

Interactive
Comment

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

A. P. S. Hettiyadura et al.

betsy-stone@uiowa.edu

Received and published: 12 March 2015

Anonymous referee #1 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.”

C5099

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Interactive
Comment

Response to referee #1 general comments: We agree with the referee that this manuscript describes a direct method for the synthesis of organosulfate standards and a method to quantify polar organosulfates in the atmosphere. As suggested by the referee we have added a paragraph that compares the optimized HILIC method using BEH amide column to the underivatized BEH HILIC column as discussed in response to comment #2. Specific comments are addressed point-by-point below.

Referee #1 comment 1- 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 MW216 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.”

Response to referee #1 comment 1: As suggested by the reviewer, we have added this reference to the introduction section. Specifically, the text at line 26 page 12592 to line 3 page 12593 have been removed: “Other modes of LC separation, such as hydrophilic interaction liquid chromatography (HILIC), are specifically designed to retain molecules with ionic and polar functional groups (Hemstrom and Irgum, 2006). HILIC chromatography has previously been shown to retain hydroxycarboxylic acid organosulfates, such as glycolic acid sulfate and lactic acid sulfate, which are among the most abundant atmospheric organosulfates quantified to date (Olson et al., 2011).”

The text at line 26 page 12592 to line 3 page 12593 have been replaced with: “Other modes of LC separation such as ion pairing (IP) with dibutylammonium acetate (DBAA) shown better separation and retention of isoprene derived organosulfates (Wang et al.,

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

2013), but has not been used quantitatively. Hydrophilic liquid interaction chromatography (HILIC) is specifically designed to retain molecules with ionic and polar functional groups (Hemström and Irgum, 2006) and shown promise in retaining hydroxycarboxylic acid containing organosulfates, such as glycolic acid sulfate and lactic acid sulfate, which are among the most abundant atmospheric organosulfates quantified to date (Olson et al., 2011).”

Referee #1 comment 2 - 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.”

Response to referee #1 comment 2: As suggested by the reviewer, we have added a discussion of the retention of organosulfates on a BEH amide versus BEH HILIC column which is undervatized. Specifically, the following text is added as a new section to the manuscript entitled “3.3 Comparison of BEH amide and BEH HILIC retention” at page 12601, line 22:

“3.3 Comparison of BEH amide and BEH HILIC retention. Organosulfates were retained significantly longer on the BEH amide column compared to the undervatized BEH HILIC column. On the BEH HILIC column, glycolic acid sulfate and lactic acid sulfate were retained for less than two minutes ($t_R < 2$ minutes), while benzyl sulfate, ethyl sulfate and methyl sulfate were co-eluted ($t_R < 0.6$ min). In comparison, longer retention times were observed for these standards on the BEH amide column (Table 1 and Fig. 2 A). The improvement in retention results from the amide-functionalization of silanol groups on BEH particles. The amide functional groups interact with organosulfates through hydrogen bonding, dipolar, and dispersion forces, and interact most strongly with oxygenated organosulfates. Meanwhile, the BEH HILIC column may contain more surface silanol groups on BEH particles that become negatively charged at

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

basic pH, repelling anionic organosulfates, leading to shorter retention times and lower resolution. For the reasons of better retention and resolution, the BEH amide column was selected for further optimization and aerosol analysis.”

Referee #1 comment 3 - Page 12599 – line 16: “I am not sure that the bisulfate m/z 97 anion (HSO_4^-) is formed by a cyclic syn-elimination pathway, suggested by Attygalle et al. (2001). Another pathway, involving a hydroxylic hydrogen atom and discussed in Wang et al. (2013) has also been suggested.”

Response to referee #1 comment 3: We agree with the referee that the m/z 97 fragment ion from organosulfates may form as proposed by Wang et al. 2013. However, this would require a hydroxyl group in the C-2 position, which is not the case in organosulfate standards used in our study. But the formation of m/z 97 in glycolic acid sulfate and hydroxyacetone sulfate cannot be explained by the cyclic syn-elimination pathway proposed by Attygalle et al., 2001 due to absence of a hydrogen at C-2 position. These may form m/z 97 in a similar pathway as proposed by Shalamzari et al., 2013.

The text at line 16 - 20 page 12599 has been removed: “. . .and the bisulfate anion (HSO_4^- at m/z 97) that is postulated to form via a cyclic syn-elimination pathway (Attygalle et al., 2001). Notably, the bisulfate anion is absent in the MS/MS spectrum of methyl sulfate, because there is no C2 position from which a hydrogen may be abstracted.”

