Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2019-349-AC1, 2020

Atmospheric Measurement Techniques
Discussions

Interactive comment on "Performance of SIFT-MS and PTR-MS in the measurement of volatile organic compounds at different humidities" *by* Ann-Sophie Lehnert et al.

Ann-Sophie Lehnert et al.

alehnert@bgc-jena.mpg.de

Received and published: 19 May 2020

General response:
We thank both Reviewers for their overall positive evaluations and the very helpful comments that helped to improve the quality of our manuscript. Our detailed responses to each comment made are provided below. As noted by both reviewers, the instruments used for measuring volatile organic gases are evolving rapidly, which means the actual results for the tests made in our manuscript may differ in newer instruments. However, we think the value of the work here is twofold: (1) these tests point to issues with current instrumentation that can help in further instrument

developments and use of existing instruments and (2) the types of tests made indicate issues that need to be addressed when evaluating instrument performance. To reflect these issues we have also changed the title of the overall manuscript, now "SIFT-MS optimization for atmospheric trace gas measurements at varying humidity." Both reviewers also requested that materials previously presented in the Supplemental Information (SI) be moved to the main text. We have done this, and this is responsible for most of the text changes in the revised document. Finally, we have gone through the text to remove imprecise language and improve grammar. We hope that the editor and reviewers will agree with the improvements to the revised manuscript.

Response to Reviewer 1

Reviewer 1: 1) The authors portray a very old quadrupole PTR-MS as a generic PTR instrument representative of all PTR-MS instruments. There are many different PTR-MS instruments with different performance levels. Importantly, almost all of them have higher performance characteristics than the PTR-QMS 500, which has not been state-of-the art for a long time.Lately, newer models such as the PTR Qi-TOF (Sulzer et al. 2014), PTR6000 X2, PTR3 (Breitenlechner et al.), and Vocus (Krechmer, Lopez-Hilfiker, et al.) have much higher sensitivity and much lower LODs. The PTR-MS sensitivities in Figure 4 are poor relative to those of the PTR3, which have been demonstrated to be three orders of magnitude larger. And very relevant to this work, the Vocus PTR-MS has been shown to have no quantitative humidity dependence, making the broad statement on P10 L39 no longer true.The PTR-MS field has largely moved to time-of-flight mass analyzers that offer much higher mass resolution (as opposed to the quadrupole demonstrated here), fast full spectrum acquisitions, high sensitivity, and low backgrounds. While the authors are fair and unbiased in their comparisons here, I fear that measuring a highly modified SIFT against a much older PTR is not representative, nor does it offer useful information to the field. As *they acknowledge, SIFT/PTR intercomparisons have been published before for other applications. I do not think there is enough different about the proposed application here that warrants another intercomparison.*

The reviewer is correct, that PTR-TOF-MS is now the state-of-the-art instrument used by many researchers. However, the PTR-QMS which we used is still used in a number of laboratories and remains useful for general atmospheric measurements; we did not have a PTR-TOF-MS available for further comparisons. As noted above (and also be Reviewer 2), instruments evolve and the exact results – while important for evaluating the instruments we tested – will clearly differ as instruments evolve. What is important are the approaches we used for determining instrument performance. We do see the point made by Reviewer 1 that comparisons between an old instrument and a newer one might give a false impression about general performance. Therefore, we limited the direct comparisons likely to be instrument-dependent. Specifically, we removed the sections about humidity-dependence and the upper limit of the dynamic range, moving the sensitivity and SNR and humidity-dependence plot to the supporting information (now Fig. S18-S20). We also included references to literature values of newer PTR instruments and discussed the newer developments of PTR-MS in the introduction. We also made sure that it is clear we are talking about the specific PTR-MS instrument we tested. Examples:
P3 L6: All ions are then analysed by a mass spectrometer (MS), usually a quadrupole-MS for SIFT-MS and a time of flight-MS for PTR-MS, separating the ions by their m/z ratio and then counting the number of ions hitting the multiplier.
P11 L37: . . . and for PTR-MS, the PTR-Qi-TOF (Sulzer et al., 2014) and the Vocus PTR-TOF (Krechmer et al., 2018) even having LODs reported below ppt for 1 s scan time.
P12 L4: These results are different from the results of Lourenço, C. et al. (2017), where PTR-MS shows a higher sensitivity by a factor of 10 and even higher sensitivities have been reported for the most recent PTR-MS developments (Sulzer et al, 2014,

Breitenlechner et al., 2017, Krechmer et al., 2018), but match the reports of Prince et al. (2010) for SIFT-MS sensitivity.
P12 L22: However again, with the higher sensitivity and lower LODs mentioned in the literature (Yuan et al., 2017), a higher signal to noise ratio should be found on state-of-the-art PTR-TOF-MS instruments.
P12 L35: However, the Vocus PTR-TOF has overcome the humidity-dependence by having a high humidity in the drift tube (Krechmer et al., 2018).

