

Response to Reviewer #2

General comment:

In this manuscript rather new technique - Vocus Inlet for Aerosols (VIA) is briefly described and coupled with NO₃-CIMS applied for measurement and characterization of organic aerosol. VIA is traditionally coupled with Vocus PTR, therefore this study represents an important extension of VIA's usability in atmospheric science by showing successful real time measurement of complex composition of secondary aerosol with impressive detection limits. Authors have put significant thought into the experimental set up, background corrections and themselves highlight the pros and cons of such technique for reliable aerosol measurement. It would be interesting to see such measurement in comparison to techniques targeting similar goal such as EESI or Figaero. As first attempt to make aerosol measurements with this coupling I find the study well done and recommend for publication after addressing minor comments.

We thank the reviewer for the positive feedback and answer the comments point-by-point below:

Comment #1:

135: The temperature profile inside the unit was not uniform'' - Could authors provide the numbers of these measurements? I assume 300°C is the maximum temperature VIA can reach and at recommended flow not sufficient for total evaporation as authors state. Or would this be compensated through losses and decreased particle transmission. The particle transmission was measured at 1 l/min however 1.5 l/min or 2 l/min were used throughout the experiment without clarification why. Again, could authors provide results of the size dependence measurement.

Response:

We added a figure on the measured temperature profile to the appendix of the manuscript (Fig. A1). The reviewer is correct that the maximum temperature of VIA is roughly 300 °C and that 70 % of the mass of ammonium sulfate was evaporated at this temperature. However, for SOA, almost all (> 99%) of the mass evaporated at 300 °C. As particle losses decrease with higher flow rates, we measured the particle transmission at 1 l/min to provide the lower limit. Unfortunately, we have not measured the size dependence, but we will do it soon in the future.

Comment #2:

160: The way the calibration is presented is a bit confusing. Shall the reader understand that three time-separate calibrations were made corresponding to presented calibration factors of $1 - 3 \times 10^{10} \text{ cm}^{-3}$? It is not clear that these calibration factors originate from separate measurements. How do these calibration factors compare to literature? How do authors explain the non linear step between 0.8 – 1 ng/m³ for all the curves? Could losses explain the discrepancy in the calibrations? Did authors calibrate higher than 1 ng/m³? Please clarify.

Response:

The calibration factors do not originate from separate measurements. We performed the experiment with the purpose of determining the instrument sensitivity, i.e. the calibration factor. In Figure 2, we simply converted the signals measured by the NO₃-CIMS to mass concentrations by applying three different calibration factors that make the results between the instruments match. It turned out that these factors were close to values reported earlier in literature (Jokinen et al., 2012; Kürten et al., 2012; Ehn et al., 2014). The nonlinear step could be due to enhanced nucleation under a high concentration of sulfuric acid, but it can also simply be uncertainty in the measurements. We emphasize that the three curves describe the same experiment, and thus are not independent from each other, and therefore there is no clear systematic trend to be seen. To limit potential sulfuric acid nucleation affecting our results, we did not use higher mass concentrations than 1 ng/m³.

We modified the text discussing Fig. 2 as follows: “The calibration curves are not as steep as the 1:1 line. This could be due to nucleation under a high concentration of sulfuric acid in the tubing between the VIA and the NO₃-CIMS. Nucleation would lead to a decrease in the gaseous sulfuric acid, resulting in lower mass concentration detected by the NO₃-CIMS compared to the SMPS (which simply measures the evaporation from the larger particles) as a function of the evaporated sulfuric acid. Wall losses between the VIA and the NO₃-CIMS will certainly also take place, but this should to a first approximation be a constant factor, and as such, becomes included in the calibration factor (Jokinen et al., 2012). On average, the difference between the concentrations measured by the SMPS and the NO₃-CIMS is smallest when a calibration factor of $2 \times 10^{10} \text{ cm}^{-3}$ is used. Therefore, we decided to use the calibration factor of $2 \times 10^{10} \text{ cm}^{-3}$ when converting the NO₃-CIMS signals to concentrations. This value is close to the literature calibration factor values that range between 1.1×10^{10} and 1.89×10^{10} (Jokinen et al., 2012; Kürten et al., 2012; Ehn et al., 2014). We acknowledge that our estimate comes with a very large uncertainty, and thus provides concentrations of highly oxygenated compounds with large uncertainties. Hence, we focus more on the qualitative than on the quantitative analysis of the measured data.”

