

This study couples a VIA with NO₃-CIMS and presents its first deployment for continuous measurements of ambient particles at a suburban site in Nanjing. The authors investigate particle-phase OOMs from three perspectives: molecular composition, gas-particle compositional differences, and PMF-based source apportionment. The online measurement of particle-phase highly oxygenated organic molecules at high time resolution has clear methodological value. The integration of VIA-NO₃-CIMS measurements with HR-ToF-AMS, VOC, meteorological, and trajectory data also gives this dataset potentially important scientific significance. The manuscript is generally well structured and contains a comprehensive set of figures. If the key methodological issues are adequately resolved, this work could become an important case study for the application of VIA-NO₃-CIMS to ambient aerosol measurements.

However, the current conclusions require more robust support from instrument characterization and statistical analyses, or alternatively, more cautious wording. I would be willing to recommend this study for publication after the issues below have been addressed.

Response: We sincerely thank the reviewer for the careful evaluation of our manuscript and for the constructive comments. These comments have helped us substantially improve the instrument characterization, clarify the scope of the quantitative analysis, and make the interpretation of the field observations more rigorous. In the revised manuscript, we have added further evaluations of the thermal-desorption behavior and measurement stability, clarified the empirical and semi-quantitative nature of the OOM concentration estimates, strengthened the treatment of methodological uncertainties, and revised statements that were not sufficiently supported. Our point-by-point responses are provided below. The corresponding changes in the manuscript and Supplementary Information are marked in green.

Reviewer: Quantification of oxygenated organic molecules (L275-309)

The authors derived an empirical calibration coefficient by regressing the normalized HSO₄⁻ signal measured by VIA-NO₃-CIMS against particulate sulfate mass concentrations measured by the AMS, and subsequently applied this single coefficient to all detected organic molecules. This approach raises several concerns, such as the conversion efficiency of particulate sulfur-containing salts into detectable H₂SO₄/HSO₄⁻ at 300 °C, post-evaporation wall losses, and compound-dependent NO₃⁻ ionization responses for different organic molecules. The response to sulfuric acid cannot automatically be assumed to represent the responses of multifunctional organic compounds, peroxides, and organic nitrates. Moreover, the contribution of OOMs to AMS-derived SOA additionally depends on both the AMS-PMF separation of SOA and the VIA calibration. I recognize that quantifying all uncertainties associated with the VIA-NO₃-CIMS analytical and quantification process, as well as the AMS-PMF analysis, is challenging. Nevertheless, I suggest that the uncertainties that can be reasonably estimated should be explicitly reported in the results. Accordingly, the statements in the manuscript (including the Abstract and Conclusions) regarding "quantitative capability" and absolute concentration or contribution values should be explicitly described as "semi-quantitative" or "empirical estimates".

Response:

Thank you for this important and constructive comment. We agree with the reviewer that the sulfate-derived empirical response coefficient cannot be regarded as an absolute or compound-independent

calibration coefficient for all detected OOMs. In particular, the semi-quantitative estimation is subject to uncertainties associated with (1) compound-dependent evaporation efficiency, including the volatilization/conversion of particulate sulfate into detectable $\text{H}_2\text{SO}_4/\text{HSO}_4^-$ highlighted by the reviewer, (2) post-evaporation transmission and wall losses, and (3) compound-dependent NO_3^- ionization sensitivity.

We carefully considered whether these uncertainties could be quantitatively estimated from the available measurements. However, these effects cannot be independently constrained with the present experimental configuration. The measured relationship between the VIA- NO_3 -CIMS HSO_4^- signal and AMS particulate sulfate reflects the combined effects of evaporation, post-evaporation transmission and wall losses, and subsequent NO_3^- ionization, rather than any of these processes individually. Moreover, corresponding compound-specific information is not available for the large number of OOMs detected in this study. We therefore consider that assigning numerical uncertainties to these individual processes, or propagating them into a single overall uncertainty for the OOM concentrations, would not be sufficiently supported by the available measurements.

