Atmos. Meas. Tech. Discuss., 7, C2774–C2782, 2014
www.atmos-meas-tech-discuss.net/7/C2774/2014/

Atmospheric Measurement Techniques Discussions

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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Received and published: 19 September 2014

General 1) There are not too many references in this paper. I am specifically missing links to other recent airborne studies (e.g. in California) which could provide a better context for the current airborne VOC research.

We have cited the review by de Gouw and Warneke (2007) where the airborne PTR-QMS instrument is described in great detail. The instruments that have been flown more recently do not differ in any significant way from the one described in that review. Given that our paper is purely instrumental, we believe that a reference to these studies would not add any relevant information.

2) In this compact methods paper, I am also missing a data inter-comparison with other

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instruments. The authors nicely demonstrate the in-flight calibration curves, detection limits, etc., but it would greatly add to the value of the paper if the authors actually compared the data to those from a different instrument (which may be particularly important to substantiate more strongly the results from Figure 10, in particular ammonia – see comment below).

We agree that it would be nice to include results from inter-comparison measurements. There were, however, no redundant VOC measurements on the NASA P-3B aircraft. Regarding ammonia, please see comment 3.

3) Because the methods for ammonia are not provided, I am somewhat unconvinced about ammonia results included to VOC results and perhaps they are diluting the otherwise coherent message. It is well known that measurements of ammonia are very challenging due to losses in the inlet and there are more dedicated instruments to measurements of ammonia (e.g. von Bobrutzki et al., 2010). PTR-MS is typically used in O2+ ionization mode to measure ammonia (e.g. Norman et al., 2007), while I suspect the authors operated exclusively in H3O+ mode. Is this correct? If so, was the residual O2+ sufficiently high and stable (e.g. when humidity changed) to ensure efficient ammonia detection? Was the signal for ammonia normalized in the same way as VOC ions resulting from H3O+ chemistry? Furthermore, it is not clear to the reader which m/z authors attributed to ammonia as it is not included in Table 1.

We have provided additional analytical details in paragraph 2.7: “Ambient ammonia was detected at m/z 18.033 (NH4+) in spite of a high intrinsic background from the ion source. An isobaric peak at m/z 18.010 (H2O+) was clearly resolvable. Data accuracy is +/- 35% based on a calibration with a NOAA permeation source (Neuman et al., 2003) performed during ground operation. PTR-ToF-MS ammonia data agreed well with data obtained using a Picarro G2103 instrument (see Figure S3 in the Supplementary Information). More details regarding airborne ammonia measurements by PTR-ToF-MS will be given in a forthcoming publication (Müller et al., in preparation).

4) While the authors did an excellent job in advertising instrumental advantages, I wonder if it would be worth balance a little with some of its limitations (challenges, future direction).

We have modified the conclusions to include some of the reviewer's suggestions. "An airborne PTR-ToF-MS instrument for high spatio-temporal VOC measurements (1 Hz, 110 m horizontal, 8 m vertical) has been successfully developed and the first airborne PTR-ToF-MS data have been reported. 2sigma-detection limits range from tens to hundreds of pptV, which makes the instrument well suited for 1-Hz VOC measurements in the continental boundary layer. Longer signal integration times (up to 10 s) are required when measuring in the remote boundary layer and in the upper troposphere. To be able to measure at 1 Hz even under clean conditions, the instrument sensitivity needs to be increased by at least one order of magnitude. A recent study by Sulzer et al. (2014) has demonstrated that such a sensitivity increase can realistically be achieved. Still, our new instrument records full mass spectra at 1 Hz which constitutes a significant improvement over conventional airborne PTR-QMS measurements. It allows studying continental VOC point sources even if the resulting plumes are spatially constrained to less than 1 km. We have also shown that the instrument is capable of resolving important isobaric ion pairs in the low mass range. Future instrument improvements should aim at an improved mass resolution for better isobar distinction. Deployment of the new instrument during the NASA DISCOVER-AQ mission generated vertical profile data of VOCs for satellite retrievals and chemistry transport model validation. Future deployments may include airborne eddy-covariant flux measurements of VOCs."

