

Response to review RC1

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 were 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 diameter 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 measurable 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-NO_x conditions”. Please be more specific about the range of NO_x 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 were 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 μ L 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

Response to review RC2

This manuscript proposes a new method to determine elemental ratios of microgram level samples using offline AMS technique. Such technique would be quite useful and valuable, and therefore the paper merits publication. The description, justification and discussion of the technique is overall solid, this reviewer has a few comments for the authors to consider before its publication:

We thank the reviewer for their comments/questions/and suggestions and we have made changes to the manuscript to address their concerns as detailed below.

(1) The manuscript aims to do elemental analysis, but as shown in the paper, it seems like you can also do mass quantification by using an internal standard. So why only mention elemental analysis?

We are very interested in the quantification capabilities of the technique. The discussion on quantification in section 3.2 and figure 4 are laying the groundwork for this type of analysis. We have added a note in the conclusions that the SVN will be used to generate aerosol for quantitative and qualitative analysis of environmental samples in the future.

(2) Does the size distribution influence the measured particle composition? Also, for different samples, did you observe different size distributions?

The current model of the SVN is better suited for discrete samples and particle size measurements tend to require a continuous source of aerosol for at least a minute or two. Initial tests were carried out using continuous flow in the SVN and these results are shown in Figures 2 and S1. Figure S1 shows that lower concentrations make smaller sized particles. It also shows that we observe homogenous particles indicating that the size range sampled will not vary the composition measured in the AMS.

We have added a sentence to the caption on Figure S1 to highlight this: "For these samples, the size distribution of the components is fairly uniform consistent with the formation of homogenous particles in the nebulizer."

(3) Dehumidification is not applied in current experiments (although it can be done as you mentioned), therefore there might be extra H₂O signals influencing quantification of organics? I think you should add dehumidification procedure.

We agree with the reviewer that care with quantification is very important. The AMS software used to process these data sets limits the organic H₂O signal to 0.225 of the CO₂⁺ signal measured in the sample to account for the presence of water in the particles. The addition of a dehumidification procedure may provide valuable insights for some studies which is why it is raised in the paper. However, we caution against the assumption that after the particles have passed through a dehumidifier all the water observed in the AMS is due to organic pyrolysis/fragmentation as this may not be true across all sample types.

(4) You mentioned there might be significant background signals if organic solvent is used to extract the samples. Did you try to use activated carbon to remove organic solvent?

We thank the reviewer for this suggestion. The lead author is currently working on characterizing background signals from organic solvents and is excited to test this idea out as a denuder before sampling into the AMS. This method will likely improve the removal of organic solvent from the particles, which will help characterize lower-volatility organic contaminants present in the solvent.

(5) You mentioned the ultrasonic nebulization may increase the temperature of your sample solution. This may lead to evaporation of some organics and therefore the composition and elemental ratios of your analysis. How to avoid this and how to consider such uncertainty?

We have begun the characterization of this feature by the offline vs. online comparisons. Our initial tests, shown in Figure 5a and 5b show very good reproducibility between the chemical composition measured in the AMS after SVN nebulization and what has not been ultrasonically nebulized. To further reinforce this we have added text to the conclusions (italic = additional text): “A direct comparison between the mass spectra generated by commercial spray atomizers or by real-time aerosol particles sampled directly from the atmosphere showed high degrees of agreement, *indicating minimal composition changes during nebulization.*”

(6) Regarding the comparison of AMS mass spectra determined by SVN and online data, you need to be careful that the difference can attribute to a couple of factors: online measurement is for PM1 and can measure both water-soluble and water-insoluble species, while the SVN only determine water-soluble portion and your samples are PM2.5?

We agree that the differences in size distribution and the effects of solubility may influence the composition observed. We address this for both the chamber and the ambient comparisons in section 3.3 and have added text highlighting the size differences for the chamber experiment between what the measured online (PM1) and what is collected on the filters (no cut-off was applied).

(7) Why not use Canagaratna 2015 (Atmos. Chem. Phys. 2015, 15, (1), 253-272.) method to calculate H/C and O/C?

H/C and O/C values for the HR-ToF-AMS data sets were calculated using the above reference. We have clarified this in the manuscript by adding (new text italics): “For samples compared to chamber or ambient online-AMS data sets, house air was the carrier gas, standard empirical estimates were used, *and the improved-ambient method for elemental ratios was applied* (Canagaratna et al., 2015).”

Other typos: Line 307 3.1 mass spectral analysis. It is not 3.1

This has been corrected

Line 316 atomizer (black) and the SVN (green), the colors are inconsistent Line 323 offline (red) vs. online (black) the colors are inconsistent

This has been corrected

Response to review RC3

This is an interesting paper by developing a small volume nebulizer for elemental analysis with aerosol mass spectrometer. The major advantage of this technique is the volume of samples needed for analysis. This manuscript is generally well written, and I recommend it for publication after addressing the following comments.

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

1. The future applications of this technique can be expanded, particularly compared with previous AMS offline analysis. In general, the volume of DI-water extracted solutions from filter samples collected with high-volume samplers are not an issue for elemental analysis with AMS. Then why we need such a technique for offline AMS analysis?

The smaller droplet sizes generated in the nebulizer, compared to commercial atomizers minimizes the influence of background material from the solvent. For a single injection of an aqueous solution, the SVN-AMS requires only 400 ng of material and preliminary work on organic solvents shows an even better nebulization efficiency. This small size enables the analysis of trace samples as, for example, samples collected with impactors over short periods of time. Additionally, the SVN-AMS is a platform that enables direct comparison of samples prepared for other offline analyses, including both liquid chromatography and direct electrospray ionization of samples into mass spectrometers, as the concentrations needed for both analyses are similar. Finally, this platform decouples the gas flow rate from the atomization process enabling a concentration of the aerosol packet, if needed.

All of these advantages are mentioned in the manuscript except for the comparison with soft ionization techniques and the decoupling of the gas flow rate with the nebulization process. Text has been added to the end of the introduction and the conclusions:

“The concentration ranges needed (described below) are comparable to the concentrations used for other offline characterizations including soft ionization with electrospray ionization into mass spectrometers. Thus, this technique provides a platform for direct comparison between offline-AMS samples and other analytical techniques.”

“Finally, in contrast to atomizers (where the carrier gas generates the aerosol), ultrasonic nebulizers decouple the aerosol formation from the carrier gas flow rate, enabling potential concentration of the aerosol prior to sampling.”

2. The authors didn't show any high resolution mass spectra of compounds or samples analyzed in this study. For example, North Pacific Ocean sample in Figure 5d. Clear signals of m/z 78 (CH_2SO_2^+) and 79 (CH_3SO_2^+) are expected, which were not. Another question is the minimum concentration used for the SVN-AMS analysis. Because “fast MS” mode was used for discrete samples, signal-to-noise ratio could can be an issue for high resolution peak fitting.

The DOM from the North Pacific Ocean is the high molecular weight fraction of the organic material and, as such, has had the lower molecular weight compounds (including any possible methane sulfonic acid) removed. We do not expect signals from methane sulfonic acid derivatives in our samples. The North Pacific sample is not total DOM, but the polysaccharide fraction (~ 25% total DOM) isolated as described between lines 197 and 204. To further clarify this point, we have explicitly changed the text in the abstract, experimental, and results and discussion to clarify that this is the polysaccharide fraction of DOM. We have also added text to the end of section 3.3 clarifying this:

“Here we demonstrate the analysis of the high molecular weight fraction of the polysaccharide fraction of dissolved organic matter (DOM) with the SVN-AMS. The DOM sample was prepared using a standard protocol for the isolation of this fraction of the organic material (see section 2.3). This preparation removes the lower molecular weight compounds so chemicals such as methane sulfonic acid are not expected to be observed.”

We agree that signal to noise can be a concern for peak fitting. For all analyses at least three replicate injections are carried out. The average mass spectra across these injections is then used for the peak fitting. If the observed signal is low during collection, more replicate injections are carried out to help improve the S/N during analysis.

We have added the following text to the experimental to clarify this:

“For the high resolution peak fitting and the analysis of the mass spectrum and the elemental ratios, the average mass spectrum across all injections is used. For quantification, the total signal under each injection pulse (see below, Figure 2a) is used.”

3. It is not recommended to directly compare the mass spectra between ACSM and AMS. ACSM often presents much higher m/z 44 than AMS [Fröhlich et al., 2015], and O/C estimated with f44 can also have a large uncertainty.

We agree that comparisons between ACSM and the AMS should be carried out very carefully and only present the comparison because no on-line AMS data was available for the Look Rock samples. We have added text to the Results and Discussion section (3.3) highlighting and clarifying this:

“The high degree of overlap in the intensities of the dominant ions between the online (AMS/ACSM) measurements and offline (SVN-AMS) results indicates that the ensemble organic composition for these aerosol samples is generally well-represented by the SVN-AMS measurements (Table 1). However, the estimated elemental ratios from a lower resolution AMS are more uncertain than from the HR-ToF-AMS. Thus, the ratios for these samples in Table 1 are provided only as a demonstration of the overall agreement between the two techniques.”

4. Typos of “FIGERO-CIMS”(line 82) and “Figure 3d” (line 356).

These have been corrected.

Fröhlich, R., et al. (2015), ACTRIS ACSM intercomparison – Part 2: Intercomparison of ME-2 organic source apportionment results from 15 individual, co-located aerosol mass spectrometers, *Atmos. Meas. Tech.*, 8(6), 2555-2576, doi:10.5194/amt-8-2555-2015.

Response to review RC4

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.

We would like to thank the reviewer for their helpful and thorough comments. We have made the requested corrections and have used the authors comments, questions, and suggestions to clarify material covered in the manuscript. Specifically, we have added text that communicates the sample preparation processes that are necessary for some samples and the corresponding limitations/care that must be exercised.

The samples provided as examples in the text are demonstrations of the technique applied to different types of systems. Work is actively being carried out to expand these examples to other systems including the characterization of the internal standard method for ambient samples. The work communicated in this manuscript is an explanation of the method and a demonstration of its potential. Given the linearity of the response to the calibration curves with the internal standard, we believe that the applicability of the technique is only limited by the correct choice of standard to serve as the calibrant. Fortunately, this technique also provides a platform to test multiple different standards, enabling later adjustments as more knowledge of the system is gained via other analyses.

The information in the experimental on sample preparation has been expanded as requested. The pretreatments for DOM were necessary to investigate the elemental ratios of the organic mixture in the samples. Marine dissolved organic matter is a very complex mixture of organic compounds that together occur at low concentrations (~ 0.5-1 mg/L) within a very saline solution (~ 35 g/L). Given the very high ratio of salt to organic C and N (up to $1 \times 10^6:1$), it is unlikely that direct measurement of elemental DOM ratios in seawater itself would be successful. There are reasonably sensitive techniques to measure total DOC, DON, and DOP in seawater. The AMS method described here is not offered as an alternative to these methods but does provide a platform for generating comparable data with decreased sample mass requirements.

Virtually all analytical and experimental work designed to study DOM composition and microbial cycling use some form of physical or chemical concentration of DOM from seawater. The ultrafiltration isolation technique used here for our DOM sample is commonly applied by marine chemists to study DOM cycling of this semi-labile fraction. Elemental analyses of this fraction are ill suited for high throughput experimental work. Indeed, we expect the AMS method might be a game changer in the ability to perform high throughput analyses of DOM elemental ratios in experimental studies. Since the same pre-treatments must be applied to the sample before either CHNS or SVN-AMS analysis, this data set provides a good test of the technique to characterize very complex organic mixtures.

We agree with the reviewer that the effects of pretreatment steps should be investigated and are excited for the idea to compare samples prepared with the method used for SVN (which is also often carried out to prepare samples for electrospray ionization/MS) to samples prepared and atomized with commercial atomizers. Bridging the gap between different techniques in terms of sample preparation is a challenging problem and the quantitative and qualitative capabilities of the AMS, when coupled to the SVN and other atomizers, may provide a powerful tool to characterize these effects.

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 N_2 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.

We thank the reviewer for this comment, the comparison between different atomization techniques is an important area of research as we characterize environmental samples with different offline techniques.

For most filter samples, the SVN requires pre-concentration. We have added text to the introduction highlighting this:

“In some cases, depending on the sample, pre-concentration is required to generate suitable solutions for analysis. The concentration ranges needed (described below) are comparable to the concentrations used for other offline characterizations including soft ionization with electrospray ionization into mass spectrometers. Thus, this technique provides a platform for direct comparison between offline-AMS samples and other analytical techniques.”

We agree that care should always be taken with sample handling. We have also added text to the conclusions highlighting this fact.

“For these samples, pre-concentration was required to prepare a suitable solution concentration for analysis. This will be required for some types of environmental samples and care should be taken to minimize artifacts during solution preparation.”

Here, the SVN-AMS is not presented as a replacement for atomizer-AMS techniques and we agree that some atomizer-AMS techniques could be used to characterize samples prepared in the manner discussed in this manuscript. The SVN is presented as a new, additional, option for aerosol generation with strengths that will make it very suitable for the analysis of certain types of samples. The SVN requires very small sample volumes per injection (2-4 μL), it generates small aerosols thus reducing the effect of organic contamination from the solvent, and it enables increases in the aerosol particles per

unit volume by decoupling the aerosol formation process from the carrier gas flow rate. Text communicating these strengths has been added to the introduction and conclusion sections.

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

This study used Argon for the DOM and for the citric acid comparison. As the chamber and ambient samples had air background, we used zero air for those samples. We have added the following text (additions in italics)

“With the SVN, inert carrier gases such as argon can also be used, allowing for the direct measurement of the CO⁺ ion intensity (as demonstrated below for dissolved organic matter, *the majority of the other samples were run with zero air*).”

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.

The particles that were measured in the SMPS were likely partially dried as the carrier gas was dry zero air. The minimum size necessary for sampling into the AMS is ~70 nm. If the particles dry during transit between the nebulizer and the AMS to diameters less than this, they will have very low transmission into the AMS.

If the solution that is being atomized is too dilute, the particles that are formed may be too small to pass into the AMS.

