Reviewer #2

In the response, referee comments are given in black, and our responses are given in blue. Changes made to the manuscript are marked in underlined blue. The line number is for the Revised manuscript.

This manuscript describes and characterizes the use of the FIGAERO-CIMS to analyze particle composition via off-line filter analysis (i.e. filters that are collected outside of the instrument and later inserted in the instrument for analysis). This technique can enable FIGAERO-CIMS analysis of particle composition in a greater number and variety of environments as it does not require moving the instrument. The manuscript is well written and of interest to readers of AMT. I suggest publication of the manuscript after my comments below have been addressed.

Reply: We are very grateful for the positive comments and helpful suggestions. We have carefully revised our manuscript accordingly.

Major comments:

Correction and analysis methods: The manuscript is generally unclear on which methods are suggested for future use. For example, the authors conducted background correction in six different ways (e.g. Fig 2), and conducted some analyses to decide which corrections were most consistent with their data. For future work do they recommend that others also correct the background in six different ways? Or are the insights from their analyses sufficient to recommend a subset of methods for future use?

Reply: We thank the reviewer for pointing out this shortcoming. It was our aim with this study to present an overview of various background determination methods and to assess their performance in order for future users of this method to be guided by our analyses. We have added the following discussion in the revised manuscript to clarify this aim:

Line 334 – Line 343

"With the thermal baseline subtraction method (Method 4), results were comparable between 2.5-h and five 0.5-h samples. For the approach using filter reheating (Method 3), there was a lesser agreement between the sum of the 0.5-h samples and the 2.5-h sample (Figs. 3e and 3f). We speculate that this could be improved with a reheating cycle for every sample. For future offline FIGAERO-CIMS analyses, we recommend carefully determining the background. Following our assessment of blank determination methods, we suggest regular collections of field blanks and scaling their signal (Methods 2a/b), and if field blanks are not available, computing a thermal baseline (Method 4). If using the reheating approach as in a previous study with FIGAERO-CIMS in offline mode (Siegel et al., 2021), the background should be determined by conducting reheating desorption cycles for each sample and blank individually."

Reagent ion depletion: The authors mention that reagent ion depletion is not desired (e.g. line 155). It was unclear to me from reading the manuscript whether and how they corrected for reagent ion depletion (e.g. by dividing the analyte signal by reagent ion concentration)?

Reply: Reagent in depletion is indeed not desired, as we state in the manuscript. We, therefore, present several measures in this manuscript to reduce reagent ion depletion:

1) We decreased the sample loading by punching only a small area (*d*=2mm) from the whole sampled filter and then use the "sandwich technique" to analyze with FIGAERO-CIMS. Therefore, the mass loadings and reagent ion depletion can be greatly reduced. (Line 159 – Line 166)

2) We applied a non-uniform ramping protocol in order to reduce reagent ion depletion between 60 °C to 105 °C desorption temperature, where HNO_3 exhibits a maximum signal. (Line 187 – Line 193)

Normalization of signal to reagent ion is normally done for FIGAERO-CIMS data regardless of reagent ion depletion.

We now added more explanation to the normalization process in this study:

Line 224:

"The total signal of a compound per filter sample, defined as the integrated signals (*Is*), calculated by first normalizing by the signals of the primary ions (I^-) and then integrating the entire thermogram (ramping and soaking)."

Data from the FIGAERO-CIMS and the ACSM are found to correlate well (e.g. Fig. 7). Do the authors have any information about their quantitative agreement?

Reply: We have added more information regarding the quantification of offline FIGAERO-CIMS to the revised manuscript (Line 505 – Line 508) and SI:

"Following the same method, after calibrations, the quantified CHOX mass concentrations of offline FIGAERO-CIMS were found to be highly correlated with OA and SOA from ToF-ACSM in another dataset at the Peking University campus (PKU) in Beijing, indicating offline FIGAERO-CIMS analysis can be more quantitative with appropriate calibrations (shown in Fig. S12 (Zheng et al., 2021))."