Sulzer, P., et al.: A Proton Transfer Reaction-Quadrupole interface Time-Of-Flight Mass Spectrometer (PTR-QiTOF): High speed due to extreme sensitivity, Int. J. M. Spectrom., 368, 1-5, doi: 10.1016/j.ijms.2014.05.004, 2014. Specific

5) Title. The word “compact” might suggest the instrument is compact, while it probably refers here to the compact ToF detector and not to the dimensions or weight of the instrument. Can you include (e.g. in Sect. 2) the info on instrument dimensions and

weight?

We have included the requested details in section 2: “The entire instrument is installed in a double bay 19 inch aircraft rack (ca. 140 cm high) and has an overall weight of approximately 340 kg.”

6) The mass resolution looks much better than nominal but certainly not as good as in ToF 8000 detectors. As delta m degrades with increasing m/z, this may be particularly relevant for measurements of larger m/z and can make separation of heavier compounds (e.g. >100 Th) difficult. It might be worth making more clear in the text how mass resolving power and resolution relate to m/z and where exactly in the m/z range the limitations start to appear.

We have included a clarifying statement: “At higher m/z it also becomes more difficult to resolve isobaric peaks, but a lot of other factors (e.g. peak shape, stability of the peak shape, signal-to-noise) play an equally important role. Peak resolvability needs to be assessed on a case-by-case basis.”

7) P5534 L4 “The new instrument resolves isobaric ions” is not strictly true, because the instrument cannot resolve the species of exactly the same mass (isobaric). Consider saying something like: “. . .can resolve compounds of the same nominal mass but different exact mass. . .”

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).

8) P5534 L5-7 “. . .records full mass spectra at 1 Hz and thus overcomes some of the major analytical deficiencies of quadrupole-MS based airborne instruments.” Consider replacing with a more positive expression (e.g. “. . .simultaneously at 1 Hz and thus is a major step forward from quadrupole-based instruments which had to sequentially analyze consecutive m/z.”

We think it is correct to state that quadrupole-MS based instruments have major analytical deficiencies, especially when flown on an aircraft. These deficiencies are so significant that PTR-QMS instruments are anticipated to become obsolete in airborne research.

9) P5534 L8 It should probably be “total monoterpenes” as ïĄą-pinene has the same exact mass as other monoterpenes, so cannot be separated using the PTR-ToF-MS (at least at a constant E/N as typically used).

The text has been changed accordingly.

10) P5534 L7 “detection limits…making the instrument well suited for fast measurements in the continental boundary layer”. I suggest to clarify “…measurements of abundant VOCs in the continental boundary layer”.

The text has been changed accordingly.

11) P5534 L22 VOC mixing ratios range from pptV… I would say VOC range from less than pptV… .

The text has been changed accordingly.

12) P5535 L16 Consider providing a context here to other recent airborne deployments (e.g. INTEX, MILAGRO, CALNEX, CABERNET) which took place after the review by de Gouw and Warneke (2007).

The PTR-MS instruments that have been flown on more recent campaigns do not differ from the one described by de Gouw and Warneke (2007). Given that our paper is purely instrumental, the inclusion of these studies would not add any relevant information.

13) P5538 L18 “heated silanized stainless steel line”. Did you notice any memory effects or problems for methanol? Why was this material chosen for VOCs/ammonia?

We did not notice any memory effects or problems for methanol, probably also because the inlet flow was very high (19-27 slpm). The material was chosen because it gives less inlet artefacts than Teflon. This was, however, not studied systematically which is why we prefer not to discuss this issue in the manuscript.

14) P5539 L12-15 “For in-flight calibration, the flow of VOC-free air is spiked with 5 ppbV of the target VOCs. Spiking is also carried out at different altitudes to characterize any humidity dependence of instrumental response factors. We use a certified 11-15 component VOC mixture…”. How long did it take to equilibrate post these 5-ppb spikes before ambient signal was measured/reported? Did these spikes raise the detection limits for the sticky compounds?

The equilibration time from 5 ppbV calibration gas to ambient air was less than 1 second. We did not calibrate before zeroing, meaning that there is no influence of the 5-ppb spikes on the detection limit.

15) P5539 L22 “A three-way valve”. What kind of valve, what materials?

The details have been included: “A three-way stainless steel ball valve (Parker-Hannifin, Jacksonville, AL, USA) is used to divert . . .”

