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Measurement
Techniques

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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.

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Reviewer 2: The paper presents results of extensive an thorough comparison of the current SIFT-MS instrument Voice 200 ultra with an older version of PTR-MS: QMS 500. Whilst the data are interesting, the results must not be interpreted as a test showing advantages and disadvantages of the current products on the market. The results are nevertheless based on honest and independent experimental work and should be published, as they do represent important contribution to validation of SIFT-MS in particular for VOC emissions from soils at different humidity. It is worthy of note that PTR-MS is used at 136 Td, some clear justification should be given for this

value. Perhaps a lower value would reduce fragmentation?

Response: See P. 11 L 21: "The authors are aware that this increases fragmentation reactions, however, we found the settings to work well for humid samples: The formation of m/z = 37 u and water clusters of product ions is reduced substantially. Also, we reduced the risk of water and VOCs condensing in the inlet tubes by using the stated high inlet temperature and drift tube temperature. "

Reviewer 2: The important realization is, that the background to a large degree originates from impurities in the instrument components. A very interesting finding relates to comparatively novel use of N2 carrier: "Nitrogen carrier gas lead to a higher sensitivity, but worse LODs and SNRs at 1 ppb and showed a higher humidity-sensitivity of the reagent ions, so we decided to use helium." Clearly more research needs to be done on the N2 carrier gas. "Final running conditions for the SIFT-MS were: 40 V, 140° C, 158 sccm Helium, and 100 sccm sample." This is a comparatively large proportion of sample, presumably following the work of Marvin Shaw, as indicated in section 2.2.

Response: We were aware of Mavin Shaw's work, however, we mainly chose to test the increase in the sample gas flow, because we expected it to increase the amount of analyte in the flow tube and thus the number of product ions formed. But since we were inspired by his work, we put a statement in to acknowledge it:
P. 7 L. 1: "Several changes were applied to the SIFT-MS to improve its limit of detection, inspired by the optimizations done by Marvin Shaw (University of York, unpublished results), but considering different sample humidities:"

Reviewer 2: Does the worse LOD for nitrogen mean a higher background? If so, is it

the purity of the nitrogen that is the problem?

Response: Yes, it generally meant a higher background. However, since we already used nitrogen 6.0 with an additional scrubber, there is not much that one can improve here. Plus, the helium had the same quality and did not show so many impurities. The higher collisional cross section of nitrogen molecules might also just lead to an increased visibility of impurities, as it could increase ionization efficiency.
Included in P. 8 L. 16ff: "Further, humidity-sensitivity of the reagent ions was also higher with nitrogen carrier gas, as was instrument background. In both cases 6.0 quality gases were used and the nitrogen was even further purified with a filter, so that total amount of impurities should be similar for both gases. We thus attribute the higher background we observed with nitrogen to the higher collisional cross-section of nitrogen molecules compared to helium atoms, which might have caused a higher ionization efficiency of the impurities in the nitrogen and the instrument itself, basically increasing the visibility of the impurities by increasing the amount of ionized background analytes. To this, we also attribute the higher sensitivity we observed with nitrogen."

Reviewer 2: Added P. 9 L 17 ff: "As in both cases 6.0 quality gases were used and the nitrogen was even further purified with a filter, the total amount of impurities should be similar and cannot explain the difference in instrument background. We thus attribute the higher background we observed with nitrogen to the higher collisional cross-section of nitrogen molecules compared to helium atoms, which might have caused a higher ionization efficiency of the impurities in the nitrogen and the instrument itself. To this, we also attribute the higher sensitivity we observed with nitrogen. The ion chemistry discussed in 3.2 would perhaps deserve better terminology and insight instead of "intensity loss" of m/z 33 and gain of 51 it would be better to mention, for example, occurence of three body association of protonated methanol with water. Was m/z 69

C3

present at all for methanol at 140C?

Response: On P. 9 L 20 ff: we exchanged the words "gain" and "loss" with "increase" and "decrease" and added a brief discussion what might happen to the ions in L 21 ff: "This could reflect either an increased association of water to protonated methanol in a three-body association involving a third collision partner M that takes up excess energy ($CH_3OH \cdot H^+ + H_2O + M \rightarrow CH_3OH \cdot H^+ \cdot H_2O + M^*$), or an increased ionization of methanol by $H_3O^+ \cdot H_2O$, where one water ligand is exchanged for methanol ($CH_3OH + H_3O^+ \cdot H_2O \rightarrow CH_3OH \cdot H_3O^+ + H_2O$) "
Discussion on whether m/z 69 for methanol is present, cf P. 9 L 24 ff: " $CH_3OH \cdot H^+ \cdot 2H_2O$ (m/z(H_3O^+) = 69 u) could not be observed directly, as we used a mixed VOC standard and at this m/z, isoprene is also detected. A quick calculation of the isoprene signal we should see based on the isoprene signal we see at m/z(NO^+) = 68 u showed us that most of the observed signal should be from isoprene and if at all only a minor amount of the methanol dihydrate ion should be present. For the exact calculation, please refer to the Supporting Information, S4.1."

Reviewer 2: The discussion on acetaldehyde and proton affinity would also do with use of established terminology. The term "deionize" does not seem to be the best choice. What is likely to happen is a sequence of association reactions followed by final ligand switching to form $H_3O^+ \cdot (H_2O)_n$
$MH^+ \cdot H_2O_{(n)} + H_2O \rightarrow H_3O^+ \cdot H_2O_{(n)} + M$ So the charge moves back into the reagent ion system. See for example our early paper on formaldehyde Spanel et al. RCM 13, 1354 (1999) or on hydrocarbons, equation 7 in Spanel Smith IJMS 181 (1998) 1. "In accordance with Wilson et al. (2003), we conclude that a back reaction of the product ion with water might deionize the product ion to form a thermally colder reagent ion again and that this might correspond to the proton affinity of the compound" This is more to do with apparent H_3O^+ affinity than H^+ affinity.

C4

Response: This is the reaction we tried to describe by the word deionize, as essentially the analyte is not ionized anymore. We agree that it might not be the best wording and changed the paragraph to the following (P. 9 L 35):

"In accordance with Wilson et al. (2003), we conclude that a back-reaction of the product ion with water occurs by a ligand exchange of $H_3O^+ \cdot M$: The analyte M is exchanged by water again and thus not part of the ion anymore, leaving a thermally colder reagent ion behind: e.g. $CH_3CHO \cdot H_3O^+ + H_2O \rightarrow H_3O^+ \cdot H_2O + CH_3CHO$ (Spanel and Smith, 1998). This affinity to H_3O^+ should correspond to the proton affinity of the compound, as H_3O^+ is essentially a proton with one water ligand associated." (P. 9, L 30 ff). Also, "gain" and "loss" were exchanged for "decrease" and "increase" again.

Reviewer 2: I agree with the other referee in that much of the data could be in the text and not in Suppl.

Response: As also stated in our response to Reviewer 1, 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 part of the manuscript. We moved the section about the SIFT-MS robustness from the comparison with the PTR-MS to an own section and also extended the section on the SIFT-MS humidity-dependence a bit, also moving two graphs to the main paper from this part (now Fig. 7 and 8).