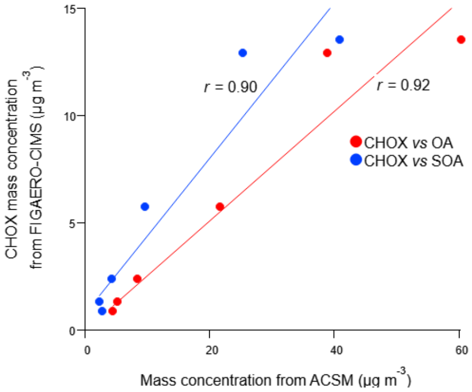

Figure R1 (revised Figure S12). Comparison between CHOX mass concentrations from FIGAERO-CIMS, organic aerosols (OA), and secondary organic aerosols (SOA) derived from ToF-ACSM at the Peking University Campus (PKU) site. Calibrations for FIGAERO-CIMS were conducted for a series of chemical compounds with both the permeation tube and micro-syringes. The details of the site, comparison setting up, calibrations, and calculations can be found in Zheng et al. (2021). In total, CHOX accounts for about 32–60% of SOA measured by the TOF-ACSM in their study.

We also refer the reader to the response to reviewer 1´s comments (Comment 10) on this topic.

The authors find that (lines 540-542) "The variability in Tmax induced by varying PM loadings is within 5°C for 29% of compounds and within 15°C for 54% of all compounds for Quartz filters, and 35% and 57% of compounds, respectively, for Teflon samples." They also summarize (in the abstract) that "we find that Tmax can be determined with high repeatability for one filter type". Taken together, this seems to imply that e.g. a 10°C difference in Tmax (due to filter loading) is acceptable. Is that the case? What volatility difference is associated with a 10°C difference in Tmax? Is that uncertainty / variability acceptable for volatility analysis?

Reply

We thank the reviewer for pointing out the implications of our statements regarding volatility determination using T_{max}, which were not fully intentional from our side. A ~5°C difference in T_{max} from the duplicate tests would translate into less than one order of magnitude in the saturation concentration (C*) estimation (69% – 30% changes to the original C*) from different empirical equations in previous studies (Ylisirniö et al., 2021; Bannan et al., 2018; Lopez-Hilfiker et al., 2014; Stark et al., 2017; Nah et al., 2019; Ye et al., 2019)). However, more recent studies (Huang et al., 2018; Ylisirniö et al., 2021; Wu et al., 2021) present the challenges of determining the volatility of SOA particles through thermogram analysis and T_{max}, indicating that such analyses may (for complex mixtures with not fully defined phase state such as SOA particles) merely be qualitative. It is not within the scope of this study to assess the relationship between T_{max} and volatility as such. Our goal here is to show the reproducibility of thermograms in general for individual filter samples and especially for the thermograms resulting from non-uniform ramping procedures. In the duplicate tests from the same sample, the majority of compounds (52%–70%) have T_{max} difference within 5 °C (Line 597, Fig.9b).

We added additional information in the revised manuscript (Line 642 – Line 646):

"The variability in T_{max} induced by varying PM loadings is within 5°C for 29% of compounds, and within 15°C for 54% of all compounds for Quartz filters, and 35% and 57% of compounds, respectively, for Teflon samples. The higher T_{max} variation for different OA loading samples compared to the duplicate samples (±5.7°C, Fig.9 b) is likely caused by other factors, such as particle viscosity, the particles on the filter, and/or mass loadings on the filter (Huang et al., 2018; Ylisirniö et al., 2021; Wu et al., 2021; Graham et al., 2022)."

We also changed the expression in the abstract (Line 36 – Line 37):

"While we find that T_{max} can be determined with high repeatability (±5.7°C) from the duplicate tests for one filter type,"

Editorial comments:

- Line 62: The FIGAERO-CIMS data from HOMEChem was recently published in AS&T: https://doi.org/10.1080/02786826.2022.2133593.

Reply: Thanks for the information. The reference has been added to the revised manuscript and Line 62 has been revised as follows:

"Having the advantage of combining molecular composition and volatility information, the FIGAERO-CIMS has been widely used for measuring OA compounds in many different environments including e.g. forests (Lopez-Hilfiker et al., 2016; Lee et al., 2016; Lee et al., 2018; Mohr et al., 2019), rural and urban areas (Le Breton et al., 2019; Huang et al., 2019; Cai et al., 2022), indoor air (Farmer et al., 2019), and cooking emissions (Masoud et al., 2022)."

- Line 312: I suggest replacing "right" with a different word (and maybe reorganizing the sentence); e.g. "This shows the importance of correctly assessing instrument background…"

Reply: Line 350 has been revised and rephrased as suggested.

