

This manuscript reports on the long-term deployment of a newly developed charge transfer orthogonal ToF-MS (oToF-MS) in Athens, Greece, for online VOC measurements. My major concern is with the scope of the manuscript. The introduction gives the impression that the primary focus of this study is to evaluate the long-term deployment of this new instrument. To achieve this goal, it is essential to compare the measurements to an established method, such as GC-MS or GC-FID. Unfortunately, this comparison is missing in the manuscript. The "Results and Discussion" section extensively discusses the sources and geographical origins of VOCs, which deviates from the main focus. If source apportionment of VOCs is indeed the primary focus, the analysis presented here is superficial, and several conclusions are not well supported. Therefore, my overall recommendation is to better define the scope, include the necessary measurements to support it, and remove the distracting analysis. I do not want to discourage the authors. The development of a highly sensitive instrument with ~20,000 mass resolution is very impressive. I hope to see more detailed characterization, evaluation, and results from this instrument in the future.

The authors appreciate the concerns raised by the reviewer, but would like to point out that a prior study has evaluated the qualitative and quantitative performance of this novel charge transfer MS using a standard mixture (Kaltsonoudis et al., 2023). The scope of the current study is to assess the instrument's performance under real ambient conditions during field measurements. The authors aimed at deploying the instrument in-situ at a running station and in parallel with other instrumentation measuring atmospheric aerosol properties, chemical characteristics and environmental parameters.

This work evaluates the ability of the novel instrument to perform unattended real-time, online, in-situ measurements. Since the authors agree that a comparison as the one the reviewer suggested will be indeed interesting as a next step, the following was added in the conclusions section of the manuscript:

Line 373: "A complete evaluation is pending for the instrument, where comparison of the field measurements to an established method, such as GC-MS or GC-FID, will have to be performed."

Nevertheless, the authors would like the reviewer and the editor to consider this manuscript for publication following the revisions, given that the results of this study support the successful implementation of this novel instrument. This is a preliminary study presenting the first deployment of this instrument that highlights its impressive capabilities, including high sensitivity and low detection limits. Therefore the authors feel that a study demonstrating its successful four-month in-situ deployment would be a valuable contribution to the scientific community.

Other comments:

1. *Line 39: It is true that proton transfer causes less fragmentation than electron impact ionization. However, the strong electric field in the PTR still causes significant fragmentation, which introduces challenges in product identification. A recent study by Coggon et al.¹ showed that fragmentation from higher-carbon aldehydes and cycloalkanes substantially contributes to m/z 69 and interferes with isoprene measurements.*

The reviewer raises an interesting concern that falls however outside of the scope of this study. Whether interferences in the isoprene signal caused by higher-carbon aldehydes and cycloalkanes fragmentation took place, this is a topic to be studied in the future, both for PTR-MS systems in general, and for this charge transfer instrument in particular. For now we could state in our manuscript that this recent study has not been taken into account, and therefore there lies the possibility that the measured isoprene signal could contain interferences.

2. *Line 71: Heated SS tubing may cause measurement interference. For example, hydroperoxides may convert to carbonyls on metal surfaces². Again, this is why validation of VOC measurements by an independent instrument should be included in this study.*

The reviewer's point here needs to be taken into account in the future, and could be the focus of another study. As far as our measurements are concerned, the SS tubing length was the lowest possible, in order to avoid such interferences, and we therefore believe that such bias was not introduced in our measurements, but could be the topic of a future study.

3. *Table 1: Are the relative abundances reported in this study from calibration or ambient measurements? As mentioned above, ambient measurements may have interferences.*

The relative abundancies reported here are from ambient measurements and are compared to laboratory conditions relative abundancies from Kaltsonoudis et al (2023) for the same instrument.

4. *Figure 5: Why is benzene shown in the same plot as MO-OOA, as they do not have a strong correlation?*

The reviewer is right, MO-OOA was seen to present quite similar diurnal pattern with benzene, but that's only due to poor correlation with other

markers, and since there isn't any correlation expected, MO-OOA was removed from the respective plot.

5. *Lines 346-349: The logic here is problematic. Comparing VOCs and OA factors is useful for understanding their sources. However, given that both have complex sources in the atmosphere, it is challenging to use one measurement to evaluate the reliability of the other. In other words, it is difficult to use "the relationship between VOCs and OA factors" to demonstrate "the successful implementation of the new oToF-MS."*

The reviewer is correct. In this study, following the absence of any instrument that measures VOCs, we used a combination of other measurements to evaluate the instrument, only in the sense that the obtained results are environmentally reasonable. That being said, we used tracers to compare VOCs with similar emission sources, as well as polar plots, to reassure the expected geographical origin of such emission sources, and based on previous studies (Kaltsonoudis et al., 2016). Finally, we compared the overall average values with previous values recorded at the same station, concluding that VOCs levels did not vary much between the years.

Reference

Kaltsonoudis, C., Zografou, O., Matrali, A., Panagiotopoulos, E., Lekkas, A., Kosmopoulou, M., Papanastasiou, D., Eleftheriadis, K., and Pandis, S. N.: Measurement of Atmospheric Volatile and Intermediate Volatility Organic Compounds: Development of a New Time-of-Flight Mass Spectrometer, *Atmosphere*, 14, 336, <https://doi.org/10.3390/atmos14020336>, 2023.