

Response to Reviewer #RC1

General comment

The manuscript “Characterization of the Vaporization Inlet for Aerosols (VIA) for Online Measurements of Particulate Highly Oxygenated Organic Molecules (HOMs)” report a systematic test of VIA used with NO₃-CIMS to detect HOM, including the transmission efficiency, evaporation efficiency, quantification of particle-phase HOM as well as applicability for volatility measurement.

The authors found that transmission efficiency of particles (NaCl>50 nm) is >90%. Transmission efficiency of VOC was also high. Also the transmission loss for sulfuric acid vapors was negligible according to the evaporated AS particles measured by SMPS and sulfuric acid measured by NO₃-CIMS. Adding a sheath flow after VIA reduced markedly the wall loss of HOM. The signal of HOM increased with T first and then decreased, indicating the loss of HOM in VIA. T_{max} correlated with T_{max} obtained from FIGAERO-I-CIMS, but much higher (~100-150 °C) than T_{max} from FIGAERO. The loss efficiency of HOM obtained by a one-dimensional model was high (3-9) and correction factor depended on molecular weight.

Determination of particle-phase organic components on-line and on molecular level is critical to understand the formation, fate and impacts of organic aerosol. In this regard, this study presents a valuable attempt to evaluate and to optimize VIA combined with NO₃-CIMS to be used for HOM measurement, although there is a number of limitations and challenges to use VIA for the quantification of particle-phase HOM. This manuscript is generally well-written. I have a few comments for the authors to consider before its publication in AMT.

We thank the reviewer for the positive and insightful comments, and we answer the specific comments point-by-point below. The reviewer’s comments are in **blue**, and our answers are in **black**.

Specific comments

Comment #1:

In this study, it was assumed that the loss of HOM was due to the collision with hot walls. What is the evidence for this assumption? It is possible that it was due to the decomposition in the air within VIA, which was not included in the model of this study as mentioned by the authors?

Response:

We wish to make the causality clear by saying that we had no a priori expectations or assumptions that decomposition on the walls would be a dominant loss process when starting these studies. Rather, we found that we could initially not explain the shapes of the obtained thermograms, but once we allowed for efficient decomposition on the walls, the observations made more sense.

Consider for example Fig. 5a, where C₁₀H₁₄O₇ has peaked and almost been completely lost at 150 °C, but some dimers only start to show up at this temperature. We expect that the HOM, both monomers and dimers, largely consist of similar functional groups (carbonyls, alcohols, and peroxides). If decomposition was purely a function of temperature, and some monomers start to decompose around 100C, then we would not expect to see any HOM above 200 °C. However, we still detect compounds peaking above 250 °C, suggesting that there has been only marginal loss of these compounds before evaporation, but then the decomposition is fairly rapid. This makes us believe that the decomposition within the particles is very limited. Our observations could also be explained by fast decomposition after evaporation to the gas phase, but if rapid particle-phase decomposition was negligible, we did not feel that rapid gas-phase decomposition should be expected either. However, contact with a hot metal

surface could be expected to lead to fast decomposition, as the heat transfer to the molecule is likely to be much larger in this case.

In addition, as our model was able to capture the thermogram shape with this assumption of efficient wall decomposition, we felt that it was motivated to suggest this as the major loss pathway. But we acknowledge that there are uncertainties involved as explained in Comment #2, and therefore use terminology like in the abstract (“*Our results indicate that...*”) when discussing this topic. In order to clarify this point to the reviewer and future readers clearly, we added the above argument in line 399.

Comment #2:

How was the uncertainty in Fig. 9 derived? I suggest the authors to further discuss the uncertainty/limitations of correction factor, e.g. how the factors not considered in the model influence CF, as it is key to the quantification of particle-phase HOM.

Response:

The uncertainties include two main parts, calibration factor of the NO₃-CIMS (100%) and correction factor, which includes the proportionality constant *c* (40%), diffusion constants (10%), and other uncertainties (30%), as we discussed in Section 3.3.1 “*However, the CF is quite sensitive to the proportionality constant *c*, which also has some uncertainties associated with it (Figure S2 and Table S5). This means that while the relative correction factors between different compounds may be well known, the absolute values can still vary by an order of magnitude. An additional source of error in the CF values is the estimated diffusion constants, these may be off by up to 10%. There is also little information available about how the Fuller method estimated diffusion coefficients scale up to temperatures of >300 °C (Tang et al., 2015). In addition, the lighter species show more erratic and less consistent thermograms, and this may introduce larger uncertainties compared to low-volatile larger molecules.*” In the end, summing up the uncertainties mentioned above as sort of an upper limit leads to 180%, i.e. an uncertainty of a factor 2.8. Thus, the values of error bars used in Figure 9 are $x \cdot 2.8$ and $x/2.8$. We added the above discussion in line 482 in the revised manuscript.

About the details, the uncertainty from *c* is an estimate from Table S5, where the *c* values we considered reasonable (between 4e6 and 7e6) result in a maximum deviation in the CF of 40% from the value used (*c* = 5.5e6). The uncertainty arising from molecules decomposing in the gas phase instead of on impact with the walls is already captured in this variation in *c*, since it determines the loss rate of the species. There may be differences between individual compounds, but *c* is determined to match the thermogram shape for all ions, so for the total mass this uncertainty should be fairly well accounted for. In addition, there is the uncertainty arising from the model being one dimensional, not being able to truly capture variation in the radial direction, which together with the uncertainty in diffusion coefficients makes up the “other uncertainties”. Of course, this is not quantifiable, but based on comparisons with 3 dimensional models we believe this to be reasonable.