"This shows the importance of correctly assessing the instrument background, especially for compounds with low signal."

- Fig 4d) – should the horizontal axis also be "Quartz"?

Reply: The reviewer is correct, the label of Fig. 4 b) has been corrected as suggested:

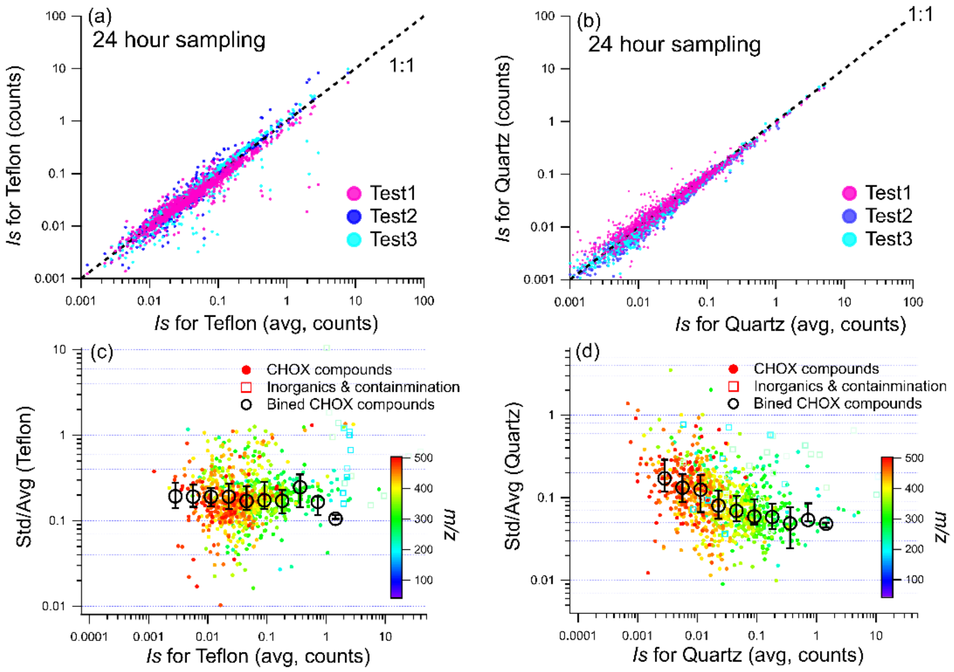

Figure R2 (revised Figure 4). Comparison of the integrated signals from duplicate tests of the same 24-h sample for (a) Teflon and (b) Quartz fiber filters. The relative error (*Is* ratio of standard deviation/average) value of the 3 duplicate tests as a function of *Is* for (d) Teflon and (d) Quartz filters. In (c) and (d), CHOX compounds are shown as dots, inorganics as well as contaminants as squares colored by the m/z. The black cycles in (c) and (d) represent median values of signal intensity bins (with log Is intervals of 0.3 for the Is range of 0 to 2) and error bars represent the 25th and 75th percentile of binned values of Std(*Is*)/Avg(*Is*) for CHOX.

- Fig 6b) – should horizontal axis be "Q-punch"?

Reply: The reviewer is right. The label of Fig. 6 (b) has been corrected as suggested.