We have added text to the manuscript to clarify this (added text in italics):

“Assuming that the density of the dried particle is 1.3 g/cm³ (Nakao et al., 2013), the minimum sample concentration that will form a 100 nm dried particle is approximately 0.3 g/L. *More dilute solutions do not generate signal in the AMS because the majority of the aerosol particles that are formed are too small for transmission through the aerodynamic lens of the AMS (Figure 2b)*. To generate large enough aerosol particles from more dilute solutions, larger initial droplets could be formed by changing the transducer *to one that vibrates at a lower frequency.*”

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).

The PTOF data is not used to determine the minimum sample concentration. We have added text to the caption of Figure S1 to clarify this.

The total signal observed in the AMS was used to determine the minimum concentration needed. The text added addressing the comment above also covers this idea. The limitation for sample concentration comes dominantly from the maximum aerosol particle size that can be formed. Enough material is needed to form aerosols that can be sampled in the AMS. Beyond this, the limitations in the AMS roughly match what is observed with online work: measured particle concentrations below $\sim 4 \mu\text{g}/\text{m}^3$ have higher noise and are not ideal for chemical analysis. We find that concentrations greater than 0.2 g/L provide consistently good quantitative and qualitative results for organic samples. That is where the lower value for the range comes from (4 μg of material). For the lower concentrations, the addition of the internal standard actually benefits the results, as the overall sample concentration is higher.

We have added text to the manuscript to clarify how this can be done 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. This allows an analysis of any trace material present in the blank by creating an aerosol population to transfer the trace material into the AMS and allows for a background subtraction using the internal standard."

Line 170-172: Was the chamber run in a batch or continuous mode? Is the seed concentration of 60 $\mu\text{g}/\text{m}^3$ 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?

The chamber was run in constant-volume, semi-batch mode. Further details on loadings have also been added:

"Chamber aerosol (enabling offline vs. online comparisons) was generated in the MIT 7.5- m^3 Teflon environmental chamber, run in continuous-volume, "semi-batch" mode. Details on the facility are given elsewhere (Hunter et al., 2014). Experiments were run at 20 °C, < 5% RH, in the dark, and under low- NO_x (< 10 ppb) conditions using ozone as the oxidant. Ammonium sulfate seeds were added for an initial concentration of $\sim 60 \mu\text{g}/\text{m}^3$. The VOC, α -pinene, had an initial mixing ratio of 100 ppb; a penray lamp (Jelight model 600) was used to add an initial ozone concentration of ~ 700 ppb ozone. The ozone concentration decreased due to consumption and dilution to 400 ppb by the end of the experiment. The initial organic loading was $\sim 70 \mu\text{g}/\text{m}^3$ and decayed due to dilution, sampling, and wall loss to a final value of $\sim 18 \mu\text{g}/\text{m}^3$."

Yes, in Figure 5b, the online AMS is the average spectra over that 10 hour period. We have added text to section 3.3 clarifying this.

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.**

The blank tested here is a filter blank that gives the background on any organic material present on the teflon filter as well as any organic material added during the sample preparation process. For blanks, the standard protocol is to carry out the same procedures as the sampling. Thus, placing the filter in the holder is more to test the contamination that comes from the lab and/or filter handling instruments (tweezers) than to actually sample anything in the filter holder itself. The filter holder is usually thoroughly cleaned between runs and we believe that 10 min is sufficient time to pick up any remaining, easily transferred, material in the filter itself. We have added text clarifying this to section 3.3:

“These blanks provide the background for any trace organic material on the filters before collection as well as any background organic material added during sample preparation.”

The blank subtraction was carried out by using the ratio of the organic to the internal standard for the blank and for the sample. The scaling factor was found to be 12% for this sample, thus the total intensity of the blank mass spectrum was multiplied by this value before subtracting it from the chamber filter. For these analysis, we spike every sample with ~0.5-1 g/L internal standard in order to enable this type of analysis. Text clarifying this has been added to the manuscript and is detailed in this document two comments above this one.

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.

The time frame for the SOAS campaign is given in the experimental. The time frame for the sample shown in the manuscript is given in the section discussing that mass spectrum (section 3.3). This sample is a night sample collected on July 4 from 8 pm to 7 am the following day.

Yes, here blow down to dryness means completely dry. We also agree that this process will affect semivolatile SOA species. Thus, the volatility and the solubility of the compounds in the sample will likely affect the mass spectrum observed compared to ambient. We mention that the loss of volatile compounds during sample preparation will likely be a factor influencing the differences we observe in the text in section 3.3

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

All reagents were 99% purity or more, text communicating this has been added.

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

The DOM was dissolved in MilliQ water at ~ 1 g/L, this has been added to the experimental.

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

We did not need to combine filters to generate sufficient mass for each sample and the DOM sample provided by our collaborators was sufficient to generate more than one mL of 1 g/L solution. Thus each mass spectrum shown in the figure is a data set from one filter sample or DOM sample. We have added text addressing this to the experimental:

“For all analyses presented here (chamber and ambient) sufficient mass was extracted to enable the analysis of individual filter samples, with no combination of extracts from different samples required.”

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.

The variations we observe are in the amount of material that is sampled into the AMS. We use the internal standard to account for these variations. The ratio of the analyte to the internal standard is consistent, despite variations in the total aerosol mass produced. The calibration curves in figure 4 demonstrate this fact. To quantify unknowns, known amounts of the internal standard are added to each sample. The ratio of the signals for the unknown to the internal standard can then be used, with the calibration curve, to calculate the unknown concentration by multiplying by the known concentration of the internal standard in the solution.

We have added text clarifying some additional details for how this type of analysis can be carried out for ambient samples in section 3.2.2:

*“For the calibration curve, the ratios of the AMS signals for the analyte over the internal standard are compared to the ratios for known solution concentrations, thus correcting any variations in the mass of analyte nebulized. 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 280-281: Where are the background coming from? If adding the internal standard to a sample solution, what happens?

The background can come from many different sources. For the sample shown in Figure 4a it is likely trace material on the Kapton surface. There may also be trace material in the syringe used to load the sample. When the internal standard is added to the solution, we produce a solution that has enough material to form aerosols that can be measured in the AMS when the sample is nebulized. Text added section 3.3 clarifies this:

“Typically, the internal standards are added at the same order of magnitude concentration as the sample. 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 to generate aerosols of sufficient size for the AMS. This allows an analysis of any trace material present in the blank by creating an aerosol population to transfer the trace material into the AMS and allows for a background subtraction using the internal standard.”

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.

We thank the reviewer for this comment, testing the method with ambient samples is a current project that the first author is working on and is beyond the scope of this work. The use of an appropriate calibration standard is a challenge for any quantification of unknown organic mixtures. We recommend a slope of 1.4 as a starting point as that is the currently accepted RIE for atmospheric organic material.

We have clarified this by adding the following text to the end of section 3.2.2:

“For extracts of atmospheric aerosol or other smaller organic mixtures, the RIE of 1.4, which is typically used for AMS measurements (Canagaratna et al., 2007; Jimenez et al., 2016; Xu et al., 2018), is likely the best value to use as an initial calibration slope. For extracts of other types of organic mixtures, compounds that have a structure similar to the average organic composition should be used to calibrate the samples.”

For the mass spectral analysis, the average mass spectrum across multiple injections is used for the analysis. This improves the S/N for the analysis and we have added text to the experimental clarifying this:

“For the work shown here, mass spectra were collected every 0.5 seconds for ~15-18 seconds in the “open” state, followed by 3 seconds in the closed state. The closed spectrum provides information on the instrument background, including contributions from gas phase species, and is subtracted from the open spectrum in data processing. For the analysis of the mass spectrum and the elemental ratios, the average mass spectrum across all injections is used. For quantification, the total signal under each injection pulse (see below, Figure 2a) is used.”

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

The atomizer is a TSI 3076 aerosol generator and the backing gas pressure was 40 psi. This information has been added to section 3.3.

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

The dot product used here is the dot product between the intensities of matching peaks in the two mass spectra. Larger dot products indicate a greater degree of similarity between the two mass spectra. We have added text clarifying this to the beginning of section 3.3:

"The degree of agreement can be described by the dot product of the intensities for matching peaks in the two spectra, as well as the log of the intensities before taking the dot product (log-dot product), which gives the lower intensity peaks greater weight."

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.

We agree that the degree of overlap for the ambient sample is lower than what is observed for the chamber experiment.

The high degree of overlap we mention is characterized by the high dot product between the spectra (0.98). We qualify this by discussing the substantially larger variation in the lower intensity peaks and use the log-dot product to provide a better representation of this variation (0.90).

To clarify that the "high degree of overlap" is referring specifically to the dominant ion intensities and to discuss the limitations of the elemental ratios measured by this analysis we adding the following text:

"Additional work is necessary to quantify the importance of these effects and care should be taken when comparing the full mass spectra for on-line compared to off-line SVN-AMS analysis. The high degree of overlap in the intensities of the dominant ions between the online (AMS/ACSM) measurements and offline (SVN-AMS) results indicates that the ensemble organic composition for these aerosol samples is generally well-represented by the SVN-AMS measurements (Table 1). However, the estimated elemental ratios from a lower resolution AMS are more uncertain than from the HR-ToF-AMS. Thus, the ratios for these samples in Table 1 are provided only as a demonstration of the overall agreement between the two techniques."

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).

We have added the following text to address this comment:

“For the SVN, the small sample volume requirements can make it attractive for the analysis of other environmental samples that are soluble in water (or organic solvents) and that have low enough vapor pressures to remain in the condensed phase *during sample preparation and after nebulization.*”

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.

The pretreatments for the DOM are necessary because the concentration of organic relative to salts in ocean water is $\sim 30 \times 10^{-6}$. Thus, if pure ocean water is sampled, the dominant signals will be salts present in the sea water with very trace organic signal. The sample pre-treatment steps are standard steps carried out for the analysis of the high molecular weight fraction of DOM. We add the following text to clarify this at the end of section 3.3.

“Here we demonstrate the analysis of the high molecular weight fraction of dissolved organic matter (DOM) with the SVN-AMS. The DOM sample was prepared using a standard protocol for the isolation of this fraction of the organic material (see section 2.3). Figure 5d shows an example AMS mass spectrum from DOM collected from the Pacific Ocean.

Technical Remarks:

Line 27: What kind of “diameter”? Also, to be clear, this diameter is for dry particles.

The diameter measurements were made using an SMPS so they are electrical mobility diameters. This diameter is for particles that have dried during transit to the SMPS. Text clarifying both these topics has been added to the beginning of the results and discussion.

“The particles have size distributions centered at 150-200 nm (electrical mobility diameter). These particles were sampled into the SMPS without passing through a drier. The SVN was approximately three meters further away from the inlet of the SMPS so the particles are likely to be somewhat smaller than those entering the AMS, due to water evaporation in the dry carrier gas.”

Line 29 and Line 281: Please add “material” after “organic”.

This has been added

Figure 2: Please properly write the ions in the legend.

This has been corrected

Line 240: “Slowly” is an improper word here, maybe “slightly”.

This section has been reworded and that sentence has been removed.

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”?

Changes have been made.

Line 307: “3.1” should be “3.3”.

This has been corrected.

1 Ultrasonic Nebulization for the Elemental Analysis of 2 Microgram-Level Samples with Offline Aerosol Mass 3 Spectrometry

4 Rachel E. O'Brien^{1*}, Kelsey J. Ridley², Manjula R. Canagaratna³, John T. Jayne³, Philip L.
5 Croteau³, Douglas R. Worsnop³, Sri Hapsari Budisulistiorini^{4†}, Jason D. Surratt⁴, Christopher L.
6 Follett⁵, Daniel J. Repeta⁵, Jesse H. Kroll²

7 [1] Department of Chemistry, College of William and Mary, Williamsburg, Virginia, 23185, USA

8 [2] Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge,
9 Massachusetts 02139, USA

10 [3] Center for Aerosol and Cloud Chemistry, Aerodyne Research Inc., Billerica, Massachusetts 01821, USA

11 [4] Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, University of
12 North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA

13 [5] Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole,
14 Massachusetts 02540, USA

15 † Now at: Earth Observatory of Singapore, Nanyang Technological University, Singapore 638789, Singapore

16 Corresponding author: Rachel O'Brien, reobrien@wm.edu

17
18
19
20
21
22 **Abstract.** The elemental composition of organic material in environmental samples – including atmospheric organic
23 aerosol, dissolved organic matter, and other complex mixtures – provides insights into their sources and environmental
24 processing. However, standard analytical techniques for measuring elemental ratios typically require large sample
25 sizes (milligrams of material or more). Here we characterize a method for measuring elemental ratios in environmental
26 samples, requiring only micrograms of material, using a Small Volume Nebulizer (SVN). The technique uses
27 ultrasonic nebulization of samples to generate aerosol particles (100-300 nm diameter), which are then analyzed using
28 an aerosol mass spectrometer (AMS). We demonstrate that the technique generates aerosol from complex organic
29 mixtures with minimal changes to the elemental composition of the organic **material** and that quantification is possible
30 using internal standards (e.g., $\text{NH}_4^{15}\text{NO}_3$). Sample volumes of 2-4 μL with total solution concentrations of at least 0.2
31 g/L form sufficient particle mass for elemental ratio measurement by the AMS, despite only a small fraction (~0.1%)
32 of the sample forming fine particles **after nebulization (with-while the remainder ending up as larger droplets)**. The
33 method was applied to aerosol filter extracts from the field and laboratory, as well as to **the polysaccharide fraction of**
34 dissolved organic matter (DOM) from the North Pacific Ocean. In the case of aerosol particles, the mass spectra and
35 elemental ratios from the SVN-AMS agree with those from online AMS sampling; similarly, for DOM, the elemental
36 ratios determined from the SVN-AMS agree with those determined using combustion analysis. The SVN-AMS
37 provides a platform for the rapid quantitative analysis of the elemental composition of complex organic mixtures and

38 non-refractory inorganic salts from microgram samples with applications that include analysis of aerosol extracts, and
39 terrestrial, [aquatic](#), and atmospheric dissolved organic matter.

