

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.

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 $\text{NH}_4^{15}\text{NO}_3$?). 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 $\text{NH}_4^{15}\text{NO}_3$. With increasing mass is only the concentration of organics increased in the solution and $\text{NH}_4^{15}\text{NO}_3$ 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 were provided in the supplement.

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.

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

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

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, NO_3 , SO_4 and $\text{NH}_4^{15}\text{NO}_3$ 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.

Figure 3: $\text{NH}_4^{15}\text{NO}_3$ 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 $\text{NH}_4^{15}\text{NO}_3$ compared to the other components in the solution? Why was for $\text{NH}_4^{15}\text{NO}_3$ a higher concentration used than for the citric acid, NH_4SO_4 , NH_4NO_3 ? Additionally it would be much more informative if for the y-axis error bars or at least some estimates were provided to judge better how significant the variability within the measurement error is.

Line 290ff: Compared are e.g. ratios of the signal of organic to the signal of $\text{NH}_4^{15}\text{NO}_3$ in the AMS to known ratios of organic to $\text{NH}_4^{15}\text{NO}_3$ in the solution. To correct for the variability due to the nebulization process a known amount of $\text{NH}_4^{15}\text{NO}_3$ is added to the sample. However e.g. if the composition of the sample is unknown the ratio of organics to the added $\text{NH}_4^{15}\text{NO}_3$ is also unknown. It is not clear to me since only the ratios of e.g. organics to $\text{NH}_4^{15}\text{NO}_3$ is used on the calibrations

curves how robust this method actually is if the ratio of organics to $\text{NH}_4^{15}\text{NO}_3$ 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 $\text{NH}_4^{15}\text{NO}_3$. 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 $\text{NH}_4^{15}\text{NO}_3$ varied or only the organics or both?

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.

Technical comments

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

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.

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

Line 307: Section number should be 3.3 instead of 3.1

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