Atmos. Meas. Tech. Discuss., 7, C2783–C2787, 2014 www.atmos-meas-tech-discuss.net/7/C2783/2014/

© Author(s) 2014. This work is distributed under the Creative Commons Attribute 3.0 License.



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

## M. Müller et al.

armin.wisthaler@uibk.ac.at

Received and published: 19 September 2014

1) It would be insightful for the reader to know the overall, mass, dimensions (volume), power requirements. These are critical aspects of aircraft measurement and would indicate the compactness of the system. Perhaps a table can be included? (If the other VOC systems on-board take more space/weight it could be mentioned in the text.). Perhaps the new EUFAR book (Wendisch and Brenguier) Wiley Airborne Measurements for Environmental Research could be used to broadly compare this instrument with others currently in use?

The requested details have been included in the revised manuscript (see also response to comment 5 of reviewer 2). Unfortunately we do not have access to the mentioned

C2783

## book.

2) There are several occasions when it is claimed that the instrument resolves isobaric ions (e.g. abstract line 4, Introduction, page 5536, line 6, section 3.2 CO2 and acetaldehyde (line 13,14). While I understand what is meant (two species having nominally the same mass when unit amu mass scales are used) I am uncomfortable with the wording since true isobaric pairs cannot be resolved with this method. While it may seem tedious to always add the caveat given unity mass resolution or nominal mass, it needs to be clear.

We point out that in mass spectrometry an isobar is defined as an "atomic or molecular species with the same nominal mass but different exact masses." (see for example Pure Appl. Chem., Vol. 85, No. 7, pp. 1515–1609, 2013). We consider our wording to be scientifically accurate.

3) In section 2.7 the total accuracy of the measurement is given as 5.2%. How accurate was the gas standard itself? Normally this is 5% which would be 0.2% inaccuracy in dilution flows which seems to be too little given normal MFC variance.

The number is the result of an error propagation calculation (5 % error in gas mixing ratio and 1 % error in the mass flows). We have, however, made a rounding error. The correct value is 5.1 %.

4) A nice example is given showing the relative importance of furan to the m/z 69 signal in biomass burning plumes. In order to also represent the more "normal" situation could an additional plot be added to figure 5 to show the typical look of the peak (i.e. isoprene dominated) outside the plume. It may be worth noting that there has been some recent evidence of a soil source of furan (Huber et al ES&T 2010). This information further strengthens the need to separate both isoprene and furan. Finally a reference to furan being "known" to be emitted from biomass burning plumes should be given (page 5542, line 19).

We have modified the figure according to the suggestions by the reviewer. We also thank the reviewer for bringing the Huber et al. (2010) paper to our attention. The scope of this paper is, however, to describe the performance of analytical instrument on the basis of selected examples. We feel that a discussion of the furan soil source would be more distractive than informative.

5) Page 5543, line 10. Why was the ToF instrument originally conceived for nominal mass analysis only? Did the instrument represent a step forward in other aspects such as weight, volume, power? (See also point 1).

A main driving force in this development was the reduction of costs (rather than an improvement in weight, volume or power). Commercial high-end ToFs are not affordable for most academic institutions, especially if additional airworthiness modifications are needed.

6) In Figure 3 it is clear that both methanol and acetaldehyde exhibit significant offsets in their calibration plots. What is the reason for this? It is mentioned in section 3.1 that power downs increase the background (hence detection limit) of the OVOC yet acetone appears to pass perfectly through the origin?

We don't know the cause of the high instrumental background in methanol and acetaldehyde. Acetone also showed elevated background levels upon instrument start-up but it quickly dropped to tens of cps (not discernable from zero in Figure 3) during the 3-hour instrument warm-up period.

7) In figure 4 the resolution of the two mass peaks HO2+ and CH5O+ is shown. To what extent does the protonated oxygen-17 mass contribute to this peak, i.e. molecular oxygen with one atom with mass number 17?

We have modified the text to discuss the contribution from 1700+ ions: "1700+ ions with a calculated exact m/z of 32.994 cannot be resolved from HO2+ ions at a mass resolving power of 900. They cause a broadening of the HO2+ peak and in our instru-

C2785

ment their contribution to the HO2+ peak was typically on the order of 15 %.

8) Figure 10 shows ammonia data. How were these data calibrated, presumably not from the same Apel Riemer VOC standard? Were inlet losses taken into account. Can it be added to table 1? This molecule is known to be problematic and so greater detail in the quantification method is required.

We refer to our response to comment 3 of reviewer 2.

9) The sensitivity (in cps ppbV-1) given in Table 1 is impressive. In order for future practitioners to compare with these figures it would be helpful to add typical primary ion counts of the system, so normalized counts can be compared. Were these sensitivity figures corrected by the duty cycle correction mentioned in Müller et al. 2013? If so it should be stated (also if the primary ions are corrected in this way) so that newcomers comparing initial sensitivity of their system are not disappointed.

The sensitivity values are actually not so impressive because we are reporting "true" counts per second (cps) as measured by the detection system. Instrument performance should not be compared on the basis of normalized counts per second (ncps) or primary ion counts per second. It is the "true" count rate of the analyte ion signal that defines the instrument sensitivity and the detection limit. We thus refrain from making the suggested changes not to mislead newcomers.

10) The paper would benefit from a schematic figure of the component parts (inlet, cal connection, catalyst, MFCs, pumps etc) inserted between figures 1 and 2 or as an extension to figure 1. This would make clear to what extent the inlet was calibrated, show the overall layout better than the 3D sketch and be easier to refer to in the accompanying text.

For the reader interested in inlet details, the figure will be provided in the Supplement.

11) Please explain briefly why glycoaldehyde is believed to be low during wintertime, the reader is currently left wondering why.

We have included an explanation: "The acetic acid data are potentially biased by a gly-colaldehyde interference. Glycolaldehyde, an isomer of acetic acid, is directly emitted from biomass burning or photo-chemically formed from isoprene and 2-methyl-3-buten-2-ol (MBO) (St. Clair et al., 2014 and references therein). Given that no biomass burning markers were observed and that biogenic emissions are low in winter, we expect the glycolaldehyde interference to be small."

- St. Clair, J. M., Spencer, K. M., Beaver, M. R., Crounse, J. D., Paulot, F., and Wennberg, P. O.: Quantification of hydroxyacetone and glycolaldehyde using chemical ionization mass spectrometry, Atmos. Chem. Phys., 14, 4251-4262, doi:10.5194/acp-14-4251-2014, 2014.
- 12) Could add the words "robustness" to introduction, p 5534, line 23 after "time response."

The text has been changed accordingly.

13) Page 5536, line 6. Insert "nominally" before "isobaric." Also page 5541, line 16.

Not corrected. See definition of "isobaric" (see response to comment 2).

14) Page 5543, line 27 "signals" should be "signal" Corrected.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 5533, 2014.