40 1 Introduction

41 A large number of environmental systems, including the atmosphere, natural waters, and terrestrial systems,
42 contain complex organic mixtures composed of hundreds to thousands of molecular species. Our ability to understand
43 and model such complex chemical systems is often greatly improved when we characterize them in terms of simple
44 chemical frameworks. On the simplest level, the analysis of average elemental ratios can provide important
45 information on potential sources of organic matter samples, as well as the chemical and/or biological transformation
46 processes that modify their composition. For example, the elemental ratios of atmospheric organic aerosol – e.g.,
47 oxygen/carbon ratio (O:C), hydrogen/carbon ratio (H:C), and nitrogen/carbon ratio (N:C) – provide information on
48 aerosol sources and aging (Aiken et al., 2008; Canagaratna et al., 2015; Chen et al., 2015; Daumit et al., 2013; Heald
49 et al., 2010; Jimenez et al., 2009; Kroll et al., 2011). Similarly, in water and soil samples, the elemental ratios of
50 carbon, nitrogen, and phosphorous reveal insights into sources and processing of dissolved and particulate organic
51 matter (Becker et al., 2014; Hansman et al., 2015; Koch et al., 2005; Lu et al., 2015).

52 The most widespread technique for elemental analysis is high-temperature combustion followed by elemental
53 ([carbon, hydrogen, nitrogen, and sulfur](#) (CHNS)) analysis, which is highly accurate but can require milligrams of
54 material (Skoog et al., 1998). For many trace environmental samples, like atmospheric aerosol, this can require
55 extremely long collection times which lead to low time resolution, limiting the amount of information provided for
56 systems that exhibit high temporal variability, [such as air masses in major urban regions](#). An alternative approach for
57 measuring the elemental ratios of aerosol is online (real-time) techniques. The most widely-used instrument for such
58 measurements is the Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) (Decarlo
59 et al., 2006), which can measure elemental ratios of ambient aerosol using just nanograms of material. Over the last
60 decade, in-situ analysis of aerosol particles with the AMS has enabled rapid, sensitive characterization of aerosol
61 concentrations, sources, and atmospheric aging, improving our ability to model atmospheric aerosol and consequently
62 its climate and health effects (Kroll et al. 2015; Ng et al. 2011; Jimenez et al. 2009; Canagaratna et al. 2007).

63 Recently, a number of researchers have used the AMS in an “offline mode,” in which atmospheric samples
64 are collected on filters, extracted, and then atomized into the AMS. Examples include the analysis of sources and
65 aging of atmospheric organic material from aerosol filter extracts (Bozzetti et al., 2017; Huang et al., 2014; Sun et al.,
66 2011; Xu et al., 2015; Ye et al., 2017), cloud/fog water samples (Kaul et al., 2014; Lee et al., 2012), and organic
67 material in glaciers (Xu et al., 2013). Offline AMS has proven especially useful for the analysis of aerosol particles
68 larger than 1 μm (Bozzetti et al., 2016; Daellenbach et al., 2016; Ge et al., 2017). Offline AMS has also proven useful
69 in investigating fractionation and solubility of atmospheric organic material in water and organic solvents
70 (Daellenbach et al., 2016; Mihara and Mochida, 2011; Xu et al., 2016). These studies used both custom-made and
71 commercial atomizers with solvent volumes of at least 5-15 mL. To generate aerosol particles in the size range needed
72 for the AMS, this corresponds to necessary sample masses on the order of 50 μg . While this represents a substantial
73 improvement over the sample mass requirements of conventional CHNS analysis, it is still sufficiently large to limit

74 the applicability of the approach since it can require relatively large organic samples collected with high-volume
75 samplers, often over 24 hours or more.

76 In this work, we characterize a new technique for the elemental analysis of very small sample masses, using
77 ultrasonic nebulization. Aerosol generation with a small volume nebulizer (SVN) expands the range of environmental
78 samples that can be measured, where either sample size is limited or solvent contamination is a concern. The SVN
79 generates aerosol suitable for analysis with aerosol instrumentation, including not only the AMS but also Scanning
80 Mobility Particle Sizers (SMPS); single particle mass spectrometers (e.g. Particle Analysis by Laser Mass
81 Spectrometry (PALMS) (Murphy et al., 1998)); soft ionization sources (e.g. Extractive Electrospray Ionization (EESI)
82 (Gallimore and Kalberer, 2013)); and thermal desorption chemical ionization mass spectrometers (e.g. Filter Inlet for
83 Gases and AEROsols, (FIGAERO-CIMS) (Lopez-Hilfiker et al., 2014)). Here, we present results characterizing the
84 SVN using an HR-ToF-AMS and an SMPS and demonstrate production and elemental analysis of aerosol using 2-4
85 μL of liquid samples, with masses of organic material as low as $\sim 0.4 \mu\text{g}$. In some cases, depending on the sample,
86 pre-concentration is required to generate suitable solutions for analysis. The concentration ranges needed (described
87 below) are comparable to the concentrations used for other offline characterizations including soft ionization with
88 electrospray ionization into mass spectrometers. Thus, this technique provides a platform for direct comparison
89 between offline-AMS samples and other analytical techniques. Quantification of total organic concentrations is
90 demonstrated using internal standards. We examine the effects of aerosol collection, extraction, and nebulization on
91 the mass spectra and elemental ratios observed for offline and online AMS. The aim of this work is to demonstrate
92 that offline analysis of organic mixtures with the SVN-AMS can provide quantitative characteristic elemental ratios
93 for trace environmental and biological samples using just micrograms of sample.

94 **2 Experimental**

95 **2.1 Small Volume Nebulizer**

96 The SVN, shown-illustrated in Figure 1, creates an aerosol by ultrasonically nebulizing a small droplet placed
97 on a thin film stretched across a water reservoir. The aerosol is then carried by a gentle flow of either house air (zero
98 air, Aadco Instruments) or argon (Airgas, 99.999% purity) into the AMS. The three main components of the SVN,
99 described in detail below, are (1) a bottom cylinder with an ultrasonic transducer and water bath, (2) a thin film that
100 is press-fit onto the top of the water bath by an upper cylinder with a slightly larger ID, and (3) a vertical glass tube
101 that connects to the AMS. The connections between all components are airtight, but the apparatus is easily
102 disassembled to inject samples onto the film, as well as to clean the thin film and change the water bath.

103 In the bottom section of the SVN, the 2.4 MHz ultrasonic transducer (Sonaer, Inc., Model 241VM) is located
104 just under the liquid reservoir, with a thin film stretched across the top of the reservoir to provide a clean nebulization
105 surface for the sample. We use a 0.001" thick Kapton film or Teflon film, as these two were found to have the lowest
106 background signal and the best performance in terms of the amount of aerosol generated compared to other materials
107 tested. Press-fit onto the bottom piece is another PVC cylinder that has two side ports with carrier gas inlets, and a
108 larger hole in the top into which a 15 cm glass tube is seated. The distance from the thin film to the bottom of the glass

109 tube is ~1.5 cm. During experiments, the nebulized aerosol is carried up through the vertical glass tube, into the
110 stainless steel tubing that leads to the AMS. Additional components such as Nafion™ (Perma Pure LLC) driers can
111 be placed inline if desired, but such modifications were not investigated in the present work.

112 Samples can be introduced into the SVN using two different approaches: discrete injections of individual
113 samples (for individual “one-shot” measurements) or continuous addition of a sample flow (for continual analysis,
114 enabling signal averaging). For most studies, MilliQ water was used as the solvent; in some cases we used HPLC-
115 grade methanol, though the organic background signal is higher in that case, likely due to a combination of increased
116 organic background in organic solvents and incomplete evaporation of methanol prior to measurement. For most of
117 the work described here, we used discrete injections of 2-5 μL of aqueous solutions manually deposited directly onto
118 the center of the Kapton film. For continuous injections, solutions made with MilliQ or organic solvents were
119 introduced via a syringe pump (Harvard Apparatus Model 22), which sends liquid flow (20-40 $\mu\text{L}/\text{min}$) through a
120 borosilicate capillary entering the SVN via a small downward-facing hole in the upper PVC piece (Figure 1). In the
121 future, such a port could also be used to provide automated discrete sample introduction using an autosampler.

122 For aqueous samples containing salts and small organic molecules, only 1-2% of the original sample mass
123 was observed to remain on the thin film after a discrete injection (Figure S2). To ensure a clean surface between
124 different samples, the surface was cleaned by nebulizing 2-8 μL of MilliQ water off the surface 5-10 times over
125 approximately one minute. The cleanliness of the surface was then verified by ~~running~~ nebulizing a salt solution (at
126 least 0.5 g/L) between each sample. The salt solution is necessary to ensure that any contaminants can be seen, since
127 pure water risks generating aerosol particles that are too small to be measured in the AMS. For samples in which
128 carryover was observed (for example, the dissolved organic matter solutions discussed in section 3.1), additional
129 cleaning of the film was undertaken with sonication in a deionized water bath followed by rinsing with HPLC-grade
130 methanol for > 30 seconds. Careful maintenance of the surface ensures uncontaminated mass spectra and accurate
131 quantification of the solution components.

132 2.2 AMS Data Collection and Analysis

133 While a number of different aerosols instruments could be used with the SVN, here we focus primarily on
134 elemental analysis by the HR-ToF-AMS. The AMS has previously been described in detail (Canagaratna et al., 2007;
135 Decarlo et al., 2006) and provides quantitative measurements of non-refractory material (organics, ammonium sulfate,
136 ammonium nitrate, etc.) for aerosol particles between approximately 40 and 1,000 nm. The mass spectrometer used
137 in the AMS is a high resolution time-of-flight mass spectrometer (HTOF-MS, ToFwerk AG), run under “V mode” for
138 a mass resolution of 2,000-3,000 $m/\Delta m$. This mass-resolving power enables peak fitting and identification of all
139 organic fragment ions observed here ($< 130 m/z$), which enables the calculation of quantitative elemental ratios for
140 the organic mixture, after correcting for fragmentation bias during electron ionization (Aiken et al., 2007, 2008;
141 Canagaratna et al., 2015). For AMS data collected using indoor or outdoor air, the intensities of CO^+ and H_2O^+ are
142 complicated by gas-phase interferences (N_2^+ and gas-phase H_2O^+). -For samples compared to chamber or ambient
143 online-AMS data sets, house air was the carrier gas, ~~and~~ standard empirical estimates were used, and the improved-
144 ambient method for elemental ratios was applied (Canagaratna et al., 2015). With the SVN, inert carrier gases such

145 as argon can also be used, allowing for the direct measurement of the CO⁺ ion intensity (as demonstrated below for
146 dissolved organic matter, the majority of the other samples were run with zero air).

147 For discrete sampling, “fast MS” mode (Kimmel et al., 2010) was used because the pulse length of a single
148 injection is ~30-60 seconds long. Fast MS mode generates mass spectra every 0.5-2 seconds and the instrument cycles
149 between the “closed” state, in which the aerosol beam is blocked, and the “open” state, in which the aerosol beam can
150 reach the vaporization/ionization region for detection. For the work shown here, mass spectra were collected every
151 0.5 seconds for ~15-18 seconds in the “open” state, followed by 3 seconds in the closed state. The closed spectrum
152 provides information on the instrument background, including contributions from gas phase species, and is subtracted
153 from the open spectrum in data processing. For the high resolution peak fitting and the analysis of the mass spectrum
154 and the elemental ratios, the average mass spectrum across all injections is used. For quantification, the total signal
155 under each injection pulse is used. For continuous injections, the standard AMS operating mode (“GenAlt mode”)
156 was used. This provides an average mass spectrum (by subtracting the closed signal from the open signal), as well as
157 particle time-of-flight (PToF) data (providing aerosol size distributions for all aerosol components), once per minute.
158 All AMS data were ~~analysed~~analyzed using software packages SQUIRREL (v1.57I) and PIKA (v1.16I), available at
159 <http://cires1.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/>.

160 The aerodynamic lens on the AMS has a transmission efficiency of nearly 100% for particles with
161 aerodynamic diameters of 70-500 nm; for somewhat smaller particles (~~3040~~-70 nm), this transmission is lower but
162 not negligible (Jimenez et al., 2003). Thus, high enough solution concentrations are used such that the dried particles
163 formed in the nebulizer are larger than ~100 nm aerodynamic diameter. Collection efficiencies (CE) in the AMS can
164 vary depending on the extent to which aerosol particles bounce off the thermal element prior to vaporization
165 (Docherty et al., 2013). This can impact the absolute concentrations observed, but for internally mixed samples, the
166 relative concentrations of different aerosol components are independent of CE. In this work, most measurements
167 (including elemental ratios) are reported as relative measurements, and thus no CE correction is applied. Some biases
168 may arise if the aerosol is not internally mixed, but for all systems examined so far in PToF, no size-dependence in
169 composition was observed (Figure S1).

170 2.3 Sample Collection and Solution Preparation

171 As described below, samples were prepared from a number of sources, including commercially available
172 standards, the extracts of chamber and ambient aerosol particles collected on filters, and dissolved organic matter from
173 the Pacific Ocean. For all solutions, either ultrapure water (18.2 M Ω cm, MilliQ) or HPLC-grade methanol was used.
174 Prior to use, all glassware was cleaned with a methanol solvent wash and baked at 450°C for 6 hours.

