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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 #2

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Authors Ye et al. comprehensively present here a very nice dataset based on urban measurements using the FIGAERO-I-CIMS. This kind of results are still rather rare, so I think this dataset will be of good interest to readers of ACP, and in particular to users of that instrumentation. I want to positively highlight especially the comprehensive sensitivity calibrations that were done for this study, but are often overlooked or neglected in other studies: direct calibrations for many compounds, including humidity dependence; the voltage scanning method; and determination of the transmission function. Also the figures are well done overall and clear, thanks! Overall, the paper is also well written, especially the intro (compact but detailed enough) and methods sections (detailed enough without being too messy). However, the manuscript does also feel a bit like a collection of snapshot results. It is all interesting bits and pieces, and well supported by the diligent methodology. A storyline, however, is missing; or clearer indications why certain results were chosen to be presented; or deeper investigations of some aspects; or at least some summarizing consolidation showing how the bits and pieces come together... The results are definitely of interest and worth publishing (ideally after addressing some concerns/issues below, but which I should not be dealbreakers). However, I suggest considering publishing the manuscript as a "measurement report", rather than a "research article", at least in its current form. (A random example of that lack of going "deeper" would be in line 488: results are acknowledged to be useful for investigating OA evolution, but that investigation is not actually done. That is a pattern through much of the manuscript. Interesting observations are reported, but not or hardly investigated. Instead, it is the next observation's turn.)

Some additional general comments:

I would suggest a slightly more specific title, along the lines of mentioning the actual location of the measurement campaign, and/or time of the year, etc.

I wonder if the paper would gain from flipping Chapter 3 (Results), i.e. to start with the more general bulk analysis, and then going into the details, rather than the other way round. But that may also be a matter of taste.

Table 1 is not referenced in the text, and hence I also found it very late. That should be fixed, as it is a very useful summary table indeed.

Throughout the paper there are some minor typos/grammatical erros (e.g., line 106: check prepositions; line 140: missing article; line 145: adverb used instead of adjective; etc.). I tried to point theose out for the Abstract only, in my minor comments below, but the issue persists throughout all sections. The paper still reads well, with few exceptions, but those errors should be fixed nonetheless.

Major comments:

1. My main major concern is the complete lack of temperature-resolved thermal desorption data ("thermograms"), which the FIGAERO technique typically provides by default. Those thermograms can provide a wealth of additional information (see, e.g. Ylisirniö et al., AMTD, 2020; doi.org/10.5194/amt-2020-254; or Ye et al., Environ. Sci. Technol., 2019; doi.org/10.1021/acs.est.9b03265; many others...). So I am curious as for why they are omitted? I would at least like to see a general discussion of that aspect of the data, possibly depending on the reasons for their absence.

2. Related to that, there is hardly a mention of the possible role of thermal decomposition in producing observed compositions, which may be evident from thermograms (e.g., if desorption temperatures are unreasonably high, given the volatility one would expect from a certain composition) or even directly from the composition (if said volatility would suggest a particulate fraction (Fp) much lower than observed). A non-negligible role of such thermal decomposition has been repeatedly reported from FIGAERO measurements on SOA (e.g. Lopez-Hilfiker et al., 2014, doi.org/10.5194/amt-7-983-2014; Stark et al., 2017; doi.org/10.1021/acs.est.7b00160; D'Ambro et al., 2018, doi.org/10.1021/acsearthspacechem.8b00084; etc.), and that issue is indeed on of the method's major drawbacks, so I would expect similar issues in this study. For example, I would not be surprised if the compositions identified as oxalic and malonic acids (section 3.4) would turn out decomposition products of the thermal desorption process due to their relatively high vapor pressure (although mass loadings presumably were high too, and I have not seen the observed thermograms...)

3. There should be some description of the conditions prevailing during the campaign, along with some more general measurement results. Probably in the beginning of section 3. E.g., meteorological data, oxidants/radicals if measured, aerosol mass loadings, time series of the AMS main composition classes (e.g. OA, nitrate, ammonium, sulfate, etc.), and whatever is available and the authors consider might be important for the reader to set the presented results into the appropriate context.

4. Also, I have gotten caught switching back and forth between the main text and the supplement. What was the rationale behind which figures are shown in the main text, vs. which in the supplement? That choice appears somewhat random. Indeed I think that the figures discussed in the main text should be included in the main article as well, and rather dismiss those figures to the supplement that the reader does not necessarily need to see while still believing the story.

Minor comments:

Abstract

- line 29: measurements "by" instead of "of"

- line 34: typo: "form" -> "from"

- line 38: missing "of" after "formation"

- line 42: possibly hint at the uncertainties behind the number 24%?

- line 43: "systematically" -> "systematical"

- line 44: some word or words missing or extraneous around "urban"

Methods:

- line 121: unclear procedure (probably due to some wrong language)

- line 132: j(NO2) should be defined, and could be a bit clearer how it is derived

- line 148: might be worth pointing out here that only elemental compositions can directly be determined (provided sufficient mass accuracy and resolving power)

- line 156: "m/Δm" should possibly be explained

- In Section 2.2.1, I would mention in the main text also the temperature range used for the thermal desorption phase. Otherwise, I think the somewhat complex sampling/measurement setup is sufficiently explained with the support by the nice figures in the supplement. (Although I am familiar with the FIGAERO, so that view may be biased.)

