Review of amt-2018-326 "Ultrasonic Nebulization for the Elemental Analysis of Microgram Level Samples with Offline Aerosol Mass Spectrometry"

General comments

In the manuscript by O'Brien et al. "Ultrasonic Nebulization for the Elemental Analysis of Microgram Level Samples with Offline Aerosol Mass Spectrometry" a novel analysis method combining aerosol generation with an ultrasonic nebulizer and an Aerosol Mass Spectrometer as a detector is presented. This work demonstrates the potential of the AMS to determine elemental composition of microgram-level of filter extracts or liquid samples. The manuscript describes the calibration process and investigates the effectiveness of this method for different samples of known and unknown composition. It fits in the scope of AMT and I would recommend it for publication after addressing specific comments listed below.

We thank the reviewer for their helpful comments and suggestions. We have added text to the manuscript clarifying questions and comments raised by the reviewer.

Specific comments

In general I find that there is some lack of information on the preparation and exact composition of the solutions used to test the effectiveness of the nebulization process (e.g. line 238/239 only a range is provided) and to determine the calibration curves (Fig. 4b e.g. what are the ratios of organic to NH4 15NO3?). The paper could be improved by providing more detailed information on the solutions. E.g. in Fig. 4b one cannot access what determines the ratio in the solution of organics to NH4 15NO3. With increasing mass is only the concentration of organics increased in the solution and NH4 15NO3 concentration is kept constant? Or the other way around? Are both concentrations varied for the different points on the calibration curve? Please provide more details. Also the reader would benefit much more if e.g. tables with the exact details of the used solution/mixtures where provided in the supplement.

We thank the reviewer for this suggestion and have added a table showing the concentrations used in the samples that generated figures 3 and 4 in the supplemental. We have also added text to the manuscript directing the reader there for further information.

In the manuscript the background signal of solvents (Milli-Q water and methanol) is mentioned several times but no graph or numbers are provided. It would be informative if e.g. in the supplemental material a graph could be shown to give the reader an estimate how much a background signal could contribute for both Milli-Q water and methanol to the actual signal of the sample.

When we atomize pure solvents, we observe no signal in the AMS because the concentration of trace components/contaminants is too small to generate aerosols of a large enough dimeter to pass through the aerodynamic lens and reach the vaporizer of the AMS. We address this in the second paragraph in section 3.1. To show the very low background observed for Milli-Q samples run with sufficient analyte to generate aerosols measureable in the AMS, we provide Figure 4a. To clarify this point we have added

the following text to the end of the second paragraph in section 3.2.2: "*For all tests of background signals and blanks, the internal standard is added to the solutions at concentrations between 0.5-1 g/L in order generate aerosols of sufficient size for the AMS.*"

Analysis of the background signal from methanol and other organic solvents, when sufficient analyte is present in the solution to generate aerosols, is an area of active research for the first author as mentioned in the conclusions.

line 54: it would be informative to give an example/a number of what "high temporal variability" means

We have added text that provides the example of air masses in major urban regions being a system with a relatively rapidly varying aerosol composition.

line 92, line 138 and caption of Figure 1: What do you mean with "house air"? Please explain. line 169: what does "low-NOx conditions". Please be more specific about the range of NOx concentrations during the experiments

House air is zero air from an Aadco zero air generator. This information has been added to the beginning of the experimental and the figure caption has been changed to "zero air". In the chamber NO_x was less than 10 ppb. This information has been added to the text.

Line 240 and Figure 3: "The amount of mass measured in the AMS increases slowly compared to the amount placed on the film…" This cannot be clearly seen from the graph because there is no information which combination of signals of citric acid, NO3, SO4 and NH4 15NO3 belong to one solution which was nebulized at the same time. According to the text the relative composition was changed for different samples only the sum of the solved components was kept constant. To better access a trend or the lack thereof it would be helpful if the reader could identify clearly the different samples in Figure 3.

The samples used to generate Figure 3 are the sample solutions run for the citric acid calibration curve in Figure 4. For the efficiency analysis, 4 μL of each solution was placed on the kapton film and atomized with six replicates run for each sample. Information on the samples used and their corresponding locations in Figure 3 has been added to the supplemental and text directing the reader to that information has been added to the manuscript text.