175 Chamber aerosol (enabling offline vs. online comparisons) was generated in the MIT 7.5-m³ Teflon
176 environmental chamber, run in continuous-volume, “semi-batch” mode. Details on the facility are given elsewhere
177 (Hunter et al., 2014). Experiments were run at 20 °C, < 5% RH, in the dark, and under low-NO_x (< 10 ppb) conditions
178 using ozone as the oxidant. Ammonium sulfate seeds were added ~~to~~for an initial concentration of ~60 $\mu\text{g}/\text{m}^3$. The
179 VOC, α -pinene, had an initial mixing ratio of 100 ppb; a penray lamp (Jelight model 600) was used to add an initial
180 ozone concentration of ~500-700 ppb ozone. The ozone concentration decreased due to consumption and dilution to

181 400 ppb by the end of the experiment. The initial organic loading was $\sim 70 \mu\text{g}/\text{m}^3$ and decayed due to dilution,
182 sampling, and wall loss to a final value of $\sim 18 \mu\text{g}/\text{m}^3$. Filter samples were collected on Zeflour® PTFE Membrane
183 Filters (0.5 μm pore size) at flow rates of $\sim 5 \text{ L}/\text{min}$ for 10 hr. Laboratory blank filters were prepared by placing
184 separate filters in the filter holder for 10 minutes before the start of the experiments. All filters were stored in baked
185 aluminum foil packets, sealed in plastic bags, and placed in a freezer at $-20 \text{ }^\circ\text{C}$ until extraction. Filters were extracted
186 with $\sim 4 \text{ mL}$ of HPLC-grade methanol. In order to avoid oxidation of the organic species in the extract, no sonication
187 was used; instead, the vials were gently agitated by hand intermittently over 3 hours. Solutions were concentrated by
188 evaporating to dryness under a gentle stream of ultra-high purity N_2 . Dried samples were stored in the freezer at -20
189 $^\circ\text{C}$ until reconstitution with MilliQ water and analysis by the SVN-AMS. Blank subtraction was carried out with a
190 scaling of the filter blank to 12% of the sample signal, as determined from the internal standard in each sample.

191 Field samples from the Southern Oxidant and Aerosol Study (SOAS) in 2013 were collected on pre-baked
192 Tissuquartz™ Filters (Pall Life Science, 8 x 10 in) at Look Rock, TN starting on 06/16/2013 using a high-volume
193 aerosol filter sampler with a $\text{PM}_{2.5}$ cyclone (Tisch Environmental, Inc.) as described by Budisulistiorini et al. (2015).
194 For filter extraction, a 37 mm punch was extracted in a pre-cleaned scintillation vials with 20 mL high-purity methanol
195 (LC-MS Chromasolv-grade®, Sigma Aldrich) by sonication for 45 min. Filter extract was filtered through 0.2 μm
196 syringe filter (Acrodisc® PTFE membrane, Pall Life Sciences) to remove suspended filter fibers. The filtered extract
197 was then blown down to dryness under a gentle $\text{N}_2(\text{g})$ stream at room temperature. An aerosol chemical speciation
198 monitor (ACSM) (Ng et al., 2011a) was deployed at the same field site (Budisulistiorini et al., 2015); the average mass
199 spectrum for the length of the filter sample was used for comparison with the present SVN-AMS measurements. For
200 all analyses presented here (chamber and ambient) sufficient mass was extracted to enable the analysis of individual
201 filter samples, with no combination of extracts from different samples required.

202 Standard solutions were prepared from commercially available compounds dissolved in MilliQ water.
203 Reagents used included ammonium sulfate, ammonium nitrate, isotopically-labelled ammonium nitrate ($\text{NH}_4^{15}\text{NO}_3$),
204 citric acid, mannitol, PEG-400, 4-hydroxy-3-methoxy-DL-mandelic acid (HMMA), and HPLC grade methanol, all
205 from Sigma-Aldrich, all at $\geq 99\%$ purity.

206 The DOM polysaccharide sample was collected at the Natural Energy Laboratory Hawaii Authority facility
207 in Kona, Hawaii. Seawater from a depth of 20 m was pumped through a 0.2 μm filter to remove particles and the high
208 molecular weight fraction of organic matter in the filtrate was concentrated by ultrafiltration using a membrane with
209 a 1 nm pore size and a nominal 1,000 ~~Dalton~~ molecular weight cut off. This fraction was desalted by serial
210 dilution/concentration with MilliQ water and then freeze-dried. Low-molecular weight humic substances and residual
211 salts were removed by stirring with anion (hydroxide form) and cation exchange resins (hydrogen form). The final
212 product was freeze-dried to yield a fluffy white powder. Conventional CHNS analysis was carried out using a CE-440
213 Elemental Analyzer (Exeter Analytical). This powder was dissolved in MilliQ water at approximately 1 g/L to prepare
214 solutions for analysis.

Formatted: Not Superscript/ Subscript

215 3 Results and Discussion

216 3.1 Nebulization and Aerosol Size

217 Figure 2a shows a time series of measured aerosol mass concentrations of a typical nebulized aerosol pulse
218 from a 4 μL solution containing approximately 0.33 g/L each of mannitol, ammonium sulfate, and ammonium nitrate.
219 The nebulizer is turned on at $t = 0$ and shortly afterwards ($t \sim 10$ s) the aerosol packet is observed in the AMS. The
220 start of the nebulization is timed so that a closed (background) measurement occurs during the downslope of the signal
221 ($t \sim 16$ -21 s, dashed lines/gaps). This background is subtracted from the aerosol particle signal during data processing.
222 Measurements are collected until the signal returns to the baseline ($t \sim 44$ s).

223 Figure 2b shows the size distribution of the particles generated by nebulizing an aqueous solution of citric
224 acid with continuous injection via syringe pump and a total concentration of ~ 1 g/L into an SMPS (TSI). The particles
225 have size distributions centered at 150-200 nm (electrical mobility diameter). These particles were sampled into the
226 SMPS without passing through a drier. The SVN was approximately three meters further away from the inlet of the
227 SMPS so the particles are likely to be somewhat smaller than those entering the AMS, due to water evaporation in the
228 dry carrier gas. We find injections of solutions with total concentrations above 0.2 g/L provide sufficient aerosol mass
229 for analysis (Figure S1). These measurements compare well with calculations based on the size of droplets reported
230 by the manufacturer (Sonaer inc.) of approximately 1.7 μm using water solutions. Assuming that the density of the
231 dried particle is 1.3 g/cm^3 (Nakao et al., 2013), the minimum sample concentration that will form a 100 nm dried
232 particle is approximately 0.3 g/L. More dilute solutions do not generate signal in the AMS because the majority of the
233 aerosol particles that are formed are too small for transmission through the aerodynamic lens of the AMS (Figure 2b).
234 To generate large enough aerosol particles from more dilute solutions, larger initial droplets could be formed by
235 changing the piezo to a transducer to one that vibrates at a lower frequency. However, for these larger droplets, drying
236 will require the loss of a greater amount of solvent, so that any impurities in the solvent will make up a larger (and
237 possibly even dominant) fraction of the resulting fine particles. Thus the use of ultrasonic nebulization at lower
238 frequencies was not investigated here.

239 3.2 Quantification

240 3.2.1 Nebulization Efficiency

241 A key quantity describing the potential sensitivity of the SVN-AMS is the SVN nebulization efficiency, the
242 ratio of the mass measured in the AMS compared to the mass of analyte placed on the thin film. This was determined
243 by loading 4 μL of a known solution onto the film and measuring the mass of each component in the AMS integrated
244 over the injection pulse, determined by:

$$245 M_{AMS} = \int_{t_1}^{t_2} f(t) dt \times v_{AMS}$$

246 where M_{AMS} is the mass measured by the AMS in μg , $f(t)$ is the instantaneous mass concentration measured in the
247 AMS ($\mu\text{g}/\text{m}^3$), and v_{AMS} is the gas flow rate into the AMS in m^3/s . For each injection, the background-subtracted AMS
248 signal is calculated (Figure 2a). The gaps due to closed cycles are bridged by interpolation and the area under the
249

250 injection curve is calculated via trapezoidal integration from time points before and after the pulse (t_1 and t_2 ,
251 respectively) with the time steps (dt) corresponding to the MS cycle time (here 0.5 s). The mass measured in the AMS
252 is affected by three factors: the amount of aerosol formed and transported out of the SVN, the fraction of the gas flow
253 from the SVN that is sampled by the AMS (typically $\sim 1/2$), and the fraction of aerosol that bounces off the heater
254 element before vaporizing (the AMS CE).

Formatted: Font: Italic

255 Figure 3 shows the mass measured in the AMS compared to the mass deposited on the nebulizer for replicate
256 injections of four different aqueous solutions of citric acid, ammonium nitrate, ammonium sulfate, and isotopically-
257 labeled ammonium nitrate ($\text{NH}_4^{15}\text{NO}_3$, used later as an internal standard) with concentrations ranging between
258 approximately 0.1 and 0.2 g/L for each of the components (but with the same total concentration, 0.75 g/L). Six
259 replicate injections of 4 μL drops of the solutions from one of the calibration curves (section 3.2.2 below) were
260 atomized, and the total mass observed in the AMS was calculated as described above. (Details on the concentrations
261 of analytes in these calibration solutions for Figures 3 and 4 are provided in the supplemental.) There are variations in
262 the efficiency from sample to sample and run to run, thus the trends shown in Figure 3 are illustrative only. The key
263 trait observed is that the measured nebulization efficiencies are on the order of 0.02-0.06%, indicating that the aerosol
264 mass detected with the AMS is approximately three orders of magnitude lower than the mass originally deposited on
265 the thin film. The amount of mass measured in the AMS increases slowly compared to the amount placed on the film,
266 and variations in measured masses are observed for replicate injections of the same sample. The observed increase in
267 the mass measured for these samples is likely partially related to CE on the vaporizer, as the highest efficiency was
268 observed for samples with the largest mass fractions of organic. The measured nebulization efficiencies are on the
269 order of 0.02-0.06%, indicating that the aerosol mass detected with the AMS is approximately three orders of
270 magnitude lower than the mass originally deposited on the thin film.

Formatted: Font: Symbol

271 The majority of the sample mass loss likely occurs during the nebulization process itself. For aqueous
272 solutions in the SVN, large droplets are observed to be ejected off the surface of the film at the same time as the
273 aerosol is generated. These ejected droplets are then lost to the walls of the SVN. The ejection of these droplets
274 appears to be a necessary part of the nebulization mechanism for water samples as smaller volumes ($< 1 \mu\text{L}$) of water
275 do not generate such droplets and also do not appear to form aerosol. This observed mechanism is in agreement with
276 previous studies of aerosol generation for ultrasonic nebulization, in which cavitation within the droplet (Lang, 1962)
277 and boiling and/or jetting from a droplet chain (Simon et al., 2015) have been observed.

278 The size distribution and number of aerosol particles from ultrasonic nebulization have been shown to be
279 affected by the frequency of the ultrasonic vibration, the properties of the liquid including surface tension, density,
280 and viscosity, and the concentration of the solution (Donnelly et al., 2005; Lang, 1962; Simon et al., 2015). The present
281 application involves relatively dilute solution, so the only parameter that is likely to vary is ~~could be varied was~~ the
282 surface tension, by use of different solvents. Nebulization of solvents with lower surface tension, such as methanol,
283 led to the ejection of much smaller droplets, and consequently substantially higher nebulization efficiencies ($\sim 10\%$).
284 However, methanol (and other HPLC-grade organic solvents) was found to give higher background signals in the
285 AMS than MilliQ water, likely due to higher levels of low-volatility contaminants. This difference was also observed
286 by Daellenbach *et al.* (2016); therefore, MilliQ water appears to be the ideal solvent to use for most environmental

287 samples. However, with adequate solvent background characterization, organic solvents may be optimal for
288 environmental samples with more non-polar components (e.g. petroleum or fresh tail pipe emissions).

289 3.2.2 Internal Standards and Calibration Curves

290 In Figure 3, the vertical spread of data points ~~illustrates~~ shows the variation in nebulization efficiency from
291 one injection to the next. This is likely the result of small differences in the droplet shape or position on the film,
292 leading to differences in how the droplets are ejected from the surface during aerosol formation. This run-to-run
293 variability in nebulization efficiency, as well as the lack of a linear correlation between the mass placed on the film
294 and the mass observed, complicates quantification, and necessitates the use of an internal standard to quantify the
295 concentration of organic species within the original sample. In some cases, an inorganic ion that is independently
296 quantified, such as sulfate, can serve as this internal standard (Daellenbach et al., 2016). However, in many cases
297 such an independent measurement is not available; additionally, some environmental samples may not contain
298 appreciable levels of measurable inorganic species, or else such species may not be soluble in the solvent of choice
299 (e.g. ionic species in organic solvents). In these cases, an internal standard needs to be added to the solution prior to
300 nebulization.

301 For use with the AMS, the internal standard must meet a number of requirements: it must be non-refractory,
302 soluble, unreactive with the other sample components, not already present in the solution, and easily distinguishable
303 from other species in the sample. For nebulization of samples dissolved in organic solvents, organic internal standards
304 (e.g., phthalic acid (Chen et al., 2016; Han et al., 2016)) meet these requirements. In the present work, which focuses
305 on aqueous samples only, we use an inorganic internal standard of isotopically-labelled ammonium nitrate
306 ($\text{NH}_4^{15}\text{NO}_3$). An example mass spectrum for an internal standard solution is shown in Figure 4a. The background
307 signal from other components (organic ~~material~~, sulfate, and nitrate) is very low. Another tested option is ammonium
308 iodide (NH_4I). Both of these salts work well as internal standards for both laboratory and ambient samples, since
309 neither $^{15}\text{NO}_3$ nor iodide are present in appreciable amounts in the atmosphere and there is usually a very small
310 contribution of organic fragments at the fragment masses observed for those salts. ~~Typically, T~~he internal standards
311 are added at the same order of magnitude concentration as the sample. For all tests of background signals and blanks,
312 the internal standard is added to the solutions at concentrations between 0.5-1 g/L in order to generate aerosols of
313 sufficient size for the AMS. This allows an analysis of any trace material present in the blank by creating an aerosol
314 population to transfer the trace material into the AMS and allows for a background subtraction using the internal
315 standard.

316 Figure 4b shows calibration curves with linear responses for three different organic compounds (citric acid,
317 4-hydroxy-3-methoxy-DL-mandelic acid (HMMA), and polyethylene glycol 400 (PEG-400)) at four concentrations
318 using $\text{NH}_4^{15}\text{NO}_3$ as the internal standard. For the calibration curve, the ratios of the AMS signals for the analyte over
319 the internal standard are compared to the ratios for known solution concentrations, thus correcting any variations in
320 the mass of analyte nebulized. For quantification of unknowns, known concentrations of the internal standard are
321 added to the samples at ratios comparable to what is used for the calibration curve. The ratio of the measured AMS
322 signals can then be used to calculate the unknown analyte concentration from the calibration curve.

