

Online gas and particle measurements of organosulfates, organosulfonates and nitroxyorganosulfates in Beijing utilizing a FIGAERO ToF-CIMS

This paper describes the application of a FIGAERO ToF-CIMS to the characterisation of organic aerosol in Beijing, with a specific emphasis on the heteroatom containing CHOS and CHONS groups. The authors have attempted to quantify these species during a field campaign and then compare the temporal evolution to various chemical and metrological factors. I have no issue with the methods used to try and understand the data in the later part of the paper. While the idea has merit, and would be a very useful addition to the field, I cannot accept that the technique is actually measuring the species of interest based on the data provided in this paper. The extraction of very small and obscured signals from poorly resolved peaks, exemplified for the two OS species in Figure 1, has not been justified in any way. The description of the peak deconvolution is short and contains no evidence that this method has been validated. Have the authors measured the mass resolution to ensure that it really is 4000? The peaks widths used in the fitting require this to be known and the mass calibration across the entire range has to have sufficient accuracy. Has this approach been tested in the lab or are there previous publications? Also no uncertainties are provided. The entire paper and conclusions rests entirely on this component and as such I cannot recommend this paper be accepted to ACP at present. There is mention of a comparison to offline methods in the paper as being "outside the scope of this work". To me this is absolutely critical to provide validation of the method.

General comment:

Within the text both OS and SCO are used. Are these meant to be different things? It is hard to work out if they are being used interchangeably. The results section contains a large number of typos and some very unclear sentences.

Specific comments

Abstract, line 33: "biogenic emissions contributed to only 19 % of the total SCO detected." While understand you want to make a split between these two sources, this is very much dependent of the spread of SCO you measure. Previous offline MS studies of OS in China, such as Wang et al., 2016 identified over 200 OS species in PM_{2.5}. Therefore, your limited subset is very much biased depending on the choice of OS included, in this case only 17 species. You need to be very careful about making generalisation about the relative strength of the two sources based on this. Also, the C₁₀H₁₆NSO₇ ion usually appears as a series of peaks in offline HPLC analysis and therefore is better described as monoterpene derived.

Page 6: SCO identification: There s not enough information here as outlined above. If this instrument has a mass resolution of 4000 (which is not explicitly stated) then at m/z 287, the minimum peak separation ΔM , which allows two ion species to be distinguished, should be around 0.07. Thus in figure 1 (top, right), the light blue and yellow ions should be better resolved. How are the peak

centroids determined? The precision in which the intensity of very low s/n OS peaks (where the measured ion signal shows no evidence of this ion) can be retrieved is likely to be very poor. See Cubison and Jimenez, 2015.

Figure 1: The figure is difficult to understand and read. Why in the middle left hand panel have you not zoomed in so the labelled peaks can be observed? Also, the bottom plot does not really convey any information that is useful to the reader. The I- spectra seems irrelevant to the data being presented. Are there any peaks where the OS dominates the observed ion, rather than being a very small obscured peak?

Table 1 and 2: I am confused why there are two tables showing very similar information. Both tables contain a "mean" value but they are different? For example C₁₁H₁₁S₇O has the same mean %OA and %SCO in both tables but different mean concentrations (by a large amount 40 ng m⁻³ v 120 µg m⁻³)

Page 7, line 26: There doesn't appear to be any sulphur compounds in your reaction mixture?

Page 8, line 4: Figure 2 doesn't actually show a three point calibration. It shows the peaks obtained for three concentrations but it does show a calibration curve comparing concentration with response.

Page 8, line 14-21: I don't follow the reasoning that the low concentration of OS relative to the organic precursors results in little error. I would like to see some examples of the double thermogram and know how widespread this effect is. Can you provide evidence that using only 1 species to determine the error is valid?

Page 8, line 27: This statement only holds true for species that desorb below 250 C.

Page 10, line 3: I do not understand this sentence at all. Quite often through the paper sentences are not very direct and contain many extra words.

Page 10, line 30: What does "mean presence" mean? Again this section lack clarity. I don't think a p:g ratio can be "prominent"? What is the 7.1 % referring to?

Page 11, section 4.1: I assume the PTR-MS measurements have been converted to daily averages? This is what the figure seems to present. The sentence starting on line 20 is very long and doesn't make sense. You are not measuring an attribution but using the measurements to test your attribution. Why do you give average toluene mixing ratios and then change to benzene? Be very clear here you are talking about your 17 SCO only.

Page 11, section 4.1.1: Green leaf volatiles and sesquiterpenes have also been identified as biogenic OS sources.

Page 12, section 4.1.2: I cannot see any of the trends you discuss here in Figure 6. You don't include any diurnal profiles, only a full time series and therefore the temporal evolution is not clear. At the end of the section I was confused as to whether you thought the NP OS concentration was driven by traffic (hence the second peak) or biomass burning? I guess in reality it's a combination of the two, but this needs to be clearer.

Figure 2: The legend says “time series” but none of the plots have a time axis? Should say these are m/z intensities. Is the average stick spectrum collected at the desorption temperature with the highest ion count?

Figure 3: The SCO times series coloured by time is really hard to see when sitting on top of the other signals. I would separate these out.

Figure 5: this legend needs work. The benzene to isoprene ratio is on the lower panel not the upper one. The AMS data is in the upper panel and should be stated. How does the anthropogenic SCO concentration change with the b:iso ratio? Most of the variability seems to be driven by the unknowns.

Reference

Cubison, M. J. and Jimenez, J. L.: Statistical precision of the intensities retrieved from constrained fitting of overlapping peaks in high-resolution mass spectra, *Atmos. Meas. Tech.*, 8, 2333-2345, <https://doi.org/10.5194/amt-8-2333-2015>, 2015.

Wang, X. K., Rosignol, S., Ma, Y., Yao, L., Wang, M. Y., Chen, J. M., George, C., and Wang, L.: Molecular characterization of atmospheric particulate organosulfates in three megacities at the middle and lower reaches of the Yangtze River, *Atmos. Chem. Phys.*, 16, 2285-2298, <https://doi.org/10.5194/acp-16-2285-2016>, 2016