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Comment

Interactive comment on “A compact PTR-ToF-MS instrument for airborne measurements of VOCs at high spatio-temporal resolution” by M. Müller et al.

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1 Introduction Page 5534, line 26 onwards: The instrument is compared to other techniques using the TOGA instrument as an example of a fast aircraft GC. Canister sampling from aircraft is perhaps the most common method of sampling VOCs aboard aircraft, yet this is not mentioned in the text, this should be addressed with a brief comparison here.

The reviewer must have overlooked the relevant sentence (page 5535, lines 1-3): “... whole air sampling (WAS) grabs 1 min integrated samples into a pre-evacuated canister every 1–2 min during intensive sampling periods (Hornbrook et al., 2011; and references therein).”

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2.7 In-flight zeroing and calibration system Page 5539, line 8: The heated catalyst used to create a zero/blank gas for the instrument is described in the text as "...efficiently destroys all VOC in the air ...". Was this zero measured with another instrument? If so, details of this should be given here.

The zero was not measured with another instrument, nor was an alternative method for zeroing used and results compared. We are aware that some groups have experienced problems with catalyst-based zeroing of their PTR-MS instruments, but we have no evidence or data to discuss this issue in our manuscript.

Page 5539, line 14: The discussion of the calibration of the system describes the use of a high concentration standard mixture being diluted into a zero air flow, a sentence to describe why lower concentration standards aren't / can't be used should be included here.

We have modified the text according to the reviewer's suggestion: "We use a certified custom-made 11-component VOC mixture (1 ppmV of methanol, acetonitrile, acetaldehyde, acetone, isoprene, methyl ethyl ketone, benzene, toluene, m-xylene, 1,3,5-trimethylbenzene, α -pinene; Apel Riemer Environmental Inc., Broomfield, CO, USA) for instrument calibration. Based on our experience, ppmV-levels of oxygenated VOCs are stably preserved in a treated aluminum cylinder for at least one year and dynamic dilution generates accurate low-ppbV calibration gas mixtures."

3.2 Mass resolving power, mass accuracy Page 5541, line 18: Discussion of the high resolving power of the instrument uses methanol as an example. The calculated and measured exact masses differ slightly and a sentence to explain these differences should be included here.

We have modified the text according to the reviewer's suggestion: "These results demonstrate that two isobaric peaks at m/z 33 are well resolved even with a relatively low mass resolving power of 900. The absolute mass accuracy of the measurement, i.e. the difference between the calculated exact m/z and the measured accurate m/z ,

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is less than 2 mDa. The mass accuracy is limited by the mass resolving power of the instrument, by the presence of isobaric peaks, by the accuracy of the mass axis calibration and by the obtained signal-to-noise ratio. Further details are discussed in Müller et al. (2011).”

3.3 Field data

Page 5543, line 25: The data plotted in figure 7 shows non-zero intercepts for both isoprene and furan. While the field data are used to highlight the instrument capabilities rather than necessarily provide a full scientific explanation, a short description of reasons for this should be included here – is it an instrumental artefact or is it “real”?

We have included a short explanation: “We find that $\Delta\text{furan}/\Delta\text{acetonitrile}$ is 1.70, while $\Delta\text{isoprene}/\Delta\text{acetonitrile}$ is only 0.66. Biogenic isoprene outside the plume causes the positive y-axis offset in the isoprene data regression line. The negative y-axis offset in the furan data regression line is caused by background levels of acetonitrile ubiquitously found in the atmosphere.”

Page 5544, line 5: The data shown in figure 8 highlights one of the real strengths of the PTR-ToF over the PTR-QMS in that all data (albeit within the defined range) are recorded without any pre-selecting of compounds of interest. Compounds which may not have originally been thought of as important may be found to be significant in a particular data set. Parallels can be drawn here to the GC-MS community where instruments are often run in selected ion monitoring (SIM) mode to improve the sensitivity of the instrument (but this may lead to the loss of potentially significant findings?). I wonder if such a comparison could be drawn here to demonstrate that technological advances in instrumentation are leading to real-life improvements and advances in data sets and scientific outcomes?

Although we agree with the referee, our data analysis is not yet at the stage where we can demonstrate “real-life improvements and advances in data sets and scientific outcomes”. We thus refer to future publications.

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Page 5544, line 17: During the discussion of the toluene-to-benzene ratio it is stated that the ratio corresponding to the traffic emission spike is 4.0 – it should be stated that this is in-line with the ratio expected from traffic related emissions inventories.

The text was changed accordingly. “The toluene-to-benzene ratio derived from a bivariate regression analysis of the 5 s traffic emission spike is 4.0. This value is in good agreement with ratios from ambient and emission inventory data previously reported for nearby site (Reid et al., 2007)”

Reid, S. B., Chinkin, L. R., Penfold, B. M., Gilliland, E. K.: Emissions Inventory Validation and Improvement: a Central California Case Study, Conference paper prepared for the U.S. Environmental Protection Agency’s 16th Annual Emission Inventory Conference, Raleigh, NC, May 14-17, by Sonoma Technology, Inc., Petaluma, CA (STI-3109), 2007.

TECHNICAL CORRECTIONS:

3.2 Mass resolving power, mass accuracy

Page 5542, line 12: The first sentence in this paragraph doesn’t read well: “The new airborne PTR-ToF-MS does not only resolve organic ions from their inorganic isobars.” Suggest changing to something along the lines of “Further examples of resolvable isobaric signals include organic isobars such as. . .”

We have modified the sentence according to the reviewer’s suggestion: ”Further examples of resolvable isobaric signals include organic isobars such as protonated formic acid, CH_3O_2^+ , with a calculated exact m/z of 47.013, and protonated ethanol, $\text{C}_2\text{H}_7\text{O}^+$, with a calculated exact m/z of 47.049.”

3.2 Mass resolving power, mass accuracy Page 5543, line 7: The final couple of sentences in this section don’t read well here. Does the statement about reproducibility refer to masses above m/z 100 or all m/z ’s? If to all m/z ’s then I suggest creating a new paragraph beginning “We find that the measured accurate m/z is highly reproducible...”

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If only to m/z's above 100 then suggest including a linking sentence or two to explicitly state that this is the case.

We agree that the sentence “We also find that the measured accurate m/z is highly reproducible with 2σ variations in the range between 0.5 mDa and 2 mDa (3 mDa for methanol)” is misplaced. We moved the sentence to avoid confusion. “The given examples have already demonstrated the excellent absolute mass accuracy of the measurements in the lower mass range, i.e. where the mass axis is calibrated using the intrinsic m/z 21.022, 39.033 and 55.039 signals. We also note that in the lower mass range the measured accurate m/z is highly reproducible with 2σ variations in the range between 0.5 mDa and 2 mDa (3 mDa for methanol).”

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