Formatted: Indent: First line: 0.5"

323 For quantification of complex organic mixtures using this technique, the most accurate organic calibration
324 standards will have chemical structures similar to the average structure of the mixture. The slope of each line is related
325 to the relative ionization efficiency (RIE) of the organic compound in the AMS (Jimenez et al., 2003). The RIE values
326 in Figure 4b for HMMA and citric acid (1.01 and 1.95, respectively) bracket the range of RIE values for different
327 types of organics measured using standard AMS calibration techniques (Jimenez et al., 2016). This range likely arises
328 from differences in how the organic compounds dissociate during volatilization on the heater. The heater in the AMS
329 is typically set at 600°C, and so most organic molecules found in organic aerosol thermally decompose prior to electron
330 impact ionization (Canagaratna et al., 2015) leading to RIEs in the range of 1.0-2.0. In contrast, the slope of 2.62 for
331 PEG-400 is substantially outside of the range of values. However, with the AMS, complex mixtures are less likely to
332 show large variations in RIE than different individual compounds, such as those used in Figure 4. For extracts of
333 atmospheric aerosol or other smaller organic mixtures, the RIE of 1.4, which is typically used for AMS measurements
334 (Canagaratna et al., 2007; Jimenez et al., 2016; Xu et al., 2018), is likely the best value to use as an initial calibration
335 slope. For extracts of other types of organic mixtures, compounds that have a structure similar to the average organic
336 composition should be used to calibrate the samples.

337 **3.4.3 Mass Spectral Analysis**

338 The primary goal of the SVN-AMS is to measure quantitative chemical information, specifically elemental
339 ratios, from complex organic mixtures. We have characterized these for a number of different chemical systems,
340 described below. Results are summarized in Figure 5 (comparing SVN-AMS and online AMS mass spectra) and Table
341 1 (comparing elemental ratios measured with SVN-AMS with those measured by either online AMS or CHNS
342 analysis).

343 One concern with using ultrasonic nebulization to generate aerosol particles is the possibility that the high
344 temperatures possibly reached by the solution during nebulization may degrade the organic compounds, affecting their
345 mass spectra (and hence measured elemental composition). Figure 5a shows a comparison of a solution containing 1
346 g/L citric acid aerosolized with a TSI atomizer (TSI 3076, 40 psi gas) (black) and the SVN (greengold), with the inset
347 showing a direct comparison between the intensities measured for each ion in the mass spectrum. The degree of
348 agreement can be described by the dot product of the intensities for matching peaks in of the two spectra, as well as
349 the log of the intensities before taking the dot product (log-dot product), which gives the lower intensity peaks greater
350 weight. Very good overlap between the two mass spectra is observed, with a dot product of 0.99 and a log-dot product
351 of 0.96. This indicates minimal degradation of the citric acid by ultrasonic nebulization.

352 A high degree of similarity is also observed between offline and online aerosol measurements for more
353 complex mixtures. Figure 5b shows mass spectra for a comparison of offline (redgold) vs. online (black) SOA sample,
354 generated from the dark ozonolysis of α -pinene. The online mass spectra is the average real-time AMS mass spectrum
355 averaged over the 10 hours of filter collection. For all filter samples, spectra from the SVN are background subtracted
356 using spectra collected from blank filter samples. These blanks provide the background for any trace organic material
357 on the filters before collection as well as any background organic material introduced during sample preparation. The
358 overlap in Figure 5b between the mass spectra is very good, with a dot product of 0.98 and a log-dot product of 0.98.

359 The elemental ratios are also very similar between the two samples with an H:C of 1.6 for both and O:C of 0.48 for
360 the chamber and 0.49 for the SVN samples (Table 1). The largest difference is observed at m/z 44 (CO_2^+) and m/z 43
361 ($\text{C}_2\text{H}_3\text{O}^+$) with a larger fraction of CO_2^+ in the offline sample. The intensity of CO^+ (m/z 28) is also different, but only
362 because it is set equal to the intensity of the CO_2^+ ion, as is commonly done for ambient sampling with the AMS
363 (given that the CO^+ ion generally cannot be distinguished from the much more abundant N_2^+ ion (Aiken et al., 2007)).
364 The organic contribution from H_2O^+ , OH^+ , and O^+ is also constrained by the CO_2^+ signal so any differences in CO_2^+
365 intensity will also show up in those ions (Aiken et al., 2008). The observed difference in CO_2^+ and $\text{C}_2\text{H}_3\text{O}^+$ ion intensity
366 is likely a result of the extraction step prior to nebulization, which may preferentially dissolve the most water-soluble
367 (oxidized) SOA components. Additionally, the online measurement is for PM1 while offline measurement is collecting
368 the full range of particle sizes on the filter. However, based on the agreement in H:C and O:C in the online and
369 offline cases, these factors does not appear to bias elemental ratio measurements substantially.

Formatted: Not Superscript/ Subscript

370 Figure 5c shows a comparison of online and offline measurements of ambient organic aerosol, specifically
371 ACSM measurements and SVN-AMS measurements of a filter extract collected simultaneously during the 2013
372 SOAS field campaign in Look Rock, TN (8 pm July 4 to 7am July 5, 2013; EST). Since the ACSM is a unit-mass-
373 resolution instrument, the HR-AMS data are degraded to unit mass resolution, and ions that are determined from the
374 m/z 44 signal ($m/z=15, 16, 17, 18, \text{ and } 28$) are excluded from the analysis. Additionally, ions at m/z 30 and 31 were
375 removed from comparison because of interferences from the internal standard (m/z 31) and nitrate in the sample (m/z
376 30).

377 The two mass spectra in Figure 5c have a high degree of agreement between the major ions (dot product of
378 0.98). However, there is substantially more variation between the two techniques than in the chamber study, especially
379 in the lower-abundance peaks ($m/z > 45$; see inset), as reflected in the lower log-dot product of only 0.90. Possible
380 reasons for this lower correlation include fractionation from the extraction step, the different sizes measured ($\text{PM}_{2.5}$
381 for the filter vs. PM_1 for the ACSM) (Daellenbach et al., 2016), the uncertainty in ACSM signals at higher masses due
382 to uncertainty in the relative ion transmission curve (Ng et al., 2011a), and/or the losses of more volatile compounds
383 during collection, extraction, and handling. Additional work is necessary to quantify the importance of these effects
384 and care should be taken when comparing the full mass spectra for on-line compared to off-line SVN-AMS analysis.
385 Regardless, The high degree of overlap in the intensities of the dominant ions between the online (AMS/ACSM)
386 measurements and offline (SVN-AMS) results indicates that the ensemble organic composition for these aerosol
387 samples is generally well-represented by the SVN-AMS measurements (Table 1). However, the estimated elemental
388 ratios from a lower resolution AMS are more uncertain than from the HR-ToF-AMS. Thus, the ratios for these samples
389 in Table 1 are provided only as a demonstration of the overall agreement between the two techniques.

390 For the SVN, the small sample volume requirements can make it attractive for the analysis of other
391 environmental samples that are soluble in water (or organic solvents), and that have low enough vapor pressures to
392 remain in the condensed phase after sample preparation and after nebulization. Here we demonstrate the analysis of
393 the high molecular weight fraction of the polysaccharide fraction of dissolved organic matter (DOM) with the SVN-
394 AMS. The DOM sample was prepared using a standard protocol for the isolation of this fraction of the organic
395 material (see section 2.3). This preparation removes the lower molecular weight compounds so chemicals such as

396 ~~methane sulfonic acid are not expected to be observed.~~ Figure ~~34-5d~~ shows an example AMS mass spectrum from
397 ~~dissolved-organic-matter-(DOM) collected~~ from the Pacific Ocean. The mass spectrum is dominated by oxidized
398 fragments containing one or more oxygen atoms with smaller amounts of nitrogen-containing fragments. ~~The sample~~
399 ~~preparation for the DOM removed all salts, thus the ammonium fragments were assumed to be from organonitrogen~~
400 ~~species and were assigned to the organic fraction.~~ The measured N:C and H:C values of 0.081 and 1.7, respectively,
401 matches those measured by CHNS analysis (0.080 and 1.74, respectively). This demonstrates that with the SVN,
402 microgram quantities of dissolved environmental mixtures can be nebulized and sampled into the AMS providing a
403 rapid, quantitative method to determine elemental ratios in these complex organic mixtures.

404 **4 Conclusions**

405 A new ultrasonic nebulizer has been described and characterized for generation of aerosol from very small
406 sample masses. We demonstrate the application of this technique to offline AMS analysis of complex organic
407 mixtures from aerosol filter extracts and DOM. Data sets that include quantitative organic mass, characteristic mass
408 spectra, and quantitative elemental ratios can be generated from only 0.4-1.2 µg of material. ~~For these samples, pre-~~
409 ~~concentration was required to prepare a suitable solution concentration for analysis. This will be required for some~~
410 ~~types of environmental samples and care should be taken to minimize artifacts during solution preparation.~~ -A direct
411 comparison between the mass spectra generated by commercial spray atomizers or by ~~real-time aerosol~~-particles
412 sampled directly from the atmosphere showed high degrees of agreement, ~~indicating minimal composition changes~~
413 ~~during sample preparation and nebulization.~~ Nebulization of aqueous samples generated measurable aerosol from
414 0.1% of the sample mass. Higher nebulization efficiencies (and smaller ejected droplets) were observed for methanol,
415 likely due to its lower surface tension. The SVN, combined with offline-AMS, provides rapid analysis of non-
416 refractory organic and inorganic compounds. For other types of characterization, including analysis of refractory
417 material or organic molecular composition, the SVN can also be coupled with other aerosol instrumentation such as
418 PALMS or CIMS instruments.

419 Future improvements in the nebulization and collection efficiency of the SVN-AMS will enable analysis with
420 even lower sample mass requirements. The use of organic internal standards is one method to potentially improve
421 collection efficiency in the AMS ~~as the higher organic content may decrease the bounce of particles off the vaporizer.~~
422 Additionally, the use of solvents with lower surface tension than water shows promise for improved nebulization
423 efficiencies. ~~Finally, in contrast to atomizers (where the carrier gas generates the aerosol), ultrasonic nebulizers~~
424 ~~decouple the aerosol formation from the carrier gas flow rate, enabling potential concentration of the aerosol prior to~~
425 ~~sampling.~~ A useful future direction for this technique will be to characterize the background signal in different organic
426 solvents and optimize the continuous flow configuration to minimize the return of large ejected droplets back onto the
427 film. Continuous flow with organic solutions will also enable the analysis of more hydrophobic organic samples such
428 as fresh vehicle emissions, cooking oils, and petrochemical samples. In the future, the SVN can be used to generate
429 aerosol for ~~quantitative and qualitative~~ analysis of other environmental samples to investigate sources or
430 processing/aging of these organic mixtures. The SVN, combined with aerosol measurement techniques such as the

431 AMS, provides a rapid, quantitative method to characterize the chemical and elemental properties of complex organic
432 mixtures, producing rich data sets for the exploration of exceptionally trace environmental samples.

433

434 **Supporting Information**

435 The supporting information is available free of charge at DOI:xxx. The document contains additional information on
436 particle sizes and memory effects between runs, (file type, PDF).

437 **Corresponding Author**

438 Rachel E. O'Brien, College of William and Mary, reobrien@wm.edu.

439 **Author Contributions**

440 MRC, JTJ, PLC, DRW, JHK, and KJR designed and built the SVN. SHB, JDS, CLF, DJR provided ambient aerosol
441 samples and DOM. REO and JHK designed experiments and REO carried them out. REO prepared the manuscript
442 with contributions from all authors.

443 **Data availability**

444 All data sets including mass spectra and SMPS data are available on request from REO, reobrien@wm.edu.

445 **Acknowledgement**

446 This work was supported by National Oceanic and Atmospheric Administration Grants No. NA13OAR4310072 and
447 NA140AR4310132. KJB acknowledges support from the National Science Foundation. SHB and JDS acknowledges
448 support from the US Environmental Protection Agency Award No. 835404, Electric Power Research Institute (EPRI),
449 and National Oceanic and Atmospheric Administration Grant No. NA13OAR4310064. Special thanks to Dr. David
450 Karl and Mr. Eric Grabowski, University of Hawaii, for the CHNS elemental analysis of DOM. DJR acknowledges
451 support from the Gordan and Betty Moore Foundation award 6000 and the Simons Foundation SCOPE award 329108.

452 **References**

453 Aiken, A. C., DeCarlo, P. F. and Jimenez, J. L.: Elemental analysis of organic species with electron ionization high-
454 resolution mass spectrometry, *Anal. Chem.*, 79(21), 8350–8358, doi:10.1021/ac071150w, 2007.

455 Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C.,
456 Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R.,

457 Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Balensperger, U. and Jimenez,
458 J. L.: O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-
459 Flight Aerosol Mass Spectrometry, *Environ. Sci. Technol.*, 42, 4478–4485, doi:10.1021/es703009q, 2008.

460 Becker, J. W., Berube, P. M., Follett, C. L., Waterbury, J. B., Chisholm, S. W., Delong, E. F., Repeta, D. J. and Metz,
461 T.: Closely related phytoplankton species produce similar suites of dissolved organic matter, *Front. Microbiol.*, 5(111),
462 1–14, doi:10.3389/fmicb.2014.00111, 2014.

463 Bozzetti, C., Daellenbach, K. R., Hueglin, C., Fermo, P., Sciare, J., Kasper-Giebl, A., Mazar, Y., Abbaszade, L., El
464 Kazzi, M., Gonzalez, R., Shuster-Meiseles, T., Flasch, M., Wolf, R., Kr, A., Francesco Canonaco, E., Schnelle-Kreis,
465 R., Slowik, J. G., Zimmermann, R., Rudich, Y., Baltensperger, U., El Haddad, I. and Preo, A. H.: Size-Resolved
466 Identification, Characterization, and Quantification of Primary Biological Organic Aerosol at a European Rural Site,
467 *Environ. Sci. Technol.*, 50, 3425–3434, doi:10.1021/acs.est.5b05960, 2016.

