Response to reviews

1.Authors pointed out that the previous method has the co-elution problem that affecting the quantification of OSs, especially for lower-molecular weight and highly polar OSs. Thus, they employed the method of HILIC using amide stationary phase to measure OSs, finding that this method can successfully separate some isoprene-derived OSs (i.e., $C_4H_7SO_7^-$ and $C_5H_{11}SO_7^-$) from other atmospheric OA components. However, as shown in Tables 7 and 8, the retention time of most OSs listed is still less than 1 minute. Authors need think more about it. Otherwise, they should clearly claim that the aim of this work is to improve the measurement of specific compounds (i.e., $C_5H_{11}SO_7^-$).

Reply:

The separation of typical organosulfates (OSs) such as $C_5H_{11}SO_7^-$ (*m/z* 215) and $C_4H_7SO_7^-$ (*m/z* 199) was notably enhanced using this method, as illustrated in Fig. 1, which compares the separation with the previous reversed-phase column. Specifically, for $C_5H_{11}SO_7^-$ (*m/z* 215), the separation of six peaks by this method is superior to reversed-phase chromatography, in which these IEPOX-derived OSs isomers co-elute in two peaks (Stone et al., 2012). The resolution of isomers is significant, because $C_5H_{11}SO_7^-$ have generated the greatest OSs signal in prior field studies (Froyd et al., 2010; Lin et al., 2013) and may prove useful in elucidating different OSs formation pathways.
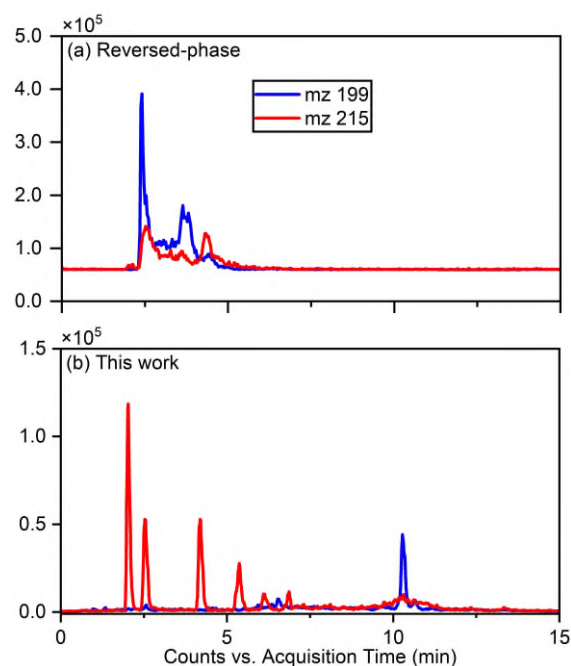

Figure 1. Comparison of the effects of separation of *m/z* 199 ($C_4H_7SO_7^-$) and *m/z* 215 ($C_5H_{11}SO_7^-$) using the previous method and this work.

Due to co-eluting effects, the retention time for *m/z* 139, 153, 155, 167 and 169 under the traditional method was 1.30 min (Stone et al., 2012). However, employing the HILIC method, significant shifts in retention times were observed, Specifically, retention times for *m/z* 139 were 0.83 & 1.58 min, *m/z* 153

were 0.79 & 0.82 min, for *m/z* 155, 167, and 169 were 10.48, 0.69 & 1.00 and 1.46 min respectively. Additionally, Fig. 2 displays chromatograms of isoprene organosulfates (iOSs) with retention times of less than 1 min. While some co-elution persists, their retention times do not precisely overlap. This observation underscores the method's potential for effectively separating lower molecular weight and highly polar OSs.
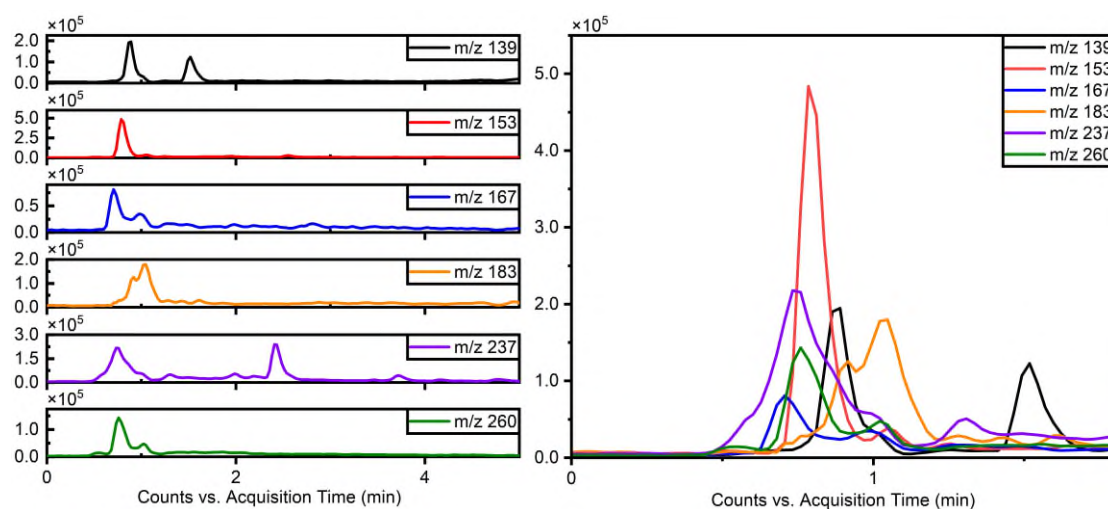

Figure 2. Chromatograms of iOSs with retention times less than 1 min.