Comment #3:

Moreover, how applicable is the correction factor for one compound (molecular formula)? For example, if one does not ramp up temperature, can the correction factor be used (considering that ramping up temperature largely limits the time resolution of the method)? Or it has to be used with a thermogram? Does the correction factor depend on functional groups other than molecular weight as shown in Fig. 8b?

Response:

The correction factor is derived from a fitting method that relies on the measured thermograms, so determining it requires a temperature ramp. The exact shape of the thermogram depends on the setup

(e.g. flow rates and tubing length), and cannot be assumed to be “universal”. In addition, the way we defined the correction factor, relates the true particle concentration to the peak of the thermogram. Without a temperature ramp, one would need to assume where the thermogram for a compound’s peaks. In our experience, the temperature ramping provides so much valuable information that we would recommend running in temperature-ramping mode despite the obvious drawback of poorer time resolution.

It is possible that future improvement in the design of the VIA could limit the decomposition, and thereby make the quantification easier. Alternatively, the ramping could be done much faster if active cooling was introduced, in which case the thermogram information would remain, while still improving the time resolution. We added more discussions on the correction factor in Sec. 3.4.

The correction factor might be related to functional groups as the reviewer mentioned, but without information on real molecular-level measurements, we used molecular weight as the x-axis to show the general trend of the correction factor in Figure 8b.

Comment #4:

I would suggest the authors to briefly discuss the advantages and disadvantages in Sect. 3.4 compared with other techniques mentioned in the introduction part.

Response:

Section 3.4 “Current challenges and future improvements” was primarily aimed at discussing limitations of the VIA-NO₃-CIMS system and potential future hardware upgrades. A comparison to other techniques inevitably requires detailed knowledge about those techniques, for example, their sensitivity towards HOM. As the NO₃-CIMS was selected as the detector for this purpose in our study, we are not selective towards less oxygenated species, which a PTR or I-CIMS likely would be. Overall, we prefer to not make too explicit comparisons to how other instruments perform, but we did add a section highlighting the strengths and weaknesses of the VIA-NO₃-CIM more generally in Line 522.

“In comparison to other online techniques used for aerosol phase characterization, the VIA-NO₃-CIMS has both benefits and drawbacks. The NO₃-CIMS was chosen due to its sensitivity and selectivity towards HOMs, which ultimately means that we can use it to measure OA composition with a low detection limit, but will not be able to detect all the evaporated species. This was particularly clear from the fact that we do not detect any of the decomposition products of the HOM, as they are going to be smaller and less oxygenated, whereby they do not readily cluster with the nitrate ions in our CIMS.”

Comment #5:

2b, in the legend, is “140 °C” the set temperature?

Response:

All figures used the read temperatures (i.e. recorded by the Eyeon software). We added one sentence in line 150 to clarify this point.

“A thermocouple attached to the surface of this vaporization tube was used to monitor the temperature, and the recorded temperature was used for thermogram analysis.”

Comment #6:

7b, is the normalize frequency of ΔT obtained from each molecular formula? Can the difference in chemical composition at different aerosol loading influence the distribution of the frequency?

Response:

Yes, the ΔT distributions were calculated based on the identified molecular formula. We used the same peak list during the high-resolution peak fitting process for all experiments. If there were peaks that showed very low signals (i.e. a “bad” shape of thermogram) in at least one experiment so that a reliable T_{\max} could not be obtained, the peaks were excluded from the statistics. We tried to compare the same peaks among several experiments with different SOA loadings. However, if the same molecular formula is in fact different compounds, this will affect the distribution, but this limitation is related to mass spectrometry in general.

Comment #7:

L433, Ren et al 2022 could be mentioned here.

Response:

The work by Ren et al. (2022) compared the effects of calibration method (syringe deposition vs. atomization) and matrix effects of inorganics on the volatility calibration of FIGAERO calibration. Thus, we cited this work followed reviewer’s suggestion in line 433.

“The calibration method (syringe deposition vs. atomization), solution/mass concentration, particle size, matrix effects of inorganics, and heating ramp rate are factors that have been reported to affect the determined volatility (i.e. T_{\max}) in the FIGAERO-iodide-CIMS system (Ylisirniö et al., 2021; Ren et al., 2022).”

Comment #8:

L511, what does the “correlation coefficient” denote?

Response:

The correlation coefficient refers to the mass concentrations measured by the VIA-NO₃-CIMS system vs the SMPS/AMS. We acknowledge that this was poorly formulated and in order to better clarify this part, we modified the sentence in line 511.

“On the one hand, the uncertainty of this correction factor could potentially be reduced significantly if the detection efficiency could be determined experimentally (i.e. mass concentration of standards measured by the VIA system vs. the SMPS).”

Reference:

Ren, S., Yao, L., Wang, Y., Yang, G., Liu, Y., Li, Y., Lu, Y., Wang, L., and Wang, L.: Volatility parameterization of ambient organic aerosols at a rural site of the North China Plain, Atmos. Chem. Phys., 22, 9283-9297, <https://doi.org/10.5194/acp-22-9283-2022>, 2022.