

Interactive comment on “Chemical characterization of oxygenated organic compounds in gas-phase and particle-phase using iodide-CIMS with FIGAERO in urban air” by Chenshuo Ye et al.

Anonymous Referee #4

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Overview

In this work the authors use a FIGAERO-I-CIMS to make calibrated and uncalibrated measurements of oxygenated organic and inorganic compounds in the urban atmosphere Guangzhou over several days. Their observations demonstrate an effective ability to quantify a number of oxygenated organics in both the gas and particle phases and are well-grounded through supporting measurements made by an aerosol mass spectrometer and PTR-MS, in particular. Their findings highlight the limitation of the I-CIMS analytical toolset in urban environments where fresh emissions of organics are

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abundant, when the objective is to close the atmosphere organic carbon budget. Their findings also highlight the capacity for the I-CIMS to place limits on the contribution of organics to aerosols, for molecules containing up to 5 O atoms. Overall, this work is highly suited for publication in Atmospheric Chemistry & Physics, pending minor revisions for improved accessibility to the scope of the measurements.

Minor Revisions

1. Limitations of long inlet lines for gas sampling on instrument response, accuracy of field blanks, or creation of bias from wall loss of aerosols followed by their volatilization are not accounted for in the presented data analysis. The authors go to great extents to conduct calibrations for their target analytes, but do not present response times for a subset of these gases using the full inlet line length under field conditions nor to simulate them in the laboratory. The partitioning and delay of organic gases has been previously demonstrated and warrants some consideration and comment in this work (Deming et al., 2019; Liu et al., 2019). With increasing oxidation of organics, time responses would be expected to increase for analytes traversing the inlet, despite the short residence time of air in it (0.35 s). The authors state the inlet was heated to minimize sorption but do not provide sufficient detail (e.g. what was the temperature? How was it chosen?). The gas inlet has a further concern related to bias introduced from the volatilization of particles lost to the tubing surfaces. Such effects are well documented for NH_4NO_3 and expected for semi-volatile organics. Were particles excluded from the gas inlet? If yes, how? If no, how was the impact of volatilized particles on the gas phase measurements accounted for? Finally, the technical details of the DCOOH addition to the instrument during the campaign to track gaseous response factors for all analytes are not given. Was this added to the instrument inlet? Or just in front of the IMR, as per the zero air for blanks?

One way the authors could have determined an approximation of these effects is by analyzing their signal decays for all ions during the field blanks where the inlet was overflowed with zero air, but the blanks presented in the manuscript appear to be limited

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at being performed only just upstream of the IMR of the CIMS.

In the case of highly oxygenated organics and inorganics (e.g. HNO₃), there is also a concern of long desorption time constants for these molecules during background assessments. Were these quantified in order to set the 3-minute background of the instrument? If yes, can the authors present a summary table of such time constants meeting this criteria using their calibration data? The calibrated compounds cover a nice range of atmospheric species and would strengthen the quality of the dataset.

2. The authors present extensive work to calibrate for many atmospheric gas and particulate species expected in real samples. They present field calibrations for the FIGAERO that have up to 50 % variance in response, but no discussion on how this may impact the interpretation of their results or improved upon for future work. Some additions need to be made throughout the manuscript to capture the impact that this variance could have (e.g. when evaluating the contribution of the particulate organics detected to the total OA from the AMS, can a +/- on these numbers be derived?).

Technical Revisions

Page 4, Line 105: The quantitative threshold for 'sufficient sunshine' should be presented here in place of these words.

Page 4, Line 106: 'south to the mountains' should be 'south of the mountains'

Page 5, Line 108: delete 'in Guangzhou' as it is redundant

Page 6, Line 145: 'thermally' should be 'thermal'

Page 6, Line 146: 'very' is not required here. Delete.

Page 7, Lines 172-173: 'overflushing' should be 'overflowing'

Page 7, Line 174: It would be useful to provide a basic description of the TD program in the text (e.g. ramping rate and max temp).

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Page 7, Line 177: The description of the particle background measurements is unclear. Please revise for clarity.

Page 8, Lines 197-199: This is good, but could matrix effects from other particle components change the sensitivity of a given analyte? Have standard additions for particulate organics been previously performed to provide context on the validity of this approach? Please provide some additional rationale on the robustness of this calibration technique here.

