, 2013.

Page 12599 – line 14: replace “fragment” by “product”. Again, see IUPAC guidelines for terms relating to mass spectrometry.

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Interactive comment on *Atmos. Meas. Tech. Discuss.*, 7, 12589, 2014.

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