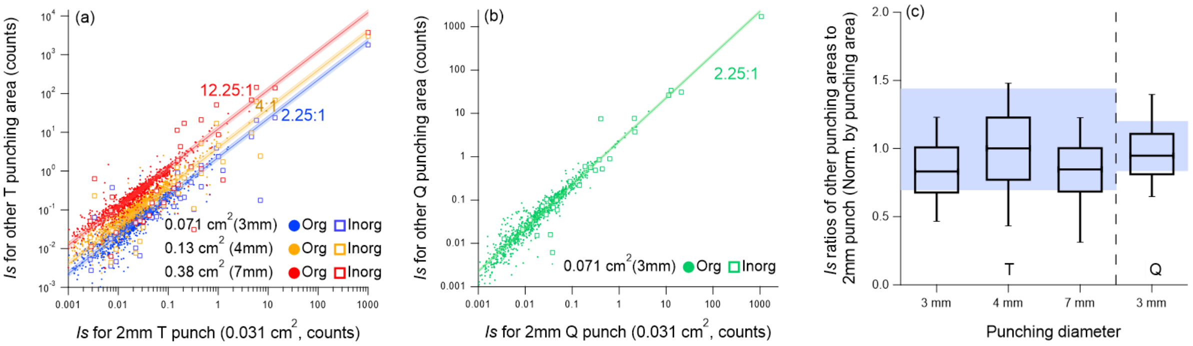

Figure R3 (Figure 6). Comparison of the Is between signals from punches (a) with 3 mm, 4 mm, 7 mm, and 2 mm in diameter for the same Teflon (T) filter, and (b) with 3mm and 2 mm in diameter for the same Quartz (Q) filter. The lines in (a) and (b) represent the punching area ratios. The shaded areas in (a) and (b) represent the area ratio plus/minus the relative errors (9% for Quartz, and 18% for Teflon) from the reproducibility tests. (c) Distribution of Is ratios normalized by the punching area ratios (3 mm, 4 mm, and 7 mm to 2 mm diameter punches for Teflon, 3 mm to 2 mm diameter punches for Quartz). Within each box, the median (middle horizontal line), 25th and 75th percentiles (lower and upper ends of the box), and 10th and 90th percentiles (lower and upper whiskers) are shown. The shaded area in (c) represents the possible distribution of the Is ratios due to the relative error established from the 24-h sample reproducibility tests (18% for Teflon and 9% for Quartz filters). The upper and lower limits for the Teflon *Is* ratio distribution are calculated as (1+18%)/(1-18%) and (1-18%)/(1+18%), respectively.

The upper and lower limits for the Quartz Is ratio distribution are calculated as (1+9%)/(1-9%) and (1-9%)/(1+9%), respectively.

Reference

Cai, J., Wu, C., Wang, J., Du, W., Zheng, F., Hakala, S., Fan, X., Chu, B., Yao, L., Feng, Z., Liu, Y., Sun, Y., Zheng, J., Yan, C., Bianchi, F., Kulmala, M., Mohr, C., and Daellenbach, K. R.: Influence of organic aerosol molecular composition on particle absorptive properties in autumn Beijing, Atmospheric Chemistry and Physics, 22, 1251-1269, 10.5194/acp-22-1251-2022, 2022.

Farmer, D. K., Vance, M. E., Abbatt, J. P. D., Abeleira, A., Alves, M. R., Arata, C., Boedicker, E., Bourne, S., Cardoso-Saldana, F., Corsi, R., DeCarlo, P. F., Goldstein, A. H., Grassian, V. H., Hildebrandt Ruiz, L., Jimenez, J. L., Kahan, T. F., Katz, E. F., Mattila, J. M., Nazaroff, W. W., Novoselac, A., O'Brien, R. E., Or, V. W., Patel, S., Sankhyan, S., Stevens, P. S., Tian, Y., Wade, M., Wang, C., Zhou, S., and Zhou, Y.: Overview of HOMEChem: House Observations of Microbial and Environmental Chemistry, Environ Sci Process Impacts, 21, 1280-1300, 10.1039/c9em00228f, 2019.

Graham, E. L., Wu, C., Bell, D. M., Bertrand, A., Haslett, S. L., Baltensperger, U., El Haddad, I., Krejci, R., Riipinen, I., and Mohr, C., 10.5194/egusphere-2022-1043, 2022.

Huang, W., Saathoff, H., Shen, X., Ramisetty, R., Leisner, T., and Mohr, C.: Chemical Characterization of Highly Functionalized Organonitrates Contributing to Night-Time Organic Aerosol Mass Loadings and Particle Growth, Environ Sci Technol, 53, 1165-1174, 10.1021/acs.est.8b05826, 2019.

Huang, W., Saathoff, H., Pajunoja, A., Shen, X., Naumann, K.-H., Wagner, R., Virtanen, A., Leisner, T., and Mohr, C.: <i>α</i>-Pinene secondary organic aerosol at low temperature: chemical composition and implications for particle viscosity, Atmospheric Chemistry and Physics, 18, 2883-2898, 10.5194/acp-18-2883-2018, 2018.

Le Breton, M., Psichoudaki, M., Hallquist, M., Watne, Å. K., Lutz, A., and Hallquist, Å. M.: Application of a FIGAERO ToF CIMS for on-line characterization of real-world fresh and aged particle emissions from buses, Aerosol Science and Technology, 53, 244-259, 10.1080/02786826.2019.1566592, 2019.