We have therefore substantially revised Sect. 2.4.2 (Lines 321–380) to explicitly describe the reported OOM concentrations as semi-quantitative, sulfate-equivalent estimates. The sulfate-derived coefficient is now defined as an empirical system response coefficient, C_{emp} , representing the aggregate response of the field-configured VIA- NO_3 -CIMS system to particulate sulfate detected as HSO_4^- . The uncertainty that can be directly estimated from the sulfate comparison is reported for C_{emp} , while the compound-dependent systematic uncertainties described above are explicitly acknowledged but not assigned numerical values.

Accordingly, the campaign-average OOM concentration of $1.67 \mu\text{g m}^{-3}$ and the approximately 22% contribution to AMS-derived SOA are retained only as semi-quantitative observational estimates. We further clarify that the estimated contribution should not be interpreted as the absolute fraction of SOA detected by VIA- NO_3 -CIMS or as the calibrated recovery efficiency of the measurement system.

The Abstract and Conclusions have been revised accordingly. The expressions “quantitative capability” and “quantitative molecular-level characterization” have been removed, and the correlation between the estimated particle-phase OOM mass and AMS-derived SOA ($r=0.88$) is now used only to demonstrate that VIA- NO_3 -CIMS captures the temporal variability of the detectable particle-phase OOM fraction, rather than to validate the accuracy of the absolute mass concentration.

Reviewer: Selection of thermal desorption temperature (L162-173)

The total particle-phase OA signal reached a maximum at 300°C (Fig. S1a). Therefore, the authors selected 300°C as the operating temperature for field measurements. However, maximizing the total signal does not necessarily mean that the original particle-phase molecules are measured most accurately. The continued increase in signal from above 200°C to 300°C may reflect more complete evaporation, but it may also arise from thermal decomposition of oligomers, peroxides, carboxylic acids, or organic nitrates, as well as dehydration, decarboxylation, and fragmentation or recombination processes. Have the authors compared the complete molecular spectra at different temperatures? The authors state that thermal decomposition cannot be fully excluded during the desorption process, but that this effect is generally considered limited under the current operating conditions. The authors should provide a more substantial justification or supporting evidence for this assertion.

Response: Thank you for this important and constructive comment. We agree that the maximum total signal at 300 °C does not by itself demonstrate the most accurate recovery of the original particle-phase molecular composition. In response, we conducted an additional comparison of the complete assigned particle-phase OOM spectra obtained from 160 to 300 °C at 20 °C intervals. The pairwise cosine similarities were calculated and are now presented as a similarity matrix in Fig. S2a, see below). We also compared the independently normalized compound-level spectra measured at 220 and 300 °C (Fig. S2b). These two spectra yielded a cosine similarity of 0.933, indicating that their broad relative molecular-composition patterns remained similar, although compound-specific changes were present.

Accordingly, we have revised Sect. 2.2.1 (Lines 184-200) and added Sect. S1.5 (Lines 116-141) to describe this evaluation. The revised manuscript no longer states that thermal decomposition is generally limited under the selected operating conditions. Instead, we explicitly acknowledge that increasing temperature may simultaneously enhance volatilization and induce compound-dependent thermal transformation. Therefore, 300 °C was selected empirically because it produced the maximum assigned OOM signal under the tested conditions, rather than because it guarantees complete and artifact-free recovery of the original particle composition. Possible incomplete volatilization and thermal decomposition are now identified as methodological uncertainties, and temperature-programmed heating is proposed as an important direction for future instrument development.