Reviewer 1: 2) There is little-to-no mention of "current" PTR literature or instrumental developments to put this paper in context. For example, the improvements made to the SIFT instrument in this work seem to be similar in spirit to those made to the PTR QMS in Deming et al. 2018. Indeed, additional information about the SIFT-MS's time dependence from an experiment similar to Deming et al. would be useful in this paper.

We have included reference to the more recent PTR-MS literature, see above. With regards to the suggestion to include experiments similar to Deming et al., 2018: we usually do not observe delay times in the signal developments of more than 30 s. The inlet capillary is also much shorter than the other lines connecting the multi-port inlet to the actual flow-tube, so we do not think the effect is large. With the needle valve, we could also shorten the length of silcosteel lines from the inlet to the detector.

Reviewer 1: Separately, I believe the authors left far too much information in the SI. Many of the SI plots are important to understanding the SIFT's performance characteristics and are referenced several times. They also clearly involved a lot of work and would be useful to many users. I think it would be a shame if they remained hidden. I would suggest cleaning some of them up and moving them back to the main paper. There is, after all, no length limit in AMT. In summary, I recommend that this paper be published but suggest that the authors reframe the narrative of the *paper around improving and characterizing the SIFT instrument, deemphasize the comparison with the PTR instrument, and bring a large portion of the impressive SI work into the main paper.*

Reviewer 2 also made the same point. In response, we moved the flow tube voltage, temperature, and carrier gas and sample gas flow optimization plots (now Fig. 2-5) to the main paper as those were the most thoroughly and systematically tested parameters. We also moved up the short discussion parts of the extended figure captions of the SI into the main paper, so that the optimization done by us is now the main focus of the manuscript. We moved the section about the SIFT-MS robustness from the comparison with the PTR-MS to its own section. We extended the section on the SIFT-MS humidity-dependence, also moving two graphs from the SI to the main paper as support (now Fig. 7 and 8). To reframe the narrative around the optimization of the SIFT-MS and minimize direct comparison with PTR-MS we changed text in the abstract, introduction, and conclusion and changed the title of the paper.

Examples:

P2 L5: "Here we present several improvements to a Voice 200 ultra SIFT-MS instrument to reduce background levels and enhance sensitivity. Increasing the sample gas flow to 125 sccm enables LODs at sub-ppb level, and the resulting humidity-dependence is overcome by calibrating for humidity as well. A comparison with a PTR-QMS 500 indicated that detection limits of the PTR-MS were an order of magnitude lower, whereas sensitivity was higher for SIFT-MS and its calibration was still more robust against humidity. Overall, SIFT-MS is a suitable, lower-cost and easy-to-use method for atmospheric trace gas measurements of more complex mixtures, even with isomers, at a varying humidity range."

P3 L22: "As mentioned above, the high limits of detection (LODs) for SIFT-MS can be an issue when measuring atmospheric trace gases, so we optimized the Voice 200 ultra SIFT-MS (Syft Technologies, New Zealand) to meet our requirements of LODs at sub-ppb level and systematically characterized the performance of the SIFT-MS under different humidity-conditions. Lastly, the instrument's performance was compared to the performance of a PTR-QMS 500 (Ionicon, Austria)."

P12 L18: "We successfully improved a purchased SIFT-MS to meet the requirements of sub-ppb atmospheric trace gas measurements. Hardware improvements like changing o-rings in the purchased instrument for materials with lower degassing, and exchanging the capillary in the inlet system with a VICI valve helped reduce the SIFT-MS background. Increasing the sample gas flow by a factor of 5 also improved sensitivity greatly, but made adjustments of the carrier gas flow, the flow tube voltage and temperature necessary. In total, we achieved a decrease of the SIFT-MS' LOD by a factor of 10."

Reviewer 1: Specific comments: Section 3.1 seems to repeat a large amount of the material in Section 2.2. A description of the SIFT improvements should be in one or the other, but not both.

We shortened Section 2.2 to make sure it contains only a description of what was done.