Figure 3: NH4 15NO3 seem to show a somewhat linear response or at least a trend the other components are missing. This is not discussed in the text. Is this possibly due to the higher concentrations of NH4 15NO3 compared to the other components in the solution? Why was for NH4 15NO3 a higher concentration used than for the citric acid, NH4SO4, NH4NO3? Additionally it would be much more informative if for the y-axis error bars or at least some estimates where provided to judge better how significant the variability within the measurement error is.

We thank the reviewer for this comment and have added material to both the supplemental as well as the manuscript to clarify this topic.

We have added detailed information on the solutions used to generate Figure 3 to the supplemental material. A higher concentration of the labeled ammonium nitrate was used because it is the internal standard and the concentrations of the other components are varied relative to it. The vertical column of data points are 6 replicate injections of the same solution and are shown to provide a measure of the variability. The relative amounts of total signal observed for any given sample can vary, and we find that the trend shown here is not always observed. Thus, the trend the reviewer observes is not inherent to the measurement but was observed for this sample. What is consistent across all measurements is the efficiencies on the order of 0.02-0.06% and the ratios between the internal standards and the analyte being proportional to the solutions.

We have modified this section of the text to clarify this:

"Six replicate injections of 4 μL drops of the solutions from one of the calibration curves (section 3.2.2 below) were atomized, and the total mass observed in the AMS was calculated as described above. (Details on the concentrations of analytes in these calibration solutions for Figures 3 and 4 are provided in the supplemental.) There are variations in the efficiency from sample to sample and run to run, thus the trends shown in Figure 3 are illustrative only. The key trait observed is that the measured nebulization efficiencies are on the order of 0.02-0.06%, indicating that the aerosol mass detected with the AMS is approximately three orders of magnitude lower than the mass originally deposited on the thin film."

Line 290ff: Compared are e.g. ratios of the signal of organic to the signal of NH4 15NO3 in the AMS to known ratios of organic to NH4 15NO3 in the solution. To correct for the variability due to the nebulization process a known amount of NH4 15NO3 is added to the sample. However e.g. if the composition of the sample is unknown the ratio of organics to the added NH4 15NO3 is also unknown. It is not clear to me since only the ratios of e.g. organics to NH4 15NO3 is used on the calibrations curves how robust this method actually is if the ratio of organics to NH4 15NO3 is significantly different between what was used for the calibration curve and an unknown sample. The response might be different for different ratios of organics to NH4 15NO3 . Unfortunately from the calibration curve it is not possible to access how the ratio on the x-axis for the known solution is composed. Was only NH4 15NO3 varied or only the organics or both?

This question raises an important point about how to implement the use of internal standards for quantification. When the concentration of the analyte is unknown in a sample, initial tests must be run to verify the range of concentrations. Then, an appropriate amount of internal standard can be added such that the ratio of analyte to internal standard matches the range used in the calibration solutions. If this is not possible, possibly due to sample mass limitations, the calibration curve can be subsequently remade to encompass the observed approximate concentrations. For the solutions run here, the IS standard was kept the same and the analyte concentrations were varied.

The concentrations for the solutions used here have been added to the supplemental and we have added text to the third paragraph in section 3.2.2 clarifying this for the reader.

"For quantification of unknowns, known concentrations of the internal standard are added to the samples *at ratios comparable to what is used for the calibration curve.* The ratio of the measured AMS signals can then be used to calculate the unknown analyte concentration from the calibration curve."

Line 376: How does the internal standard improves CE of the AMS? If I am not mistaken that was not discussed in any of the previous sections of the paper. Please explain.

The use of an organic internal standard may improve collection efficiency as it may reduce particle bounce off the vaporizer in the AMS. This has been added to the sentence in the conclusions.

Technical comments

line 52: please explain once the abbreviation (CHNS) since not everyone necessary know what it stands for.

We have added "carbon, hydrogen, nitrogen, and sulfur" in front of CHNS.

Figure S1: "((a) 2 g/L; size distribution centered at 200-300 nm) or more dilute solutions ((b) 0.2 g/L; size distribution centered at 100-200 nm)" Judging from the x-axis the maximum of the curves in both graphs seem to be centered around higher values. Please explain or correct.

This has been corrected.

Figure S1, S2: please add on both graph legends for the different traces shown

These have been added

Line 307: Section number should be 3.3 instead of 3.1

This has been corrected

Line 356: it is Figure 5d instead of 3d

This has been corrected