Reply to anonymous Referee #1

We thank referee #1 for the constructive comments, which improved the manuscript. Original comments are written in black, our replies in blue as well as comprehensible excerpts from the text highlighting the tracked changes.

1.Lines 86-88: The authors state in their summary of existing online measurement techniques for particulate organic components that VIA experiences fragmentation at 250°C, emphasizing that the APCI-Orbitrap-MS mitigates this fragmentation. Figure 2 depicts the effect of temperature on signal intensity for different compounds. However, this figure alone does not demonstrate that fragmentation in the APCI-Orbitrap-MS is less severe than in VIA. Thermal decomposition/fragmentation remains a key challenge for the online measurement of organic components in particulates. The argument presented here would be substantially strengthened if the authors could include a direct comparison of thermal decomposition between the two instruments or provide a comparative analysis against relevant published data in the literature.

Response:
We acknowledge that Figure 2 does not provide sufficient information about thermal fragmentation. The primary focus of this figure was to determine optimal vaporizer temperatures for efficiently evaporating molecules from the particle phase, using a complex SOA matrix. While we did monitor specific tracers, including those highlighted by Zhao et al. (2023), and did not observe any thermal fragmentation during our experiments, we recognize that the potential for fragmentation can vary based on the stability of each individual compound against thermal decomposition. Certainly, compounds like peroxides are prone to thermal decomposition also with the presented method.
To address the reviewer's concern, we will revise the X-axis description of Figure 2 to clarify that the vaporizer temperatures represent set points, and the actual temperature of the gas stream is expected to be lower. Additionally, we will include additional explanations that highlight this issue of thermal stability and the potential for fragmentation.

recording thermograms, for which precise knowledge on the effective temperatures would be necessary, we were solely
245 evaluating the effectiveness of evaporation and potential signs of thermal decomposition. Additionally, even though not observed during this experiment (Fig. S7) the thermal decomposition of compounds cannot be ruled out, as it is dependent on the structural stability of each individual compound. Finally, we selected an operating temperature of 350 °C for continuous ambient measurements, as the laboratory experiments indicated that at this temperature monomers and dimers are sufficiently

2.Figure 7: I have reservations about the normalization of units applied by the authors in this figure. This normalization obscures true concentration levels and makes it impossible to assess the original mass spectral intensity information. Consequently, the processed data significantly hinders its utility for meaningful interpretation and fails to support critical information assessment.

Response:
We appreciate your feedback regarding the normalization of units applied in Figure 7. We understand your concern that this normalization may obscure true concentration levels and hinder meaningful interpretation of the original mass spectral intensity data. To clarify, the

aerosol used in our study was generated in the laboratory, which resulted in considerable variation in aerosol mass. To facilitate a meaningful comparison of instrument sensitivity to specific compounds, we normalized the data to account for the differences in compound-specific sensitivity per aerosol mass.

While we believe that this normalization approach is essential for comparing the response of the different compounds per aerosol mass, we also acknowledge the importance of providing complete transparency in our data presentation. Therefore, we will include a table in the SI to allow for a comprehensive understanding of the original mass spectral intensity levels.

Table S3: Instrumental sensitivity experiments with different reference standards and their respective concentration in standard solution [ug L−1], average signal background intensity, average signal intensity and produced mass concentration [µg m−3] used for normalization of Fig. 7.