Reviewer 1: P3 L7: ": : :usually a quadrupole MS". Do the authors have evidence of this? For SIFT this is true, but TOF has been the dominant technique for PTR for almost a decade now. This is not trivial, as the issues with how the authors characterize PTR are serious throughout the work.

Changed to "…usually a quadrupole-MS for SIFT-MS and a time of flight-MS for PTR-MS,…" (P3 L6)

Reviewer 1: P4 L16-18: The authors judge the success of their instrument modifications here by evaluating the background. Did they also evaluate response time, which is a critical parameter for ambient atmospheric measurements? PEEK may have a higher background, but its response time has been shown to be significantly better than stainless steel (coated and non). (Deming et al., 2018)

See above, we usually do not observe lag times on the instruments after 30 s, and the silcosteel lines from the multi-port inlet to the flow tube are longer (approximately 15-20 cm) than the capillaries (approx.. 6-8 cm), so we do not think the capillary has such a big effect here. Plus, we shortened the silcosteel lines by using the needle valve instead of a capillary by approximately 10 cm.

Reviewer 1: P10 L17: Mass-to-charge ratios should have a label as such everywhere in the paper. e.g. m/z 19 or m/Q 75

We introduced this way of describing the ion in the methods section (P5 L16 "For the sake of simplicity, we will refer to the individual ions by m/z(reagent ion) / m/z(product ion) / analyte, e.g. 19 u / 33 u / methanol throughout the paper."), but the reviewer is right, we should at least have used the unit of the ions, so we added "u" to each m/z ratio to make clear it is an m/z value.

Reviewer 1: Technical corrections: P4 L33: This is the methods section. Are the authors referring to a different methods section?

Sorry, this was an error, we removed the "As described in the methods section" part – what we meant was described directly above.

Reviewer 1: P5 L20: should be "it more strongly punishes a larger number of parameters"

Corrected.

Reviewer 1: P6 L25: "workdaily" I'm not familiar with this word.

Corrected to "on each working day".

References: Breitenlechner, M., Fischer, L., Hainer, M., Heinritzi, M., Curtius, J., and Hansel, A.: PTR3: An Instrument for Studying the Lifecycle of Reactive Organic Carbon in the Atmosphere, Anal. Chem., 89, 5824-5831, 2017. Deming, B. L., Pagonis, D., Liu, X., Day, D. A., Talukdar, R., Krechmer, J. E., de Gouw, J. A., Jimenez, J. L., and Ziemann, P. J.: Measurements of delays of gas-phase compounds in a wide variety of tubing materials due to gas–wall interactions, Atmos. Meas. Tech., 12, 3453-3461, 2019. Krechmer, J., Lopez-Hilfiker, F., Koss, A., Hutterli, M., Stoermer, C., Deming, B., Kimmel, J., Warneke, C., Holzinger, R., Jayne, J., Worsnop, D., Fuhrer, K., Gonin, M., and de Gouw, J.: Evaluation of a New Reagent-Ion Source and Focusing Ion-Molecule Reactor for Use in Proton-Transfer-Reaction Mass Spectrometry, Anal. Chem., 90, 12011-12018, 2018. Lourenço, C., González-Méndez, R., Reich, F., Mason, N., and Turner, C.: A potential method for comparing instrumental analysis of volatile organic compounds using standards calibrated for the gas phase, Int. J. Mass spectrom., 419, 1-10, 2017. Prince, B. J., Milligan, D. B., and McEwan, M. J.: Application of selected ion flow tube mass spectrometry to real-time atmospheric monitoring, Rapid Commun.

Mass Spectrom., 24, 1763-1769, 2010. Sulzer, P., Hartungen, E., Hanel, G., Feil, S., Winkler, K., Mutschlechner, P., Haidacher, S., Schottkowsky, R., Gunsch, D., Seehauser, H., Striednig, M., Jürschik, S., Breiev, K., Lanza, M., Herbig, J., Märk, L., Märk, T. D., and Jordan, A.: A Proton Transfer Reaction-Quadrupole interface Time-Of-Flight Mass Spectrometer (PTR-QiTOF): High speed due to extreme sensitivity, Int. J. Mass spectrom., 368, 1-5, 2014. Yuan, B., Koss, A. R., Warneke, C., Coggon, M., Sekimoto, K., and de Gouw, J. A.: Proton-Transfer-Reaction Mass Spectrometry: Applications in Atmospheric Sciences, Chem. Rev., 117, 13187-13229, 2017.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2019-349, 2019.