2. Following Comment 1, there also exist co-elution phenomena for OSs standards by the fact that the retention of time of OSs standards (m/z 148-372) is less than 1 minute. Did authors compare the signal (or area in MS) of pure standard alone to the mixing standards to evaluate the effect of co-elution.

Reply:

In this experiment, six OS standards were analyzed. Table 1 compares the retention times and peak areas of pure and mixing standards. The results indicate that the retention times for all standards remained unchanged. Furthermore, there was no co-elution observed between the pure and mixing standards of small molecular weight iOSs, such as $CH_3SO_4^-$ & $C_2H_5SO_4^-$. The peak area ratios of pure to mixing standards were 1.00 and 0.96, respectively. However, co-elution exists for the long-chain alkane OSs ($C_{12}H_{25}SO_4^-$, $C_{16}H_{33}SO_4^-$, $C_{18}H_{37}SO_4^-$), with peak area ratios of 0.57, 0.60, and 0.67, respectively. The mixing standards reduced the signal by almost half, possibly due to a retention time of approximately 0.5 min, falling within the column deadtime.

The ratio of the standards with retention time (*t*R) were 0.8-1 min are close to 1, showing that even though some of the standards closely elute this doesn't effect the instrument response, suggesting no matrix effect. But the long chain OSs, which elute in the dead volume have a large matrix effect. Meaning

that the small amount of retention in this method is much better than the no retention in the reverse phase method. This is also give a evidence to comment 1.

This observation suggests that the analytical effectiveness of this method on iOSs with high polarity surpasses that of long-chain alkane OSs.

Table 1. Comparison of retention time and peak aera in MS between pure standards and mixing standards.

Compounds	[M-H]⁻		Standards	tR (min)	Peak area	Peak area ratio (Pure/mixing)
	m/z	Formula				
Sodium methyl sulfate	111	$CH_3SO_4^-$	pure	0.92	19059629	1.00
			mixing	0.92	19009710	
Sodium ethyl sulfate	125	$C_2H_5SO_4^-$	pure	0.81	15696871	0.96
			mixing	0.81	16315513	
Sodium octyl sulfate	209	$C_8H_{17}SO_4^-$	pure	0.56	44588250	0.86
			mixing	0.56	51744174	
Sodium dodecyl sulfate	265	$C_{12}H_{25}SO_4^-$	pure	0.52	34579898	0.57
			mixing	0.52	60595452	
Sodium hexadecyl sulfate	321	$C_{16}H_{33}SO_4^-$	pure	0.51	31064839	0.60
			mixing	0.51	51815669	
Sodium octadecyl sulfate	349	$C_{18}H_{37}SO_4^-$	pure	0.50	36757474	0.67
			mixing	0.50	55209165	

3. *It is better to give the detailed equations or calculation processes when extrapolate the result of detection limits in instrument (ug/mL) to that in the atmosphere (ng/m³).*

Reply:

Thanks for your suggestion! We also add these equations in the main text, see new line 233-234.

$$MDLs = IDLs * \frac{V_1}{V_2} \tag{1}$$

$$V_2 = V_0 * \frac{S_1}{S_2} \tag{2}$$

Where IDLs is instrument detection limits, MDLs is method detection limits. The area of a sampling filter (82mm diameter) for OSs analysis (S_1) was 52.78 cm², and the total area of a sampling filter (S_2) was 411.84 cm². The total air volume of 4 h sampling at a flow rate of 1.13 m³ min⁻¹ (V_0) was 271.2 m³, the solution volume in the vial for LC/MS analysis (V_1) was 300 μL, which same as the volume for

internal standard added, and the air volume responding to the filter analyzed (V_2) was 34.76 m^3.

4. Line 184-186. It is better to show the standard curves.

Reply:

Thanks for your suggestion! Also see new line 226.
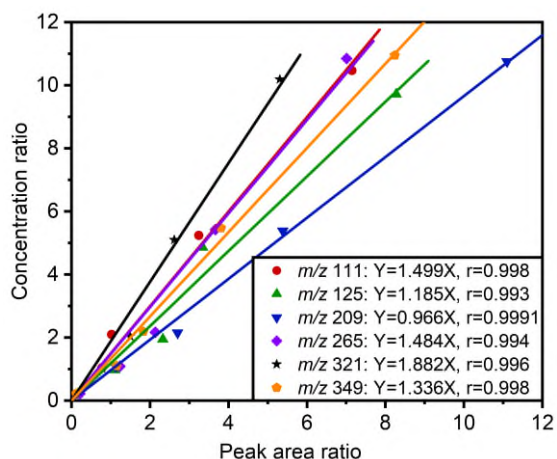

Figure 3. Correlations between concentration ratios and area ratios of standards to the internal standard, r is the correlation coefficient.

References

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 of the United States of America, 107, 21360-21365, http://doi.org/10.1073/pnas.1012561107, 2010.

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, Atmospheric Chemistry and Physics, 13, 8457-8470, http://doi.org/10.5194/acp-13-8457-2013, 2013.

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