*MS No.: egusphere-2025-899*

## Authors’ Response to Referee #2

This paper reported synthesis and quantification of organosulfate compounds in atmospheric aerosols. The method is useful, while the following comments need to be carefully addressed before publication:

***Response:*** We thank the referee for his/her critical reading of the manuscript, appreciation of our work and constructive comments and suggestions, which helped to improve the quality of the MS. The MS is revised according to all the comments from the referee. Our point-by-point responses to all the comments are provided below. Please see the revised MS for details of the revisions.

General comments:

1. There have been several published papers on synthesized and quantification of OS compounds. For example, Hettiyadura et al., AMT, 2015; Huang et al., AMT, 2018; Wang et al., ES&T, 2017; Wang et al., ES&T, 2021 etc. What’s the novelty of this work or the improvement of the method here?

   ***Response:*** Because most of the organosulfate derivatives are not commercially available to use as authentic standards, many researchers have synthesized the required organosulfate derivatives, following the previously reported protocols, and used them as the standards in aerosol studies. The existing literature predominantly reports the synthesis and quantification of compounds such as methyl sulfate, ethyl sulfate, lactic acid sulfate, benzyl sulfate, hydroxyacetone sulfate, and glycolic acid sulfate.

   However, organosulfate derivatives like 3-methylbenzyl sulfate, cyclohexyl sulfate, and phenethyl sulfate have not been reported and are not available commercially. Therefore, in this study, we synthesized these specific sulfate derivatives based on procedures reported by Kundu et al. (2013), Olson et al. (2011), Staudt et al. (2014), and Li et al. (2010), with modifications to the reaction conditions. Notably, we employed a strong base, sodium hydride, instead of weaker bases such as dimethylaminopyridine (DMAP) or pyridine. This modification enabled the efficient synthesis of the target sulfate derivatives with high yields and purity within a short time frame. Furthermore, this method is also applicable to the synthesis of other derivatives, including ethyl sulfate and benzyl sulfate.

On the other hand, we combined these synthesized five novel OSs standards (ethyl sulfate, 3-methylbenzyl sulfate, cyclohexyl sulfate, benzyl sulfate, and phenethyl sulfate) with four commercially available standards (methyl, phenyl, octyl, and 4-nitrophenyl sulfate), covering multiple types of OSs such as aliphatic, aromatic, and long-chain alkyl groups, and thus filled the gap in the previous reference standard library.

Furthermore, the gradient elution program was optimized using the HSS T3 chromatographic column, and the isomers PES (phenethyl sulfate) and 3MBS (3-methylbenzyl sulfate) with the same molecular weight (m/z 201) were successfully separated (with retention times of 8.49 min and 9.20 min, respectively). In fact, previous studies have not reported the effective separation of such isomers. 3) The limit of detection (LOD) of all target OSs reached 0.10 ng mL$^{-1}$, and the limit of quantization (LOQ) was 0.10-0.50 ng mL$^{-1}$. Superior to Ding et al. (2022) for LOD (1.0 ng mL$^{-1}$) of methyl sulfate and Hettiyadura et al. (2015), the LOD and LOQ of methyl sulfate ethyl sulfate and benzyl sulfate were 2.6, 3.4, 3.9 and 8.6, 11.2, 13.2 ng mL$^{-1}$, respectively.

2. The HSS T3 column was used in this study. While previous studies (e.g., Hettiyadura et al., AMT, 2015; Huang et al., AMT, 2018 etc.) have suggested that HILIC column should be employed to quantify the low-molecular-weight and polar OS compounds. The performance of C18 column is not quite well for quantifying the water-soluble and polar OSs. The targeted OSs in this study include several low-molecular-weight compounds, and I notice the retention of MS and ES may not so well in T3 column based on the retention time in figure 2. The limitation of this method should be detailed. If possible, a comparison between the performance of T3 column and HILIC column to quantify the LMW OSs should be discussed.