468 Bozzetti, C., Sosedova, Y., Xiao, M., Daellenbach, K. R., Ulevicius, V., Dudoitis, V., Mordas, G., Byčenkienė, S.,
469 E., Plauškaitė, K., Vlachou, A., Golly, B., Chazéau, B., Besombes, J.-L., Baltensperger, U., Jaffrezo, J.-L., Slowik,
470 J. G., Haddad, I. El and Prévôt, A. S. H.: Argon offline-AMS source apportionment of organic aerosol over yearly
471 cycles for an urban, rural, and marine site in northern Europe, *Atmos. Chem. Phys.*, 17, 117–141, doi:10.5194/acp-17-
472 117-2017, 2017.

473 Budisulistiorini, S. H., Li, X., Bairai, S. T., Renfro, J., Liu, Y., Liu, Y. J., McKinney, K. A., Martin, S. T., McNeill, V.
474 F., Pye, H. O. T., Nenes, A., Neff, M. E., Stone, E. A., Mueller, S., Knote, C., Shaw, S. L., Zhang, Z., Gold, A. and
475 Surratt, J. D.: Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol
476 formation during the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee ground site,
477 *Atmos. Chem. Phys.*, 15, 8871–8888, doi:10.5194/acp-15-8871-2015, 2015.

478 Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F.,
479 Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., Decarlo, P. F., Kolb, C. E.,
480 Davidovits, P. and Worsnop, D. R.: Chemical and Microphysical Characterization of Ambient Aerosols with the
481 Aerodyne Aerosol Mass Spectrometer, *Mass Spec Rev.*, 26, 185–222, doi:10.1002/mas.20115, 2007.

482 Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner,
483 E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T. and Worsnop, D. R.: Elemental ratio
484 measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and
485 implications, *Atmos. Chem. Phys.*, 15, 253–272, doi:10.5194/acp-15-253-2015, 2015.

486 Chen, Q., Heald, C. L., Jimenez, J. L., Canagaratna, M. R., Zhang, Q., He, L.-Y., Huang, X.-F., Campuzano-Jost, P.,
487 Palm, B. B., Poulain, L., Kuwata, M., Martin, S. T., Abbatt, J. P. D., Lee, A. K. Y. and Liggio, J.: Elemental
488 composition of organic aerosol: The gap between ambient and laboratory measurements, *Geophys. Res. Lett.*, 42(10),
489 4182–4189, doi:10.1002/2015GL063693, 2015.

490 Chen, Q., Ikemori, F. and Mochida, M.: Light Absorption and Excitation–Emission Fluorescence of Urban Organic
491 Aerosol Components and Their Relationship to Chemical Structure, *Environ. Sci. Technol.*, 50, 10859–10868,
492 doi:10.1021/acs.est.6b02541, 2016.

493 Daellenbach, K. R., Bozzetti, C., Křepelová, A., Canonaco, F., Wolf, R., Zotter, P., Fermo, P., Crippa, M., Slowik, J.
494 G., Sosedova, Y., Zhang, Y., Huang, R. J., Poulain, L., Szidat, S., Baltensperger, U., El Haddad, I. and Prévôt, A. S.
495 H.: Characterization and source apportionment of organic aerosol using offline aerosol mass spectrometry, *Atmos.*
496 *Meas. Tech.*, 9(1), 23–39, doi:10.5194/amt-9-23-2016, 2016.

497 Daumit, K. E., Kessler, S. H. and Kroll, J. H.: Average chemical properties and potential formation pathways of highly
498 oxidized organic aerosol, *Faraday Discuss.*, 165, 181–201, doi:10.1039/c3fd00045a, 2013.

499 Decarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K.,
500 Horvath, T., Docherty, K. S., Worsnop, D. R. and Jimenez, J. L.: Field-Deployable, High-Resolution, Time-of-Flight
501 Aerosol Mass Spectrometer, *Anal. Chem.*, 78(24), 8281–8289, doi:10.1029/2001JD001213, *Analytical*, 2006.

502 Docherty, K. S., Jaoui, M., Corse, E., Jimenez, J. L., Offenberg, J. H., Lewandowski, M. and Kleindienst, T. E.:
503 Collection Efficiency of the Aerosol Mass Spectrometer for Chamber-Generated Secondary Organic Aerosols,
504 *Aerosol Sci. Technol.*, 47, 294–309, doi:10.1080/02786826.2012.752572, 2013.

505 Donnelly, T. D., Hogan, J., Mugler, A., Schubmehl, M., Schommer, N., Bernoff, A. J., Dasnurkar, S. and Ditmire, T.:
506 Using ultrasonic atomization to produce an aerosol of micron-scale particles, *Rev. Sci. Instrum.*, 76(11), 1–10,
507 doi:10.1063/1.2130336, 2005.

508 Gallimore, P. J. and Kalberer, M.: Characterizing an Extractive Electrospray Ionization (EESI) Source for the Online
509 Mass Spectrometry Analysis of Organic Aerosols, *Environ. Sci. Technol.*, (47), 734–7331, doi:10.1021/es305199h,
510 2013.

511 Ge, X., Li, L., Chen, Y., Chen, H., Wu, D., Wang, J., Xie, X., Ge, S., Ye, Z., Xu, J. and Chen, M.: Aerosol
512 characteristics and sources in Yangzhou, China resolved by offline aerosol mass spectrometry and other techniques,
513 *Environ. Pollut.*, 225, 74–85, doi:10.1016/j.envpol.2017.03.044, 2017.

514 Han, Y., Kawamura, K., Chen, Q. and Mochida, M.: Formation of high-molecular-weight compounds via the
515 heterogeneous reactions of gaseous C8–C10 n-aldehydes in the presence of atmospheric aerosol components, *Atmos.*
516 *Environ.*, 126, 290–297, doi:10.1016/j.atmosenv.2015.11.050, 2016.

517 Hansman, R. L., Dittmar, T. and Herndl, G. J.: Conservation of dissolved organic matter molecular composition during
518 mixing of the deep water masses of the northeast Atlantic Ocean, *Mar. Chem.*, 177, 288–297,
519 doi:10.1016/j.marchem.2015.06.001, 2015.

520 Heald, C. L., Kroll, J. H., Jimenez, J. L., Docherty, K. S., Decarlo, P. F., Aiken, A. C., Chen, Q., Martin, S. T., Farmer,
521 D. K. and Artaxo, P.: A simplified description of the evolution of organic aerosol composition in the atmosphere,
522 *Geophys. Res. Lett.*, 37(L08803), 1–5, doi:10.1029/2010GL042737, 2010.

523 Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M.,
524 Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski,
525 M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad, I. El and
526 Prévôt, A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China, *Nature*,
527 514, doi:10.1038/nature13774, 2014.

528 Hunter, J. F., Carrasquillo, A. J., Daumit, K. E. and Kroll, J. H.: Secondary Organic Aerosol Formation from Acyclic,
529 Monocyclic, and Polycyclic Alkanes, *Environ. Sci. Technol.*, 48, 10227–10234, doi:10.1021/es502674s, 2014.

530 Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang,
531 X., Smith, K. A., Morris, J. W. and Davidovits, P.: Ambient aerosol sampling using the Aerodyne Aerosol Mass
532 Spectrometer, *J. Geophys. Res.*, 108, 8425, doi:10.1029/2001JD001213, 2003.

533 Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., Decarlo, P. F., Allan, J.
534 D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J.,
535 Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen,
536 J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman,
537 J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S.,
538 Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono,
539 A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M.,
540 Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U. and Worsnop, D. R.: Evolution of
541 Organic Aerosols in the Atmosphere, *Science* (80-.), 326, 1525–1529, doi:10.1126/science.1179518, 2009.

542 Jimenez, J. L., Canagaratna, M. R., Drewnick, F., Allan, J. D., Alfarra, M. R., Middlebrook, A. M., Slowik, J. G.,
543 Zhang, Q., Coe, H., Jayne, J. T. and Worsnop, D. R.: Comment on “The effects of molecular weight and thermal
544 decomposition on the sensitivity of a thermal desorption aerosol mass spectrometer,” *Aerosol Sci. Technol.*, 50, i–xv,
545 doi:10.1080/02786826.2016.1205728, 2016.

546 Kaul, D. S., Gupta, T. and Tripathi, S. N.: Source Apportionment for Water Soluble Organic Matter of Submicron
547 Aerosol: A Comparison between Foggy and Nonfoggy Episodes, *Aerosol Air Qual. Res.*, 14, 1527–1533,
548 doi:10.4209/aaqr.2013.10.0319, 2014.

549 Kimmel, J. R., Farmer, D. K., Cubison, M. J., Sueper, D., Tanner, C., Nemitz, E., Worsnop, D. R., Gonin, M. and
550 Jimenez, J. L.: Real-time aerosol mass spectrometry with millisecond resolution, *Int. J. Mass Spectrom.*, 303, 15–26,
551 doi:10.1016/j.ijms.2010.12.004, 2010.

552 Koch, B. P., Witt, M., Engbrodt, R., Dittmar, T. and Kattner, G.: Molecular formulae of marine and terrigenous
553 dissolved organic matter detected by electrospray ionization Fourier transform ion cyclotron resonance mass
554 spectrometry, *Geochim. Cosmochim. Acta*, 69(13), 3299–3308, doi:10.1016/j.gca.2005.02.027, 2005.

555 Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E.,
556 Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D. and Kolb, C. E.: Carbon oxidation state as a
557 metric for describing the chemistry of atmospheric organic aerosol, *Nat. Chem.*, 3, 133–139,
558 doi:10.1038/NCHEM.948, 2011.

559 Kroll, J. H., Lim, C. Y., Kessler, S. H. and Wilson, K. R.: Heterogeneous Oxidation of Atmospheric Organic Aerosol:
560 Kinetics of Changes to the Amount and Oxidation State of Particle-Phase Organic Carbon, *J. Phys. Chem. A*, 119,
561 10767–10783, doi:10.1021/acs.jpca.5b06946, 2015.

562 Lang, R. J.: Ultrasonic Atomization of Liquids, *J. Acoust. Soc. Am.*, 34(1), 6–8, 1962.

563 Lee, A. K. Y., Hayden, K. L., Herckes, P., Leitch, W. R., Liggio, J., Macdonald, A. M. and Abbatt, J. P. D.:
564 Characterization of aerosol and cloud water at a mountain site during WACS 2010: secondary organic aerosol
565 formation through oxidative cloud processing, *Atmos. Chem. Phys. Atmos. Chem. Phys.*, 12, 7103–7116,
566 doi:10.5194/acp-12-7103-2012, 2012.

567 Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Lutz, A., Hallquist, M.,
568 Worsnop, D. and Thornton, J. A.: A novel method for online analysis of gas and particle composition: description and
569 evaluation of a Filter Inlet for Gases and AEROSols (FIGAERO), *Atmos. Meas. Tech*, 7, 983–1001, doi:10.5194/amt-
570 7-983-2014, 2014.

571 Lu, Y., Li, X., Mesfioui, R., Bauer, J. E., Chambers, R. M., Canuel, E. A. and Hatcher, P. G.: Use of ESI-FTICR-MS
572 to Characterize Dissolved Organic Matter in Headwater Streams Draining Forest-Dominated and Pasture-Dominated
573 Watersheds, *PLoS One*, 1–21, doi:10.1371/journal.pone.0145639, 2015.

574 Mihara, T. and Mochida, M.: Characterization of Solvent-Extractable Organics in Urban Aerosols Based on Mass
575 Spectrum Analysis and Hygroscopic Growth Measurement, *Environ. Sci. Technol.*, 45, 9168–9174,
576 doi:10.1021/es201271w, 2011.

577 Murphy, D. M., Thomson, D. S. and Mahoney, M. J.: In Situ Measurements of Organics, Meteoritic Material,
578 Mercury, and Other Elements in Aerosols at 5 to 19 Kilometers, *Science (80-.)*, 282, 1664–1669, 1998.

579 Nakao, S., Tang, P., Tang, X., Clark, C. H., Qi, L., Seo, E., Asa-Awuku, A. and Iii, D. C.: Density and elemental ratios
580 of secondary organic aerosol: Application of a density prediction method, *Atmos. Environ.*, 68, 273–277,
581 doi:10.1016/j.atmosenv.2012.11.006, 2013.

582 Ng, N. L., Herndon, S. C., Trimborn, a., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D.
583 R., Zhang, Q., Sun, Y. L. and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring
584 of the Composition and Mass Concentrations of Ambient Aerosol, *Aerosol Sci. Technol.*, 45(7), 780–794,
585 doi:10.1080/02786826.2011.560211, 2011a.

586 Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H. and Worsnop, D. R.: Changes in organic
587 aerosol composition with aging inferred from aerosol mass spectra, *Atmos. Chem. Phys. Atmos. Chem. Phys.*, 11,
588 6465–6474, doi:10.5194/acp-11-6465-2011, 2011b.

589 Simon, J. C., Sapozhnikov, O. A., Khokhlova, V. A., Crum, L. A. and Bailey, M. R.: Ultrasonic atomization of liquids
590 in drop-chain acoustic fountains, *J Fluid Mech.*, 766, 129–146, doi:10.1017/jfm.2015.11.Ultrasonic, 2015.

591 Skoog, D. F., Holler, F. J. and Nieman, T. A.: *Principles of Instrumental Analysis*, Saunders College Pub,
592 Philadelphia., 1998.

593 Sun, Y., Zhang, Q., Zheng, M., Ding, X., Edgerton, E. S. and Wang, X.: Characterization and Source Apportionment
594 of Water-Soluble Organic Matter in Atmospheric Fine Particles (PM 2.5) with High-Resolution Aerosol Mass
595 Spectrometry and GC-MS, *Environ. Sci. Technol.*, 45, 4854–4861, doi:10.1021/es200162h, 2011.