Comment #3:

165: For readers not having experience with Nitrate Cims, please explain the unit for the calibration factor.

Response:

To clarify this, we modified Sec. 2.2.1 as follows: “The signal intensity of highly oxygenated compound X can be converted to a concentration by normalizing the measured signal intensity (ions s⁻¹) with the total measured reagent ion signal (ions s⁻¹), which cancels out the unit. Then the normalized value is multiplied by the calibration factor (cm⁻³), yielding the concentration of X in units cm⁻³, which describes the number of molecules of X in a cubic centimeter of gas (Eq. (2), Jokinen et al., 2012).”

Comment #4:

170: What role does the gas-particle equilibrium play? This equilibrium is distorted 1. Via the denuder and 2. via the dilution with clean air on potentially still present particles. Would this somehow effect your results? Or is this effect negligible?

Response:

The reviewer is correct that the denuder and dilution can disturb the gas-particle equilibrium. However, since VOC oxidation will be on-going up until the VIA denuder, the gases and particles will not be in true equilibrium before the denuder either. As an example, almost all typically detected gas-phase HOM are only detected because they have not had enough time to condense (i.e. the partitioning equilibrium is heavily on the particle side). Nevertheless, the residence times are so short (seconds or less) that we indeed expect the effects to be every small. For some SVOC, which the NO₃-CIMS typically is not very good at detecting, the effects should be the largest. As discussed in Sec. 4.1, we detected some organic compounds of higher volatility (mainly C5 compounds) evaporating when VIA was set to 25 °C. This net evaporation is likely a result of the disturbed gas-particle equilibrium, i.e. that the gas phase was removed in the denuder. In addition, at the point of dilution, the particles have already undergone heating, and therefore there should be negligible amounts of compounds left that would be affected by the dilution at room temperature.

Comment #5:

175: In this case is the author talking about background (filter) NO₃-CIMS corrected signal?

Response:

This is correct; the NO₃-CIMS background signal is subtracted from the NO₃-CIMS signal we show in Fig. 3.

Comment #6:

190: With detection limits as low as 1 ug/m³ why did authors choose to investigate SOA at such high loadings?

Response:

We wanted to generate high enough loadings of SOA to ensure that we measure well above the detection limit, as we determined the exact value of the detection limit after the experiments.

Comment #7:

215: There has been studies showing that the prevalence of oligomers is linked to total SOA mass. I encourage authors to consider this option and provide references.

Response:

The reviewer is correct that higher concentration of precursors (higher SOA loading) may cause higher amount of oligomers formed in the gas or particle phase (Kourtchev et al., 2016). However, in our follow-up publication using VIA and NO₃-CIMS, we performed experiments with lower SOA loadings (1-14 µg m⁻³) and still detected oligomers (Zhao et al, 2022).

Comment #8:

250: What does prevent the author to use calibration factor for sucrose from direct sucrose calibration? This would be technically possible the same way as for ammonium sulfate and could diminish the discrepancy in the figure at high temperature

Response:

In Fig. 10f, we show the evaporated mass from sucrose particles measured by the SMPS and the NO₃-CIMS. We included all compounds with m/z ratio larger than 200 Th in this analysis and used calibration factor of $2 \times 10^{10} \text{ cm}^{-3}$ to convert the NO₃-CIMS signals to concentrations. In order to reach similar mass concentrations than the SMPS measured for sucrose, the NO₃-CIMS calibration factor would need to be $\sim 9 \times 10^{10} \text{ cm}^{-3}$. The signal from sucrose particles was spread out over wide m/z range (see Fig. 4f), and we detected smaller and larger compounds than sucrose itself evaporating from the particles, potentially due to fragmentation and particle-phase reactions. In addition to this, we cannot be sure that we are sensitive to all the evaporating species from sucrose particles. In the sulfuric acid calibration, the signal of the evaporated sulfuric acid from ammonium sulfate particles was distributed to H₂SO₄NO₃⁻ and HSO₄⁻ ions, giving a calibration factor close to the literature values.

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