Page 9, Lines 225-226: Was the concentration too high for all the analytes? Figure S6 says this was the case only for levoglucosan. Please explain the effect observed for the use of too high concentration in the calibration standards, such that the community can benefit from this observation.

Page 9, Lines 236-238: Depending on the time responses of the analytes in the instrument for desorption (see Minor Comment 1 above), many of these background corrections may be much higher than if the blanks had been performed for a longer period of time. Overall, the impact of this is not particularly serious because the result is a conservative estimate of mixing ratios and mass loadings (i.e. the presented values may be lower than they truly are due to over-correcting). It would be nice to see the data for the backgrounds of species spanning the range of calibrated analytes in the SI.

Page 12, Lines 319-322: There are no lines on Figure 5 depicting the two different slopes. Suggest adding these.

Page 14, Lines 389-390: 'with 4 or 5 carbon atoms' for a molecular formula denoted as C₄. Revise.

Page 15, Lines 415-416: Revise for clarity.

Page 16, Lines 432-435: Can the authors specify or expand on the relative roles of thermolytic versus ionization cleavage of the S-O bond for particulate organosulfates?

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Page 16, Lines 452-454: Is the AMS data inclusive of NaCl-detection (Ovadnevaite et al., 2012)? Or is the chloride detected here mostly derived from NH₄Cl? If it is the latter, then the presence or absence of aerosol chloride may be more ambiguous than stated and this should be clarified here.

Page 17, Lines 457-461: The long lines and known volatility of NH₄NO₃ under atmospheric conditions could result in a significant bias to the gaseous HNO₃ measurement, which is suggested from the early morning shoulder in the presented diurnal HNO₃ data in Figure 11b. This growth of this shoulder corresponds to the period when most aerosol nitrate is observed. While it may not be possible to correct for this bias, its existence and impact should be stated and assessed.

Page 17, Lines 464-471: This argument for the bias in particulate nitrate quantitation can be strengthened by separating the dataset around a threshold of 1 µg/m³ or orgN (I determined this by visually inspecting the figure. There may be a better value that can be applied and the authors should identify the best value.). Do the slopes and correlations have marked differences and how can that be related to the AMS ON measurement? Can the authors propose a reasonable correction to account for this bias if AMS ON data is available for other FIGAERO users?

Page 19, Lines 522-523: Expand the analysis here. Again, it may be worthwhile to determine the range of pON for both instruments where the relationship is more robust (visual inspection suggests 5 µg/m³?).

Page 20, Line 549: 'of' at the end of the sentence is not needed. Delete.

Page 20, Lines 559-564: In the figure the abbreviation UMR is used, but it is not defined here or in the figure caption. Please do so.

Figures: When stating 'standard deviation' the number should be presented (e.g. one standard deviation).

References: Given the extensive number of references, the authors are highly encour-

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aged to thoroughly assess their correctness.

References

Deming, B. L., Pagonis, D., Liu, X., Day, D. A., Talukdar, R., Krechmer, J. E., De Gouw, J. A., Jimenez, J. L. and Ziemann, P. J.: Measurements of delays of gas-phase compounds in a wide variety of tubing materials due to gas-wall interactions, *Atmos. Meas. Tech.*, 12(6), 3453–3461, doi:10.5194/amt-12-3453-2019, 2019.

Liu, X., Deming, B., Pagonis, D., Day, D. A., Palm, B. B., Talukdar, R., Roberts, J. M., Veres, P. R., Krechmer, J. E., Thornton, J. A., De Gouw, J. A., Ziemann, P. J. and Jimenez, J. L.: Effects of gas-wall interactions on measurements of semivolatile compounds and small polar molecules, *Atmos. Meas. Tech.*, 12(6), 3137–3149, doi:10.5194/amt-12-3137-2019, 2019.

Ovadnevaite, J., Ceburnis, D., Canagaratna, M., Berresheim, H., Bialek, J., Martucci, G., Worsnop, D. R. and O'Dowd, C.: On the effect of wind speed on submicron sea salt mass concentrations and source fluxes, *J. Geophys. Res. Atmos.*, 117(16), 1–11, doi:10.1029/2011JD017379, 2012.

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