596 Xu, J., Zhang, Q., Li, X., Ge, X., Xiao, C., Ren, J. and Qin, D.: Dissolved Organic Matter and Inorganic Ions in a
597 Central Himalayan Glacier-Insights into Chemical Composition and Atmospheric Sources, *Environ. Sci. Technol.*,
598 47, 6181–6188, doi:10.1021/es4009882, 2013.

599 Xu, J. Z., Zhang, Q., Wang, Z. B., Yu, G. M., Ge, X. L. and Qin, X.: Chemical composition and size distribution of
600 summertime PM_{2.5} at a high altitude remote location in the northeast of the Qinghai-Xizang (Tibet) Plateau: Insights
601 into aerosol sources and processing in free troposphere, *Atmos. Chem. Phys.*, 15(9), 5069–5081, doi:10.5194/acp-15-
602 5069-2015, 2015.

603 Xu, L., Guo, H., Weber, R. J. and Ng, N. L.: Chemical Characterization of Water-Soluble Organic Aerosol in
604 Contrasting Rural and Urban Environments in the Southeastern United States, *Environ. Sci. Technol.*, 51, 78–88,
605 doi:10.1021/acs.est.6b05002, 2016.

606 Xu, W., Lambe, A., Silva, P., Hu, W., Onasch, T., Williams, L., Croteau, P., Zhang, X., Renbaum-Wolff, L., Fortner,
607 E., Jimenez, J. L., Jayne, J., Worsnop, D. and Canagaratna, M.: Laboratory evaluation of species-dependent relative
608 ionization efficiencies in the Aerodyne Aerosol Mass Spectrometer Laboratory evaluation of species-dependent
609 relative ionization efficiencies in the Aerodyne Laboratory eva, *Aerosol Sci. Technol.*, 52(6), 626–641,
610 doi:10.1080/02786826.2018.1439570, 2018.

611 Ye, Z., Liu, J., Gu, A., Feng, F., Liu, Y., Bi, C., Xu, J., Li, L., Chen, H., Chen, Y., Dai, L., Zhou, Q. and Ge, X.:
612 Chemical characterization of fine particulate matter in Changzhou, China, and source apportionment with offline

613 aerosol mass spectrometry, *Atmos. Chem. Phys.*, 17, 2573–2592, doi:10.5194/acp-17-2573-2017, 2017.

614

615

616

617

618

619

620

621

622

623

624

625

626

627

628

629

630

631 **Figures and Tables**

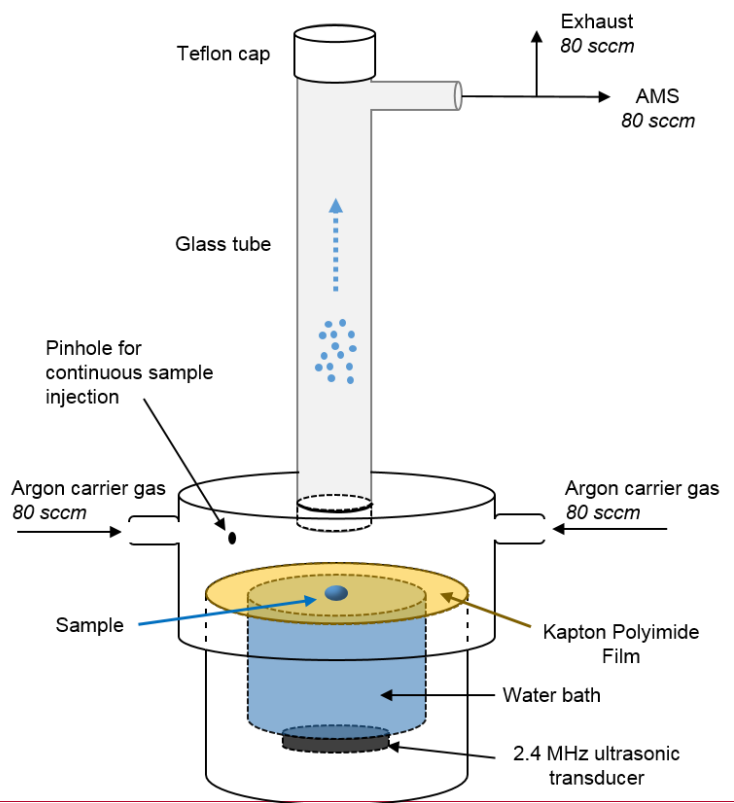
632 Table 1. Elemental ratios measured by SVN-AMS vs. other techniques for the various mixtures examined in this work.

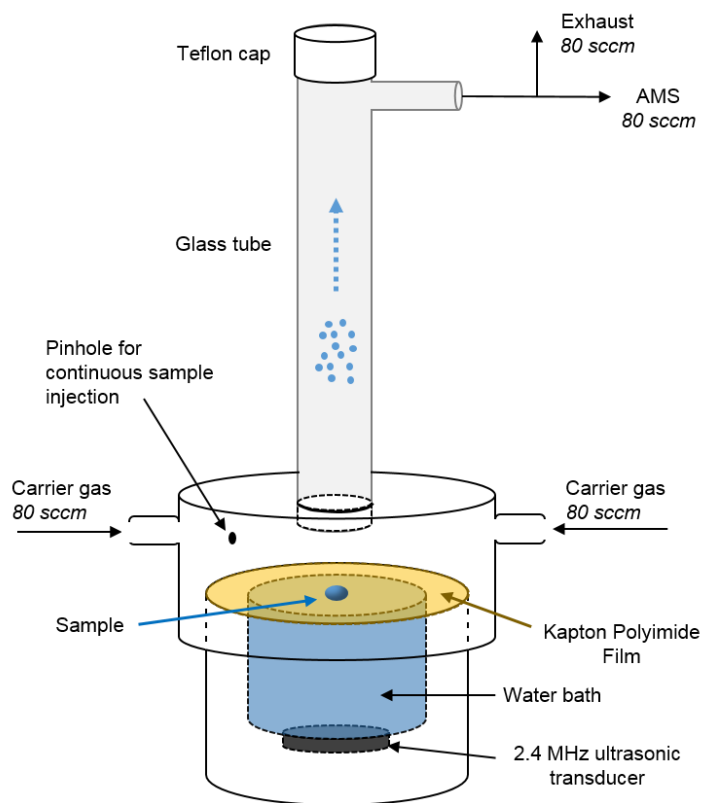
Sample		O:C	H:C	N:C
Citric acid	Atomizer-AMS	1.0	1.4	--
	SVN-AMS	1.1	1.3	--
	<u>Actual</u>	<u>1.2</u>	<u>1.3</u>	<u>--</u>
α -pinene SOA	Online-AMS	0.48	1.6	< 0.002
	SVN-AMS	0.50	1.6	< 0.002
Look Rock	Online-ACSM ^a	0.13 ($f_{44}=0.19$)	1.3 ($f_{43}=0.062$)	-- ^b
	SVN-AMS ^a	0.13 ($f_{44}=0.16$)	1.3 ($f_{43}=0.051$)	-- ^b
DOM	CHNS analyzer	ND	1.74	0.080
	SVN-AMS	0.77	1.7	0.081

633

634 a. Elemental ratios are estimated from parameterizations for f_{44} and f_{43} (Aiken et al., 2008; Ng et al., 2011b).635 b. There is no established parameterization method for determining N/C from UMR data.

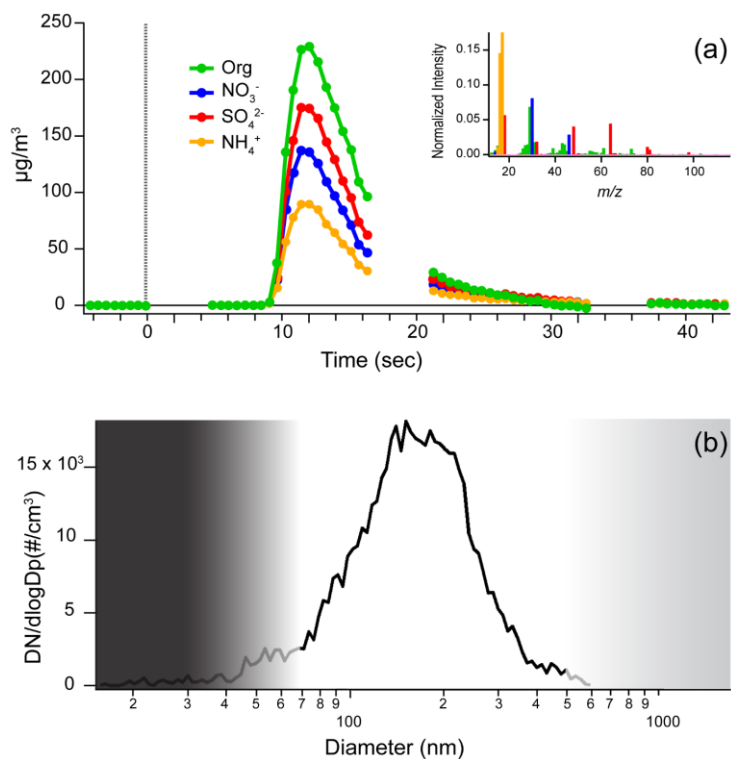
Formatted Table



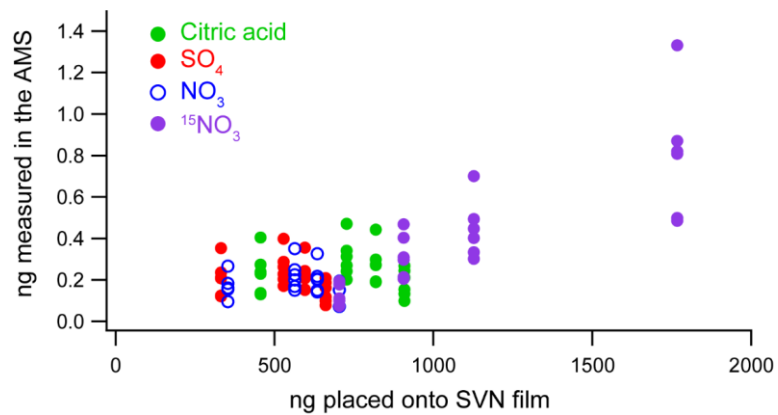
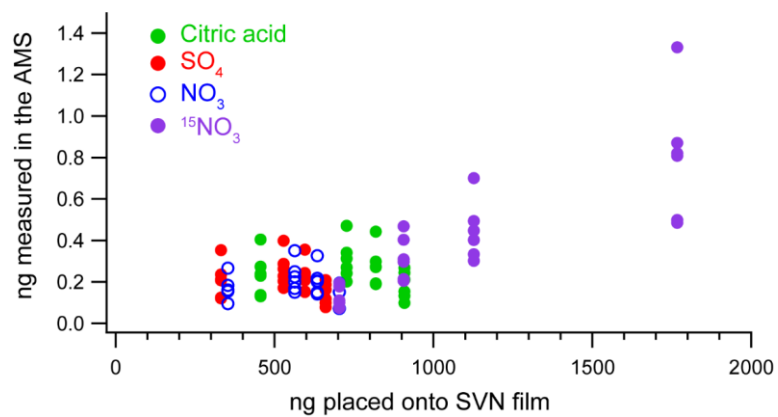


637

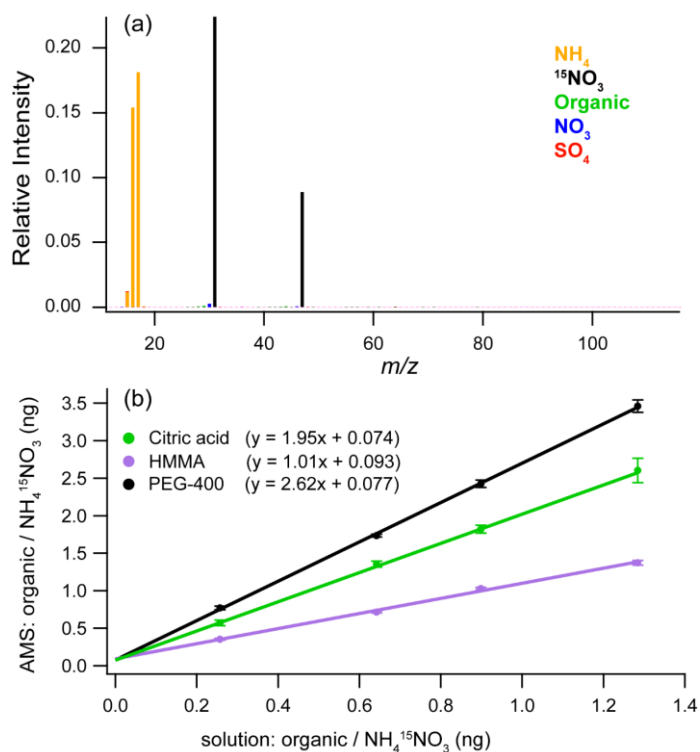
638 Figure 1. Schematic diagram of the small volume ultrasonic nebulizer (SVN). Samples (2-4 μ L) are loaded on the Kapton
 639 (or Teflon) film through either the hole in which the glass tube is seated (for discrete injections) or through the pinhole (for
 640 continuous injections). After the transducer is turned on, the aerosol is carried up through the glass tube and into the
 641 instrument by a ~160 sccm flow of house air/zero air or argon carrier gas. The water bath between the transducer and the
 642 Kapton film carries ultrasonic waves up to the film and serves to cool the ultrasonic transducer.