- line 195 (and later): I assume that solution droplets were deposited onto the filter, in which case I believe that "injected" is incorrect.

Fig. S5: What is the meaning diamonds vs. triangels vs. circles? I think there are some discrepancies with humidity-dependences determined by Lee et al. (EST, 2014; doi.org/10.1021/es500362a), e.g.: 1) missing positive slope for formic acid for very low humidities (or at only at lower ones than in Lee et al.) 2) mostly negative slope for nitric acid (for > 2.5 mmol/mol), whereas positive slope in Lee et al. (for < 8 hPa) 3) the slope of succinic acid is slightly negative, but slightly positive in Lee et al. If I am not mistaken, the range of humidities covered by Lee et al. corresponds to mixing ratios up to 8 mmol/mol, which is only the driest third of the data in Fig. S5. But I think above observations (1-3) still hold. It appears like water has a "more negative impact" on sensitivity overall for Ye et al. here, compared to Lee et al. (2014). Such sensitivity calibrations, in particular also for humidity dependence, are rare and therefore very useful. But it would be better still if the authors could include some discussion of potential discrepancies to earlier sensitivity calibrations and speculate on their reasons. On a side note, I just wondered what Fig. S5 would look like with logarithmic scales? Could be worth considering if that maybe straightened out some lines, for example.

Fig. S6a-f: Would be good to mark in the graphs when the new solution was used. And in light of recent results indicating the importance of solution concentration on Tmax (Ylisirniö et al., AMTD, 2020; doi.org/10.5194/amt-2020-254), it could be interesting to report the concentrations used here (Fig. S6b, d, f; even though it seems like Tmax information was not actually used in this study – not yet anyway).

In 2.2.3, 1st paragraph: It is unclear what is meant by "integrating the sum signals" (integrating the signal time series during desorption?) and "peak area" (presumably that same thing?). The latter term is often used for the areas under mass spectral

peaks, so I would avoid using it here, unless some more detailed explanation is given (provided I have understood correctly).

Results:

In general, I was thinking the "organic acids" group should be more clearly defined, and possibly renamed. What was the criteria to fall into this group? And it is probably reasonable to assume that also a subset of compounds assigned to other groups qualify as organic acids.

- lines 319-322: It would be good to elaborate on the conclusion of primary and secondary sources from Fig. 5. I fail to see how that distinction can be made here, or under what assumptions.

Fig. S13a: I suggest expressing also right-hand y-axis in units of ppt

$C_{10}H_{15}NO_6I^-$ and Fig. S13b: What kind of correlation was expected? Certainly, gas-phase mixing ratios would not be the only variable affecting particle-phase concentrations. Other factors might play a role too, e.g. OA loading, and factors possibly influencing the distribution of isomers, e.g. NOx and O3. The main text (line 416) points out that the correlation is not good, but I might miss the attempt of explaining that. The following sentences might be the hypothesis, but that would not be clear to me from reading this paragraph. In any case, I think that looking at more data could support the authors' hypotheses.

Fig. S14: Very interesting figure, both panels, yet S14b is not discussed anywhere.

- lines 427-428: I do not actually see where the cited Lee et al. study reports that organosulfates are detected via deprotonation. Le Breton et al. do make the case, and I believe there are LC-ESI-MS measurements that also detect such compounds in deprotonated form, which might make for more suitable works to cite here in addition.

- line 432: reference should be specifically to panel b in Fig. S15.

- lines 440-444: I agree that wall losses are an issue, but then what about other likely low-volatility compounds that are reported as concentrations (e.g. Fig. S11)? It might actually be useful to estimate wall losses, if possible (it has remained unclear, by the way, if the gas-phase sampling flow was laminar or turbulent). Reporting reliable mixing ratios or concentrations is tricky business with these methods. But I think it is OK to report results in those ways, as long as caveats and uncertainties are clearly stated (better yet quantified (or estimated)...)

- Fig. 10, panels b and d lack legends.

- Fig. S16 lacks explanation of yellow shades.

- Reference to Fig. 11 could come sooner.

- line 486: "augmented" likely not the right word

- line 502: I think that concluding from the abundance of that group of compositions (CxHyN1,2Oz with #O=3) to the abundance of nitrophenols specifically, needs some additional evidence or argumentation or relativization, as other (in particular non-phenolic) compounds are likely member of that group as well.

- Figs. 14 and S17 (and related discussion): I fail to see the point in this analysis. Please elaborate.

∼- line 523: why do you think agreement was worse in some periods?

Fig. 16a: Could the relatively high absolute humidity also contribute to the lower mass closure, keeping in mind calibration results (Fig. S5)?

Fig. S18b: Clarify in caption or in the figure that OA is AMS-based

Conclusions: Should more suitably be called a "Summary".

- line 575: Unclear connection of BVOC products to NOx

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