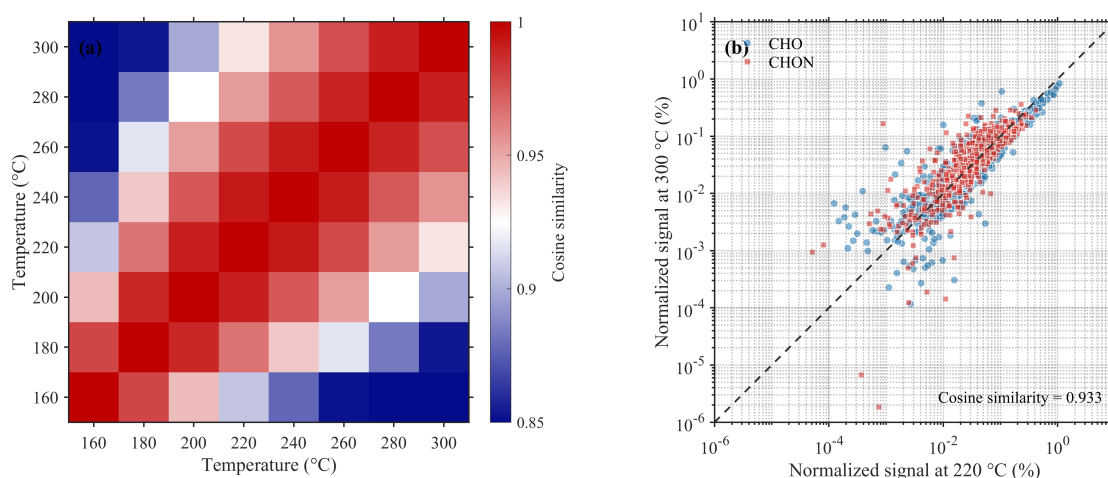


Figure S2. Temperature dependence of the assigned particle-phase OOM composition. (a) Cosine similarity matrix for OOM spectra obtained between 160 and 300 °C at 20 °C intervals. (b) Comparison of the relative signals of individual OOM molecular formulas at 220 and 300 °C. The spectra at each temperature were independently normalized to their respective total assigned OOM signals. Blue circles and red squares represent CHO and CHON compounds, respectively. The dashed line denotes the 1:1 relationship.

Reviewer: Abstract, L30–31: an *r* value of 0.88 only indicates that the two signals co-vary over time; it does not demonstrate the accuracy of the absolute concentrations. Therefore, the statements that this calibration “demonstrates quantitative capability” (L30-31) and that the study provides “quantitative molecular-level characterization” (L44) are not sufficiently accurate.

Response: Thanks for pointing out this inaccurate statement. As per your suggestion, these expressions have been removed from the Abstract. The revised text states that the summed OOM concentration covaried closely with AMS-derived SOA ($r = 0.88$), demonstrating that VIA-NO₃-CIMS effectively captures the temporal variability of particle-phase OOMs. The reported concentration is explicitly described as semi-quantitative, and no claim regarding absolute quantitative accuracy is made.

Reviewer: L168–170: The main text reports an average evaporation efficiency of approximately 70%, whereas Sect. S1.5 reports a range of 70%–92%. Please reconcile these values. The description of particle-volume loss as direct volatilization of organic material should also be corrected.

Response: We agree that the previous wording conflated particle-volume loss with the volatilization efficiency of organic material and could therefore be misleading. We have removed the statement describing the observed particle-volume reduction as a direct measure of organic-material evaporation efficiency. The revised manuscript instead reports the measured particle-transmission or volume-response behavior under the tested conditions without interpreting it as compound-independent volatilization efficiency. The inconsistent values of approximately 70% and 70%–92% have consequently been removed/reconciled in the main text (Lines201-211) and Supplement (Lines142-168).

Reviewer: L249–255: Please explain how the alternating 10 min sample and background periods were paired. Background interpolation during rapidly changing conditions may introduce either positive or negative biases. A representative measurement cycle and the stability of the zero-air/HEPA-filter background should be shown.

Response: Thanks for the comment. We have clarified the sample–background pairing procedure in the revised manuscript (Section2.4.1, Lines288-299). The VIA alternated between 10 min HEPA-filter background and 10 min sample periods. To minimize switching-related transients, data acquired during the 1 min before and after each solenoid-valve switching event were excluded, leaving 8 min of stable measurements within each period. Each sample period was paired with the immediately preceding HEPA period, and no temporal interpolation of the background was performed. We have also added Fig. S5, which shows a representative 1 h HEPA–sample switching cycle and the stability of the HEPA-filter background over a representative 20 h period. These additions provide a direct illustration of the switching procedure, the retained stable measurement windows, and the temporal stability of the background signal.

