

Dong et al. used five synthetic and four commercial authentic organosulfates to optimize UPLC-ESI-MS/MS method, which the authors applied to quantify OSs in PM_{2.5} samples collected during wintertime in Tianjin, China.

General Comments:

The motivation and objectives of the present work are not clearly articulated by the authors. There is a lack of explanation on why the specific nine organosulfates were chosen. Were they previously identified as significant in earlier studies, thus necessitating authentic standards for enhanced quantification? Some of these synthetic OS standards have been synthesized and applied in past studies to characterize OS in ambient particulate matter. Alternatively, are they representative enough to optimize a separation method intended to improve the resolution of a broader range of ambient OSs within a matrix? The use of reversed-phase C18 column in the present work has known limitation of resolving low molecule-weight and hydrophilic compounds because of early co-elution. It would be helpful if the authors clarified the specific optimization made, with a clear identification of existing gaps, comparison with prior studies, and discussion of limitations. Moreover, the intro is overall undercited. The supposedly improved methods lack sufficient detail in relation to previous methods and related studies.

Furthermore, neither the synthetic method nor UPLC method introduced by the authors bears substantial novelty. Therefore, the expectation is that a substantial improvement was achieved compared to established methods. However, the presentation of the manuscript does not clearly demonstrate such advancements. In the results section regarding the ambient PM_{2.5} samples, only the quantification of nine OSs was presented, along with their contributions to total sulfur (~1%) and total OC (~0.1%). In my opinion, this is sufficient to substantiate the conclusion that “anthropogenic emissions and subsequent secondary processes are the main sources of OSs”. The extent of sulfur closure aligns with previous measurements by Ding et al. in Tianjing during the same sampling season, which indicated that more than 95% of organic sulfur is still unaccounted for. I wonder if authors have looked for the presence other OSs in their samples, even qualitatively? Is there any improvement in resolving additional OSs with their optimized method? Addressing these questions would greatly strengthen the author’s statement that “the optimized method has enhanced sensitivity and specificity, making it appropriate for the quantitative analysis of OSs in atmospheric PM_{2.5}”. Additionally, the authors could consider using the nine OSs as surrogate standards to quantify additional OSs resolved by UPLC-ESI-MS/MS to give an upper/lower bound estimate. While uncertainties exist, this approach can highlight future directions.

In summary, although the topic of the manuscript falls within the scope of AMT but the significance of the method improvements and the overall presentation do not meet the journal's expectation. I recommend the authors to consider submitting to other journals, such as ACP, after improving the clarity and incorporating additional results suggested above.

Detailed Comments:

Lines 129-145: The NMR information, if presented as is, can go to the SI. key information should be summarized and phrased in sentences (like lines 146-148) in the main text to improve readability.

Lines 159-160: Does the 2 mL contain 20% methanol by volume? The remainder is 5 $\mu\text{g L}^{-1}$ CA solution? Is the CA solution aqueous? Please clarify.

Line 154: Please describe more about the dehumidification process.

Lines 195-199: I don't see any mass spectra shown in Figure 1. They are simply fragmentation schemes of those molecules under MS/MS. Please include product ion spectra to demonstrate resemblance to previous studies.

Lines 207-210: Please clarify the new elution program employed to achieve separation of 3MBS and PES. By looking at Figure 2, 3MBS clearly has a retention time longer than 10 min. Please also clarify the inserts for the BS and PES EIC in Figure 2 caption. It looks like the BS insert is simply a zoom-in view of the original EIC while the PES insert is the new EIC with shifted retention time.

Lines 221-222: Can authors explain why ambient samples that may contain some of those reference OSs were used for recovery test instead of blank filters? Was a mixture of known quantity of reference OSs spiked on one filter or was each reference OS spiked on individual filter to determine the recoveries?

Table 2. Please clarify why LOD and LOQ are the same for 3-methylbenzyl sulfate, octyl sulfate, and 4-nitrophenyl sulfate. Plus, the lower bound of the linear range is lower than the LOQ of these species.

Line 250: It is worth noting that the cited measurements in the U.S. were conducted in summer and early fall. Wintertime measurements of methyl sulfate in the U.S. are available in the literature, which is more comparable to the current work. One example is: Chen, Y. *et al.* Seasonal Contribution of Isoprene-Derived Organosulfates to Total Water-Soluble Fine

Particulate Organic Sulfur in the United States. *ACS Earth Space Chem.* **5**, 2419–2432 (2021).

Line 266: this is the first time that phenyl methyl sulfate and 3-methyl phenyl sulfate were mentioned in the manuscript. Is it a typo? There are no corresponding labels for these two compounds in Figure 4.

Line 274: Where are the total sulfur data and how are they obtained? Only SO_4^{2-} concentration is shown in Figure 4.

Line 281: The author claimed an improved synthetic procedure but the comparison with literature procedure was not discussed in detail.

Lines 283-284: The only improvement seems to be the separation of PES and 3MBS with a potential compromise on the PES sensitivity (Figure 3). As mentioned in my earlier comment, author did not provide detailed discussion on the improved UPLC-ESI- MS/MS method. How is it compared to previous studies using similar RPLC methods (e.g., Want et al., <https://doi.org/10.1021/acs.est.3c01422> and Ding et al., <https://doi.org/10.1016/j.scitotenv.2022.155314>)?

Technical corrections:

Lines 188-189: mass-to-charge ratio

Line 251: the sentence is incomplete before the parenthetical citation.

SI Figure S1: the labeling for (b) and (c) in the caption is incorrect.