Compound	Polarity	Concentration in standard solution [ug L^{-1}]	Average signal background intensity	Average signal intensity	Produced particle mass concentration [µg m^{-3}]
MBTCA	$[M-H]^-$	5.11	1.55×10^5	9.11×10^7	35.43
MBTCA	$[M+H]^+$	5.11	1.69×10^4	8.03×10^6	35.43
Pinic Acid	$[M-H]^-$	2.4	1.22×10^6	1.17×10^7	1.77
Pinic Acid	$[M+H]^+$	2.4	1.72×10^5	2.95×10^6	1.77
Levoglucosan	$[M-H]^-$	1.2	1.85×10^5	3.02×10^6	0.44
Levoglucosan	$[M+H]^+$	1.2	1.74×10^3	3.91×10^4	0.42
Vanillin	$[M-H]^-$	116	7.99×10^5	2.69×10^6	2.23
Vanillin	$[M+H]^+$	116	3.56×10^4	4.48×10^5	2.22
Nitrocatechol	$[M-H]^-$	3.2	2.18×10^6	2.87×10^7	0.60
Nitrocatechol	$[M+H]^+$	3.2	1.12×10^3	1.12×10^5	0.72
Camphorsulfonic acid	$[M-H]^-$	3.3	0	7.70×10^7	4.28
Camphorsulfonic acid	$[M+H]^+$	3.3	9.19×10^3	3.37×10^6	4.26
Glyphosate	$[M-H]^-$	3.5	0	1.06×10^5	52.37
Glyphosate	$[M+H]^+$	3.5	0	1.20×10^4	52.37
Acridin	$[M+H]^+$	1.6	0	8.06×10^3	0.09
$C_{21}H_{23}O_4P$	$[M+H]^+$	2.1	0	2.44×10^6	20.86
$C_{29}H_{53}O_8$	$[M+H]^+$	2.1	0	4.28×10^5	20.86

3.Line422-423: “4-nitrocatechol had the highest ionization efficiency”. This does not necessarily reflect ionization efficiency, but could also be affected by ion transmission efficiency.

Response:

We acknowledge that the phrasing "4-nitrocatechol had the highest ionization efficiency" should more accurately be the instrument sensitivity rather than ionization efficiency alone.

matrix effects and possible losses in the inlet system.

All experimentally investigated B-OA and BB-OA compounds, along with camphorsulfonic acid and glyphosate (A-OA), showed higher sensitivity in APCI negative ion-mode compared to the positive ion-mode. The highest instrumental sensitivity showed 4-nitrocatechol ~~had the highest ionization efficiency~~ in negative ion-mode followed by camphorsulfonic acid, pinic-acid, levoglucosan and MBTCA. Explained by their elevated gas-phase acidity, which is associated with the presence of electrophilic functional groups, such as carboxylic acids among others (Carroll et al., 1975; Sharon and Bartmess; Derpmann

4.Figure S7: The concentration of organic molecules is a critical limiting factor for online structural identification of compounds. The figure indicates that the maximum intensity of organic molecule signals reaches 1.8E7. This represents an exceptionally high signal level for online measurements. What causes such elevated signal intensities in organic molecules, and whether the authors implement optimizations to enhance instrument sensitivity?

Response:

We agree with Reviewer #1 that during the experiments elevated signal intensities were reached. When again looking into the raw data the TIC reached 1.15E9, which is definitely a high signal, but is still within the linear range of the instrument and not at risk for oversaturation of the detector.

The experiment Figure S7 is based on SOA generated from the ozonolysis of α-pinene, achieving an average particle mass concentration of 306.6 µg m^{-3} with a laboratory setup. While the SOA production in the laboratory often is only a simulation of ambient processes, accurate levels of precursors in an oxidative system are challenging to achieve and maintain. However, during the field campaigns the concentration of organics measured by the ACSM reached up to 127 µg m^{-3}. This indicates that our experimental conditions adequately cover the expected range of aerosol mass concentrations.

We recognize the importance of providing more detailed information regarding the optimization of instrument sensitivity. To address this, we have included several key strategies in the revised section '3.4 Instrumental Sensitivity of the APCI-Orbitrap-MS'.

3.4 Instrumental sensitivity of the APCI-Orbitrap-MS

In addition to the importance of high mass resolution, we also want to highlight the versatility of the APCI-Orbitrap-MS for its ability to detect compounds over a wide chemical range. The sensitivity of the instrument for a specific compound is based on the ionization efficiency, the ion transmission efficiency, and the detection performance. To enhance the instrument sensitivity, particularly for a targeted approach, conducting online measurements in selected ion monitoring (SIM) mode can significantly improve sensitivity by focusing on one or a few selected *m/z*. Additional sensitivity improvements can be achieved by optimizing the radio frequency (RF) amplitude applied to the S-lense and the automatic gain control (AGC). Adjusting the RF amplitude enhances ion transmission in specific mass ranges, while optimizing the AGC target value controls the number of ions accumulated in the C-trap for subsequent introduction into the mass analyzer. To test the sensitivity of the APCI-