The text at line 16 - 20 page 12599 have been revised to read: “. . .and the bisulfate anion (HSO_4^- at m/z 97) in ethyl sulfate can be postulated to form via a cyclic syn-elimination pathway (Attygalle et al., 2001) in which a proton is abstracted from the C-2 position. Notably, the bisulfate anion is absent in the MS/MS spectrum of methyl sulfate, as there is no C-2 position. For hydroxyacetone sulfate, the proton likely comes from the C-3 position. For in glycolic acid sulfate and lactic acid sulfate, the proton may come from carboxylic acid group, as described by Shalamzari et al. (2013).

Referee #1 comment 4 - 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 chromatography, reported in Wang et al. (2013)."

Response to referee #1 Comment 4: The reviewer's comment points out the need to clarify that the extracted ion chromatograms shown in Figure 3 were obtained on a high-resolution mass spectrometer. We have clarified this in the caption and text. In addition, we provide exact mass and qualitative MS/MS to further support the identification of six compounds with m/z 215. Specific changes are:

The following text at Page 12601 – line 7 – 17 has been removed: "As shown in Fig. 3a, six methyltetrol sulfate isomers derived from isoprene epoxide (IEPOX) (Gomez-Gonzalez et al., 2008; Surratt et al., 2008) with a precursor ion of m/z 215 ($C_5H_{11}O_7S^-$) are baseline resolved. The separation of these isomers by this method is superior to reversed phase chromatography, in which these IEPOX-derived organosulfate isomers co-elute in two peaks (Stone et al., 2012). The resolution of individual IEPOX-derived organosulfate isomers is significant, because their separation will support future quantification of individual isoprene SOA products that may prove useful in elucidating different organosulfates formation pathways (Surratt et al., 2010) and because IEPOX-derived organosulfates have generated the greatest organosulfates signals in prior field studies (Froyd et al., 2010; Lin et al., 2013)."

The text at Page 12601 – line 7-17 has been revised to read: "As shown in Fig. 3A, four major and two minor molecular ion signals with m/z 215 ($C_5H_{11}O_7S^-$; measured mass: 215.0225) are baseline resolved. Peak retention times (and error in the observed m/z) are 1.40 (-0.5 mDa), 1.74 (0.5 mDa), 2.87 (-0.3 mDa), 3.65 (-1.8 mDa), 4.51 (-0.2 mDa) and 4.81 (0.1 mDa). All MS/MS spectra (collected by Q-ToF)

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

showed m/z 97 as a product ion. Prior studies have shown that m/z 215 corresponds to methyltetrol sulfates derived from isoprene epoxide (IEPOX) (Gómez-González et al., 2008; Surratt et al., 2008). The separation of four major and two minor isomers by this method is superior to reversed-phase chromatography, in which these IEPOX-derived organosulfate isomers co-elute in two peaks (Stone et al., 2012). The HILIC separation is also better than the reversed-phase separation achieved with ion pairing which also given only two peaks for m/z 215 (Wang et al., 2013). The resolution of isomers is significant, because methyltetrol sulfates have generated the greatest organosulfate signal in prior field studies (Froyd et al., 2010; Lin et al., 2013) and may prove useful in elucidating different organosulfate formation pathways.”

Referee #1 comment 5 - 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 NorthWest Europe during spring. *Atmos. Environ.* 45, 4546-4556, 2011.

Response to referee #1 comment 5: As suggested by the reviewer, we have added a comment that acetonitrile provides many advantages as an extraction solvent.

The text at line 5 – 8 page 12602 previously read: “It has been previously shown that methanol converts carboxy-organosulfates to methyl esters and should be avoided in quantitative analysis of organosulfates (Olson et al., 2011). Instead, ACN and water (95: 5, by volume) were used as the extracting solvent in this study.”

The text at line 5 – 8 page 12602 have been revised to read: “It has been previously shown that methanol converts carboxy-organosulfates to methyl esters and should be avoided in quantitative analysis of organosulfates (Olson et al., 2011), while ACN is ef-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

fective extracting carboxylic acids in ambient aerosols (Kristensen and Glasius, 2011). In this study, ACN and ultra-pure water (95: 5, by volume) were used as the extracting solvent.”

Referee #1 comment 6 - 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.”

Response to referee #1 comment 6: As suggested by the reviewer, we have revised the text to reflect that m/z 213 has precursors other than isoprene, such as 2-E-pentenal as mentioned in Gómez-González et al. (2008).

Specifically, the text at line 17 - 20 page 12601 has been removed: “Two additional organosulfates derived from isoprene, with precursor ions of m/z 213 (C₅H₉O₇S⁻) and m/z 211 (C₅H₇O₇S⁻) (Gomez-Gonzalez et al., 2008; Surratt et al., 2008) shown in Fig. 3b and c, respectively, were retained although not fully resolved by this method.”

The text at line 17 - 20 page 12601 has been replaced with: “Figure 3B-E shows m/z 213, which is associated with 2-E-pentenal, a photolysis product of the green leaf volatile 3-Z-hexenal (Gómez-González et al., 2008). . .

