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Interactive comment on "Ultrasonic Nebulization for the Elemental Analysis of Microgram-Level Samples with Offline Aerosol Mass Spectrometry" *by* Rachel E. O'Brien et al.

Anonymous Referee #4

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The work presented by O'Brien et al. tested a new offline method (an ultrasonic nebulizer combined with an AMS) for detecting organic matter in environmental samples. This method is of interest because it requires only small sample volume. However, the advantage of this technique is overlooked in the paper. For example, the authors need to consider the preparation process of the sample liquid as I commented below. The samples tested in this study are very limited. Thus the conclusions need careful modifications to avoid misleading. Moreover, the description about the sample preparations need substantial improvements. The internal standard method is not yet fully applicable, which could be tested in real ambient samples. The pretreatments for DOM samples seems intensive. Whether if it is necessary for SVN-AMS is unclear. I would

suggest to use the SVN-AMS method directly for water samples for DOM and the effects of pretreatment steps should be investigated. Overall, this manuscript needs a major revision before publishing on AMT.

Specific comments:

Line 69-74 and Line 83-84: While the analysis of SVN-AMS uses only a few μL (0.4 μg solute), preparing the sample liquids require additional volume. For examples, for ambient aerosol particles, it perhaps still takes at least a few mL to dissolve the material on filters into a solution. Then, to achieve the advantage of less required material, the SVN-AMS method needs substantial preconcentration (e.g., drying by purging N2 as described in Line 180-188). If preconcentration is applicable for organic aerosol, the atomizer-AMS method can go with it too. The real difference of this method compared to the atomizer-AMS method seems the acceptable preconcentration magnitude, meaning the sample material into μL can be much more concentrated than into mL liquid. But intensive concentration may cause artifacts and only work for some environmental samples. Please clarify and avoid misleading.

Line 139-140: This study did not use Argon, right? Please clarify.

Line 152-155, Line 209-215, and Figure 2 caption: I am confused about the description of particle size and necessary sample concentration. This study did not use a dryer (Line 104-105). Was SMPS data for dried or wet particles? Why the diameters of dried nebulized particles is important for AMS transmission? My understanding of this approach is that the AMS only samples whatever wet aerosols were partially dried in aerodynamic lens and went through.

Figure S1. The SVN-AMS uses fast MS mode which is different from PTOF. Why to use PTOF data to determine the minimum sample concentration. The authors need to identify the minimum sample concentration for AMS detection at normal operation conditions (i.e., the integrated mass compared to the detection limit and the background levels).

Line 170-172: Was the chamber run in a batch or continuous mode? Is the seed concentration of 60 μg/m3 the initial concentration in the chamber? What about the 500 ppbv ozone? Is that initial concentration as well? Do the concentrations vary over time? The filter samples were collected for 10 hr. How did the particle concentration vary over that 10 hr period? In Figure 5b, is the online AMS spectra averaged for that 10 hours?

Line 172-173, Line 178-179, and Line 324: It is not clear to me how the 10-min sampling can represent the "blank". What kind of blank? Before the start of the experiments, what do the filters collect? Can 10 min be enough? What do the authors mean "blank subtraction was carried out with a scaling of the filter blank to 12% of the sample signal, as determined from the internal standard in each sample"? The internal standard is not mentioned in the previous text.

Line 180-186: Although the filter samples are from another study, the authors should provide enough details about the sample/samples used in this study. What is the sampling period? "Blown down to dryness" means completely dry? I suspect completely dryness affects the semivolatile SOA species. If not, how concentrated the solution is used for SVN-AMS measurements compared to ambient loading.

Line 190-191: The grade of the reagents should be provided.

Line 198-199: How is this white power prepared for the SVN-AMS analysis? Dissolve into additional water or just melt?

Line 200: Please clarify for each case (chamber, SOAS, and DOM), how many fiters/samples were used in this study.

Line 240: The description about the variations should be more quantitative. Given such big variations, I think it is necessary to clearly state that this method is not good for quantitative analysis of the mass concentrations of the samples.

Line 280-281: Where are the background coming from? If adding the internal standard

to a sample solution, what happens?

Line 293-306: The internal standard method should be tested for ambient samples with the suggested RIE of 1.4; otherwise the goodness of this method remains unclear.

Section 3.3: The run-to-run variations is large for nebulization efficiency. What about the run-to-run variations of elemental composition and mass spectra. Please provide.

Line 316: The model of the TSI atomizer as well as the operating conditions should be provided.

Line 320: I don't understand how the dot product (of what?) represents the similarity of the two spectra.

Line 344-353: The mass spectra showed in Figure 5c are indeed quite different in terms of many distinguished ions. I think saying the two mass spectra have a high degree of agreement (Line 344) or one is well represented by the other (Line 351-352) is improper and misleading. Since the major similarity appears for m/z 41-44, the authors may present some of the major peak ratios (e.g., f44-to-f43) instead. Also, in Table 1, the uncertainty of elemental ratios should be provided. Using f44 to derive O:C is associated with much greater uncertainty than the AMS method does. The comparison for Look Rock somewhat indicates that the elemental ratios are less sensitive to the method.

Line 355-356: Not only "remain in the condensed phase after nebulization" but also after intensive pretreatments (e.g., serial dilution/concentration etc. in Line 197-198).

Line 365-366: Why the pretreatments in Line 197-198 are needed for the SVN-AMS method for DOM? Tests on real water samples should be presented. The effects of dilution or concentration on the analysis deserve further discussions.

Technical Remarks: Line 27: What kind of "diameter"? Also, to be clear, this diameter is for dry particles. Line 29 and Line 281: Please add "material" after "organic". Figure 2: Please properly write the ions in the legend. Line 240: "Slowly" is an improper word

here, maybe "slightly". Figure 5: To be clear, the "SVN" in panels b), c), d) is indeed "SVN-AMS". In panel a), the legend of "TSI" should be "Atomizer". And the "Online" in panel c) should be "AMS"? Line 307: "3.1" should be "3.3".