***Response:*** Following the reviewer’s advice, we added the comparison in retention between the experiments with the BEH amide column and the HSS T3 column. The experimental results indicated that the separation effect of the BEH amide column was not good, and all OSs peaks emerged within 2 minutes. On the contrary, the retention time of the HSS T3 column was longer. Although the retention time for low-molecular-weight organosulfates (methyl sulfates, ethyl sulfates) is very short, there are no significant interference peaks. Therefore, we chose the HSS T3 column for separation. For detailed content, please refer to Section 3.2 in the revised MS.

3. The universal of selected OS species should be introduced. Have they been observed in ambient aerosol samples? Why the authors choose these compounds to synthesize and quantify?

   ***Response:*** In previous studies, organosulfates were classified into isoprene derived OSs, monoterpene derived OSs, aliphatic OSs, aromatic OSs, $C_2$/$C_3$ OSs, and organosulfates of unknown origin based on the sources of their precursors. Among them, there are more quantitative research works on the types of organosulfates derived from isoprene and monoterpenes, but there are relatively few quantitative studies on anthropogenic organosulfates (long-chain aliphatic OSs, aromatic OSs, etc.). Therefore, in this study, ethyl-, 3-methylbenzyl-, cyclohexyl-, benzyl- and phenethyl sulfate were selected for synthesis and quantification to expand the types of quantitative analysis of organosulfates in environmental samples. We added these points in the revised MS (please lines 82-89).

4. In the figure 2, the EIC are the results obtained from OS standards or ambient aerosol samples? If it represents the standards, the OS ion spectrum of ambient aerosol samples should also be displayed and compared with those of OS standards. I also suggest to combine the extracted ion chromatogram in Figure 2 into one panel, to clearly show the separation of the target ions.

   ***Response:*** The EIC result in Figure 2 (modified to Figure 3) is the result of the OSs authentic standard solution. Because the responses of each organoulfates are different and the peak intensities vary greatly, it is difficult to clearly display the separation effects of the two isomers, PES and 3MBS, after synthesizing one panel. Therefore, we chose to display them separately. However, following the reviewer's suggestion, we placed the OSs chromatograms of the standard substances and aerosol samples displayed on the same panel in the Supplementary Material.

5. Please describe how to determine the LOD and LOQ in more details. Why the LOD and LOQ of different OS compounds are the same, as shown in figure 2? I notice the statements on OS recoveries in lines 284-285 were different from the data in Table 2.

   ***Response:*** For the determination of the limit of quantification (LOQ) and the limit of detection (LOD), we employed a mixed solution containing standard substances with known concentrations for testing. The respective concentrations of these standard substances in the mixture were as follows: 0.01 ng mL$^{-1}$, 0.1 ng mL$^{-1}$, 0.5 ng mL$^{-1}$, 1 ng mL$^{-1}$, 5 ng mL$^{-1}$, 10 ng mL$^{-1}$, 20 ng mL$^{-1}$, 50 ng mL$^{-1}$, 70 ng mL$^{-1}$, 100 ng mL$^{-1}$, 120 ng mL$^{-1}$, 150 ng mL$^{-1}$, 170 ng mL$^{-1}$, 200 ng mL$^{-1}$. We determined the concentration of the limit of detection (LOD) based on a signal-to-noise ratio (S/N) greater than 3, and the concentration of the limit of quantification (LOQ) was established when the S/N ratio exceeded 10. For 3-methylbenzyl sulfate, octyl sulfate, and 4-nitrophenyl sulfate, the S/N ratio was greater than 10 at a concentration of 0.1 ng mL$^{-1}$. However, at a concentration of 0.01 ng mL$^{-1}$, the S/N ratio did not surpass 3. Consequently, we set both the LOQ and LOD for these three substances at 0.1 ng mL$^{-1}$.

The recovery rates in lines 284-285 represent the recovery rates of aromatic organosulfates. We have corrected the recovery rates of all organosulfates to 44-126%. Please see the line 361 in the revised MS.