Lee, B. H., Lopez-Hilfiker, F. D., amp, apos, Ambro, E. L., Zhou, P., Boy, M., Petäjä, T., Hao, L., Virtanen, A., and Thornton, J. A.: Semi-volatile and highly oxygenated gaseous and particulate organic compounds observed above a boreal forest canopy, Atmospheric Chemistry and Physics, 18, 11547-11562, 10.5194/acp-18-11547-2018, 2018.

Lee, B. H., Mohr, C., Lopez-Hilfiker, F. D., Lutz, A., Hallquist, M., Lee, L., Romer, P., Cohen, R. C., Iyer, S., Kurten, T., Hu, W., Day, D. A., Campuzano-Jost, P., Jimenez, J. L., Xu, L., Ng, N. L., Guo, H., Weber, R. J., Wild, R. J., Brown, S. S., Koss, A., de Gouw, J., Olson, K., Goldstein, A. H., Seco, R., Kim, S., McAvey, K., Shepson, P. B., Starn, T., Baumann, K., Edgerton, E. S., Liu, J., Shilling, J. E., Miller, D. O., Brune, W., Schobesberger, S., D'Ambro, E. L., and Thornton, J. A.: Highly functionalized organic nitrates in the southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets, Proc Natl Acad Sci U S A, 113, 1516-1521, 10.1073/pnas.1508108113, 2016.

Lopez-Hilfiker, F. D., Mohr, C., D'Ambro, E. L., Lutz, A., Riedel, T. P., Gaston, C. J., Iyer, S., Zhang, Z., Gold, A., Surratt, J. D., Lee, B. H., Kurten, T., Hu, W. W., Jimenez, J., Hallquist, M., and Thornton, J. A.: Molecular Composition and Volatility of Organic Aerosol in the Southeastern U.S.: Implications for IEPOX Derived SOA, Environ Sci Technol, 50, 2200-2209, 10.1021/acs.est.5b04769, 2016.

Masoud, C. G., Li, Y., Wang, D. S., Katz, E. F., DeCarlo, P. F., Farmer, D. K., Vance, M. E., Shiraiwa, M., and Hildebrandt Ruiz, L.: Molecular composition and gas-particle partitioning of indoor cooking aerosol: Insights from a FIGAERO-CIMS and kinetic aerosol modeling, Aerosol Science and Technology, 56, 1156-1173, 10.1080/02786826.2022.2133593, 2022.

Mohr, C., Thornton, J. A., Heitto, A., Lopez-Hilfiker, F. D., Lutz, A., Riipinen, I., Hong, J., Donahue, N. M., Hallquist, M., Petaja, T., Kulmala, M., and Yli-Juuti, T.: Molecular identification of organic vapors driving atmospheric nanoparticle growth, Nat Commun, 10, 4442, 10.1038/s41467-019-12473-2, 2019.

Wu, C., Bell, D. M., Graham, E. L., Haslett, S., Riipinen, I., Baltensperger, U., Bertrand, A., Giannoukos, S., Schoonbaert, J., El Haddad, I., Prevot, A. S. H., Huang, W., and Mohr, C.: Photolytically induced changes in composition and volatility of biogenic secondary organic aerosol from nitrate radical oxidation during night-to-day transition, Atmospheric Chemistry and Physics, 21, 14907-14925, 10.5194/acp-21-14907-2021, 2021.

Ylisirniö, A., Barreira, L. M. F., Pullinen, I., Buchholz, A., Jayne, J., Krechmer, J. E., Worsnop, D. R., Virtanen, A., and Schobesberger, S.: On the calibration of FIGAERO-ToF-CIMS: importance and impact of calibrant delivery for the particle-phase calibration, Atmos. Meas. Tech., 14, 355-367, 10.5194/amt-14-355-2021, 2021.

Zheng, Y., Chen, Q., Cheng, X., Mohr, C., Cai, J., Huang, W., Shrivastava, M., Ye, P., Fu, P., Shi, X., Ge, Y., Liao, K., Miao, R., Qiu, X., Koenig, T. K., and Chen, S.: Precursors and Pathways Leading to Enhanced Secondary Organic Aerosol Formation during Severe Haze Episodes, Environ Sci Technol, 55, 15680-15693, 10.1021/acs.est.1c04255, 2021.