Referee #1 comment 7 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).”

Response to referee #1 comment 7: As the referee suggested we have extended Figure 3 (shown in this response as Figure 1) to include extracted chromatograms of m/z 199 and m/z 183. The revised figure includes additional sections “D” and “E” shown below. In addition, we have revised the discussion at line 17 – 20 page 12601:

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

“HILIC chromatography of atmospheric aerosol samples from Centreville, AL reveals the existence of multiple isomers of major biogenic organosulfates. Fig. 3B-E shows m/z 213, which is associated with 2-E-pentenal, a photolysis product of the green leaf volatile 3-Z-hexenal (Gómez-González et al., 2008), m/z 211 associated with isoprene (Surratt et al., 2008), m/z 199 associated with 2-methylglyceric acid, a photo-oxidation product of isoprene (Gómez-González et al., 2008; Safi Shalamzari et al., 2013), and m/z 183 which derives from isoprene and crotonaldehyde (Safi Shalamzari et al., 2013). As shown in Fig. 3B, six major signals for m/z 213 (C₅H₉O₇S⁻; measured mass: 213.0069, error \leq 1.6 mDa) were observed, but not resolved with retention times 1.10, 1.29, 1.58, 1.80, 2.07, and 2.23 minutes. Three signals for m/z 211 (C₅H₇O₇S⁻; measured mass: 210.9912, error \leq 1.5 mDa) are shown in Fig. 3C with retention times of 0.56, 0.74, and 0.85 minutes. Fig. 3D shows multiple peaks for m/z 199 (C₄H₇O₇S⁻; measured mass: 198.9912, error \leq 2.7 mDa), but only the peaks at 3.67, 3.81, 3.98, 7.19, and 8.36 minutes are assigned the formula C₄H₇O₇S⁻ with error $<$ 3 mDa. Notably, the strongest signal obtained for m/z 199 is baseline resolved and retained more than eight minutes near glycolic acid sulfate and lactic acid sulfate, suggesting that it contains a carboxylate group. Fig. 3E shows three peaks for m/z 183 (C₄H₇O₆S⁻; measured mass: 182.9963, error \leq 1.2 mDa) with retention times 0.67, 0.91, and 1.23 minutes. The combination of high-resolution mass spectrometry with HILIC chromatography reveals the presence of multiple conformational isomers for major organosulfate signals that are associated with biogenic VOC. Thus, this separation method provides reliable quantification of organosulfates and insight to the distribution of individual organosulfate isomers that may provide insight to the mechanisms of biogenic SOA formation.”

Likewise, the caption for Figure 3 page 12614 has been revised to read: “Figure 3. High-resolution extracted ion chromatograms for organosulfates qualitatively identified in PM_{2.5} collected during the daytime on July 2013 in Centreville: A) m/z : 215.0225, B) m/z 213.0069, C) m/z 210.9912, D) m/z 198.9912, E) m/z 182.9963 (smoothed 2×1 ; abs window: 0.01 Da).”

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Referee #1 comment 8 - 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.”

Response to referee #1 comment 8: We agree with the referee and will revise this sentence to include a more generalized conclusion.

The text at line 14 - 16 page 12603 was previously read: “In addition to resolving the six model compounds used in method validation, the HILIC separation holds promise for the separation of a range of isoprene-derived organosulfates.”

The text at line 14-16 page 12603 have been revised to read: “In addition to resolving the six model compounds used in method validation, the HILIC separation holds promise for the separation of organosulfates derived from isoprene and other biogenic VOC.”

Technical corrections:

Referee #1 comment 9 - 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).”

Response to referee #1 comment 9: The text at line 23 page 12598 was previously read: “The detector operated in multiple reaction monitoring (MRM) mode, in which the molecular ion was selected in the first quadrupole, fragmented in the second quadrupole and product ions were selected in the third quadrupole.”

The text at line 23 page 12598 have been revised to read: “The detector operated in multiple reaction monitoring (MRM) mode, in which the deprotonated molecule was selected in the first quadrupole, fragmented in the second quadrupole and product ions were selected in the third quadrupole.”

Referee #1 comment 10 - Page 12599 – line 14: “replace “fragment” by “product”.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Again, see IUPAC guidelines for terms relating to mass spectrometry.”

Response to referee #1 comment 10 - Page 12598 – line 23: The text at line 14 page 12599 was previously read: “Major fragment ions included the sulfite radical (SO_3^- at m/z 80) that forms from the homolytic cleavage of an O-S bond, the sulfate radical (SO_4^- at m/z 96) that forms from the homolytic cleavage of a C-O bond, the bisulfite anion (HSO_3^- 15 at m/z 81) that forms from the heterolytic cleavage of the S-O bond,...