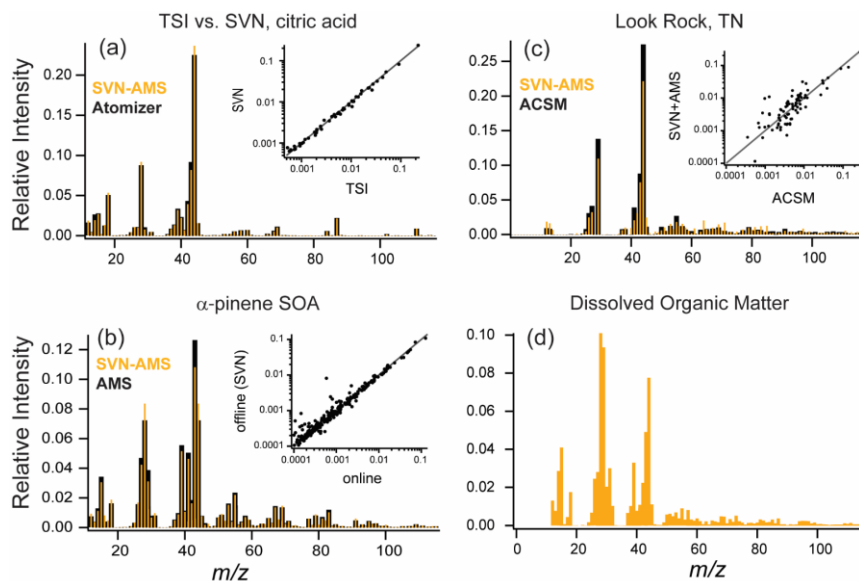
643 Figure 2. Measurements of the composition and size of nebulized samples from the SVN. (a) Time series of aerosol
 644 composition from a single 4 μL nebulization of an aqueous solution (mannitol, ammonium nitrate, and ammonium sulfate).
 645 Data were recorded using fast-mode MS for the AMS-open scans, with a mass spectrum collected every 0.5 s (filled circles).
 646 The gaps in the trace correspond to closed cycles where the aerosol beam was blocked to provide a background subtraction
 647 (gas-phase and instrument background) that was applied during data processing. Measured concentrations are not
 648 corrected for collection efficiency (CE) in the AMS, which affects the absolute values but not the relative concentrations.
 649 The inset shows the average mass spectrum acquired across the injection, normalized to total ion signal. (b) Aerosol size
 650 distribution from a $\sim 1\text{g/L}$ citric acid solution measured with an SMPS (black line). The gradient represents the
 651 transmission efficiency for particles into the AMS with nearly 100% between 70-500 nm and decreased but substantial
 652 transmission for spherical particles 30-70 nm and 500 nm to 2.5 μm (Jimenez et al., 2003); thus, the smallest particles in the
 653 distribution will not be efficiently detected by the AMS.



654 Figure 3. Mass of each component placed on the thin film vs. the mass measured by the AMS for 4 different solutions with
 655 varying concentrations of citric acid, ammonium sulfate, ammonium nitrate, and the internal standard (NH₄¹⁵NO₃), all
 656 with a total solution concentration of 0.75 g/L. Each sample had 5 replicate injections, with the vertical spread in the
 657 measured masses indicating substantial run-to-run variability (up to a factor of 3) between injections.



658 Figure 4. (a) Blank of the Kapton film using 1 g/L internal standard solution (¹⁵N- ammonium nitrate). (b) Calibration
 659 curves made using an internal standard for solutions with three different organic compounds: citric acid, 4-hydroxy-3-
 660 methoxy-DL-mandelic acid (HMMA), and polyethylene glycol 400 (PEG-400). The error bars are $\pm 1\sigma$ for five replicate
 661 injections.



663 Figure 5. Online (or TSI atomizer) (black) vs. SVN nebulizer (orange) mass spectra for (a) an aqueous solution of citric
 664 acid at 1 g/L; (b) α -pinene + O₃ chamber SOA; (c) a SOAS campaign sample from Look Rock, TN with online data collected
 665 on an ACSM. Smaller insets in a, b, and c show direct comparison of intensities for each mass spectrum on a log scale. (d)
 666 AMS mass spectra from North Pacific Ocean dissolved organic matter (polysaccharide fraction) nebulized with the SVN
 667 (since this sample was not from aerosol particles, no online samples are available).

Supplemental Information for

Ultrasonic Nebulization for the Elemental Analysis of Microgram-Level Samples with Offline Aerosol Mass Spectrometry

Rachel E. O'Brien^{1*}, Kelsey J. Ridley², Manjula R. Canagaratna³, John T. Jayne³, Philip L. Croteau³, Douglas R. Worsnop³, Sri Hapsari Budisulistiorini^{4†}, Jason D. Surratt⁴, Christopher L. Follett⁵, Daniel J. Repeta⁵, Jesse H. Kroll²

[1] Department of Chemistry, College of William and Mary, Williamsburg, Virginia, 23185, USA

[2] Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

[3] Center for Aerosol and Cloud Chemistry, Aerodyne Research Inc., Billerica, Massachusetts 01821, USA

[4] Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA

[5] Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02540, USA

† Now at: Earth Observatory of Singapore, Nanyang Technological University, Singapore 638789, Singapore

Corresponding author: Rachel O'Brien, reobrien@wm.edu

Included:

4-6 pages, 2-3 figures, 1 table and expanded information on memory effects and solution preparation.

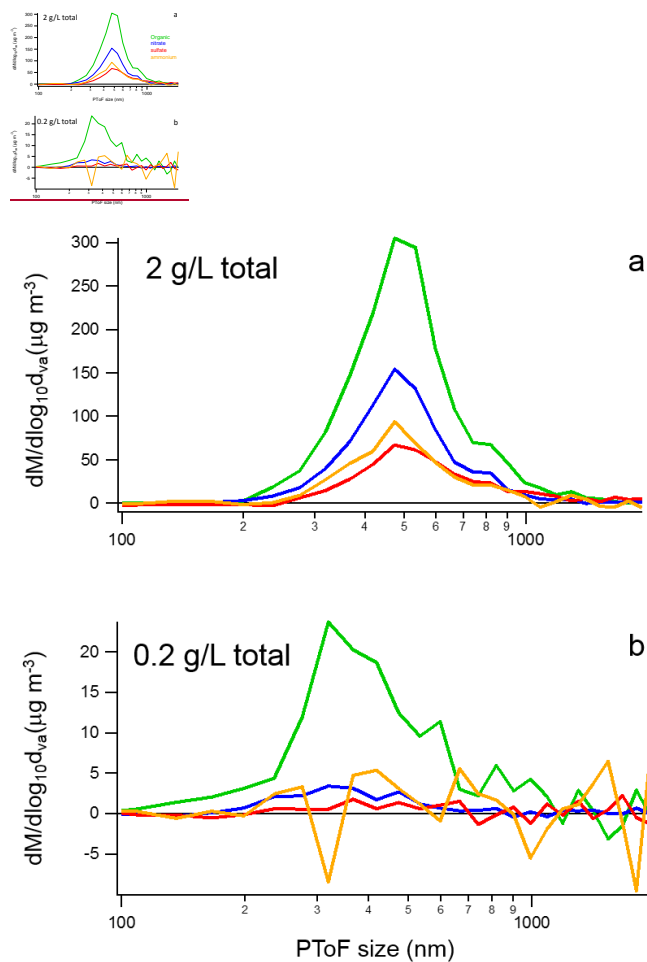


Figure S1. AMS pToF mass distributions from continuous injection of aqueous solutions of NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, and mannitol. Measurable shifts in the distribution can be achieved for more concentrated solutions ((a) 2 g/L; size distribution centered at 200–3500 nm) or more dilute solutions ((b) 0.2 g/L; size distribution centered at 100–2300 nm). Thus, these data demonstrates that fine particles formed from nebulizing solutions with concentrations greater than ~0.2 g/L have an appropriate size distribution for direct measurement by the AMS. For these samples, the size distribution of the components is fairly uniform consistent with the formation of homogenous particles in the nebulizer.

Formatted: Font: Bold

Formatted: Font: Bold

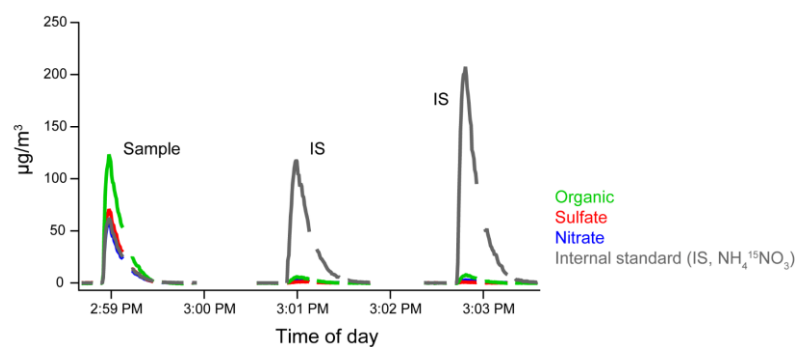


Figure S2. Discrete aerosol pulses for a solution with 0.125 g/L of each component (first pulse) followed by two nebulizations of 1 g/L solution of the internal standard (grey, $\text{NH}_4^{15}\text{NO}_3$) with no rinse on the Kapton surface.

Formatted: Font: Bold

Memory Effects

For typical solutions containing small polar organic molecules and salts, the sample mass that remains on the film surface after the nebulization is small. Figure S2 shows a time trace for a discrete injection of 4 μL of a solution of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , $\text{NH}_4^{15}\text{NO}_3$, and mannitol each at 0.125 g/L (first pulse). The two subsequent pulses are generated from 4 μL drops of a 1 g/L

solution of $\text{NH}_4^{15}\text{NO}_3$ placed directly on the same spot as the sample. The mass of SO_4 , NO_3 , and mannitol that remained on the Kapton film and ~~that is~~ observed in the next pulses is 1-2% of the original mass observed. These values are within 10% of the signal for a blank run on a freshly cleaned Kapton film. Thus, minimal cleaning of the Kapton surface was needed between runs for samples with composition similar to the one described above. To account for potential contamination, runs of the internal standard solution were included between samples.

No carryover from one run to the next has been observed due to droplets from previous discrete injections falling back down to the surface of the film after the sample has been loaded and the SVN sealed in preparation for nebulization. This is likely due to the fact that the surface area of the droplet is very small on the Kapton film and lies in the center of the film with only the open glass tube above it. Also, the time between injections is long enough for a large fraction of the droplet mass on the sides of the SVN to evaporate. However, some ejected droplets are observed to fall from the SVN sides and pool up on the film with continuous injection at 20 $\mu\text{L}/\text{min}$ with an aqueous solution. This behavior has not been observed for continuous injections of solutions with more volatile solvents such as methanol.

Nebulization Efficiency and Calibration Curves

The same solutions were run to generate the calibration curves and the nebulization efficiency plot. For the nebulization efficiency, exactly 4 μL of the solution was placed on the Kapton film for each injection. This provides the known mass of material placed on the film. The stock solution for each analyte was 10 g/L, the table below shows the volumes of each stock added to generate the solutions.

Formatted: Font: Symbol

Table S1. Volumes of stock solutions used in the standard solutions

<u>Standard name</u>	<u>NH₄¹⁵NO₃</u>	<u>(NH₄)₂SO₄</u>	<u>NH₄NO₃</u>	<u>Organic</u>	<u>H₂O dilution</u>
	<u>(μL)</u>	<u>(μL)</u>	<u>(μL)</u>	<u>(μL)</u>	<u>(mL)</u>
<u>A1</u>	<u>100</u>	<u>20</u>	<u>20</u>	<u>20</u>	<u>1.6</u>
<u>A2</u>	<u>100</u>	<u>50</u>	<u>50</u>	<u>50</u>	<u>2.5</u>
<u>A3</u>	<u>100</u>	<u>70</u>	<u>70</u>	<u>70</u>	<u>3.1</u>
<u>A4</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>4</u>

The efficiency plot in Figure 3 shows the results of six replicate injections of the above solutions.

Figure S3 shows the same plot with the solutions that contributed to each set of replicates labeled either above or below the data sets. The trends shown here, where the greatest net mass was observed for the first calibration solution, are not necessarily characteristic. What is consistently observed is efficiencies on the order of 0.02-0.06% and ratios of analytes to the internal standards that are replicable and correlate to the ratios of the components in the solutions. This last feature enables the use of the internal standard in the calibrations.

Formatted: Font: Bold

Formatted: Centered

Formatted Table

Formatted: Centered

Formatted: Centered

Formatted: Centered

Formatted: Centered

Formatted: Font: 12 pt

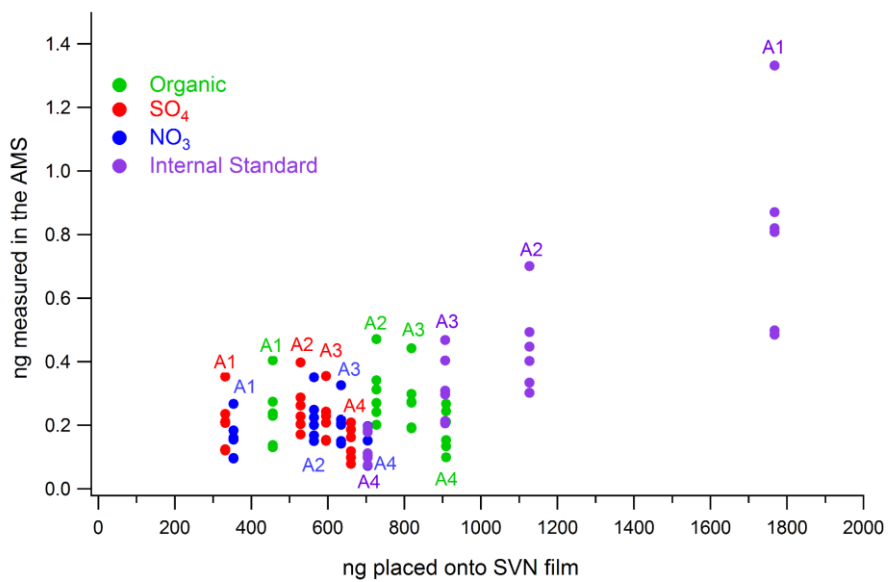


Figure S3. Replicate of Figure 3 in the text with the contributing solutions labeled above each sample set.

Formatted: Font: 12 pt

Formatted: Font: (Default) Times New Roman, 12 pt, Bold

Formatted: Font: (Default) Times New Roman, 12 pt