

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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The paper presents results of extensive and 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

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given for this value. Perhaps a lower value would reduce fragmentation?

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."

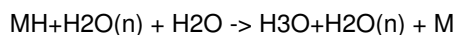
Clearly more research needs to be done on the N₂ carrier gas.

"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.

Does the worse LOD for nitrogen mean a higher background? If so, is it the purity of the nitrogen that is the problem?

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, occurrence of three body association of protonated methanol with water. Was m/z 69 present at all for methanol at 140°C?

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 H₃O⁺(H₂O)_n



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

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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.

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

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