The text at line 14 page 12599 have been revised to read: “Major product ions included the sulfite radical (SO_3^- at m/z 80) that forms from the homolytic cleavage of an O-S bond, the sulfate radical (SO_4^- at m/z 96) that forms from the homolytic cleavage of a C-O bond, the bisulfite anion (HSO_3^- 15 at m/z 81) that forms from the heterolytic cleavage of the S-O bond,...

Works Cited

Attygalle, A. B., Garcia-Rubio, S., Ta, J., and Meinwald, J.: Collisionally-induced dissociation mass spectra of organic sulfate anions, *Journal of the Chemical Society, Perkin Transactions 2*, 498-506, 10.1039/B009019K, 2001.

Froyd, K. D., Murphy, S. M., Murphy, D. M., de Gouw, J. A., Eddingsaas, N. C., and Wennberg, P. O.: Contribution of isoprene-derived organosulfates to free tropospheric aerosol mass, *Proceedings of the National Academy of Sciences*, 107, 21360-21365, 10.1073/pnas.1012561107, 2010.

Gómez-González, Y., Surratt, J. D., Cuyckens, F., Szmigielski, R., Vermeylen, R., Jaoui, M., Lewandowski, M., Offenberg, J. H., Kleindienst, T. E., Edney, E. O., Blockhuys, F., Van Alsenoy, C., Maenhaut, W., and Claeys, M.: Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(-) electrospray ionization mass spectrometry, *Journal of Mass Spectrometry*, 43, 371-382, 10.1002/jms.1329, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Hemström, P., and Irgum, K.: Hydrophilic interaction chromatography, *Journal of Separation Science*, 29, 1784-1821, 10.1002/jssc.200600199, 2006.

Kristensen, K., and Glasius, M.: Organosulfates and oxidation products from biogenic hydrocarbons in fine aerosols from a forest in North West Europe during spring, *Atmospheric Environment*, 45, 4546-4556, <http://dx.doi.org/10.1016/j.atmosenv.2011.05.063>, 2011.

Lin, Y. H., Knipping, E. M., Edgerton, E. S., Shaw, S. L., and Surratt, J. D.: Investigating the influences of SO₂ and NH₃ levels on isoprene-derived secondary organic aerosol formation using conditional sampling approaches, *Atmos. Chem. Phys.*, 13, 8457-8470, 10.5194/acp-13-8457-2013, 2013.

Olson, C. N., Galloway, M. M., Yu, G., Hedman, C. J., Lockett, M. R., Yoon, T., Stone, E. A., Smith, L. M., and Keutsch, F. N.: Hydroxycarboxylic acid-derived organosulfates: Synthesis, stability, and quantification in ambient aerosol, *Environmental Science and Technology*, 45, 6468-6474, 10.1021/es201039p, 2011.

Safi Shalamzari, M., Ryabtsova, O., Kahnt, A., Vermeylen, R., Hérent, M.-F., Quetin-Leclercq, J., Van der Veken, P., Maenhaut, W., and Claeys, M.: Mass spectrometric characterization of organosulfates related to secondary organic aerosol from isoprene, *Rapid Communications in Mass Spectrometry*, 27, 784-794, 10.1002/rcm.6511, 2013.

Stone, E. A., Yang, L., Yu, L. E., and Rupakheti, M.: Characterization of organosulfates in atmospheric aerosols at Four Asian locations, *Atmospheric Environment*, 47, 323-329, <http://dx.doi.org/10.1016/j.atmosenv.2011.10.058>, 2012.

Surratt, J. D., Gomez-Gonzalez, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, *J. Phys. Chem. A*, 112, 8345-8378, 10.1021/jp802310p, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Wang, W., Safi Shalamzari, M., Maenhaut, W., and Claeys, M.: Ion-pairing liquid chromatography/negative ion mass spectrometry for improved analysis of polar isoprene-related organosulfates, *Rapid Communications in Mass Spectrometry*, 27, 1585-1589, 2013.

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

AMTD

7, C5099–C5111, 2015

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Interactive
Comment

Figure 1 (revised Figure 3)

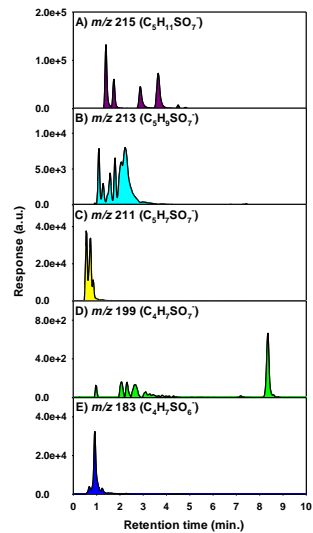


Fig. 1.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)