16) P5540 L10-11 “…signals (m/z 21.022, m/z 39.033 and m/z 55.039) are used for mass axis calibration and reference peak shape determination.” Was it not possible to use any intrinsic heavy masses to improve the accuracy in the higher mass region (e.g. >100 Th)?

Signal intensities were not high enough to use these signals for accurate mass calibration.

17) P5442 L1-3 “These results demonstrate that two isobaric peaks at m/z 33 are well resolved and accurately positioned (m < 1.0 mDa) even with a relatively low mass resolving power of 900.” The delta m for methanol seems quite good (1 mDa) but gets somewhat worse for acetone (4 mDa), isoprene (5 mDa), and as one goes along the m/z range (Table 1). This is still impressive relative to nominal and should be sufficient

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for separating the ions differing in oxygen number, at least in the low to medium mass range. I wonder though if the signal abundance can affect the accuracy of the peak positioning of a partially merged peak?

Reviewer 1 has made a related comment to paragraph 3.2. We have included the following details which should answer also the question by reviewer 2: “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).”

18) P5542 L28-29 ”. . .which identified furan as the dominating species detected at m/z 69”. Needs to make it clear that this refers to biomass burning.

The text has been changed to: “Our results confirm findings from previous biomass burning studies which identified furan as the dominating species detected at m/z 69 (e.g. Hornbrook et al., 2011, and references therein).”

19) Figure 8. I can see the peak at m/z 124 and I know at least one PTR-ToF instrument where this peak was intrinsic. Could it be intrinsic also here? If so this peak probably should be omitted from the figure, but maybe could be useful for aligning the mass scale?

The intrinsic m/z 124 signal increases with humidity and the observed enhancement is caused by higher humidity levels in the plume. The signal increase is, however, minor (0.55 ncps or less than 20 pptV in acetone equivalents) and we think it is not necessary to discuss this detail in the paper.

20) Figure 9. Top. Would it be useful to zoom in to the area with high toluene mixing ratio (>2 ppbv) (maybe as an inset)?

The zoomed figure does not reveal any relevant details.

21) Figure 10. Apart from methanol which has been thoroughly discussed, neither acetic acid, formic acid nor ammonia are discussed, or mentioned in Table 1, or seem

to have been present in the calibration standard, so it is unclear how the concentrations were derived and what is the uncertainty. See also earlier comment #3 for ammonia. Perhaps vertical profiles of other VOCs (e.g. from Table 1) could be more relevant to present as examples here or would it be possible to add an intercomparison figure?

Our collaborative research efforts and our funding are focused towards species observable from space. It is thus important that we show vertical profiles of ammonia, methanol, formic acid and acetic acid (see also page 5544, lines 23-25). We have included the requested analytical details in paragraph 2.7. “Ambient ammonia was detected at m/z 18.033 (NH_4^+) in spite of a high intrinsic background from the ion source. The isobaric H_2O^+ peak at m/z 18.010 was clearly resolvable. Data accuracy is ca-35% based on a calibration with a NOAA permeation source (Neuman et al., 2003) performed during ground operation.

Formic acid and acetic acid were calibrated post-campaign using a liquid standard nebulization device (LCU, Ionicon Analytik, Innsbruck, Austria) which has been described in detail by Fischer et al. (2013). The accuracy of the data is ca. 10 %.”

Fischer, L., Klinger, A., Herbig, J., Winkler, K., Gutmann, R., and Hansel, A.: The LCU: Versatile Trace Gas Calibration, in: Proceedings of the 6th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications, Obergurgl, Austria, 3–8 February, 192–194, 2013.

Neuman, J. A., Ryerson, T. B., Huey, L. G., Jakoubek, R., Nowak, J. B., Simons, C., and Fehsenfeld, F. C.: Calibration and evaluation of nitric acid and ammonia permeation tubes by UV optical absorption, Environ. Sci. Technol., 37, 2975–2981, doi:10.1021/es026422l, 2003

22) Conclusions. Could be expanded to include most important points from the study. For example, consider highlighting that this was the first airborne deployment of a PTR-ToF instrument.

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The text has been changed to: “An airborne PTR-ToF-MS instrument for high spatio-temporal VOC measurements (1 Hz, 110 m horizontal, 8 m vertical) has been successfully developed and the first airborne PTR-ToF-MS data have been reported.” More changes are discussed in comment 4.

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

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