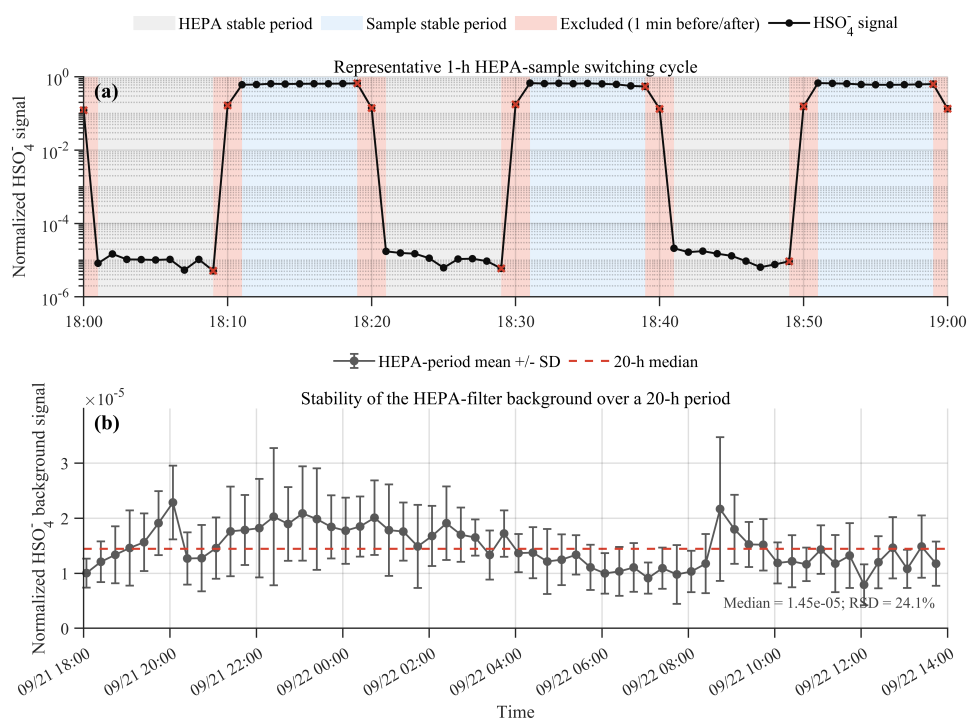


Figure S5. Representative HEPA-sample switching cycle and stability of the HEPA-filter background. (a) One-hour time series of the normalized HSO₄⁻ signal during alternating 10-min HEPA-filter background and sample periods. Data acquired during the 1 min before and after each solenoid-valve switching event were excluded to minimize switching-related transients, and the remaining 8 min within each period were retained as stable measurements. Each sample period was paired with the immediately preceding HEPA period without temporal interpolation. (b) Stability of the HEPA-filter background over a representative 20-h period. Each point represents the mean normalized HSO₄⁻ signal during the retained stable portion of one HEPA period, and the error bars denote ± 1 standard deviation of the corresponding 1-min measurements. The red dashed line indicates the median HEPA background over the 20-h period.

Reviewer: L334–339: An r^2 value of 0.70 between PM₁ and PM_{2.5} is insufficient on its own to demonstrate that “submicron particles dominated fine particulate mass.” The PM₁/PM_{2.5} mass ratio and its distribution should be reported.

Response: We agree with the reviewer that the correlation between PM₁ and PM_{2.5} alone is insufficient to demonstrate that submicron particles dominated fine particulate mass. Because this statement is not essential to the subsequent analysis, we have removed it from the revised manuscript.

The correlation between PM₁ and PM_{2.5} is now reported only to describe their temporal covariation and is no longer used to infer the relative contribution of submicron particles to PM_{2.5}.

L357–360: The cross-reference to “Sect. 2.5.2” is incorrect and should be Sect. 2.4.2.

Response: Thank you for identifying this error. The cross-reference has been corrected from Sect. 2.5.2 to Sect. 2.4.2.

Supplement: Figure S26 is used twice. The second occurrence should be renumbered as Fig. S27.

Response: Thank you for identifying the duplicate figure number. The second occurrence of Fig. S26 has been renumbered, and all subsequent figure numbers and corresponding cross-references have been checked and updated throughout the main text and Supplementary Information.